Treatment Processes for Ferruginous Discharges from Disused Coal Workings

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1. SUMMARY

This report outlines progress made during months six to nine of research on methods of treatment of coal minewater discharges. A survey on the international literature on acid mine drainage is given. Brief summaries are given of recent contacts with British Coal and of the results of the coal minewaters questionnaire (which are reported more fully in a separate document). Laboratory and preliminary site work is updated on precipitation, flocculation, adsorption and sedimentation of ochre from the Sheephouse Wood and Bullhouse discharges in conjunction with samples of selected local industrial waste materials obtained from Yorkshire Water and Stocksbridge Engineering Steels. Criteria, site survey plans and preliminary designs are given for a simple accelerated sedimentation pilot plant proposed for construction in the field immediately below the underbank reservoir (National Grid reference SK (4)253/4(3)993/4).

2. LITERATURE SURVEY ON ACID MINE DRAINAGE

2.1 Intoduction

Amongst the environmental problems created by the exploitation of mineral resources, run-off water containing acid and dissolved heavy metals (i.e. acid mine drainage, AMD), arising from mine workings, either operating or abandoned, tailings dams and waste rock dumps, is arguably the most serious. The effects of AMD can be both pernicious and far-reaching, since contamination of water courses and aquifers can carry the pollution considerable distances from the source mining area. AMD is a ubiquitous problem, whose seriousness has only recently been generally acknowledged. In North America, the past decade has seen a vast increase in the amount of legislation and regulation on the prevention of AMD at new mine sites and its mitigation at old sites. The zeal of the legislators has been matched in North America by an equally spectacular rise in the number of environmental companies and consultancies offering their services to mining companies. There is as yet, however, much debate over the most effective technical approaches to solving the problem of AMD. In recognition of the unsolved technical problems in the mitigation and elimination of AMD, the Canadian Federal Government has recently allocated funding of $20 million for research in this area

In Europe, AMD has not yet risen as high on the political agenda as in the USA and Canada, but it is only a matter of time before it does. Recent examples which highlight the problems latent in Europe include:-

- the widespread environmental pollution, some of which results from mining activities, revealed by the opening up of the former Communist states of Eastern Europe
- the recent serious river and sea pollution which occurred in Cornwall, which resulted

from the closure of the Wheal Jane mine,one of the last operating tin mines in the area.

2.2 Outline of the Problem

Rocks containing pyrite (FeS_2) and/or other sulphide minerals undergo a series of chemical reactions when exposed to air and water, which produce acidic solutions containing sulphate, iron and other metals. Factors found to influence the rate and extent of these primarily oxidation reactions include sulphide mineral content and morphology, oxygen availability, ferric ion concentration and bacterial population density. A complex series of reactions occur, which can be represented in simplified form as follows:-

$$2FeS_2 + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \qquad (1)$$

$$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O \qquad (2)$$

$$4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+ \qquad (3)$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

The rates of the oxidation reactions involving oxygen (reactions (1), (2) and (3)) are greatly increased by the catalytic activity of bacteria, principally of the *Thiobacillus* type. The main acid-generating reaction is the action of oxygen on pyrite to produce ferrous iron, sulphate and protons - reaction (1). Acid is consumed by the further oxidation of ferrous iron to ferric - reaction (2), although at pH's above about 3, this oxidation will be accompanied by hydrolysis, resulting in an overall release of acid - reaction (3). As the pH drops below 3, ferric ions remain stable in solution and the chemical oxidation of pyrite by ferric - reaction (4) - can proceed in parallel with the bacterially-assisted oxidation - reaction (1).

According to Schafer (1992), the main factors causing increases in the rate of pyrite oxidation above pH 3.5 are oxygen availability and exposed surface area of pyrite, whereas increasing acidity decreases the rate. Below pH 3.5, regeneration of ferric ion is the primary rate-limiting factor and hence factors favouring increased bacterial activity increase the rate of acid generation, namely: oxygen supply, pyrite surface area, temperature (up to 40°C) and nutrient availability.

AMD arises from two types of wastes generated by the mining industry - waste rock from mining operations and tailings from mineral processing operations. The latter are the easier of the two to deal with for two main reasons. Firstly having been through the blending, comminution and separation operations in the mineral processing plant, the tailings from a particular operation are relatively homogeneous in their chemical and physical properties. Furthermore they are disposed of in a particular place, e.g. on a tailings dam or into the mine as backfill, which enables close control to be exercised of the disposal site and procedures employed. Waste rock, on the other hand, tends to be inhomogeneous, in both chemical composition and size range. The siting of waste rock dumps is usually optimised with respect to minimisation of the overall costs of the mining operation and rarely are the potential problems of AMD taken into account in this cost optimisation.

Acid generation can also occur in the mining excavations themselves, be they underground or open pit. Wherever mining operations expose sulphide mineralisation to air and water, AMD generation becomes possible, indeed in most situations, probable.

In operating mines, measures to prevent or reduce AMD problems can and should be incorporated in the mining methods and the treatment of acidic mine waters by neutralisation is normal practice, if only to protect mining machinery from corrosion. Much more serious problems can arise from abandoned mines, where lack of preventive measures allow uncontrolled access of air and water into mining voids, thus creating long-term sources of pollution.

2.3 Current Research Strategies

Based on the reaction schemes outlined above, a number of methods of prevention or control of acid generation can be envisaged:-

- Prevention of contact with water.
- Minimising infiltration of air.
- Blending acid-generating with acid-consuming materials.
- Controlling bacterial activity.
- Coating sulphide surfaces.

The most common method of control of AMD is collection and treatment of the contaminated water. Neutralisation by lime to precipitate a metal hydroxide/gypsum sludge is widely used, but the problem then becomes one of safe disposal of the metal-containing sludges. Driven by the continuing cost implications of these methods of control, much work is under way to develop effective methods of prevention of acid formation, based on the principles outlined above. The vast majority of research into AMD has been carried out in the USA and Canada, most of it during the past decade.

2.3.1 US work

According to the US Bureau of Mines (1985), acid drainage from coal mines is one of the most persistent industrial pollution problems in the United States. The problem stems primarily from abandoned underground coal mines and it is estimated that over 5000 miles of

US waterways are adversely affected. Work at the USBM during the 1980's into the alleviation of AMD covered four main areas :-

(i) Prediction of acid-generating potential.
(ii) Improved mine planning.
(iii) At-source control of acid formation.
(iv) Improved water treatment methods.

