PREVENTING ARD FROM MINE WASTE USING COMMERCIAL ASPHALT/WATER EMULSIONS

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Abstract

In this new process for preventing acid rock drainage (ARD) from mine waste, diluted, commercial asphalt/water (A/W) emulsions are infiltrated from the surface into mine waste to provide disseminated asphalt particles in a zone several meters deep. The A/W emulsion consists of asphalt microdroplets suspended in water. The water matrix provides mine waste rock wetting and emulsion penetration identical with water. The emulsion is stabilized with an anionic surfactant. Breakdown of the A/W emulsion allows tiny asphalt particles to adhere to the mine waste rocks. The asphalt provides permanent anaerobic conditions. Oxygen dissolved in water is reduced to CO_2 and H_2O by reaction with the asphaltenes, which are the reducing agents (electron donors) in the process. Provided sulfate reducing bacteria (SRB) are present, arsenic and soluble metal sulfates are precipitated as sulfides. This process and its optimization are described, including experiments with sand-filled columns representing a vertical section through mine waste. Asphalt and metal retention results are provided. Analyses of a Nevada mine ARD were made before and after treatment in the presence of SRB. Greater than 99% precipitation of dissolved arsenic occurs in a 7 days, which is sufficient time to affect the reaction during slow infiltration of rainwater through the asphalt zone. The rate of rainwater infiltration is limited by a soil (dirt) cover laid over the mine waste to support vegetation, after emulsion application.

Introduction

Mine Closure methods for preventing ARD from mine waste fall into two categories: 1) treating drainage after it leaves mine waste and 2) treating mine waste to prevent ARD from occurring. This asphalt/water (A/W) emulsion process is in the latter category. Although meteoric water (rainwater and/or snow melt) continues to drain from the mine waste, dissolved oxygen has been removed.

Capping the mine waste with a thick, compacted clay layer to prevent water infiltration and ARD is frequently practiced. A clay cap must be engineered and constructed to be permanently impervious. Clay caps are expensive and they can fracture and leak ARD if the underlying solids settle.

Another mine closure method that has been practiced is infiltration into the mine waste of an aqueous solution of carbohydrates. This will establish anaerobic conditions and prevent further sulfide mineral oxidation. Sulfate reducing bacteria (SRB), necessary to precipitate heavy metals and arsenic as sulfides, are usually present in the mine waste. Carbohydrate is an electron donor in this biochemical process. Molasses and/or alcohols are usually the selected carbohydrates. This method is less expensive than clay capping. However, over time and with sufficient rainfall these carbohydrate solutions will drain from the mine waste, making this method impermanent. Consequently, carbohydrate solutions have more recently been confined to treating pit lakes.

Petroleum refinery products are potentially useful electron donors for anaerobic bioremediation of mine waste and they are less expensive than carbohydrates. Unfortunately, they are non-aqueous liquids and by themselves cannot wet and penetrate into mine waste. However, sticky asphalt particles, if uniformly dispersed within mine waste, will be permanently retained. A method for accomplishing this could provide *permanent* anaerobic conditions so that bioremediation processes requiring anaerobic conditions could also occur *permanently*. Converting oxygen dissolved in infiltrating water to CO_2 and H_2O and fixing heavy metal contaminants as sulfide precipitates, using SRB, are important examples of this bioremediation approach to mine waste.

Commercial Asphalt/Water Emulsions and Their Significant Properties

Asphalt, the residue of complete petroleum distillation, is water insoluble. Among petroleum refinery products asphalt has the least value, making it an inexpensive material for an anaerobic bioremediation treatment. A/W emulsions are manufactured to ASTM specifications by feeding hot, liquid asphalt (typically 60%) and an emulsifier (1%) with water into a high shear reactor, usually a colloid mill. The asphalt is dispersed as microdroplets within a continuous water phase. Several commercial grades are manufactured[1] at many locations in the United States and in other countries that have a network of paved roads. The “geographic listing of member plants” of the Asphalt Emulsion Manufacturers Association (AEMA)[2] lists more than one hundred locations in the United States, including at least one in each western State, where most of the mine waste is located.

Both anionic and cationic emulsions, with different setting rates are widely used for road repair and resurfacing. These emulsions are stabilized by their emulsifiers, which are surfactant molecules. Each surfactant molecule has an organic end that attaches to the asphalt microdroplet and an ionic end that attaches to water. Asphalt microdroplets in anionic emulsions are repelled by the anionic surfaces of the common minerals in mine waste, which is the property that allows infiltration into mine waste. Conversely, asphalt microdroplets in cationic emulsions quickly attach to these minerals and seal the mine waste surface rather than infiltrating into it.

