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Acidic and ferruginous mine drainages

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Introduction

Springs, streams and rivers draining from outcrops of coal-bearing strata are normally contaminated by small quantities of iron, manganese, aluminium and other compounds derived from the natural weathering of the exposed minerals. In the early history of mining, the presence of iron oxide (ochre) deposits in natural seepages was used as an indicator of the presence of coal seams (Plot 1686; Thomas 1698).

Compared with these natural conditions, mining operations expose relatively large areas of rock to the action of the atmosphere, with the result that abnormal quantities of water-soluble compounds of iron, manganese etc. may contaminate the drainage from the mine, and in turn, the local surface drainage system. The visible effect of such compounds on rivers and streams is the deposition of the highly coloured pigment, ochre. Such deposits are commonly associated with coal mining, and the offending discharges have become known as 'acid mine drainage'.

In the United Kingdom, most of the ochreous discharges from coal mines are not acidic in the chemical sense, the term referring to the supposed state of the chemical conditions at the point of weathering of the parent mineral, iron pyrite (FeS_2). A more correct term for the non-acidic drainages would be 'ferruginous'. It is also necessary to point out that sulphide minerals such as iron pyrite occur in rocks other than coal-bearing strata, and that the mining of minerals other than coal also leads to the discharge of acidic and ferruginous mine drainages (Bilharz 1949; Kinney 1964; Treharne 1962).

In recent years, the pollution caused by acidic and ferruginous mine drainages has achieved prominence in the press and in the technical literature (Anon. 1965), and has led to changes in legislation in some countries. The causes of this increased interest are, chiefly:

(i) A general increase in awareness of pollution;
(ii) the time-lag, often as long as several decades, in the appearance of acid mine drainage after the abandonment of certain types of mines;
(iii) the increase in the total amount of pyritic material exposed in each mining area;
(iv) the availability, at a practical cost, of methods of controlling some of the problems of acidic and ferruginous mine drainage discharges.

The majority of the discourse relating to these drainages during the last decade has come from the United States of America, where it was reported in 1962 that the total acid load from mine drainages was estimated to be 3·5 million tons/year (Anon. 1962). This quantity of acid was small compared with the alkalinity of the river systems as a whole, but had an overwhelming effect on particular rivers and streams within mining areas. In the United States, nearly 6,000 miles of streams and 1,500 acres of impoundments were reported to be polluted by acid mine drainage (Kinney 1964).

In the United Kingdom, individual acidic and ferruginous drainage problems from coal mines are qualitatively similar to those in the U.S.A. but the scale of the overall problem is smaller by two to three orders of magnitude. No major rivers in the United Kingdom are measurably affected by these drainages, but several minor rivers and a large number of streams are affected by the typical ochre deposits and a few are so contaminated as to be acidic.

The formation of acidic and ferruginous mine drainages

The mine drainages to be considered in this text arise from the sources listed below:

Underground coal mine workings

Water from the strata which penetrates into such workings must be removed. Workings below the local surface water table are drained by pumping; workings above the water table may be drained by gravity flow. After abandonment, the former type of workings usually fill to the local water table but seldom overflow, whereas the latter type of workings normally continue to drain indefinitely. The rate of flow of drainages from individual underground coal mines in the United Kingdom averages about 1 million gal/day.

Surface coal mine workings

These are also known as opencast mines, contour or area strip mines or pits. Water may enter such workings from the strata or as rainfall and may be pumped or drained by gravity. The rates of flow of such drainages vary over wide ranges.

Coal mine spoil heaps

These are also known as 'tips', 'rucks', and 'banks' in England and Wales, as 'bings' in Scotland, and as 'refuse banks' in North America. Drainages arise from the action of rainfall and may appear as surface run-off or as seepages at the toe or from perched water tables. Rates of surface drainage may be high in storms, and otherwise negligible. Rates of toe seepages caused by percolation are usually less than 10,000 gal/day but may be higher in districts of very high rainfall.

Coal stock piles

Drainages from the action of rainfall may appear at the toe of such piles. Rates of flow are usually less than 10,000 gal/day.

The factors which determine the extent of contamination of mine drainage waters by acidic and ferruginous salts have been the subject of extensive studies in the last few years. It has been found that a large number of physical, chemical and biological factors may be involved. The more important of these factors are summarized below. A comprehensive review has recently been published (Anon. 1971a).

Chemically, the contamination of coal mine drainages by acids and iron salts starts with the oxidation of the mineral, iron pyrite (FeS_2). This mineral is found throughout the coal seams and the associated shales and occasionally in the sandstones. Pyrite takes the form as brassy crystals and greenish bronze amorphous masses. The former range in size from a few μm to a few cm, and the latter appear in sizes up to over 1 m diameter.

