TREATMENTS TO COMBAT PYRITE OXIDATION IN COAL MINE SPOIL

C.A. Backes, I.D. Pulford, and H.J. Duncan[1]

Abstract. Oxidation of pyrite and its inhibition by
various waste materials were studied using pyritic
spoil from Central Scotland, with the aim of develop-
ing procedures to prevent reacidification after the
initial treatment. It had previously been shown
that the rate of pyrite oxidation could be decreased
by complexing or precipitating the iron species in-
volved. Analysis of leachate from a set of lysi-
meters showed that the rate of pyrite oxidation in-
creased with the onset of warmer weather, but was
greatly reduced during winter. A controlled tempe-
rature incubation experiment investigated the inhi-
bition of pyrite oxidation by chicken manure or coni-
fer bark at 0, 8, 18 and 30°C. There was no signifi-
cant pyrite oxidation in the limed spoil. In the un-
limed spoil more oxidation occurred at 18 and 30°C
than at 0 and 8°C. Conifer bark reduced the rate of
pyrite oxidation at all temperatures, and at 18°C it
reduced it to that found at the lower temperatures.
Chicken manure completely inhibited acid and iron pro-
duction at all temperatures. A small field trial
investigated the use of chicken manure, conifer bark,
sewage sludge, and oil shale waste in conjunction with
lime to inhibit the rate of pyrite oxidation. The
plots were seeded with grass, and vegetation yield
and spoil characteristics measured. These plots are
being continued, to study the long-term effects of
the amendments on pyrite oxidation.

INTRODUCTION

Pyrite is present in many of the
colliery spoil heaps (bings) in Central
Scotland, and is the major obstacle to
their reclamation. Acidic spoil, resul-
ting from the oxidation of the pyrite, is
traditionally neutralised by the addition
of lime. However, after a few years bings
suffer from acid regeneration, as the lime
is leached out and more pyrite oxidises.
The reacidification tends to occur in loca-
lised areas as the distribution of pyrite
in a bing is seldom homogeneous (Backes
1984). These acidified areas tend to
spread, killing any established vegetation.

Many bings receive only the initial
reclamation treatment and, even when large
quantities of lime are added in an attempt
to account for potential acidity, either
in one or a number of applications, the
bings still tend to suffer from acid
regeneration. Doubleday (1974), for
example, found that four applications of
limestone totalling 100 t/ha over a two-
year period were inadequate to neutralise
the acidity of one spoil; Costigan et al.
(1981) found spoils limed at either 50 or
100 t/ha which reacidified after one or two
years. Some bings do receive aftercare,

[1]C.A. Backes is a Post-Doctoral Research
Assistant, I.D. Pulford a Lecturer and H.J.
Duncan a Reader, Agricultural Chemistry
Section, Chemistry Department, University
of Glasgow, Glasgow G12 8QQ, Scotland, U.K.

especially if they are to be used for agricultural purposes. In these cases it may be possible to apply additional lime to small areas of the bing as they reacidify, to neutralise the acid and inhibit the spread of pyrite oxidation. However, it would be preferable if there were one initial treatment, which not only neutralised the acid already present in the bing, but also prevented further reacidification of the spoil. This paper proposes such treatments.

There are two main pathways for pyrite oxidation, either using oxygen or ferric ions as the oxidising agent. Above about pH 4.5 oxidation will only occur by the oxygen pathway. This is a relatively slow process and does not produce large quantities of acid. However, if the pH falls to below 4.5 then ferric ions act as an oxidising agent on pyrite. The ferric ions are produced by the bacterially catalysed oxidation of ferrous ions, which are liberated from the pyrite. This leads to a cyclic system, in which ferrous ions are bacterially oxidised to ferric ions, which are then reduced by their action on pyrite back to ferrous, simultaneously releasing more ferrous ions from the pyrite. This is a much faster reaction than oxidation by oxygen, leading to a rapid release and build-up of acid. Backes, Pulford and Duncan (1986, 1987) showed that the ferric ion oxidation pathway could be inhibited by the use of specific chemicals to interfere with the cycling of iron. Phosphates and silicates were used to precipitate the iron, whilst citrates were used to complex it. Use of a bactericide stopped the production of ferric ions by the action of <u>Thiobacillus ferrooxidans</u>. These studies, which were carried out in suspensions of pyritic coal waste, showed that the treatments restricted the oxidation pathway to that by oxygen alone, so decreasing the rate at which acid was released. Waste materials were also used to inhibit the oxidation of pyrite by ferric ions. Chicken manure and chopped conifer bark both complexed the iron, while pulverised fuel ash (a source of silicate) precipitated it. The work reported here extends these laboratory studies on waste materials into controlled pot and field studies.