Once in mine waste, the anionic emulsion will gradually disengage (break) to leave the asphalt microdroplets adhering to rocks in spite of the ionic repulsion forces, but emulsion breaking must not be completed before adequate penetration of the emulsion infiltrating into the waste has occurred.

Research Objectives and Results

The purposes of this research were twofold:

First, was to identify a diluted, commercial grade asphalt/water emulsion that would infiltrate mine waste to a suitable depth.[3]

Second, was to determine if the asphalt is sufficiently reactive to achieve anaerobic conditions and precipitate arsenic and heavy metals from mine water as sulfide precipitates. Asphaltenes are much slower reacting electron donors in biochemical processes than carbohydrates.

A) Infiltration of A/W Emulsions into Sand-Filled Columns

Vertical columns, 7.6 cm (3 inch) diameter x 5 m (16 feet) high, were filled with -30 mesh washed sand to replicate the finer particle fractions in mine waste and the coarser fractions of a typical mill tailing. The nominal sand grain size was 0.5 mm. Hydraulic conductivity, measured after water flooding and prior to emulsion addition, was 0.46 mm/sec. Prior to infiltration, commercial A/W emulsions were diluted with water to 20% asphalt, or less.

As described below, satisfactory emulsion infiltration results were obtained using a slow setting, anionic A/W emulsion, designated as grade SS-1 h (ASTM D977 and ASSHT M208).

1500 ml of 20% emulsion were added to the wet, drained sand-filled column at an average superficial velocity of 0.003 mm/sec, which is much less than the sand hydraulic conductivity. It corresponds to an application rate typical of an impact sprinkler or drip irrigation system used in heap leaching. The column was open to drainage at all times. Clear drain water was collected steadily, indicating transit of liquid through the column in nearly plug flow. The final amount of drainage was 1350 ml.

Large emulsion additions were made to a sand-filled column, amounting to an inserted carbon weight that was 1.5% of the sand weight. After a 21 day column rest period, 4.5 liters of water were passed through it. This rinsing is equivalent to 40 cm of rain, which is more than the total amount of rain falling during two years in most of the Western USA. Laboratory analysis showed the asphalt loss caused by the rinsing to be less than 0.5% of the asphalt in the sand-filled column. .

These experiments showed that diluted A/W emulsion SS-1 h will infiltrate mine waste, with more than 99% of the injected asphalt retained within 5 meters (16 feet) of the surface when the emulsion is applied at slow infiltration rates typical of those encountered with impact sprinklers. Infiltration rates were not limited by the sand's hydraulic conductivity. Faster emulsion application rates may drive the asphalt deeper into mine waste before emulsion breakage is completed.

B) Arsenic and Heavy Metal Removal Using A/W Emulsions

Approximately one liter batch tests (mason jars) were used to follow the removal of soluble arsenic and selected heavy metals from ARD. Each batch contained pea gravel and 100 ml of asphalt emulsion SS-1 h, and it was filled with ARD containing SRB. The ARD came from Newmont Mining Company's closed Rain Mine, near Carlin, Nevada. It was obtained there from sampling the feed to an operating lime neutralization facility. The ARD had a pH of 2.69 and contained large amounts of Group I and II metal sulfates, as well as arsenic and heavy metal sulfates. The sulfate concentration was 26 g/L.

To ensure that sufficient SRB were present in these batch tests, a biosludge inoculate containing a natural consortia of SRB was grown; 100 ml of this biosludge and 10 ml of $(NH_4)_3PO_4$ were included with each 2000 ml of ARD.

Upon completion of each batch experiment, the sealed container was opened. Solution was removed, filtered and analyzed by a certified laboratory using EPA methods, primarily ICP/MS. The reduction in arsenic and metal concentration indicated that anaerobic conditions were established in the sealed containers. Solutions were not analyzed for oxygen because they were exposed to air upon being opened and processed, making it impossible to obtain an accurate measurement.

The experimental results in Table 1 show a substantial removal of arsenic and heavy metals from Rain Mine ARD, using asphalt as the only source to obtain anaerobic conditions.

