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TREATMENT OF EARTH SURFACE AND SUB-SURFACE FOR PREVENTION OF ACIDIC DRAINAGE FROM THE SOIL

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5 Claims

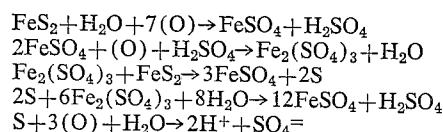
ABSTRACT OF THE DISCLOSURE

A method of lessening the rate and the extent to which sulfur compounds, e.g. pyrite and marcasite, are converted into corrosive acids which comprises applying a pulverized phosphate on the surface and/or admixing it with the top soil and rock material having sulfur-containing components therein which are contacted by water and especially which are also exposed to air especially in the presence of bacteria which accelerate the oxidation of the sulfur-containing component.

The invention encompasses a process of treating earthen and terranean materials more especially such materials in situ, e.g. earth strata, rocks, mine tailings, gob piles and the like.

Ingredients or components of the earth composing exposed and near surface strata and accumulated earth, rock, and mineral piles are frequently converted to acidic materials, which, when contacted with underground or surface water, render the water acidic. Sometimes, due to the gradient of the terrain or of subsurface impervious rocks comprising the water table, run-off waters and underground streams originating in or passing through, beneath, or lateral to an abandoned mine become acidified due to contact with acid-producing materials there present and as a result contaminate lower level areas, not only in the immediate vicinity, but also often those that are somewhat remote from the source of the acidification.

Acidification is largely a result of the presence of certain sulfur-containing compounds, e.g., sulfides of metals particularly of iron, of which FeS_2 is most common, when they are contacted by moving water, especially in the presence of oxygen and of bacteria which catalyze oxidation. Possible mechanisms of the acidification which occurs when water contacts FeS_2 in the presence of oxygen, and particularly when catalyzed by oxidation bacteria, may be represented by the following equations:



Among the strata wherein such conversion to acidic materials occurs are those associated with abandoned mines, e.g. coal mines and iron mines, especially rather shallow coal mines. Particularly bad effects occur due to acidification associated with drift mines, frequently located on a slope wherein drainage from the mine proceeds on down the slope and usually ultimately into a stream as a result of which significant portions of an entire river valley are contaminated. In such mines during disuse, the roof often caves in or at least partially subsides creating a natural depression which fills with water and serves as sort of sink from which the thus accumulated water percolates downwardly through layers of rock and earthen materials, onto the mine floor beneath, and subsequently down the hillside. During such percola-

tion the waters, particularly in the presence of air and more particularly in the presence of certain catalytic bacteria, convert sulfur-containing compounds present in the earth and rock, e.g. sulfides of Fe, Al, Mn, or the like, (illustrative of which as pyrite and marcasite, both substantially FeS_2) to iron sulfates which are subsequently hydrolyzed to H_2SO_3 and H_2SO_4 . In various areas, as of Appalachia in the United States and particularly in the Ohio River watershed for example, stream pollution from this source has become seriously damaging. Fish and game as well as vegetation and domestic water supplies are suffering seriously from such acid contamination. The above areas are suffering particularly, not only because of the large number of abandoned mines and the presence of the sulfur-containing rock, but because these areas receive a relatively high annual rainfall.

The seriousness of the acidification of mine waters has become so pronounced that recently the Director of the United States Bureau of Mines has appeared before the Congress of the United States to report on the status of the problem and to discuss the urgent need for abating such acidification.

To illustrate the seriousness of the situation in the areas above mentioned, there are an estimated 14,000 abandoned coal mines in the Ohio River Watershed from which millions of tons of sulfuric acid are flowing and being received by the drainage system from that area annually.

Examination of earthen strata associated with abandoned mines from which acidified water is draining has shown that the strata at the site of the mine contains high counts of oxidation bacteria, most illustrative of which are thiobacillus thiooxidans, and thiobacillus ferrooxidans. It has been found that the count of such bacteria increases proportionately with the acidity of the earthen material. Further examination has shown that both the high acidity and the bacteria are largely concentrated in the outer or air-containing portion, usually not over about two inches deep and of even less depth in fresh acid-forming surfaces. To demonstrate that acid-forming is localized at and near the surface of sulfur-containing earthen material, the upper two inches of the roof material of a mine in which water was dripping through the room onto the mine floor and which showed high acidity, were removed. Both the acidity and oxidation bacteria count, including the thiobacillus thiooxidans and thiobacillus ferrooxidans, were high. Shortly thereafter the dripping water was tested and was found to be neutral. However, within about 24 hours, the water dripping into the mine was found to be again acidic and tests of the surface material showed that bacteria were again present in substantial amounts. After a week both acidity and bacteria count (including both types of bacteria) were as high as they had been prior to removing the top layer of material. This examination shows that the growth of bacteria which catalyze oxidation of both the iron and sulfur materials and the increase in acidity develop more-or-less concurrently near the surface exposed to air.

There is clearly a need for inhibiting the formation of acidifying materials on and near the earth's surface. The invention meets this need.

