LABORATORY TESTING OF COATINGS FOR PREVENTION OF ACID DRAINAGE IN UNDERGROUND COAL MINES[1]

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Abstract: Laboratory research has been conducted to develop tough chemical and mineral coatings for the prevention of acid mine drainage (AMD) in unsubsided underground coal mines. Specially designed sprayed coatings have the potential for substituting for initial rock dusting, preventing AMD in unsubsided mines, and opening up more acid-producing coal reserves for mining. Fifteen liquid chemicals were sprayed onto acid-producing mine rock samples for laboratory testing of coating durability in water tanks. Eight chemicals that passed the durability tests, and 4 of these were judged suitable for further tests. These 4 chemicals were mixed with water and apatite dust and sprayed on mine rock samples for more tests involving short-term bubbler tank, soxhlet, and long-term bubbler tank procedures. Two coating types, for chemicals code-named I and G, passed these tests. These 2 chemicals were then mixed with limestone dust and water and further tested as sprayed mine rocks using the same testing procedures. These coatings also worked well in retarding AMD products. For most tests coating G (an epoxy resin) worked the best but is most expensive; coating I (a latex) worked second best. The optimum G and I limestone coatings are ones composed of a 10% (by volume) chemical to 90% water solution mixed as a slurry with 30% by weight of limestone dust. These 2 coatings are economical, durable, and should be tested in an underground mine.

Additional Key Words: acid mine drainage, underground coal mines, mine coatings, apatite, limestone.

Introduction

We thank Mr. James Laurita Jr. of MEPCO, Inc., the National Mine Land Reclamation Center and the National Research Center for Coal and Energy at West Virginia University, and Mr. William (Randy) Williams of Kiss Engineering for their financial support of collaboration on this research.

One costly and long-term consequence of coal mining is often acid mine drainage from underground mines. Current methods to remedy the problem have had limited success. Consequently, alternative techniques for mediating acid formation continue to be investigated. This report details preliminary research results for evaluating polymer-mineral coatings as inhibitors of pyrite oxidation and the generation of AMD in underground coal mines. Such inhibitions could possibly be achieved through spraying coating barriers on mine rock surfaces, to retard movement of mine air, water, and bacteria to rock and to keep the pH of adsorbed water high on rock surfaces. Successful coatings would likely target active mines for preventing AMD prior to mine abandonment and flooding.

Hart et al. (1990) have shown that phosphates reduce the oxidation of pyrite, possibly by forming iron phosphate on exposed pyrite. Texasgulf Inc.'s Code 31 apatite (about 95% apatite), was found to be very effective in suppressing AMD from mine wastes. Highly soluble at pH values below 5.5, apatite may react with ferric iron leached from pyrite to precipitate iron phosphate, disrupting acid generation. Although this theory for apatite is disputed by some, apatite was found to ameliorate AMD. Only one Appalachian area study was found in which phosphate rock was applied in an underground setting to inhibit acid mine drainage. Hause and Willison (1986) reported that a West Virginia coal mine was sealed and flooded with alkaline water, after above-high-water-table areas were dusted with ground apatite. The mine effluent required no additional treatment 14 months after treatment.

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A 1990-91 study of potential mine coatings was funded by James Laurita, Jr. and supervised by Randy Williams and Henry Rauch. They found that two chemicals were successful in binding powdered apatite to mine rocks and that these coatings were durable and did not allow AMD during short-term laboratory testing. These two coating chemicals were also incorporated into our reported research here. In another mine-coating study, Franklin and Nuzum (1975) assessed the suitability of 46 chemicals in suppressing radon gas emissions from uranium mines. Several of these chemicals were later field-tested in an underground coal mine to try preventing the weathering of mine roof shales, and proved effective for at least 1.5 years (Franklin et al. 1977).

Materials for Study

Chemicals for coating mixes were chosen from chemical manufacturers, mine stabilization companies, and previous research. Future use of the chemicals in underground mines was a major consideration in developing criteria for suitable chemicals for study. These criteria included the ability to be applied under high relative humidity conditions, nonflammability, ease of spraying application, lack of adverse environmental effects, and reasonable cost.