Pyrite begins to oxidize as soon as it is exposed to air, the rate of oxidation increasing progressively with the extent of the oxidation. The sulphates resulting from the oxidation can be detected in drainage water within a few days of first exposure of the pyrite. The immediate products of oxidation of iron pyrite are ferrous sulphate, $FeSO_4$; ferric sulphate, $Fe_2 (SO_4)_3$; sulphuric acid, H_2SO_4; and hydrated ferric oxide, $Fe_2O_3.xH_2O$.

Many investigations have been made into the processes involved in the oxidation of iron pyrite. The principal rate-controlling factors have been identified, but the interpretation of some of the test results has led to differences of opinion concerning details of the oxidation mechanism.

Increasing temperature leads to an increased rate of oxidation, it having been suggested that the rate doubles for a 10°C rise of temperature. Water appears to be essential for the reaction, the rate of oxidation increasing with the water vapour pressure until, at 100% relative humidity, the rate becomes equal to that for immersed pyrite. It has been suggested that water may be necessary not as a reactant, but as a medium for the transfer of the oxidation products from the reaction sites. The rate of oxidation is generally agreed to be determined by the pressure of the reacting oxygen, approximating to a first order reaction at atmospheric pressures.

It is claimed that the actual electron transfer associated with the oxidation of the pyrite occurs on the surface of the mineral from either adsorbed oxygen or from ferric ion. A reaction mechanism involving ferric ion would require the presence of an inorganic or biological catalyst to oxidize ferrous to ferric, a reaction which occurs at a negligible rate in acidic solutions in the absence of such a catalyst.

The rate of oxidation is also apparently related to the reactive surface area of the pyrite, thus explaining the apparent anomaly that 'brassy, museum grade' pyrite does not appear to oxidize. The various mechanisms which have been postulated for the oxidation of pyrite have recently been reviewed in a report describing a mathematical model for a pyrite oxidation system (Morth *et al.* 1972).

The role of bacteria in the formation of acidic and ferruginous drainages has been studied extensively in the last twenty-five years, partly as a means of elucidating the mechanism of the oxidation reaction and partly in the hope that some means of controlling the formation of acidic and ferruginous mine drainages by bacteriostats would be discovered (Temple & Colmer 1951; Ashmead 1956; Lundgren 1971). Acidophilic ferrous oxidizing bacteria have been found to be ubiquitous in coal mine workings and have been shown to increase the rate of oxidation of pyrite in laboratory experiments (Ashmead 1956; Baker & Wilshire 1970; Smith & Shumate 1970). The effectiveness of bacterial catalysis in the field has been questioned by the observation that the number of organisms which can develop in field conditions is limited to about 10^8 to 10^9/ml, a number which can only achieve the observed rate of production of pyrite oxidation products when the ratio of water to pyrite is very high (Lau *et al.* 1970).

Compared to the attention which has been given to the mechanism of pyrite oxidation, comparatively little interest has been shown in the hydrological and other mass transport aspects of the problem. Careful inspection of mine workings, spoil heaps and coal stock piles in the United Kingdom has revealed that only a small fraction of the total quantity of pyrite oxidation products which are produced are actually discharged in the drainage. For example, it is found that although most underground mine workings produce an iron-free neutral drainage, all of the pyrite exposed on the walls, floors and roofs of the mine roadways becomes more or less oxidized and covered with efflorescences of acidic oxidation products. In such situations, the primary factor which determines the degree of contamination of the drainage is the effectiveness with which the drainage water comes into contact with the oxidation products and not the rate of oxidation of the pyrite.

A second factor which may determine the quality of the drainage from mine workings and spoil heaps is the neutralizing and purifying effect of the clays, carbonates and other minerals in the strata. These minerals may react with pyrite oxidation products to form aluminium, manganese, calcium and magnesium sulphates. Most of the coal mine drainages encountered in the United Kingdom contain high (up to 3,000 mg/l concentrations of these neutral sulphates, which are not present in the parent ground waters, thus indicating the extent of internal neutralization of pyrite oxidation products which has occurred. The extent of this internal purification can be judged by the observation that whereas fresh spoils contain no sulphates, a well weathered spoil may contain as much as 5% of calcium sulphate.

Finally, a drainage which becomes contaminated within a mine working or a spoil heap may be purified naturally before it is discharged. The contaminated drainage may mix with naturally alkaline waters, and subsequent aeration and sedimentation of the mixture may remove appreciable quantities of what would otherwise be polluting components such as iron salts.

The quality of a mine drainage is thus seen to be determined by the following factors:

The comminution and exposure of rocks containing pyrite.

A supply of atmospheric oxygen to the vicinity of the exposed pyrite.

The efficiency of transfer of oxygen to the surface of the pyrite.

An effective catalyst for the oxidation of ferrous to ferric in an acidic medium (assuming oxidation by ferric ion to be significant in the particular situation).

A supply of water as liquid or vapour for the promotion of the oxidation reaction or the removal of reaction products from the immediate oxidation sites.