2.3.2 Canadian work

Acid mine drainage in Canada arises mainly from base metal, precious metal and uranium mining, rather than coal mining. It has been estimated by Filion *et al.* (1990) that the cost of remedial action at operating and abandoned mine sites across Canada will be of the order of Can$4 billion over the next twenty years. Research into the remediation of mine sites has been under way for over two decades. A coordinated effort between industry and government began in 1986 and currently, AMD research in Canada is organised under two programmes, one national, one provincial:-

(i) Mine Environment Neutral Drainage programme - MEND;
(ii) British Columbia Acid Mine Drainage task force - BC AMD.

The MEND programme is a cooperative research organisation, which was set up in 1989 and is financed by the Canadian mining industry, the Federal government and the provinces of British Columbia, Manitoba, Ontario, Quebec and New Brunswick. Its objectives are, firstly, to provide a comprehensive scientific, technical and economic basis for the prediction of the long-term management requirements for reactive tailings and waste rock, and secondly, to establish techniques for the operation and abandonment of acid-generating tailings and waste rock disposal areas in a predictable, timely and acceptable manner. It is estimated that to meet these objectives, a research expenditure of Can$12.5 million will be necessary. In the 1990/91 programme, 27 projects were underway, with a total value of Can$4.3 million.

The BC AMD task force was established in 1987 to solve the particular concerns of acidic drainage in the province of British Columbia, which contains in excess of 250 million tonnes of acid-generating waste rock from mining operations. The task force is divided into three technical sub-committees:- Prediction and Prevention, Treatment and Control and Environmental Monitoring. The research programme for 1990/91 involved a portfolio of 14 projects totalling Can$1.1 million.

2.4 Techniques for the Prediction of AMD

2.4.1 Computer-based predictions

An example of progress being made in computer-based predictive techniques is the Reactive Acid Tailings Assessment Program (RATAP) which has been developed by Canadian consultants under contract to CANMET (Conard B.R., 1992). The RATAP model is designed to assess acid generation and associated hydrogeochemical events brought about by the chemical and microbial oxidation of sulphide minerals in tailings deposits. In this model, the mass of tailings is divided into three regions: the saturated zone below the water table; the capillary rise zone, just above the water table; and the hydraulically unsaturated zone, where the pore spaces are only partially filled with water. Most sulphide oxidation takes place in the upper regions, i.e. the unsaturated zone and the top of the capillary rise zone. For quantitative predictions the tailings mass is divided into three-dimensional cells and mass flows of reagents and products between the cells are computed based on fundamental reaction kinetics, hydrogeological characterisation and other empirical measurements.

The RATAP model requires a number of parameters as input, such as the fluxes of atmospheric oxygen and pore water through the tailings mass and a knowledge of the oxidation kinetics of the particular sulphide minerals present in the tailings as functions of temperature, oxygen concentration, bacterial activity, pH, CO_2 concentration and moisture content. The sulphide minerals are considered to be present as distinct, unconsolidated particles, characterised by a known size distribution function. Oxidation depends on the inherent chemical and biological surface oxidation rates of the sulphide minerals present and on the transport of oxygen by diffusion through the pore spaces.

The factors affecting the fundamental rates of sulphide mineral oxidation are discussed in some detail by Byerley and Scharer (1992) in their paper on the application of the RATAP model to the release of copper and zinc from sulphide minerals into the environment. They state that the chemical and biological reaction rates for the oxidation of sulphide minerals can be expressed as functions of the temperature, pH and the dissolved oxygen concentration in the following manners:

$$\text{Chemical rate} \quad k_C = A'e^{-E'_a/RT}[O_2]^{0.5}10^{-xpH}$$

$$\text{Biological rate} \quad k_B = Ae^{-E_a/RT}\frac{[O_2]}{K_0 + [O_2]} \cdot \frac{1}{1 + 10^{2.5-pH} + 10^{pH-4}}$$

where: k_B = biological rate constant (mol/m^{2}s)

k_C = chemical rate constant (mol/m^{2}s)

E_a = Arrhenius activation energy (J/mol)

T = temperature (K)

O_2 = dissolved oxygen concentration (mol/l)

K_0 = half saturation constant for oxygen (mol/l)

x = 0.5-1

In addition to the above, biological reaction rates depend on the attachment of bacteria to the mineral surfaces, the availability of carbon dioxide as the carbon source for bacterial growth, the moisture content, nutrient availability and the effects of metabolic inhibitors.

The diffusion transport of oxygen through the hydraulically unsaturated pore spaces can be expressed as a partial differential equation:

$$\frac{\delta C}{\delta t} + D_e \frac{\delta^2 C}{\delta z^2} + v_z K_H \frac{\delta C}{\delta z} = \Sigma \sigma_i \frac{\delta M_i}{\delta t}$$

where:

C = concentration of oxygen in the air-filled pore space (mol/m^3)
D_e = effective diffusion coefficient (m^2/s)
z = depth into the tailings (m)
t = time (s)
v = water infiltration rate (m/s)
K_H = modified Henry's law constant
M_i = concentration at the ith metal sulphide (mol/m^3)
σ_i = stoichiometric coefficient

Since the effective diffusion coefficient and the water infiltration rate vary with depth and time, the differential equation has variable coefficients and analytical solution of it is not possible. Thus calibration of the model with field data is necessary to use it as a predictive tool.

According to Byerley and Scharer, results achieved to date with the RATAP model have been somewhat mixed and deficiencies in its predictive capabilities have been identified. Most serious of these is the general problem of the use of short-term laboratory data for the prediction of long-term events in the environment. It is concluded that neither the critical oxidation reactions, nor the methodology of emulating reactions in the natural environment, have yet been fully established.

2.4.2 Experimental test procedures

Because of the difficulties in simulating the conditions leading to AMD, a number of experimental test procedures have been devised to assess the acid generating potential of mineral-bearing rocks and waste. As seen above, acid generation is caused by sulphide mineralisation; however if the host rock also contains carbonate minerals, these will act as natural neutralising agents and may even impart an alkaline character to the rock. It has become the standard convention to express the potential of a rock sample to generate or neutralise acid in terms of kg $CaCO_3$ equivalent per tonne of rock. Thus the various experimental test procedures are designed to measure the acid potential (AP) or neutralisation potential (NP) of samples of rock or waste.