METHODS

Pyritic spoil was obtained from Baads Colliery, West Lothian (Ordinance Survey of Great Britain ref NT 002609), and all field work was conducted on this site. The pyritic content of the spoil had been previously measured as ranging from 0.07 to 2.92%, using the method of Dacey and Colbourn (1979). However, lumps of pyritic material could easily be found in the field which contained up to 75% FeS_2. The heterogeneity of pyritic spoil has been discussed by Backes (1984). Baads bing was originally reclaimed in 1979, when the lime requirement was 25 t/ha to account for existing acidity plus 25 t/ha for potential acidity. Large areas of the bing have since suffered from severe acid regeneration.

Field Lysimeters

A series of lysimeters was set up in the field in February 1987, five containing pyritic spoil and two with nonpyritic spoil as the controls. Each lysimeter had a volume of $0.01m^3$ and was imbedded into the surrounding spoil. The leachate was collected weekly and filtered through Whatman's No. 1 filter paper. It was analysed for pH, titratable acidity by titration with sodium hydroxide to phenolphthalein end point, and total soluble iron by atomic absorption spectrophotometry. The weekly rainfall, and maximum and minimum air temperatures were also noted. Any rain which had not penetrated the spoil was discarded (this occurred only after very heavy rainfall).

Controlled Temperature Incubation Study

Bags of pyritic spoil, previously air-dried and sieved through a 4 mm sieve, were placed at four different temperatures; 0, 8, 18 and $30^{\circ}C$. After a few days, when the spoil had equilibrated, it was used to prepare a series of pots for each temperature. To four replicate pots of 500 g spoil, the following were added: no addition (control); 15 g lime (equivalent to 15 t/ha, the nominal lime requirement); 60 g chopped conifer bark (60 t/ha); 50 g chicken manure (50 t/ha); conifer bark plus lime at the above rates; chicken manure plus lime at the above rates. The spoil and amendment were thoroughly mixed before being placed in a pot. All sets of pots were returned to their original temperature and watered regularly to maintain them at near field capacity. At intervals, all the pots were leached with 100 cm^3 distilled water, and the leachate filtered and analysed as for the lysimeter study.

Field Study

Small plots (2 m by 2 m) were prepared on the area of the bing that had suffered the most severe acid regeneration, where all the vegetation had been destroyed. All plots, apart from the controls, were treated with lime at 15 t/ha and one of the following: chicken manure at 25 t/ha, sewage sludge at 20 t/ha, conifer bark at 60 t/ha, conifer bark at 30 t/ha, oil shale waste at 50 t/ha. One plot was left as lime only. The amendments were incorporated into the top 15 cm of spoil. All treatments were replicated three times in a randomised block design. The area was then fertilised (300 kg/ha of 15:10:10 NPK compound fertilizer) and seeded with an agricultural grass mix (100 kg/ha). The plots were sown in August 1986, and at the beginning of the next spring they were refertilized. The grass was harvested in 1987, and its yield measured. The spoil

of each plot was sampled in duplicate and analysed for pH (1:2.5 spoil:water) and water-extractable iron.