The availability of carbonate or clay minerals to react with the primary oxidation products.

A supply of drainage water moving to and from the zone of pyrite oxidation.

The efficiency of secondary purification of the drainage within the mine or heap, e.g. by alkaline strata water.

Table 1. The composition of drainage water from a number of coal mining activities.

Source of Discharge	Quality	pH value	Alkalinity to pH 4·5 mg/l $CaCO_3$	Acidity to phenol-phthalein at the boiling point mg/l $CaCO_3$	Calcium mg/l Ca	Magnesium mg/l Mg	Dissolved iron mg/l Fe	Suspended iron mg/l Fe	Manganese mg/l Mn	Chloride mg/l Cl	Sulphate mg/l SO4
Underground mine working, shallow depth	Naturally purified, low salinity	8·0	290	0	90	93	1·0	0	0·4	90	700
Underground mine working, medium depth	Naturally purified, medium salinity	7·9	580	0	176	137	0	0·5	0·1	6,900	700
Underground mine working, maximum depth	Naturally purified, high salinity	7·5	190	0	2,560	720	0·6	0·2	0·9	30,800	350
Flooded underground mine workings	Alkaline and ferruginous	6·9	340	0	190	130	25	21	6	42	1,720
Shallow underground mine workings, gravity flow	Acidic and ferruginous	2·9	0	480	125	88	122	0	7	50	1,250
Spoil tip seepage	Acidic and ferruginous	4·6	5	580	250	230	23	17	10	95	2,300
Coal stock pile seepage	Acidic and ferruginous	3·1	0	1,100	n.d.	n.d.	160	0	9	80	1,220

n.d. signifies not determined

Faced with this list of conditions, it would seem to be improbable that a mine drainage could become contaminated with pyrite oxidation products. However, by an unfortunate coincidence, sufficient of these conditions occur simultaneously in the Appalachian coalfields of the United States to produce a major problem. The coals and associated rocks which are exposed apparently have a fairly high pyrite content, the mines have largely been driven above the water table and have thus remained filled with air after abandonment, the workings have been shallow and the overlying rocks have fractured easily so that water has penetrated over large areas of the workings, little or no alkalinity has been present in the natural ground waters, and the drainage has continued to flow from the mines after abandonment.

In contrast, conditions in the coal mines of the United Kingdom have been much less likely to cause problems. A few of the earliest mine workings (e.g. those in, South Wales, the Rossendale anticline in Lancashire, the fringes of the Pennine hills, and parts of Scotland), were similar to the mines of Appalachia, and these still yield small quantities of acidic and ferruginous drainages. The majority of coal mines in the United Kingdom have been driven in coal seams of relatively low pyrite content, the workings were below the water table and were covered by relatively soft shales which allowed little water to enter the mines during the active phase, and little or no overflow to occur after abandonment. The natural ground waters encountered in these mines have usually been alkaline, some having alkalinities of 2,000 mg/l (as $CaCO_3$).

Similarly, in the United Kingdom, the coincidence of conditions necessary for the discharge of acidic and ferruginous drainages from spoil heaps and coal stock piles are seldom present.

The composition of drainages from various coal mining activities are shown in Table 1.

The potentially polluting and other adverse effects of acidic and ferruginous mine drainages

From the point of view of modern society, acidic and ferruginous mine drainages cannot be claimed to have any beneficial effects. It should be remembered that these drainages are a living demonstration of a process by means of which iron has been mobilized and concentrated into iron-rich deposits in the course of geological history, but unfortunately, mankind does not have any particular need or sympathy for the continued deposition of iron ores at the present time.

A possible slight advantage of acidic and ferruginous drainages from coal stock piles is that pyritic sulphur removed by leaching is so much less sulphur remaining to pollute the atmosphere on subsequent combustion of the coal (Rogoff *et al.* 1960). However, this advantage is gained only at the risk of causing water pollution. It is estimated that the costs of preventing this pollution would be far greater than the costs of other methods of desulphurizing the coal or the flue gases resulting from its combustion.

Compared with this somewhat dubious advantage, the adverse effects of acidic and ferruginous mine drainages are many and are potentially serious. Some of these effects appear before the drainage is discharged, others appear in the environment external to the mine if the drainage is discharged in a contaminated condition. These effects will be considereed in turn.

ADVERSE EFFECTS WITHIN THE MINE, SPOIL HEAP OR COAL STOCK PILE

In mine workings, the most obvious effect of acidic and ferruginous mine drainages is the corrosion of equipment such as conveyors, roof supports, rails, chains, and steel ropes. These drainages also attack concrete and mortar, and paradoxically, although corrosive, often produce serious fouling of pumps, pipes, etc. with ochreous scale. Fortunately, acidic and ferruginous mine drainages do not contain substances which are particularly toxic to man and animals by ingestion, and do not seriously affect the skin, although clothing may be damaged by repeated immersion and drying. Drainage water contaminated by acidic and ferruginous salts is seldom suitable for use within the mine for purposes such as dust suppression, coal preparation etc.