Table 1. Analysis of Arsenic and Metals in Solution, After Batch Treatment
(Percentages Remaining are Shown in Brackets)

Treatment Period (days)	Species Concentration (micrograms per liter) Fe(T)	As	Cu	Zn
0*	370,000	4,200	14,000	9,000
7	4,200 (1.14%)	15 (0.36%)	2,300 (16.4%)	4,900 (54.5%)
7	4,300 (1.17%)	14 (0.33%)	2,300 (16.4%)	4,900 (54.5%)
28	3,400 (0.92%)	13 (0.31%)	920 (6.6%)	3,000 (33.3%)
120	1,600 (0.43%)	8 (0.19%)	520 (3.7%)	2,200 (24.5%)
EPA Method:	200.7	206.2	200.7	200.7

* As-received from the Mine, but measured by the laboratory measuring the other samples

Process for Mine Waste Closure

Mine waste, other than finely ground mill tailings, will have a high hydraulic conductivity. Consequently, a deluge of rainwater or snow melt directly onto most mine waste heaps will rapidly percolate through it. Consequently, there will be insufficient time in the disseminated asphalt zone to remove all of the dissolved oxygen in the water. However, closure of a mine waste heap, will likely require a layer of soil (dirt) placed on top of it to support planting vegetation. The hydraulic conductivity of uncompacted soils will not exceed 10^{-3} cm/sec[4]. A soil layer will limit the flow to and through the underlying mine waste to the soil's hydraulic conductivity. In a rainwater deluge, excess water will flow laterally off the soil surface (surface flooding) after saturating it.

Table 2 shows results calculated for various hydraulic conductivities of soils. The depth of water penetration into the mine waste is shown for water that has been in the mine waste for 7 days, infiltrating at a velocity limited by the listed soil hydraulic conductivity. Seven days were chosen because the preceding research shows that more than 99% of the arsenic will be precipitated by asphalt in that amount of time.

Table 2. Depth of Penetration into Mine Waste of Infiltrating Rainwater at the Expected Range of Soil Hydraulic Conductivities

Hydraulic Conductivity	Penetration Depth in 7 Days
1 x 10^{-3} cm/sec	6 meters
1 x 10^{-4}	0.6
1 x 10^{-5}	0.06

Mine waste closure will proceed as follows. The undiluted *anionic* A/W emulsion (SS-1h) will be shipped from the nearest manufacturer to the mine in highway tank trucks. For northern Nevada mines the source will by Utah. At the mine the emulsion will be diluted with water to no more than 20% asphalt.

If ARD is already seeping from the mine waste, or if substantial oxidation of sulfide minerals is thought to have occurred, carbohydrates can be included with the dilution water. Alternatively, a carbohydrate solution can be applied prior to A/W emulsion application. Either way, soluble arsenic and heavy metals already contaminating the mine waste will be precipitated as sulfides. Inoculation of a consortium of SRB may be made if needed; however, in past practice using carbohydrate solutions this has not been necessary.

If the mine waste surface has been compacted, it may be necessary to dozer rip it prior to the A/W emulsion application.

A/W emulsion and carbohydrate solution applications will be made by a tank truck, identical with mine road watering tank trucks. These same tank trucks are used to apply A/W emulsions to paved roads being resurfaced. Large hoses (e.g. fire hoses) will be used to apply emulsion to the sloping sides of mine waste heaps.

The final steps are installation of a soil layer upon the mine waste and replanting.

Brief Discussion of Economics

Using A/W emulsions to form an anaerobic zone in the top several meters of mine waste will be less expensive and more reliable than constructing a thick, compacted clay cap on top of the mine waste. The delivered emulsion cost in northern Nevada mines is about $3.00 per gallon of 60% asphalt emulsion. Assuming an annual deposit of 20 inches of rain saturated with oxygen (8 ppm), and assuming that all of the asphaltenes contained in the A/W emulsion are reactive, an emulsion dosage of 200 gallons per acre will provide 3,000 years of anaerobic protection at a cost of about $600 per acre. Inclusion of soluble carbohydrates with the diluted emulsion may double that estimate for materials. The amount will depend on an estimate of the amount of already solublized metals and arsenic that are contained in the mine waste.

The A/W emulsion volumes applied to the mine waste at the dilutions shown in Table 3 are modest. Only one pass of the tank truck distributing emulsion over the surface of the mine waste will be required with the truck speed set to provide the desired dosage per acre.

Table 3. The Volume of Diluted A/W Emulsion Require at Selected Dilutions

Asphalt Dilution	Emulsion Volume Applied
20% asphalt	600 gallons/acre
10% asphalt	1,200 " "
5% asphalt	2,400 " "

The costs of a rented tank truck and labor will be site specific and have not been estimated. The cost per acre for equipment, labor and overhead will likely be less for large mine waste heaps than for small mine waste heaps. The total cost, except soil installation and planting, should be less than $5,000 per acre for mine waste heaps covering more than 200 acres.

Contrast this cost with the cost of a clay cap. A well engineered and carefully constructed clay cap 1 to 1.5 meters thick is estimated to cost $1.00 per sq ft, which is $45,000 per acre. Soil installation over the compacted clay layer and planting will also be required.

References

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