In an attempt to compare and evaluate different test procedures, Lawrence *et al.* (1989) undertook a comparative study of 11 prediction techniques, which they tested on four waste rock and eight tailings samples from Canadian mines. The procedures tested were:

(1) Acid - Base Accounting	Sobek *et al.* (1978)
(2) BC Research Initial Test	Duncan and Bruynesteyn (1979)
(3) Alkaline Production Potential	Caruccio *et al.* (1981)
(4) Net Acid Production Test	Albright (1987).
(5) BC Research Confirmation Test	Duncan and Bruynesteyn (1979)
(6) Humidity Cell Test	Sobek *et al.* (1978).
(7) Shake Flask Test	Halbert *et al.* (1983)
(8) Soxhlet Extraction Test	Singleton and Lavkulich (1987), Sullivan and Sobek (1982).
(9) Lysimeter Test	Ritcey and Silver (1981).
(10) Hydrogen Peroxide Test	Finkelman and Griffin (1986)
(11) Manometric Pressure Carbonate Analysis	Evangelou *et al.* (1985)

The study showed that several of the test procedures could provide good predictions of the field behaviour of many of the samples tested. It was stated, however, that it was unlikely that any one particular procedure could provide a definitive assessment and that a combination of two or more different procedures was necessary in order to provide confidence in the predictions. Even so, the predictabilty of the long-term weathering characteristics of rocks and wastes is still subject to uncertainty and further work is required to develop and improve confidence the prediction techniques and procedures.

2.5 Prevention of AMD

The two key factors that are essential for the processes leading to acid generation to occur are the exposure of sulphide minerals to air and water. In the absence of either one of these, acid will not be produced. Thus most strategies for the prevention of acid mine drainage involve prevention of exposure of mineralised rock to air or to water or to both.

There are three main areas in a mining operation where preventative measures against AMD need to be taken. These are in the mine itself, at the disposal sites for waste rock and at the disposal sites for tailings from the mineral beneficiation operations.

The design and construction of dams for the disposal of mineral processing tailings has become a very sophisticated technology (Hallam *et al.*, 1991; Brown and Burden, 1992). Two basic methods are used - sub-aerial and sub-aqueous. In sub-aerial facilities, the tailings dam is constructed so that the tailings are deposited on to "beaches" which are self draining. Thus the tailings dry out and become compacted and, being out of contact with water, acid generation is not possible. On closure of the mine, at the end of its profitable life, modern practice would be to cap a sub-aerial tailings area with an impermeable layer of clay to prevent access of water or air, covering this in turn with top-soil to enable revegetation of the area. In sub-aqueous disposal facilities, the tailings are deposited under water deep enough to maintain anaerobic conditions over the deposited material. Such facilities are usually intended remain in perpetuity as artificial lakes after the cessation of mining operations.

Whereas the tailings from a mineral dressing operation are relatively homogeneous, due to comminution and blending which occurs during processing, waste rock produced by mining operations can be very variable in its chemical properties. The development of appropriate disposal strategies for waste rock requires a knowledge of the acid potential or neutralisation potential of the various types of waste rock produced at a particular operation. Hence the importance of reliable predictive tests, as discussed above. With such knowledge, it may be possible to design waste rock dumps with layers of different rock types, having an overall excess of neutralisation potential over acid potential. This and other strategies in modern mining facility design are discussed by Schafer (1992).

2.6 Remedial Action

At abandoned mine sites, or even at existing mines which have been in operation for a number of years, prevention of AMD may not be feasible and remedial action may be the only option. The most common remedial treatment is chemical neutralisation to consume acidity and precipitate metals from solution as hydroxides. While such treatment is feasible at operating mines, which can bear the costs out of operating profits, the long term cost implications of treatment at abandoned mine sites for the foreseeable future has prompted much attention to low-cost, "passive" treatment systems, which utilise natural processes for improvement of water quality.

2.6.1 Passive treatment in wetlands

Various reports, for instance by Kleinmann (1985 and 1989), indicate that passive treatment of coal mine drainage by wetlands has in some instances proven to be a feasible alternative to conventional chemical treatment. Constructed wetlands in the form of cattail marshes and peat moss bogs are employed.

The processes by which dissolved metals and acidity are removed from water in wetlands are complex and include dilution, bioaccumulation in plants, precipitation as sulphides by bacterial reduction and precipitation as oxides and hydroxides by bacterial oxidation. Oxidation and hydrolysis leads to the precipitation of iron and the production of acidity, while the reduction of sulphate consumes acidity and raises the pH of the mine waters:-

$$4Fe^{2+} + O_2 + 10H_2O = 4Fe(OH)_3 + 8H^+ \qquad (3)$$

$$SO_4^{2-} + 10H^+ + 8e^- = H_2S + 4H_2O \qquad (5)$$

The formation of H_2S by sulphate reduction also results in metal removal from the mine water by precipitation of metal sulphides. The bacteria which catalyse the sulphate reduction reactions require a carbon source as a reductant. This may be produced naturally by rotting vegetation in the wetland, or it may be deliberately introduced during construction of an artificial wetland.

Wetland constructions include collection structures, pretreatment units, primary treatment cells for aerobic and anaerobic mechanisms and polishing ponds. The sizing of wetlands in respect of metal and acid loadings is the subject of continuing debate and design principles are still under development. Full aeration of water is said to provide only enough dissolved oxygen to oxidise 50-70 mg/l ferrous iron and thus mine waters with higher concentrations of ferrous iron require treatment through a series of aeration units with their associated aerobic wetland areas for iron precipitate removal.

It is said that removal of acidity by sulphate reduction in anaerobic wetlands is best done following iron removal, since reduction of ferric iron precedes that of sulphate and thus interferes with sulphide production. Dvorak *et al.* (1991) discussed the treatment of metal-contaminated water using bacterial sulphate reduction in pilot-scale reactors consisting of tanks filled with spent mushroom compost.

A recent innovation is the use of anoxic limestone drains for pH modification ahead of wetlands (Nairn,*et al.* 1991). These consist of trenches filled with limestone and covered with a plastic liner and clay capping to inhibit oxygen penetration. On being passed through an anoxic drain, acidity in a mine water is consumed by dissolution of the limestone. The exclusion of oxygen during this process is important since oxidation of dissolved iron causes precipitation of iron oxyhydroxides which coat or "armour" the limestone, preventing further dissolution from occurring. After passing through anoxic drains, the near neutral mine water is in an ideal condition for metal removal in a constructed wetlands.

2.6.2 Active treatment by chemical neutralisation

In spite of the attractions of passive wetland water treatment systems, their limited capacities for metal and acid removal and their largely experimental stage of development account for the fact that chemical neutralisation and precipitation of iron hydroxide sludges remains the most widely used method for the treatment of acid mine waters.

A study was carried out by the US Bureau of Mines of thirty-three chemical AMD treatment plants operated by Pennsylvanian coal companies (Ackman T.E., 1982). Virtually all the treatment plants in the study used milk of lime to neutralise the AMD and precipitate an iron sludge. Only two plants used liquid sodium hydroxide and none used limestone, in spite of the latter's known superiority with respect to the settling properties of the resultant sludge. Normal lime sludges are highly voluminous and are difficult to densify.