In spoil heaps, the conditions which lead to the formation of acidic and ferruginous drainages are often directly associated with the fertility of the surface layers of the heap. A solution to a soil fertility problem will normally solve an acidic and ferruginous drainage problem. Ferruginous drainages may deposit ochreous scale in gravel and pipe drains within and beneath a spoil heap and thus affect the mechanical stability (Fischer 1970).

Apart from the obvious difficulties of disposal of a contaminated drainage discharge, acidic conditions within a coal stock pile do not pose immediate problems although concrete underlying a stock pile may be attacked, particularly if the concrete is of low quality. Acidic conditions in a coal stock pile often first reveal themselves by the corrosion of bunkers and fuel-handling equipment when the coal is subsequently utilized.

After the removal of an acidic coal stock pile which has been lying on natural ground, the quality of the surface drainage recovers rapidly provided that the coal and any inferior coal 'carpet' has been completely stripped, the sub-soil well limed, and the top soil replaced.

THE EFFECTS OF DISCHARGES OF ACID AND FERRUGINOUS MINE DRAINAGES ON MUNICIPAL SEWERS

In the United Kingdom, the discharge of acidic and ferruginous drainages to municipal sewers is not a common practice, but, providing that the drainage can be accommodated, certain compensatory beneficial effects may be obtained. In making a discharge to a sewer it is necessary to ensure that sufficient dilution is available to avoid damage to the fabric of the sewer by acids and sulphates, and to avoid interference with the biological sewage treatment processes. Provided that these limitations can be overcome, acidic and ferruginous mine drainages can have the beneficial effects of forming flocs which assist the sedimentation and filtration processes and may precipitate phosphates from the sewage (Benoit *et al.* 1971).

THE POTENTIAL EFFECTS OF ACIDIC AND FERRUGINOUS MINE DRAINAGE DISCHARGES ON RIVERS, STREAMS, CANALS, LAKES AND THE SEA

The effects of acidic and ferruginous mine drainage discharges to surface waters depend on the quality of the drainage, the quality of the receiving water and the relative dilution. The principal pollutants in acidic and ferruginous drainages from coal mines are suspensions of ferric oxide (ochre) and dissolved iron, aluminium, manganese, calcium and magnesium sulphates, and possibly free sulphuric acid. Low concentrations of the heavy metal salts of copper, nickel, zinc etc. may also be present. All of these potential pollutants are present naturally in surface water courses in the geologically exposed coalfields so that the biological systems in the receiving waters have acquired a considerable tolerance. The possible effects of these drainages will be considered under three headings.

The effect on the aesthetic value of the surface water

The principle visual effect of an acidic and ferruginous mine drainage on a surface water is the deposition of the hydrated ferric oxide, ochre, (also known as 'yellowboy' in North America). Chemically-deposited ochre is a pigment of considerable covering power, and as little as 1 mg/l (as Fe) in a stream will cause visible staining of the bed and the accumulation of opalescence in pools.

Discharges of mine drainage containing a few mg/l of iron to still waters such as canals and lakes may acumulate to produce visible coloured patches and opacity of the water. Discharges of ferruginous mine drainages to estuaries are seldom visible because of the naturally suspended silt in such waters, and discharges to coastal waters are similarly seldom perceptible provided that the rate of discharge does not exceed about 100 kg of iron a day at any one point.

In general, the discoloration of surface water by ochre does not produce a favourable reaction from a riparian owner or from the public, although some of the contaminated waters are quite spectacular and have been known to attract visitors.

It is not possible to assess objectively the loss of aesthetic value of a surface water contaminated by ochre.

The effects on the utilization of a surface water

Surface waters may be required for a wide variety of purposes including agriculture, industry and public supply, and recreation, including bathing. Acidic conditions in a surface water, as indicated by a low pH value, must be considered to reduce the value of the water for all these purposes. In the absence of acidic conditions, the neutral salts such as sulphates etc. may also be detrimental. Particular instances of this are the effects of sulphates on concrete structures such as cooling towers, the effect of magnesium salts in the drinking water of cattle, etc. Iron and maganese compounds are detrimental to industrial activities such as paper making and laundering and may increase the costs of treatment of water for public supply.

The effects on the biology of a surface water

The biological effects of an acidic and ferruginous mine drainage discharge are complex and not amenable to completely rational analysis. High concentrations of the acidic drainages are toxic to all normal forms of surface water-life, but in the absence of the mineral acid component, the other contaminants may have a less severe effect than the discoloration by ochre would suggest. It has been shown that the acute toxicity of aged ferric hydroxide is highly problematical and would be in the range of thousands of mg Fe/l (Sykoraj *et al.* 1972) and a fishery has been maintained in a strip mine pond, despite the presence of iron in concentrations from 0·16 to 11 mg/l by the application of lime to maintain a pH value greater than 6 (Davis 1971).