Fifteen chemicals were chosen for initial testing. These polymer chemicals were first tested for adhesion on rock surfaces by dunking and short-term bubbler tests. The chemicals were then diluted with water and mixed with powdered apatite (Texasgulf Inc. Code 31) in varying percentages to prepare coatings for laboratory testing. After short-term testing, chemicals for the 3 most successful apatite coatings (J, a petroleum extract; G, an epoxy resin; and I, a latex) were mixed with cheaper limestone dust (agricultural lime) and water for further coating tests.

For testing coating effectiveness, rocks were obtained from an Upper Freeport coal deep mine of northern WV, a major AMD producer. Where possible, fresh roof, coal, and pavement rock were obtained from small areas (few square feet) and small volumes of rock in the mine, to minimize effects of prior weathering and lithologic heterogeneity. Coal was the greatest soxhlet acid producer, averaging 1.16% sulfur and -34.19 net neutralization potential (NNP). Roof and pavement rock averaged respectively 0.06% and 0.03% sulfur, and 0.45 and 1.33 NNP; these rocks were at most moderate acid producers, with roof rock being the greatest acid producer from bubbler tank tests. These rocks were reduced to convenient pieces for testing, and their surface areas were estimated using wrapped aluminum foil. Surface areas for rocks ranged 50-100 cm^2 and averaged about 80 cm^2 for soxhlet tests, and ranged 570-1,750 cm^2 and averaged about 1,100 cm^2 for the 1 to 4 rock pieces per bubbler tank test.

The tested coating mixes were slurries that were applied thin enough to be economical but thick enough to cover the rock. For tested apatite coatings, coating A was prepared by adding by volume 10% A (a latex) to 90% distilled water, supplemented by 25% by weight of apatite dust (AD); this mixture is abbreviated 10% A, 25% AD. In similar fashion, coating G was 25% G, 25% AD; coating I was 10% I, 25% AD; and coating J was 20% J, 25% AD. For the tested limestone dust (LD) coatings, coating G had three versions: 15% G, 0% LD; 10% G, 30% LD; and 20% G, 60% LD. Coating I LD versions were 10% I, 0% LD; 10% I, 30% LD; and 10% I, 60% LD.

The typical thickness of wet sprayed coatings varied with composition, with thicker coatings being associated with more mineral dust. From glass plate spray tests, wet chemical-mineral coatings ranged about 0.1-0.2 mm thick. Dry coatings were less than 50% the thickness of wet coatings. The dry coating weight percentages were 71-93% for apatite mixed with chemicals A, G, I, and J, and 88-96% for limestone mixed with chemicals G and I. Both minerals (especially limestone) are cheaper than the tested chemicals per unit quantity. From glass plate tests, the estimated expense of spraying chemical-limestone coatings in a mine is 2-4 cents/ft^2 for chemicals I and G, with G being more expensive. Labor costs are most of this expense. Our wet coatings would be considerably thinner and somewhat more expensive than a single typical limestone rock dusting in an underground mine.

Laboratory Methods

Dunking tests served to identify coatings for further testing by evaluating the short-term adherence of each tested chemical to painted mine rocks under submerged conditions. Polymers that remained intact on the rock surfaces were subjected to additional tests. Short-term bubbler tank tests were next conducted to evaluate the short-term adhesion of applied coatings to mine rocks; these tests simulated flooded mine conditions using plastic tanks with 2.5 liters of distilled, aerated water. Mine rock samples about 3-8 cm in size and about 70 cm^2 in average surface area were coated with undiluted polymers, cured in a high-humidity chamber, and submerged in bubbler tanks for 5-7 days. Coating chemicals showing little or no change were used to formulate chemical-apatite coatings. These coating mixes of chemical, water, and mineral were sprayed onto more rocks, cured, and then tested submerged as before except that pH was held at 2.5 ± 0.1 by HCl addition, to simulate a harsh AMD environment. Coatings remaining durable after 5-7 day tests were visually identified. Of 8 coatings remaining intact after testing, the 4 cheapest and most convenient chemicals (A, G, I, and J) were further tested in apatite coating mixtures.