Two methods of solid/liquid separation were in use - mechanical thickeners, or ponds. The former are more expensive to operate, but ponds require extensive land area. Methods of sludge disposal were disposal into deep mines, permanent retention in ponds, disposal in active coal refuse areas and on-site burial.

The main conclusions of the study were:-

(a) The main economic and environmental problems created by sludge treatment of AMD are the enormous volumes of sludge generated and the limited availability of suitable disposal sites.

(b) Present laws mandate treatment of polluted mine waters in perpetuity, ensuring continued growth in sludge production and disposal problems.

(c) Concerted efforts to reduce sludge volumes are essential, otherwise disposal will become excessively costly and environmentally unmanageable.

(d) Sludge volumes can be reduced by developing methods for production of dense, easily handled sludges and , preferably, by preventing AMD from occurring in the first place

(e) The best disposal sites for AMD sludges are abandoned mine workings. Three major benefits can result from the underground disposal of dense sludges: (i) filling mine voids will reduce subsidence; (ii) the alkaline sludge will help to neutralise any acid generating properties of the mine workings themselves; (iii) consumption of land is reduced compared with surface disposal.

A comparative study of various neutralising agents was reported by Heunisch (1987). The settling rates and final densities of iron sludges produced by three proprietary neutralising agents, Alkament, Neutra-Fix and Neutra-Ment, were compared with those produced by conventional lime neutralisation. From compositional data given, Alkament appears to be a lime/limestone mixture, containing less water than conventional hydrated lime, whereas Neutra-Fix and Neutra-Ment are dolomitic-based materials with appreciable MgO and gypsum contents. It was found that the proprietary regents were somewhat more efficient than lime in terms of the quantities required for equivalent amounts of neutralisation, but that their rates of reaction were slower. This latter property made them less suitable for plants utilising mixing tanks for neutralisation. A marked advantage of Neutra-Ment, in particular, was a 50% reduction in settled sludge volume, compared with lime neutralisation.

Improvements in the efficiency of lime utilisation in aeration/neutralisation systems has been the subject of research at the US Bureau of Mines (Ackman and Kleinmann, 1984, 1985 and 1991) into an in-line aeration and treatment system (ILS). The ILS consists of a combination of a jet pump and a static mixer. The jet pump has a Venturi action which causes air to be sucked in and intimately mixed with a high velocity stream of mine water. This then enters the static mixer, which imparts spiral flow to the air/water mixture and provides sufficient residence time for oxidation to occur. Lime slurry or other neutralising agents can be added into the jet mixer along with the air to provide an easily controlled neutralisation capability. The violent agitation in the system improves the utilisation of lime, with savings of up to 30% reported. In addition, because there are no moving parts in the ILS, maintainence costs are low, as are the initial capital costs.

3. INDUSTRY SURVEY

3.1 Visit to Hemheath Colliery

Mr. J. Sorbie (General Manager, Trentham Colliery, nr. Stoke-on-Trent) provided a tour on June 8th of the Hemheath dissolved air flotation (DAF) plant. The DAF plant is among the more sophisticated techniques presently employed for treating ochreous minewaters and afforded a useful complement to earlier visits with Adrian England to conventional lagooning operations (Progress Report 2). Mr. M. Irwin and Mr. J. Bourne explained that the plant, which occupies relatively little volume under cover, was installed some two years ago at a cost of approximately £100,000 and has generally functioned reliably. Operating costs have not been estimated but must be significant in respect of reagents (three), power (thirteen pumps and mixers), maintenance and staff time (one operator). The plant is equipped with a control panel for data recording and process adjustment but computer control is not provided. A brief process description is given below.

Minewater containing 300-400 mg/L Fe, after adjustment to pH 5 underground, is pumped intermittently at 140 m^3/day to tanks for holding, reagent addition and metering. Solutions of soda ash and caustic soda are employed to raise the pH to 9.0-9.6 (for complete precipitation and conditioning of the ochre) and of the Chemisolv polymer PA 101 to hydrophobise the ochre flocs (for subsequent collection on air bubbles). Some 30-40 gal/min of the resulting mixture are pressurised to 5 bar, prior to injection of a separate stream at 6 bar containing dissolved air and admission to the DAF separation facility. The latter, consisting essentially of a 3 m diameter cylindrical tank with concentric partitions (to provide a circular flow and thus maximise the time available for ochre to rise to the surface), yields an overflow of ochre - which is scraped from the surface - together with an underflow of clean water. The flows are pumped to different ends of an outside lagooning system designed to treat the various mine and process effluents, such as surface runoff, to consent levels (pH 5-9, suspended solids 100 mg/L, total Fe 10 mg/L, oil 5 mg/L) ahead of final outflow to the Newstead Brook. Ochre, coal dust, etc., are periodically dredged from the upper end of the lagoon while cleaner water flowing to the lower end encounters a final treatment - in the form Deccablock flocculant blocks suspended in the stream - before discharge.

3.2. Coal minewaters discharges questionnaire

The 2-page questionnaire, first introduced (in draft form) at the November 8th 1991 'Pollution from Abandoned Mineworkings' meeting organised by Yorkshire Region and BOC Foundation at Olympia House in Leeds, was amended and sent for response to all 10 NRA regions, two RPB's (Forth and Clyde) and British Waterways in mid-January, together with a covering letter appropriate to the local level of impact of coal minewaters discharges. Replies were received by early July 1992. The results are reported in a separate document.

4. EXPERIMENTAL DESIGN AND TESTWORK

4.1 Minewater sampling and analysis

The Sheephouse Wood and Bullhouse discharges have been sampled three times since the last report. The partial analyses obtained are shown, together with those obtained during the previous periods, in Table 3.1. The main deductions from the Table were given in Progress Report 2 and are not repeated here.

New measures of the time dependence of iron precipitation in the Sheephouse Wood minewater were initiated on 30th April and 2nd June 1992. Samples taken at the point of discharge to the Little Don on 30th April gave 16, 6, 2 and zero mg/L Fe (on the full supension, the clear liquid from immediate filtration on site, that from a second filtration in London on 1st May and that from a third filtration on the 5th May, respectively) confirmed earlier results that the iron takes several days to precipitate fully. Two small samples of the clear effluent taken at the Sheephouse Wood drainage adit on 2nd June were immediately filtered through a 0.2 μm millipore sterile membrane and compared over time with an unfiltered control. After 18 hours the filter sterilised samples remainded clear while the control precipitated ochre as usual. After 10 days the amounts of iron remaining in solution were 4.1 and 0.23 mg/L in the filtered and control solutions, respectively. Similar results were obtained with samples of the Bullhouse discharge. The results indicated that the rate of precipitation was substantially slowed in the absence of microbial oxidation. Positive confirmation of the presence of iron oxidising bacteria is still needed.