Many accounts of the effects of acidic mine drainages on surface waters have appeared in the technical literature (Weaver & Nash 1968; Herricks & Cairns 1972; Riley 1960; Dugan *et al.* 1968) but little attention has been given to the effects of the alkaline or ferrous bicarbonate type of discharge which is more common in the United Kingdom.

Experiments to determine the effects of specific components of acidic and ferruginous mine drainages on different types of water in the laboratory are seldom conclusive but may help to elucidate some of the observations made in the field. Free mineral acids, as indicated by low pH values, are probably the most toxic components involved (Anon. 1968; Lloyd & Jordan 1964). It has been shown that four species of bacteria used as test organisms should be able to grow at pH values greater than 5·3, in sulphate concentrations up to 500 mg/l and in iron salt concentrations up to 100 mg/l (McCoy & Dugan 1968). Tests over a full generation of juvenile brook trout revealed a trend towards slower growth in increasing concentrations of suspended ferric hydroxide, but egg viability was high in all concentrations except 50 mg/l. Similar tests on fathead minnows showed that the highest concentration of suspended iron which did not seem to affect survival and growth was below 12 mg Fe/l. The safe concentration for reproduction and growth of Gammarus minus larvae was less than 3 mg Fe/l (Sykora *et al.* 1972). Aluminium both in solution and in the form of freshly precipitated suspensions seems to be particularly toxic. A recent report indicated that the maximum safe concentration was 0·1 mg/l to trout, and that concentrations of 1·5 mg/l could be fatal to trout (Freeman & Everhart 1971).

The ferrous salts in mine drainages do not usually have a significant effect on the dissolved oxygen content of a surface watercourse, mainly because 1 mg/l of dissolved oxygen will oxidize 7 mg/l of dissolved ferrous iron, and the rate of oxidation of ferrous iron falls rapidly with a slight fall of pH value, being negligible at pH values (about 5·5) at which the biological life is not seriously disturbed.

Prevention of the formation of acidic and ferruginous mine drainages

Prevention of the formation of an acid and ferruginous mine drainage is basically simple. Either the source of the drainage water can be cut off, contact between the water and the contaminating pyrite oxidation products can be cut, or production of the pyrite oxidation products can be prevented. Ideally, these principles should be adopted in the planning of a mining operation but, in practice, circumstances seldom permit complete control by any of these methods which are discussed below in general terms. A more detailed review of these methods of control has recently been published (Anon. 1971a).

STOPPING OF DRAINAGE WATER AT THE SOURCE

It is almost impossible to prevent surface water from entering underground strata, particularly strata which have been fractured by mine workings (Zaval & Robins 1973; Anon. 1972; Hill & Martin 1972). Occasionally, it may be possible to identify and seal surface fissures, abandoned adits, auger holes etc. and it may be possible to pump from, or to drain, aquifiers, but to attempt to prevent strata water from running into a mine working would usually be expensive and dangerous.

It is not possible to prevent natural precipitation from falling on to surface mine workings, spoil heaps and coal stock piles.

PREVENTION OF CONTACT BETWEEN DRAINAGE WATER AND PYRITE OXIDATION PRODUCTS

Since the majority of the water which flows from the strata into underground mine workings is relatively uncontaminated, it is advantageous to trap this water, if possible, at the point of entry, and to convey it directly from the mine. Unfortunately, the geological conditions in coal-bearing strata are seldom favourable, and it is more usual for water to penetrate the workings in the form of 'drippers' which cannot be trapped.

Contact between drainage water and pyrite oxidation products in spoil heaps can be controlled. In the extreme, water-tight covers of plastic or tar can be placed over the surface of a heap. Such seals seldom last for more than a few months or years due to the action of the weather or to vandalism, and cannot be considered to provide more than a temporary solution. Hydraulic seals which are efficient and permanent can be obtained by placing a layer of well compacted, low permeability spoil on the surface of the heap, but secondary problems of erosion may then be encountered. To control erosion, a comprehensive surface drainage system, with particular attention to the surface contours may be required, and this may involve considerable regrading of an existing heap. It is normally necessary to place a top layer of fertile soil stabilized with vegetation on the outer surface of a heap which has been covered with an impermeable layer of spoil in order to control erosion and the disruptive effects of frost, etc.

Contact between drainage water and pyrite oxidation products in coal stock piles can be controlled by plastic film or tar covers, subject to the limitations previously described. Such covers have other beneficial effects, including partial or complete control of spontaneous combustion and may be highly profitable if their use permits the construction of deeper stock piles than would otherwise be possible (Hall 1967; Kenyeres & Takacs 1972).