Following these further tests, various limestone dust mixtures with water and chemicals G, I, and J were tested as coatings using 5-day acid water bubbler tank tests as described above. Chemical A was not tested again because it was least successful in the apatite coating tests. Chemical J failed to be durable during these tests, so only chemicals G and I were further tested in limestone coating mixtures.

The soxhlet method (Renton et al. 1988) with modifications was used to evaluate acid-suppression ability of the coatings. Chemical-apatite coatings for chemicals A, G, I, and J, followed by 2 chemical-limestone coatings for chemicals G and I were tested. Coated mine rock samples averaging about 80 cm^2 in surface area and control specimens of uncoated rocks, chemical-coated glass marbles, and peels of chemical-limestone coatings (for chemicals G and I) were soxhlet tested in duplicate through 5 leaching and oven-warming cycles. Each leaching cycle consisted of 24-hour hot-water leaching followed by leachate collection for analyses. After each leaching cycle, the sample thimbles were oven heated at 37° C for 1 week under humid conditions (with a water tray), to increase leaching potential of sulfide minerals in the rocks and yet to not further dry and crack the coatings and to preserve any pyrite-oxidizing bacteria possibly present. After 5 leaching cycles, visual observations were made of coating durability.

The chemical-apatite and chemical-limestone coatings tested by soxhlet leaching were later subjected to long-term bubbler tank tests. One to 4 coated roof, coal, and pavement rocks, averaging about 1,100 cm^2 in total surface area, were placed in tanks containing 7 L (for apatite tests) and 8 L (for limestone tests) of continuously bubble-aerated, distilled water. The tanks were innoculated with 0.5 mL of fresh AMD from a mine source to ensure the presence of AMD bacteria. An initial tank water sample was chemically prior to test-rock immersion. Thereafter, pH readings were taken weekly and 60 mL water samples were collected at 2-week intervals for iron and sulfate analyses; a descriptive log of specimen appearance was also kept. These tests were run for a several months.

Water samples from the soxhlet and tank tests were tested for pH, total iron, and sulfate because these are the 3 primary chemical parameters indicative of AMD and pyrite weathering reactions. Elevated values of iron and sulfate concentrations and lower values of pH relative to background (initial) values indicate that AMD-generating reactions are occurring. Of these 3 parameters, sulfate is considered the most definitive indicator of AMD generation owing to its persistence, in contrast to pH and iron which change after AMD neutralization. Sulfate was measured by the turbidimetric method for the apatite-coating experiments and by ion chromatography for the limestone-coating tests. Total iron was measured by atomic absorption spectrophotometry on preacidified water samples. pH was measured with a pH meter, in water of tanks or tank samples just after sampling.

Results and Discussion

The soxhlet test results are summarized in Table 1, which contains data as hydrogen ion activity and sulfate concentration per cm^2 of exposed rock, for the first (A), fifth (E), and 5 cycles (cumulative total). Higher values may mean higher AMD leaching potential from the tested rocks. Of the control (uncoated) rocks, coal allowed the greatest acid and sulfate contents, producing a pH of about 4 for cycle 5 and about 60-100 mg/L of cumulative sulfate. Pavement rock allowed the least acid and sulfate, with a pH of about 7-8 for cycle 5 and about 15-79 mg/L of cumulative sulfate. Roof rock was intermediate in acid and sulfate, with about 7-7.6 for pH for cycle 5 and about 32-81 for cumulative sulfate. Apatite coatings allowed more sulfate than limestone coatings, probably because Code

Table 1. Hydrogen and sulfate results from soxhlet experiments.