Table 4.1 Partial analyses on minewater samples

	Samples Taken	Results Obtained (mg/L except where shown otherwise)
(1)	Sheephouse Wood (15/7/91)	
	Adit (clear effluent)	75 Fe
	Adit (sediment)	Almost entirely hydrated iron(III) oxide
	River level (suspension)	300 Fe (sample probably unrepresentative)
(2)	Sheephouse Wood (1/10/91)	
	Adit (clear effluent)	45 Fe, pH 6.4, O_2 56% of saturation
	River level (suspension)	56 Fe, pH 7.8, O_2 fully sat.
	Bullhouse (1/10/91)	
	Drainage (clear effluent)	44 Fe, pH 5.9, O_2 63% of saturation
(3)	Sheephouse Wood (8/11/91)	
	Adit (clear effluent)	21, 23 Fe
	River level (suspension)	34, 35, 36, 35 Fe
(4)	Sheephouse Wood (11/12/91)	
	River level (suspension)	27 Fe
(5)	Sheephouse Wood (6/2/92)	
	Adit	33 Fe
	Midhope	32 Fe
	River level	24 Fe, approx. (0.9 - 1.3) $\times 10^3$ m^3/day
	Bullhouse (6/2/92)	48 Fe, approx. (2.2 - 2.6) $\times 10^3$ m^3/day
(6)	Sheephouse wood (2/4/92)	
	Adit	29, 23, 22, 172 Fe, Mg, Ca, Na, resp.
	River level	23, 23, 22, 145, 450, 20, nil Fe, Mg, Ca, Na, sulphate, chloride, phosphate, resp.
	Bullhouse (2/4/92)	52, 68, 66, 113, 934, 54, 7 Fe, Mg, Ca, Na, sulphate, chloride, phosphate, resp.
(7)	Sheephouse Wood (30/4/92)	
	Adit	25/32, 23, 38/41, 64 Fe, Mg, Ca, Na, resp.
	River level	16, 23, 41, 64, Fe, Mg, Ca, Na, resp.
	Bullhouse (30/4/92)	60, 75, 141, 41, Fe, Mg, Ca, Na, resp.
(8)	Sheephouse Wood (3/6/92)	
	Adit	30 Fe
	River level	28 Fe, approx. 0.9 $\times 10^3$ m^3/day
	Bullhouse (3/6/92)	57 Fe
(9)	Sheephouse Wood (14/7/92)	
	River level	34, 40 Fe

Roughly stoichiometric amounts (relative to iron) of sodium carbonate and sodium citrate solutions were added to samples of the clear effluents emerging from the Sheephouse Wood adit. As expected there was an immediate reddening and precipitation in the first case (as iron(II) carbonate and ochre formed). It was therefore confirmed that sodium carbonate precipitates the ochre rapidly, but sodium hydroxide may be preferable because less is likely to be consumed in additionally precipitating calcium. There was no apparent immediate change in the second case (as iron was complexed by citrate anions) but a yellow/orange colour formed over 24 hours as the the complexed iron was oxidised. Precipitation occurred over several days. If desired, therefore, the iron may be retained in solution for lengthy periods. Similar results were obtained with samples of the Bullhouse discharge.

Three sets of flow data carried out on Sheephouse Wood Minewater drainage by Mr. J. Dawson (NRA) - 0.008/0.009 m^3/s (0.6 x 10^3 m^3/day) on 7th May 1992, 0.012 m^3/s (1.0 x 10^3 m^3/day) on 9th June (after overnight rain) and 0.008 m^3/s on 23rd June - correspond reasonably well with those in the table. Although precise data is difficult to obtain, it was clear that the flow rates vary considerably with the rainfall pattern, but the concentrations of dissolved metals are not closely linked to the flowrate.

4.2 Laboratory flocculation testwork

Preliminary results in Progress Report 2 (pages 12-13) indicated that Yorkshire Water filter-pressed sludges (WT waste) and Stocksbridge Engineering Steels red dust and smelter slag dust increased the rate of sedimentation of the very slow settling minewater ferric iron flocs in the presence of the Allied Colloids Magnafloc 155 flocculant. Composite particles (containing both ochre and waste flocs) were observed which were denser than the ochre alone and therefore sedimented at a greater rate. The results below represent attempts to optimise conditions with respect to flocculant dosage and quantities of sludge/dust added. Problems arose with the variable particle size distribution and dispersibility of the materials and there was some doubt about possible contamination of the the minewater by impurities from the industrial waste materials.

Because a clear mud line was not formed as the ochre sedimented and some particles adhered to the surfaces of the Imhof cones employed, earlier data on settling rates obtained under conventional conditions were questionable. A new technique was developed in which samples were taken at two set levels (at the 900 and 100 mL marks in 1 L measuring cylinders in which sedimentation was taking place) for determination of iron by atomic absorption spectrometry.

Typically, calculated quantities of red dust, slag dust or WT waste and flocculant were added to a cylinder filled nearly to the brim with 1200 mL of aged Sheephouse Wood minewater. Samples for analysis were taken at the marks mentioned above with the aid of a long pipette.

The solids ratio (dry weight of ochre in 1200 mL to dry weight supplement) was 1:2 and the flocculant concentration was varied over six levels (0.1-0.4 mL of the diluted solution) including conditions recommended by the supplier. The results obtained for the two most efficient flocculant dosages are given in Table 4.2.

Table 4.2 Comparative laboratory flocculation of Sheephouse Wood minewater with industrial waste supplements

Flocculant dosage (mL/1200 mL)	Time of settling (min)	Total iron (mg/L) at the 100 and 900 mL marks							
		Red dust		Slag dust		WT waste		Control	
		900	100	900	100	900	100	900	100
0.3	5	9.2	12.9	15.6	14.6	9.7	18.6	17.1	14.3
	15	4.9	12.6	12.1	11.6	9.9	13.3	13.1	12.6
	21	4.9	7.4	7.2	9.2	7.4	9.2	5.4	7.7
0.4	5	8.9	12.6	14.1	12.6	16.3	22.5	7.9	17.1
	15	6.4	8.7	8.9	9.2	6.4	13.9	7.9	11.0
	21	4.5	5.2	6.4	7.9	5.2	10.4	5.9	7.2

As can be seen in the table the flocculation was efficient, giving good rates of settling over 20 minutes (such low levels of iron would require several hours without flocculant addition). Addition of red dust significantly reduced the iron content in comparison with the control after 15 minutes, even though the dust itself contained a high proportion of iron. The other two wastes were less satisfactory in enhancing sedimentation rates.