PREVENTION OF THE OXIDATION OF IRON PYRITE

It is tempting to think that it should be possible to control the rate of oxidation of pyrite in air by the application of some form of inhibitory reagent, possibly a biological control agent. Various attempts to find such a reagent have been reported but none has been shown to be effective in full scale use. Reagents such as chromates and ammonia have had no effect on acidic drainages running from abandoned mine workings (Braley 1956). Research into the development of a phage for ferrous oxidizing bacteria (Shearer *et al.* 1968) was apparently not successful. Later it was claimed that oxidation could be inhibited by strains of Caulobacters (Shearer *et al.* 1970). This report also discussed the use of 15 different antibiotics, three of which were effective, and the antibiotic-producing species, *Streptomyces aureofaciens*.

Assuming that the oxidation of pyrite cannot be prevented by an inhibitory reagent, it is necessary to consider the possibility of controlling the oxidation by restricting the access of oxygen to the pyrite. During the course of active mining operations it is not possible to prevent air from coming into contact with pyrite in underground mines which are ventilated with air in order to support life.

In an attempt to prevent the oxidation of pyrite, an underground mine is to be operated in the U.S.A. in a sealed condition without ventilation, the miners being supplied with air by individual life-support systems (Anon. 1970). It is unlikely that such systems will be economically viable in Great Britain because of geological difficulties.

Although it is not possible to prevent pyrite oxidation during the active phase of underground mining, it may be possible to control the air supply to the worked-out parts of a mine which are no longer required and there is an even better chance of restricting the air supply when the whole mine, or possibly a group of adjacent mines have been abandoned. Methods of cutting off the air supply, in order of effectiveness, are:

to flood the workings completely,

to fill depressions in connecting tunnels, adits, etc. with water,

to construct air-tight masonry seals in tunnels, shafts, adits etc.

The flooding of workings will often occur naturally once pumping ceases provided that the workings are below the local water table. In order to flood workings above the water table, it would be necessary to construct hydraulic seals, a practice which is seldom feasible due to the low strength of coal-bearing strata, except when very low hydraulic pressures are involved (Foreman & McLean 1973).

Flooding effectively prevents further oxidation of pyrite, but dissolves any pyrite oxidation products which may have formed previously so that it may be necessary to deal with a problem of contaminated water disposal should the flooded workings overflow.

Seals formed by the flooding of depressions and masonry seals may be effective provided that the surrounding strata is undisturbed. However, if the workings are at a shallow depth below the surface, it is seldom possible to prevent the ingress of oxygen through fractures caused by the breathing effect of changes in the atmospheric pressure (Hill & Martin 1972; Braley 1962; Moebs & Krickovic 1970).

It is not possible to control the oxidation of pyrite in surface mine workings, and this is one of many reasons for the method of surface mining used in the United Kingdom which involves rapid extraction of the coal followed by complete restoration of the original site.

The oxidation of pyrite in spoil heaps can be controlled by the use of sealing layers as previously described for the control of water penetration. In order to prevent completely the ingress of oxygen, it may be necessary to ensure that an earth seal is not allowed to dry out. A highly compacted spoil will normally contain about 20% of voids which will be water-filled at the time of placing. The permeability of such a material to oxygen will be negligible, but if the water is displaced by drying, the permeability to oxygen will increase appreciably. However, even though some pyrite may become oxidized in this way, it is unlikely that the rate of leaching of the oxidation products in subsequent wet weather would be significant. Should it be considered necessary to avoid drying out of the surface layers of a spoil heap, large, deep-rooted plants should not be allowed to propagate, particularly on parts of a heap, e.g. steep slopes which do not receive or are unlikely to absorb, a normal proportion of the rainfall.

The oxidation of pyrite in stock piles of graded coals cannot normally be prevented, although the access of air can be reduced by the application of plastic or tar films to the pile. It may be possible to reduce the rate of oxygen penetration into stock piles of the finer grades of coal by heavy compaction.

The purification of acidic and ferruginous mine drainages by treatment

Should it be impracticable to prevent the formation of an acidic and ferruginous drainage in a mine, spoil heap or coal stock pile, it may be necessary to resort to treatment of the drainage before discharge. Technically, these drainages can be treated to any required quality standard, but it should be recognized that the costs of treatment could be so high as to render the continued operation of the mine uneconomic.

The type of treatment required will depend on the quality of the drainage and the standard to which it is to be purified. For the purposes of discussion, methods of treatment suitable for different types of acidic and ferruginous drainages will be considered individually, and finally, certain less orthodox methods of treatment suitable for various types of mine drainage will be described.

DRAINAGES CONTAINING FREE ACID AND INSIGNIFICANT CONCENTRATIONS OF IRON SALTS

Shallow underground mine workings which are well ventilated may provide conditions in which most of the iron originally dissolved from pyrite is deposited leaving essentially a dilute solution of sulphuric acid. Such drainages are almost unknown in the United Kingdom. It is possible to treat such drainages simply by the addition of an alkali such as lime or limestone. Automatic plants have been installed for the treatment of this type of drainage in remote districts in Pennsylvania (Charmbury *et al.* 1968).