RESULTS AND DISCUSSION

Lysimeter Study

The rate of acid and iron production in the lysimeter study reflected the rate of pyrite oxidation (figs 1, 2). The cumulative rate was obtained by multiplying the weekly rainfall by the concentration of acid or iron and then summing over the appropriate weeks. Although the spoil for all the pyritic lysimeters was obtained from a small area, the quantity of acid and iron produced varied considerably, reflecting the heterogeneity of the pyritic content of the spoil. Initially the rate of oxidation was very slow, but between weeks 14 and 16 (at the end of May) the rate increased dramatically. The limits of the change of rate were shown in lysimeters 1 and 5; the rate of acid production per lysimeter changed from 7 µg H^+ per week to 136 µg H^+ per week in lysimeter 1 and from 11 to 60 µg H^+ per week in lysimeter 5. The rate of iron production changed from 75 µg Fe per week to 1900 µg Fe per week for lysimeter 1 and from 54 µg Fe to 500 µg Fe per week in lysimeter 5. This increase in rate occurred in all the lysimeters (apart from the controls) over the same two-week period; the rate then stayed approximately constant for each lysimeter until week 32, when the rate decreased in all lysimeters. This increase and decrease in rate closely corresponded to the measured air temperature (fig 3). At week 16, the weekly minimum temperature began to rise above $0^{\circ}C$, whereas the maximum temperature had begun to rise about week 9. The rate of acid production would probably correlate most closely to the average temperature, rather than the maximum or minimum. The approximately constant rate after week 16 would suggest that there was a rate limiting mechanism operating during the summer period. The solubility constant (Ksp(Fe) $(OH)_3$ for ferric hydroxide ranges from 4 x 10^{-38} to 2.7 x 10^{-39}, depending on which form of hydroxide precipitates. During the summer period the leachate was supersaturated with respect to these oxides, suggesting that one of these forms was controlling the concentration of iron in solution, and thus limiting the rate of pyrite oxidation. Other iron compounds can precipitate, such as jarosite and a large number of intermediate iron products, whose solubility would be greater than that of the hydroxides. It would depend on the exact local conditions as to which iron compound precipitated (Nordstrom 1982). In the colder period, the leachate was supersaturated with respect to the stable iron oxides, but not so with respect to the more amorphous oxides. As it would be expected that the amorphous oxides would precipitate in this situation, it seems
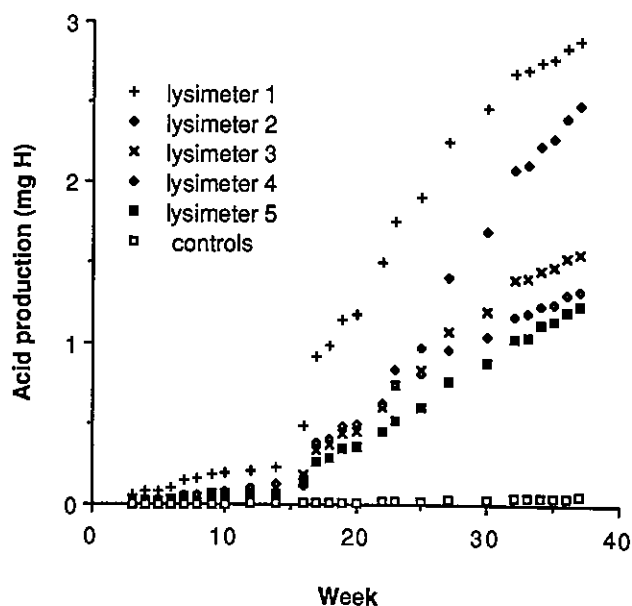

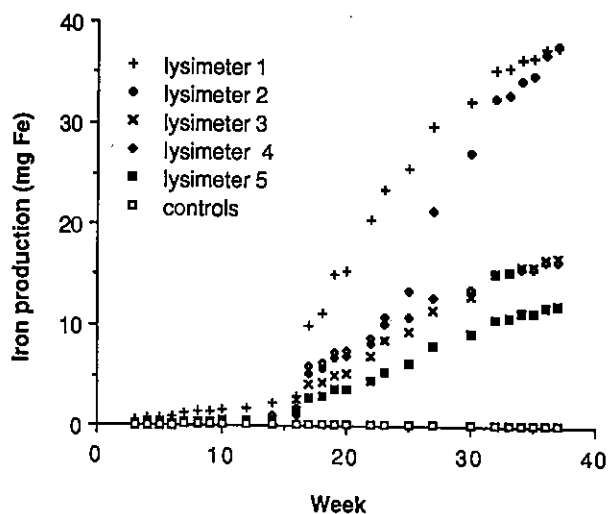
Fig 1. Cumulative acid production in lysimeters.