The invention accordingly is a method of lessening the rate and the extent to which sulfur compounds, e.g. pyrite and marcasite, are converted into corrosive acids. It comprises applying a pulverized phosphate on the surface and/or admixing it with the top soil and rock material having sulfur-containing components therein which are contacted by water and especially which are also exposed to air especially in the presence of bacteria which accelerate the oxidation of the sulfur-containing component.

Any inorganic phosphate may be used, e.g. phosphate

ores or phosphate slime by-products. A phosphate source which is quite satisfactory is naturally occurring calcium phosphate, i.e. $\text{Ca}_3(\text{PO}_4)_2$. Another source is dicalcium phosphate, i.e. CaHPO_4 . These phosphates are desirably sparingly water-soluble and gradually convert FeS_2 to CaSO_4 and to $\text{Fe}_3(\text{PO}_4)_2$. The Fe^{++} ions are thus largely eliminated. The $\text{Fe}_3(\text{PO}_4)_2$ is quite insoluble and precipitates out since it has a solubility of less than 8 milligrams in 100 milliliters of water. In time there is thus provided a phosphate coating over the sulfide mineral pieces. Any FePO_4 formed is also relatively insoluble.

The source of phosphate employed is usually a low grade material. It is recommended in the initial treatment of a stratum that H_2SO_4 be admixed with the phosphate before or during application thereof. The amount of H_2SO_4 is suggested to be up to about 10 percent of dilute sulfuric acid based on the weight of phosphate employed. The H_2SO_4 thus present initially attacks the phosphate and converts it more nearly to an ionized state so that the PO_4^- radicals are more reactive with the iron sulfates. The use of H_2SO_4 with the phosphate is particularly recommended when the phosphate employed is low grade. The amount of H_2SO_4 suggested to be employed is that which will sufficiently react with the phosphate to result in ionization of the phosphate compound thereby to react subsequently with the sulfates of the earth's stratum. From about two to about ten percent of dilute sulfuric acid based on the weight of the phosphate employed is suggested; depending upon the amount of sulfur compounds present in the stratum being treated and upon the nature of the phosphate employed.

In carrying out the practice of the invention, it is suggested that an estimate of the amount of iron sulfides present in the rock or soil to be treated, be ascertained (as by sampling and analysis) and then an excess of phosphate, reactable therewith, be provided. The phosphate may be applied in a powdered or granulated state. The particle size is not critical, although a very fine powder is more effective in a shorter time than coarse material. However, any size from chunks to less than 325 mesh may be used. It also may be slurried in water or, as aforesaid, dispersed in dilute sulfuric acid and sprayed on the surface being treated. Any of a number of means may be used for its application including mechanized spreaders, e.g. a conveyor-beater spreader, "sand-throwing" equipment, or bulldozer, a hand spreader useful for dry applications, or mechanized multiple-nozzle high-pressure sprayers or hand sprayers adaptable for slurry application.

Although the bacteria present in the stratum being treated are rendered much less damaging by reducing the FeS_2 accessible for oxidation, it is recommended (as a preferred embodiment of the invention) to include a bactericide comprising a bromine or chlorine source in the treatment to destroy or render impotent the oxidation bacteria. The bacteria which are most damaging in this situation as aforesuggested, are the thiobacillus thiooxidans which catalyze the oxidation of sulfur materials and the thiobacillus ferrooxidans which catalyze oxidation of iron materials. The bromine or chlorine when used may be dissolved in water which is subsequently sprinkled over the area of an abandoned mine or over a refuse pile from the mine, sometimes known as a gob pile (which is often produced in strip mining operations) or over the old tailings of a mine. It may also be sprinkled on the floor of an abandoned mine and, if desirable, sprayed on the ceiling. Cl_2 or Br_2 may be released as either liquid or gas to supplement the action of the applied phosphates. The Br_2 or Cl_2 may also be provided by employing a readily decomposable compound thereof such as a bromite, a chlorite, hypobromite, or hypochlorite.

The preferred technique for applying the bromine or chlorine is to introduce it under pressure from properly located openings, preferably nozzles, from which it issues as a gas.

The invention may be carried out as follows:

A sample is taken of the sulfur-containing rock or earth in the tailings, refuse pile, mine roof, or floor of the area to be treated in accordance with the invention. The sample is analyzed for its FeS_2 content and the amount of H_2SO_4 which may be formed therefrom calculated. It is advisable to measure or at least to estimate the depth of the sulfur-containing stratum, layer, tailings, or refuse pile to be treated. However, knowledge of the depth is not highly critical, since oxidation of the sulfur materials is largely limited to a relatively shallow depth. The extent of the cracks and crevices, however, must be taken into consideration since oxidation occurs along their edges. The area of the surface to be treated is also estimated. The amount of sulfur-containing component of the soil or rock to be so treated is then roughly calculated. There is thus provided a practical basis for calculating the amount of sulfuric acid which may be formed by water contacting the rock or earth which it is desired to treat, by using the following equation:



The following examples are illustrative of the practice of the invention:

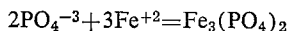
Example 1

Specified earthen material to be treated, illustrative of which are roofs and floors of mines and surfaces of refuse piles, mine tailings, or gob piles, is examined as above suggested to ascertain the extent of sulfur-containing materials therein. It has been found to be good practice to obtain a core of the stratum, to be treated, to a moderate depth, e.g. about a foot, and run an analysis of a representative sample thereof for FeS content. Calcium phosphate-containing rock is ground to a suitable size, e.g. between about 10 and 100 mesh, and spread over the exposed surface to be treated in an amount previously determined by analysis of the sample. The amount of phosphate ore required will be about the stoichiometric quantity (based on the equation, supra) or slightly in excess of that required to react with the FeS_2 present in the layer thus sampled. The phosphate material may conveniently be spread by any common spreading device, as hereinabove suggested. As aforesaid, if the phosphate rock is of rather impure quality, up to about 10 per cent by weight thereof of dilute sulfuric acid is recommended to be admixed therewith prior to or while spreading the material on the surface being treated. When sulfuric acid is employed, equipment such as a tank truck suitable for spreading slurry may advantageously be employed. The phosphate rock applied according to the invention converts any soluble iron compounds in the area comprising or immediately below the surface, to non-acid forming phosphates which in turn coat unreacted iron sulfides present, such coating hindering further solubilization thereof and at the same time fills the crevices and interstitial spaces among earthen particles of the stratum or pile being treated, thus hindering or impeding the flow of air and water (containing oxygen dissolved therein) there-through where otherwise the air and water would contact and attack the decomposable sulfide minerals. Water leaving the mine will have the pH value thereof raised substantially, i.e. from the 1.0 to 2.5 value prior to treatment to a value of 4 to 6.

Example 2

An abandoned mine situated above the permanent water table and having one or more subsidence areas on the surface above a mine and having a network of tunnels therein is producing acidified water which drains from the mine into the watershed of the area. It is desired to treat the roof and floor of the mine to inhibit the acidification of the water passing through or along the roof or floor. The surface subsidence areas are treated by apply-

ing a covering of particulated phosphate rock in an amount sufficient to satisfy the following equation:



The floor of the mine is similarly treated. Often, less phosphate is required on the mine floor since most of the water falling thereon from the ceiling will no longer be acidified and the floor of the mine often contains a lower percent of FeS_2 .

Chlorine or bromine gas supplied by steel bottles is conducted to the interior of the mine and there released into the mine at strategic locations so as to serve a maximum exposed area of the interior of the mine. The amount of the bromine or chlorine employed is initially about 1,000 parts per million based on the bacteria in the materials and thereafter reduced to about 100 parts per million and maintained at that level until the drain water from the mine shows a pH value of not less than about 4 and preferably not less than 6.

Reference to the description of the invention and the foregoing examples shows that the pH value of seeping waters from areas wherein sulfur-containing minerals form sulfurous and sulfuric acid may be raised to a substantially non-acidic and non-contaminating value.

Having described the invention, what I claim and desire to protect by Letters Patent is:

1. The method of inhibiting the conversion of iron- and sulfur-containing components, of a terranean or subterranean stratum, to acidifying materials that acidify water coming into contact therewith to form corrosive acids, which comprises obtaining and analyzing a sample of said stratum for its FeS_2 content, distributing and applying, on at least the most exposed portions of said stratum, a pulverized inorganic phosphate, in an amount sufficient to provide at least about the stoichiometric quantity of the phosphate required to react with the FeS_2 shown to be present by analysis of said sample, and from about 2 to about 10 percent of dilute sulfuric acid based on the weight of said phosphate to render the phosphate more reactive with said components, whereby water passing along, over, and through the stratum will come into contact with the so distributed and applied phosphate and sulfuric acid thereby converting the iron- and sulfur-containing components present in the stratum to substantially water-insoluble phosphates.

2. The method of inhibiting the conversion of iron- and sulfur-containing components of a terranean or subter-

ranean stratum wherein bacteria are present which accelerate the oxidation of the sulfur component to acidifying materials which acidify water coming into contact therewith to form corrosive acids, which comprises analyzing a sample of said stratum for its FeS_2 content, distributing and applying on at least the most exposed portions of said stratum a pulverized inorganic phosphate in an amount sufficient to provide at least about the stoichiometric quantity of the phosphate required to react with the FeS_2 shown to be present by analysis of said sample whereby the water passing along, over, and through the stratum will come into contact with the so distributed and applied phosphate thereby converting iron- and sulfur-containing components present in the stratum to substantially water-insoluble phosphates, and, bringing into contact with said stratum while said phosphate is in contact therewith, a bactericide selected from the group consisting of elemental bromine and chlorine and compounds containing bromine and chlorine which are decomposable to release elemental bromine and chlorine at atmospheric conditions.

3. The method according to claim 2 wherein said bactericide is a hypochlorite.

4. The method according to claim 2 wherein said stratum comprises at least a portion of the roof of a mine and the bactericide is elemental bromine which is released inside of said mine.

5. The method according to claim 2 wherein the bactericide which is released inside of said mine is elemental chlorine.

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