DRAINAGES WHICH ARE ACIDIC AND ALSO CONTAIN SIGNIFICANT CONCENTRATIONS OF FERRIC IRON

Drainages from well-ventilated underground mine workings, spoil tips and some coal stock piles may contain ferric iron in solution in concentrations up to a few thousand mg/l. The pH value of such drainages must be less than about 3·5 in order to maintain the ferric iron in solution. Drainages of this type are also relatively uncommon in the United Kingdom.

Treatment by lime neutralizes the free acidity and causes the ferric salts to precipitate as a floc of ferric oxide hydrate. The precipitation is rapid and is effective in giving a neutral supernate of low iron content, although the coagulation of the flocs becomes progressively more difficult the lower the initial iron concentration of the drainage. Lime treatment involves relatively high reagent costs, problems of dosage control, and produces a waste sludge of high water content.

Limestone may be used for the treatment of this type of drainage with the advantage of lower reagent cost, simpler dosage control and more dense sludge. The limestone must either be very finely divided, or mechanically scrubbed during the reaction in order to remove a scale of reaction products. Limestone processes are not generally applicable if the sulphate content of the drainage exceeds about 5,000 mg/l, as SO_4 (Wilmoth & Hill 1970; Lovell 1971; Glover 1967).

DRAINAGES WHICH ARE ACIDIC AND CONTAIN FERROUS SALTS IN SOLUTION

Drainages of this type may be discharged from mine workings, spoil heaps and coal stock piles and although they represent only a small fraction of all discharges from coal-mining operations in Great Britain, a few examples can be found in each coalfield, particularly in association with coals of high (e.g. more than 3% as S) sulphur content. The iron content of such drainages may be as high as 5,000 mg/l (as Fe), and the pH values may be as low as 1·5, although the flow rates of the more contaminated drainages are usually proportionately reduced. These drainages are also liable to contain appreciable concentrations of aluminium and manganese salts and trace concentrations of copper, nickel, zinc etc.

In assessing the type of treatment needed for this type of drainage, it is necessary to measure not only the free acidity revealed by the pH value, but also the concealed acidity due to the aluminium and ferrous components of the drainage which are not indicated by the pH value. For this purpose, the effective acidity can be measured by titration with sodium hydroxide at the boiling point to phenolphthalein. The acidity value so determined is a measure not only of the effective acidity of the drainage from the point of view of treatment, but also of the real alkali demand which the discharge would exhibit if it were to be discharged to a surface water.

These acidic-ferrous drainages are all amenable to treatment by lime as previously described for acidic-ferric drainages, but the sludges produced are liable to be even more voluminous. For example, the treatment by lime of a discharge of 1 m gal/day containing 1,000 mg/l of dissolved ferrous iron would produce about 100,000 to 200,000 gal/day of sludge. In lagoons such sludge would consolidate over a period of several months to a volume of about 50,000 to 100,000 gallons. The de-watering of such sludges is often difficult and expensive, for example, mechanical filtration could cost up to £5/ton of dry solids. Various methods for increasing the density of lime-precipitated sludges have been described, most of which are based on the principle of sludge recirculation to the point of neutralization (Streeter *et al.* 1971; Kostenbader & Haines 1970; Moss 1971). Whenever possible, lime-precipitated sludges are discharged to abandoned mine workings, but the number of such workings to which disposals can be made safely is very limited in the United Kingdom. The costs of treatment of acidic-ferrous drainages by lime are in the range £0.2 to £3/1,000 gallons treated.

Provided that the sulphate content does not exceed about 5,000 mg/l (as SO_4) the acidic-ferrous mine drainages can be treated by limestone as previously described. Ferrous salts will not react directly with limestone, and must be oxidized to ferric salts before a reaction will occur. The cheapest available oxidizing agent is atmospheric oxygen, but unfortunately the rate of oxidation of ferrous salts by air is negligible at pH values of less than about 5·5. In order to use limestone for treatment of drainages containing acidic ferrous salts it is thus necessary either to introduce air with the limestone and to agitate the mixture for periods of up to several hours (Hill 1969; Anon. 1971b), or to oxidize the ferrous salts whilst still acidic by the use of a catalyst. Reagents which have been proposed for this purpose include activated carbon (Ford & Boyer 1973) and gamma rays (Steinberg & Pruznsky 1970), ozone (Beller *et al.* 1970) and electrolysis (Jasinski & Gaines 1972). It is also possible to oxidize ferrous salts in acidic solutions by biochemical means using ferrous oxidizing bacteria (Glover 1967; Whitesell *et al.* 1971; Ueta *et al.* 1972). These bacteria are normally present in acid mine drainages and can be propagated, preferably in an activated sludge type of process, to cell counts sufficiently high for the oxidation of hundreds of mg/l of ferrous salts in a few hours at normal atmospheric temperatures. The overall costs of limestone processes with appropriate ferrous oxidation stages are estimated to be about one half of the equivalent costs of treatment by lime.