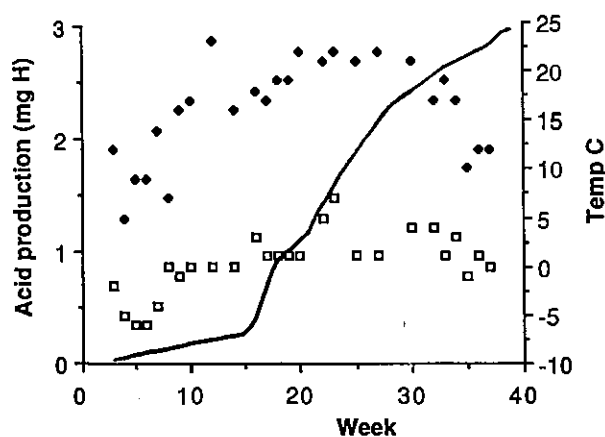Fig 2. Cumulative iron production in lysimeters.

Fig 3. Relationship of acid production to air temperature (lysimeter 1, maximum T, minimum T).

that in the cold period precipitation of ferric ions was not occurring and thus not rate limiting. Apart from the precipitation of an iron hydroxide, there are three other factors which can limit the rate of pyrite oxidation by ferric ions in the field. The rate limiting step in the oxidation pathway can be either the bacterial oxidation of ferrous to ferric ions, or the actual ferric ion oxidation of pyrite, or the surface area of the pyrite available for reaction with the ferric ions (Garrels and Thompson 1960, Bloomfield 1972, van Breemen 1973). As the rate of oxidation was much greater in the summer period than in the colder period, it would suggest that the last two mechanisms would not be rate limiting in the colder period, otherwise they would have decreased the summer rate. However, it is very probable that the rate of ferrous ion oxidation by Thiobacillus ferrooxidans was decreased due to the fall in temperature, or it is possible that this process was completely absent, restricting the oxidation of the pyrite to that by oxygen alone, which is a much slower process.

Controlled Temperature Incubation Study

The limed pots at all temperatures maintained a pH above 5.5. This high pH would restrict the rate of pyrite oxidation to that by oxygen alone, and therefore no conclusions can yet be drawn as to the effect of amendment and lime on the rate of pyrite oxidation from this study.

In the unlimed pots the rate of pyrite oxidation varied with temperature, although for the first 40 days, it was nearly the same at all temperatures. After this the rate of acid production was approxiamtely 16 μg H^+ per day at 18 and $30^\circ C$ and 6 μg H^+ per day at 0 and $8^\circ C$ (fig 4). The rate of iron production was 10 μg Fe per day at 0 and $8^\circ C$, 40 μg Fe per day at $30^\circ C$, and 70 μg Fe per day at $18^\circ C$. (Only results for acid production are presented graphically as the overall trends were the same for acid and iron). This was not such a marked difference in rate between temperatures as had occurred in the lysimeter study.

The conifer bark reduced the rate of pyrite oxidation at all temperatures, and at $18^\circ C$ it reduced it to the rate at the lower temperatures (figs 5, 6, 7). The chicken manure completely inhibited the rate of acid and iron production at all temperatures (figs 6, 7, 8).

After day 155, the pots at 0 and $8^\circ C$ were moved to 8 and $18^\circ C$ respectively to simulate the rise in temperature occurring in the field. The pots at $18^\circ C$ were not moved as it is only rarely that the spoil would maintain a temperature above this in the field in Scotland. The pots at $30^\circ C$ were indicative of the maximum acid and iron production, although more iron was actually produced in the $18^\circ C$ pots (lime-only pots). There was no discernible change in the rate of pyrite oxidation in the 0 and $8^\circ C$ pots

when the temperature was raised to 8 and $18^\circ C$ respectively.