APATITE DUST MIXTURES	CYCLE A		CYCLE E		CUMULATIVE	
	(H+)/cm2	SO4 Conc. mg/l/cm2	(H+)/cm2	SO4 Conc. mg/l/cm2	(H+)/cm2	SO4 Conc. mg/l/cm2
Roof Rock Tests						
Coating A	6.48E-11	3.59E-01	5.20E-10	2.09E-01	3.13E-09	9.07E-01
Coating G	4.17E-11	2.57E-01	5.97E-11	6.44E-02	2.33E-07	5.06E-01
Coating I	1.22E-10	4.95E-01	6.62E-11	1.04E+00	5.20E-09	1.97E+00
Coating J	2.80E-08	6.34E-01	5.24E-11	1.08E+00	3.13E-08	2.38E+00
Control Roof	**1.75E-05**	**2.73E-01**	**2.30E-09**	**1.33E-01**	**1.76E-05**	**9.99E-01**
Coal Tests						
Coating A	5.36E-11	3.70E-01	7.16E-11	1.71E-01	1.06E-05	6.75E-01
Coating G	7.87E-11	2.18E-01	4.02E-09	1.30E-01	3.47E-08	7.01E-01
Coating I	4.54E-09	4.92E-01	4.51E-11	1.15E+00	7.14E-09	1.83E+00
Coating J	9.47E-08	5.14E-01	2.26E-11	1.05E+00	9.52E-08	1.97E+00
Control Coal	**1.17E-05**	**1.85E-01**	**2.00E-06**	**2.86E-01**	**1.86E-05**	**1.13E+00**
Pavement Rock Tests						
Coating A	4.96E-11	4.21E-01	5.43E-11	2.14E-01	5.31E-10	8.76E-01
Coating G	7.19E-11	2.63E-01	8.57E-11	1.26E-01	3.78E-06	7.33E-01
Coating I	8.71E-11	4.74E-01	5.13E-11	1.28E+00	1.85E-09	2.16E+00
Coating J	2.95E-08	4.88E-01	3.11E-11	9.52E-01	2.98E-08	1.75E+00
Control Pavement	**5.93E-06**	**4.02E-01**	**1.62E-08**	**7.47E-02**	**6.14E-06**	**9.63E-01**

LIMESTONE ROCK DUST MIXTURES	CYCLE A		CYCLE E		CUMULATIVE	
	(H+)/cm2	SO4 Conc. mg/l/cm2	(H+)/cm2	SO4 Conc. mg/l/cm2	(H+)/cm2	SO4 Conc. mg/l/cm2
Roof Rock Tests						
10% Coating I Pure	1.02E-08	2.14E-01	4.88E-09	6.68E-02	1.59E-08	5.19E-01
10% Coating I/30% RD	2.67E-12	9.80E-02	7.56E-12	3.13E-02	2.91E-11	2.35E-01
10% Coating I/60% RD	5.24E-12	1.18E-01	2.40E-12	3.40E-02	1.50E-11	2.78E-01
15% Coating G Pure	1.70E-08	1.63E-01	3.45E-10	4.59E-02	4.27E-08	3.57E-01
10% Coating G/30% RD	2.49E-12	1.71E-01	5.88E-12	5.00E-02	2.16E-11	4.08E-01
20% Coating G/60% RD	4.28E-12	2.02E-01	4.28E-12	9.58E-02	1.92E-11	6.74E-01
Control - Roof	**1.37E-08**	**2.88E-01**	**5.23E-10**	**7.03E-02**	**2.41E-08**	**6.43E-01**
Coal Tests						
10% Coating I Pure	4.03E-09	7.96E-02	5.09E-09	2.16E-02	1.09E-08	1.47E-01
10% Coating I/30% RD	5.78E-12	9.74E-02	5.61E-12	2.03E-02	2.51E-11	1.75E-01
10% Coating I/60% RD	1.54E-12	8.19E-02	7.18E-13	1.46E-02	6.02E-12	1.49E-01
15% Coating G Pure	1.20E-09	1.29E-01	6.21E-10	1.66E-02	7.12E-09	2.03E-01
10% Coating G/30% RD	1.90E-12	8.32E-02	4.60E-12	2.15E-02	1.45E-11	1.61E-01
20% Coating G/60% RD	1.55E-12	1.12E-01	3.70E-12	1.12E-01	1.64E-11	5.28E-01
Control - Coal	**1.68E-08**	**1.75E-01**	**1.09E-06**	**1.30E-01**	**3.40E-06**	**6.67E-01**
Pavement Rock Tests						
10% Coating I Pure	9.89E-10	9.22E-02	1.32E-10	3.46E-02	1.39E-09	2.62E-01
10% Coating I/30% RD	4.64E-12	9.74E-02	4.10E-12	2.58E-02	2.82E-11	2.75E-01
10% Coating I/60% RD	2.90E-12	1.03E-01	3.17E-12	2.90E-02	1.12E-11	2.53E-01
15% Coating G Pure	1.77E-10	8.66E-02	9.75E-11	2.73E-02	1.60E-09	2.34E-01
10% Coating G/30% RD	2.15E-12	7.34E-02	4.67E-12	2.68E-02	1.92E-11	2.01E-01
20% Coating G/60% RD	2.98E-12	7.69E-02	3.48E-12	2.75E-02	1.36E-11	1.99E-01
Control - Pavement	**1.58E-10**	**9.29E-02**	**1.49E-10**	**2.44E-02**	**5.90E-10**	**2.12E-01**