DRAINAGES WHICH ARE CHEMICALLY NEUTRAL BUT CONTAIN DISSOLVED FERROUS IRON

Drainages of this type are discharged almost exclusively from the deeper underground mine workings and are the most common form of ferruginous mine drainage in the United Kingdom, although rare in North America because the mine workings are less deep. The iron salts in these drainages originate from the acidic oxidation products of pyrites, which have been neutralized by strata water containing sodium bicarbonate, and by carbonate and clay minerals. These drainages may contain ferrous iron in concentrations up to about 400 mg/l (as Fe) which is present effectively as ferrous bicarbonate ($Fe(HCO_3)_2$). The principle chemical characteristic of these drainages is that on aeration, all the ferrous salts are converted into the insoluble ferric form which precipitates as hydrated ferric oxide (ochre). An efficient and relatively low cost treatment process can thus be based on the use of a series of sedimentation basins with a cascade between each basin. Provided that a suitable site can be found, earth-walled basins can be used and treatment costs may be as low as 5 to 20p/1,000 gallons of water treated. The sludge formed by this method of treatment is of relatively high density and is fairly permeable so that it can be dredged and discharged to a spoil heap without much difficulty. Should it not be possible to construct basins, a more compact plant involving mechanical aeration and filtration may be necessary, the capital and operating costs of which could rise to £1,000 gallons of drainage treated.

DRAINAGES CONTAINING FERRIC IRON IN SUSPENSION

Mine drainages may contain ferric iron in the form of the hydrated oxide (ochre) either alone, or in combination with the dissolved ferric and ferrous salts as previously described. Suspensions of ferric oxide are not normally present in drainages from immobile sources such as abandoned mine workings, spoil heaps, coal stock piles etc. but are fairly common in drainages from active mines where physical disturbances may be present.

Treatment necessary for the removal of dissolved iron will incidentally remove suspended ferric oxides without a significant increase in costs. Drainages containing only ferric oxides can be treated by sedimentation, possibly with added flocculants, at a cost of up to 25p/1,000 gallons in earth-walled lagoons, and up to £1/1,000 gallons in mechanical plant.

UNCONVENTIONAL TREATMENT PROCESSES

A wide range of what may be termed unconventional treatment processes have been tested in recent years and a few are used in the U.S.A. on the full scale:

Reverse osmosis

This process which involves the application of hydraulic pressure to the drainage contained in semi-permeable membranes is applicable to the treatment of the less contaminated acidic and ferruginous mine drainages (Sleigh & Kremen 1971; Mason & Gupta 1972). The disadvantages, apart from the high capital and operating costs are that a concentrated acidic waste may be produced which will still require treatment. An advantage is that a potable water product can be produced, so that, in areas of water shortage, receipts from the sale of water may offset the costs of treatment. No full-scale plant has so far been constructed.

Flash distillation

This process involves the distillation of the drainage under reduced pressure.

Comments similar to the reverse osmosis process are applicable. Although taken to an advanced design stage in Pennsylvania (Maneval & Lemezis 1972) no full-scale plant based on this process has been constructed.

Freezing

It is possible to purify acidic and ferruginous mine drainages by selective freezing (Anon. 1971c). Process evaluation tests have not reached the stage at which cost estimates can be made. It is also possible to de-water, by freezing, the hydroxide sludges produced from alkali treatment of acidic and ferruginous mine drainages, but the costs are high (Streeter *et al.* 1971).

Ion exchange

Various processes involving the use of liquid or solid ion exchange resins in more or less complicated chemical systems have been developed (Holmes & Kreusch 1972). Advantages over some of the other less conventional processes are that the waste products may be produced in solid form and may have a market value. Two full-scale plants have been commissioned (Zaban *et al.* 1972).

Solvent extraction

It is possible to remove iron and other contaminants from mine drainage by the use of organic complexing reagents and solvent extraction, but the costs of such processes would generally be too high to be practicable.

Biochemical reduction

It is possible to cultivate in an acidic and ferruginous mine drainage, after appropriate correction of the pH value, sulphate reducing bacteria, which will produce sulphides, which will in turn precipitate the dissolved iron salts (Dugan *et al.* 1968). It is even possible to form magnetic sulphides by such a process (Freke & Tate 1961). It is considered that corrosion problems due to sulphides, the need to maintain anaerobic conditions and relatively high operating temperatures would lead to very high costs of treatment. No full-scale treatment plants have been constructed.

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Summary

The origin and potentially polluting effects of acidic and ferruginous drainages from coal mines, spoil heaps and coal stock-piles are described. Procedures available for the control of contamination at the source and for the treatment of these drainages are reviewed.

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