Conifer bark and chicken manure both complex iron (Backes 1984, Vaughan, Wheatley and Ord 1984), either by chelating it on to the solid material or by forming a stable complex in solution. Both these amendments decreased the rate of pyrite oxidation at all temperatures, presumably by complexing the iron and inhibiting the ferric ion oxidation of pyrite. The amendments could have been complexing the products of the pyrite oxidation, reducing the measurable amounts of acid and iron, leading to the false conclusion that the actual rate of oxidation was decreased. However, in view of the lysimeter results, it would seem that at least at the higher temperatures they were actually inhibiting the ferric ion oxidation of pyrite.
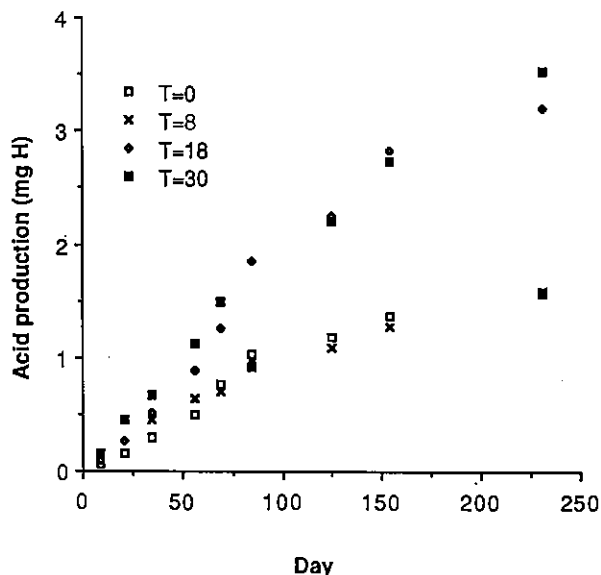
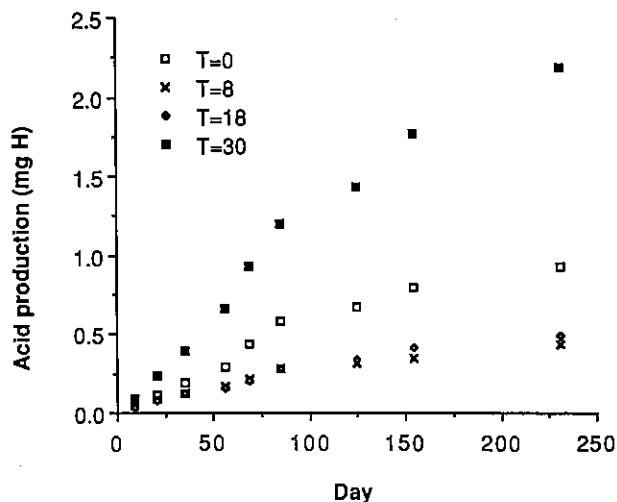Fig. 4 Cumulative acid production in control pots at all temperatures.

Fig. 5 Cumulative acid production in pots amended with conifer bark at all temperatures.
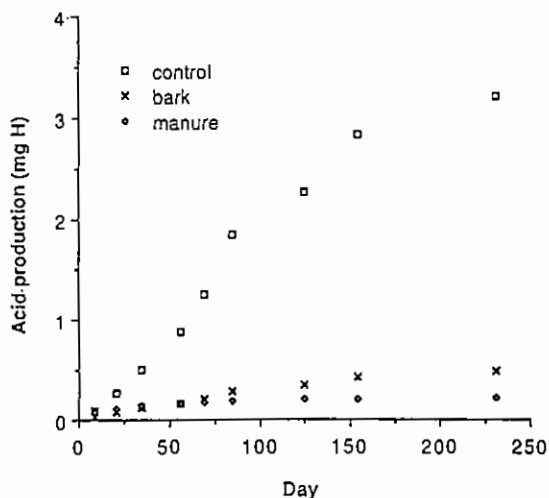
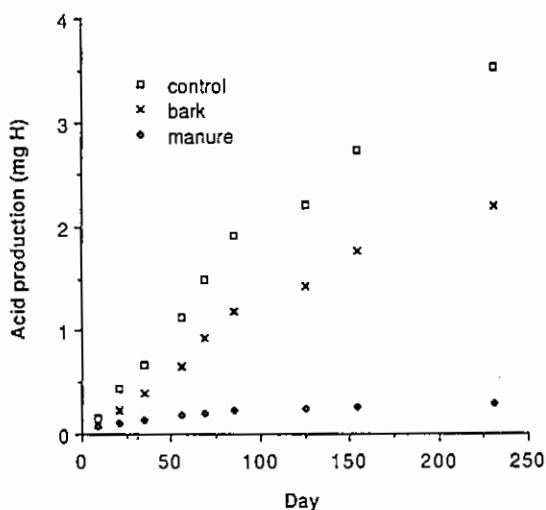Fig. 6 Cumulative acid production in unlimed pots at 18°C.