4.3 On-site flocculation and adsorption testwork

Earlier work on the Sheephouse Wood discharge indicated that varying concentrations of iron remained in solution at the point of discharge to the River Little Don, even though the minewater had become fully saturated with oxygen during its residence time of 1.5 hours in the leet track. For instance, data reported in Progress Report 2 (page 12) indicated that some 13 out of a total of 23 mg/L (i.e., more than 50%) of iron remained in solution under the conditions prevailing on 2nd April 1992. Two other sets of results in the present report (Section 4.1) gave similar data. However, laboratory work has generally been carried out over 24 hours after sampling, by which time precipitation was essentially complete. In order to take account of time-dependent changes in the properties of the minewater sedimentation, certain flocculation and adsorption tests were therefore carried out on site on 14th July.

Samples of Sheephouse Wood drainage were taken at the point of discharge to the River Little Don and immediately subjected to flocculation tests as described in Section 4.2. The results obtained (Table 4.3) were disappointing as very little enhancement of settling rates was achieved over those without flocculation. It turned out that the flocculant sample employed was defective. A further problem encountered was difficulty in adequately dispersing the particles of industrial wastes prior to flocculation. The tests will need to be repeated, in simultaneous comparison with older samples, to ascertain whether the properties of fresh and aged minewaters are significantly different.

Table 4.3 Comparative on-site flocculation of Sheephouse Wood minewater with industrial waste supplements

Flocculant dosage (mL/1200 mL)	Time of settling (min)	Total iron (mg/L) at the 100 and 900 mL marks							
		Red dust		Slag dust		WT waste		Control	
		900	100	900	100	900	100	900	100
0.4	5	36	39	36	38	39	39	40	39
	12	32	34	34	34	37	40	42	41
	20	27	24	36	31	36	37	41	38

After flocculation and filtration, the residual minewaters were clear and colourless but were nevertheless found to contain 12, 14, 14 and 15 mg/L Fe upon later analysis for red dust, slag dust, WT waste and control. Very little adsorption from solution onto the waste materials had occurred. In order to determine whether improved adsorption onto the wastes was possible in the absence of flocculant, 200 mL aliquots of freshly filtered minewater (containing about 13 mg/L Fe in solution) were shaken for one minute with 0.1 g (dry mass) of the wastes and filtered. The resulting filtrates were later found to contain 8, 13 and 13 mg/L Fe indicating that significant removal of iron occurred only with red dust. Indeed the red dust filtrate remained clear and colourless while the other two slowly sedimented residual ochre in the same way as the control.

5. PILOT PLANT DESIGN

5.1 General considerations and criteria

Pilot plant design is scheduled for the period May-September 1992. Preliminary work undertaken so far includes a general comparison of potentially suitable techniques, site selection and survey, and outline plant design. Analyses of the Sheephouse Wood and Bullhouse minewaters have confirmed that the main task is to deplete the iron content (initially 20-50 mg/L) to 5-10 mg/L at the point of discharge to the river (about 1 mg/L once diluted in the river). Although pH control will be required there will be no need to reduce the concentrations of anions or other metals. Detailed designs and costings have not yet been carried out.

Techniques potentially available for iron removal from abandoned minewater systems are (i) precipitation and sedimentation (ii) precipitation and filtration (iii) precipitation and flotation and (iv) adsorption. As has been mentioned in the literature and industrial surveys precipitation and sedimentation, in the form of oxidative cascading and lagooning, is employed at various British Coal operations and elsewhere and, in the form of containment in constructed wetlands, at numerous abandoned coal mines in North America. Filtration and flotation are used at a few sites (the latter at Hemheath Colliery as described in Section 3.1). Adsorption is not yet important for removing iron alone but a number of metals, including iron, are adsorbed/precipitated (for instance on waste biomass or growing algae) in the tailing streams at various mineral producton plants around the world. The present project deals with separations in constructed plant applicable in relatively restricted spaces. Constructed wetland techniques, which generally require much more space to treat substantial metal loads, are the subject of a separate NRA project and are not considered further here.

At British Coal operations with minewaters containing so-called 'temporary acidity' the preferred treatment - where sufficient space is available and installations can be screened from view - is often simple aeration, lagooning and dewatering on sand or gravel filters. The technology is well established; costs are minimal (10-25 pence/m^3 in 1980) because power, maintenance and supervision requirements are low; and the product may find a market as a pigment. However, the residence times needed for this full oxidative treatment are 24 hours or more. Minewaters containing 'permanent acidity' do not fully precipitate without addition of base. The space requirements may then be less when the pH is raised but reagent costs are substantial and the product may not meet specifications for use as a pigment.

Measurements of dissolved oxygen showed that the Sheephouse Wood and Bullhouse effluents emerge from underground in partially aerated and oxidised states. Once in the air, samples of the minewaters spontaneously oxidised and precipitated ochre over several days unless indigenous iron-oxidising bacteria were rigorously removed. Fully anoxic conditions may exist within the mine systems but use of this possibility as a basis for treating the minewaters at source, in a reduced state, was not possible because of lack of access. Chemical and/or biological reducing systems might be feasible to re-precipitate iron as sulphide but considerable development work would be required. Full oxidation and ochre precipitation or chemical precipitation of mixed ferrous and ferric solids by pH increase remained the most suitable bases for any treatment process in constructed plant (as against in constructed wetlands). The main initial aim was therefore to ascertain which of the techniques (i)-(iv) above best meet(s) economic and environmental criteria likely to govern the treatment of ochre from abandoned coal mines in general, and from the Sheephouse Wood and Bullhouse discharges in particular.

Although samples of the discharges retained very little dissolved iron after ageing in the open, they did not give the phenolphthalein test for 'temporary acidity' and the complete precipitation process required several days. Without the use of chemical reagents to enhance process rates large lagoons would be required - which would be difficult to screen from view on either side of the Halifax hard seam system and impossible to locate economically at Bullhouse. As samples of the minewaters also became more acidic during precipitation, the product might be too acidic to discharge, even taking account of dilution in the river. More generally, there would be little need to construct a pilot plant for such a system because the minewaters in question are not significantly different from many others for which there should be a wealth of full scale design, construction and operating experience at British Coal.