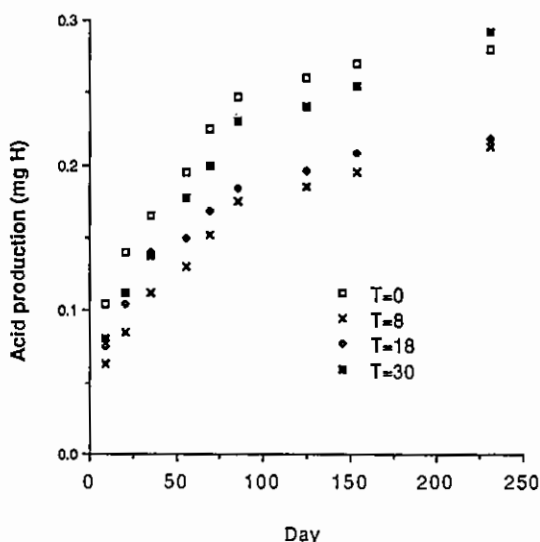Fig 7. Cumulative acid production in unlimed pots at 30°C.

Fig 8. Cumulative acid production in pots amended with chicken manure at all temperatures.

Table 1 : Vegetation yields on limed plots amended with various organic treatments, 1 year after establishment.

Treatment	Mean yield of vegetation (and s.d.) (g/m^2)
Chicken manure	374 (87)
60 t/ha conifer bark	321 (105)
Sewage sludge	320 (114)
30 t/ha conifer bark	286 (99)
Lime only	262 (56)
Oil shale	233 (28)

Field Study

After one year the pH of spoil in all the plots, apart from the unamended controls, was above 6.5. There was a large variance in the yields from each treatment, which means that statistically the differences in yields were not significant (table 1). However, the general trend was that all the amended plots, except for those treated with oil shale, gave greater yields than those treated with lime alone. In the case of the sewage sludge and chicken manure plots, this may have been due to an added nutrient effect, but this would not be the case for the conifer bark plots. Therefore there was probably some beneficial effect occurring in terms of inhibition of pyrite oxidation. The oil shale waste was rather an inert material, and may require attack by acid before it releases silica. This field trial is being continued, so that when the added lime has been neutralised or leached out the effectiveness of the amendments at inhibiting pyrite oxidation in the field can be measured.

CONCLUSIONS

The preliminary results of this study point to ways of inhibiting the reacidification of colliery spoil. Any of these amendments would have to be added to an acidic bing in conjunction with lime, by incorporation into the plough layer, as otherwise the pH would be too low to allow for the establishment of vegetation. This would lead initially to the oxidation of pyrite being inhibited due to the high pH, as ferric hydroxide would precipitate and _Thiobacillus ferrooxidans_ would be inoperative. In time the effect of the lime would be reduced, as the slow rate of pyrite oxidation produced acid which would neutralise the lime, and as lime was leached out of the spoil. The amendments would then start to be effective, by complexing any iron that came into solution, thus restricting the oxidation of pyrite to that by oxygen alone. This should prevent the rapid reacidification of the spoil, allowing a vegetation cover to be established, which itself would act as a source of organic matter for the spoil. A continual supply of organic matter to the spoil would ensure that once the original amendment had been completely degraded

95

there would still be an iron complexing source available. The build-up of a vegetation cover would also restrict the infiltration of air into the spoil, thus decreasing the rate of pyrite oxidation further. If the amendments are added in the colder period of the year, it may help to ensure that all iron produced is immediately complexed, thus precluding the onset of rapid reacidification of the spoil.

ACKNOWLEDGEMENTS

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