Ochre is often naturally coagulated in minewater systems and the particles apparently form directly on solid surfaces as well as in the bulk of the solution. However, the highly hydrous composite particles are mechanically soft and hardly denser than water so that they readily disperse and subsequently sediment, and then only slowly, when the level of turbulence becomes sufficiently low. Rates of sedimentation can be enhanced by the action of organic flocculants. Such flocculants are currently little used in minewater treatment because of their cost and because, according to conventional wisdom, high pH values are required - which would cause the water to fail discharge criteria. However, our work showed that effective flocculation was possible at near-neutral pH values. Significant reagent costs would be incurred but the installations would be smaller and less obtrusive than those employed for conventional sedimentation. It might be feasible to contact the minewater with the flocculant cheaply if the latter is in the form of so-called Dekkablocks. The solids would dewater relatively rapidly on a filter pad and would probably meet specifications as a pigment.

Our testwork suggested that local industrial wastes from the water treatment and steel industries should improve settling rates of when flocculated together with the minewater suspensions. However, the effects have proved difficult to optimise satisfactorily in the short time available and should perhaps be the subject of a separate study before applications can be attempted efficiently.

Little information is available on filtration or flotation processes as primary treatments for minewaters. The indications are that the processes, although efficient with regard to high iron removal and small space requirements, would be relatively costly to operate on discharges from abandoned mines. The use of filtration as a secondary dewatering or polishing step is more attractive; for dewatering simple filtration pads can be contemplated as above while for polishing a crude micro-filtration may be possible.

Adsorption of both solid and dissolved minerals - particularly of base metals - from tailings streams onto different forms of biomass has been the subject of much development work in recent years. Little of the work has concentrated on iron but processes based primarily on ion exchange should treat iron roughly as well as other metals. Unfortunately, our work with local waste materials did not indicate significant absorptive capability. Commercial products might be bought in but would inevitably increase treatment costs.

In summary, the preferred approach is a two stage process with (1) base addition (as sodium hydroxide, sodium carbonate, lime or magnesium hydroxide) as necessary to cause precipitation without undue increase in pH, (2) flocculant addition (as Magnafloc 155) to aid settling rates and reduce the size of equipment and (3) dewatering by simple filtration on gravel pads and polishing by re-settling or micro-filtration.

5.2 Site selection and ground survey

Two sites have been seriously considered for constructing a small pilot plant: at Midhopestones pumping station (0.5 Km downstream from the Sheephouse Wood drainage adit) and in the field next to the Unsliven Bridge and the Underbank Reservoir dam (3 Km from the adit). Both are close to the minewater leet track and have the necessary slopes for gravity flow. The former has the advantages of power, drains, a building, an adjacent farm and village facilities and hardstanding but the site is very steep and cramped. The minewater residence time to this point is 0.5 hour with little turbulence for aeration.

The latter site - hereafter called the bottom field site - was originally envisaged as the most appropriate location and is once again preferred. It has no on site facilities - which may be a more realistic situation in relation to minewater treatment in general - although the road and power sources are not far distant and there is gated access for equipment and vehicles. The site has the advantages of effectively unlimited space with a choice of slopes immediately adjacent to the minewater track. The residence time of 1.5 hours gives the maximum time for full aeration of the minewater, with a considerable slope providing a near-cascade, if required, immediately beside the proposed plant location. The site has the disadvantage of relative isolation, the need for fencing and protection against vandalism, and the possibilities of pernicious contamination of the minewater during the long passage in the leet track - but once again these factors are probably representative of many other minewaters.

The most promising area of the bottom field site was surveyed to ascertain area and elevation data by means of the standard techniques of distance measurement, triangulation, trigonometric levelling and tacheometry. A 1:625 plan (Fig.5.1) was constructed from the coordinates and elevations (Table 5.1) calculated from the raw data (not shown), and nominally aligned to the National Grid. The proposed area for the pilot plant is alongside the wall between the tacheometry points 2 and 24.

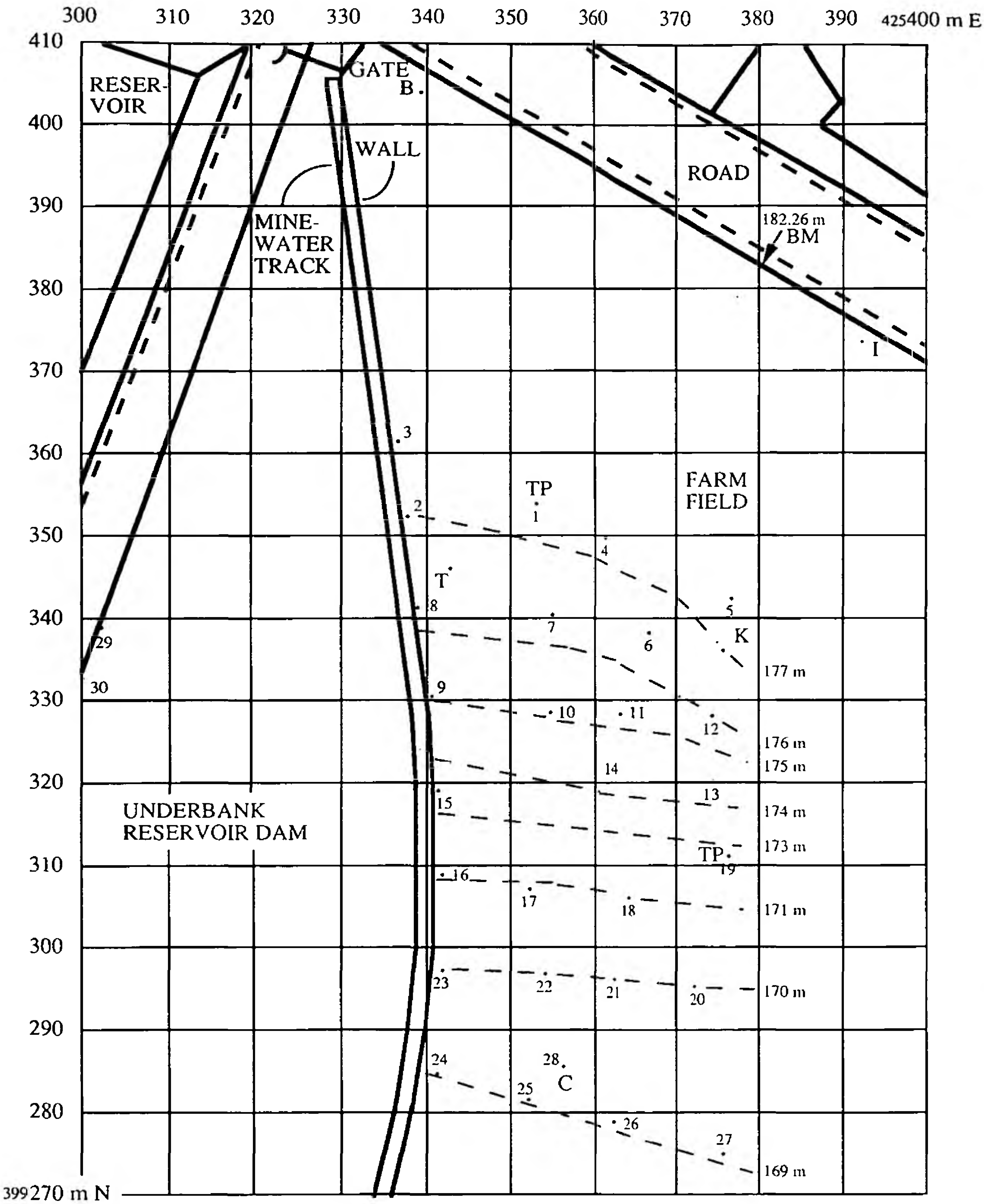

Fig. 4.1 Plan of survey results (1:625) aligned to the National Grid for the proposed pilot plant site in the field adjacent to to the Underbank Reservoir Dam. The data points are explained in Table 4.1.

Table 5.1 Survey data

	Elevation (m above Newlyn datum)	Coordinates (m) Northings	Eastings
Trianguation and trigonometric levelling points (determined in relation to the bench marks at NG refs 25389938 and 25369913 elevations 183.26 and 168.41 m, resp., on Plan SK 2599, and to a base line chained as 34.34 m between points K and T)			
I	182.46		
B	184.46		
K	177.05	336.0	376.0
T	176.76	347.0	343.0
C	169.74		
Tacheometry points (determined in relation to point K)			
1	177.61	354.1	353.6
2	177.01	352.6	337.7
3	177.81	362.2	336.5
4	177.63	350.0	362.0
5	177.45	343.4	375.7
6	176.78	338.1	366.6
7	176.57	340.3	355.5
8	176.25	342.4	339.2
9	175.54	330.7	340.7
10	175.44	327.8	355.6
11	175.71	327.9	364.2
12	176.12	327.9	375.0
13	174.63	320.2	374.6
14	174.28	319.9	362.4
15	173.60	318.8	342.2
16	171.31	308.6	342.9
17	170.79	307.3	353.2
18	171.24	306.2	365.3
19	172.87	311.4	376.8
20	170.52	295.9	373.0
21	170.22	296.6	363.5
22	170.12	297.4	354.4
23	169.98	297.7	343.1
24	169.22	285.2	341.8
25	169.30	282.3	352.9
26	169.32	278.5	363.5
27	169.81	274.7	376.1
28	169.67	285.8	357.3
29	184.81	338.1	303.1
30	185.01	330.1	300.1

5.3 Outline design

As explained above the preferred basic concept involves two tanks in series, the first for reagent addition and sedimentation and the second for cleaning the overflow from the first. It is proposed to minimise the impact of any plant by constructing equipment on as small a scale as possible consistent with representing the characteristics of a full scale plant. For the same reason, and for reasons of cost, the constructions will be as simple as possible. In particular, power requirements will be minimised.

For these purposes a nominal 1% bleed (about 10 m^3/day) from the full flow should be adequate if used in conjunction with a gravity-fed flocculation tank (of volume 0.5-1 m^3) having a nominal residence time residence of about 1 hour. The actual residence time can be varied by adjusting the precise flow rate. A second tank of about 10 times the volume of the first will be gravity fed from the first and used as a polishing system, with or without chemical or adsorbant addition. Facility will be provided to intermittently run-off the water from the flocculation tank and to slurry and run-off the sediment onto a simple filtration pad. The whole system will be gravity-drained back to the leet and fenced to discourage farm animals and possible vandals. It should be completely removable so that the field can be returned to its original state at the end of the trials.

The plant is intended to be operated in short campaigns during which adequate staffing can be provided. Samples of the overflows, in particular, will be analysed on a regular basis to determine the efficiency of the separation processes and optimise the variable parameters. As staff from both Yorkshire Water and Stocksbridge Engineering are regularly on-site, it may be possible to arrange for a watching brief between campaigns.

Although simple in concept and design, the proposed plant should nevertheless afford considerable flexibility in the choices of flow regimes, types and rates of addition of reagents, and modes of dewatering and polishing the products.

6. WORK PLANNED FOR THE PERIOD JULY - SEPTEMBER 1992

6.1 Laboratory work

Work will be carried out to assess the possibility of adsorbing residual iron from true solution and for precipitating iron, particularly with inexpensive reagents available locally. The filtration characteristics of flocculated ochre will be tested.

6.2 Site work

Further laboratory scale work on site will be needed to test fresh minewater characteristics. Lists of equipment and costings will be prepared for the preferred pilot design and a complete design will be described and costed. Preliminary construction schedules will be prepared.

7. SUMMARY OF PLANNED AND ACTUAL EXPENDITURE

All claims for the first accounting year of the contract (up to the end of March 1992) seem to have been settled. The budget and actual expenditure for the months April-June 1992 are given in Table 7.1. The table also includes planned expenditure for the next three-month period. As in previous reports the categories of expenditure have been re-grouped for convenience under the headings staff, travel and subsistence, consumables and overheads. According to our Contracts Administration, a partial claim has already been made for the last three months (total value £3530), and the shortfall (£3528) will, if agreed, be claimed next time around. Overall expenditure is some £635 over-budget, primarily because additional site work has been undertaken, and will be covered by reducing staff costs or equipment costs. Estimates of expenditure for the three months to the end of September are in accordance with Schedule 8 of the contract.

Table 7.1 Planned and Actual Expenditure 1991/2

Expenditure/£	Authority's Budget Apr 92-June 92[1]	Actual Expenditure Apr 92-June 92	Planned Expenditure July 92-Sept 92
Staff	2563	2563[2]	2563[1]
Travel and subsistence	450	810	450
Capital Items	nil	nil[3]	3250[4]
Consumables	250	611	250
Reports	69	nil[3]	69
Analyses	200	nil[3]	200
Overheads	2892	3075[2]	2892[1]
Totals	6424	7059[2]	9674

Notes:[1] Taken as 25% of 1992/93 budget on Schedule 8 less capital items

[2] Committed expenditure

[3] Small items of equipment, reporting and analyses are included under consumables.

[4] This is a nominal amount and will vary according to agreed expenditure on equipment as the pilot scale part of the project gets under way.

8. CONCLUSION

The literature, preliminary consultation and laboratory phases of the work are essentially complete. From the laboratory and site work carried out in the first nine months of the contract, flocculation (with minimal base addition) has been identified as the most promising basis for pilot scale trials. The preferred site for the plant is adjacent to the wall near the terraced part of the farm field next to the Unsliven Bridge.

Although a detailed design still remains to be agreed and some uncertainties require resolution, the work continues to proceed more or less according to plan.

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