(H+)=Hydrogen ion activity, in moles/kg, and SO4=sulfate concentration, in mg/L. All values are reported as ratios of activity or concentration to surface area of their respective tested rock samples. All values shown are averages of duplicates tested for each group of treatments and rock types. Number interpretations: 6.48E-11 = 6.48x10exp(-11).

31 apatite contains 1.2% sulfur. For the apatite tests all coatings showed less acid than control rocks. Coatings I and J allowed more sulfate than controls, perhaps because of the sulfur in apatite dust. Overall, coating G performed best, having the least acid and sulfate. For limestone tests the coal coatings performed better than the coal control, and most coatings performed better than the roof rock control. The coatings appear to be least successful for pavement rock, but this rock showed little acid (pH about 8) or sulfate (about 15 mg/L). Both 30% LD and 60% LD coatings performed well, and I coatings overall appear to have worked slightly better than G coatings.

Fig. 1 displays the results of the apatite-coating bubbler-tank leaching tests through April, 1993. For the control rocks, the roof rock allowed the most acid and sulfate and the coal was least associated with these chemicals. These rocks apparently varied in composition compared to those used in the soxhlet tests. The control roof, pavement, and coal rock produced respectively pH's of about 5, 5, and 6, and sulfates of 204, 99, and 80 mg/L on April 26th. The initially higher hydrogen ion and sulfate ratios for the first tested control samples of some bubbler tank tests cannot be readily explained and may be from experimental error; the only acid and sulfate sources for initial samples should be the 0.5 mL of AMD added to the tanks. In general, apatite coatings allowed less acid and sulfate than control rocks. Overall, coatings G and I performed very well, and better than coatings J and A. Coating J and especially coating A developed concentrated fungus growth after several months of tank testing, indicating that these chemicals are fungus-culture mediums and should not be used in mines. Also, coating J showed significant wear. Based on chemical results and visual appearances, coatings G and I performed best.

Fig. 2 and Fig. 3 show results of the limestone-coating bubbler-tank tests up to October, 1993, for coating types G and I respectively. For control rocks, the roof rock allowed the most acid and sulfate, while the coal also showed much acid and sulfate. The pavement exhibited the least AMD products. For the last reported October date, the control roof, coal, and pavement rocks allowed respectively pH values of about 3, 3, and 6.5, and sulfate values of 151, 67, and 12 mg/L. In general, the G and I coatings worked well in preventing sulfuric acid compared to the control rocks, with the exception of pavement rocks whereby the control allowed about as much acid and sulfate as the average G and I coated rocks; however, the control pavement rock allowed very little acid and sulfate and is considered an alkaline rock. Overall, G coatings worked better (with less sulfuric acid) than I coatings. The 30% LD G coatings worked better than 60% LD and 0% LD G coatings for 2 out of 3 tested rock types, with the exception of the alkaline pavement rock. The 0% LD I coating allowed more acid and sulfate than did 30% LD and 60% LD I coatings. Although 60% LD I coatings worked better than 30% LD I coatings with less AMD products, 60% LD I coatings tended to spall from tested rocks, probably because they are thicker and have less chemical cement. Therefore 30% LD G and I coatings are preferred over 60% LD G and I coatings to prevent AMD.

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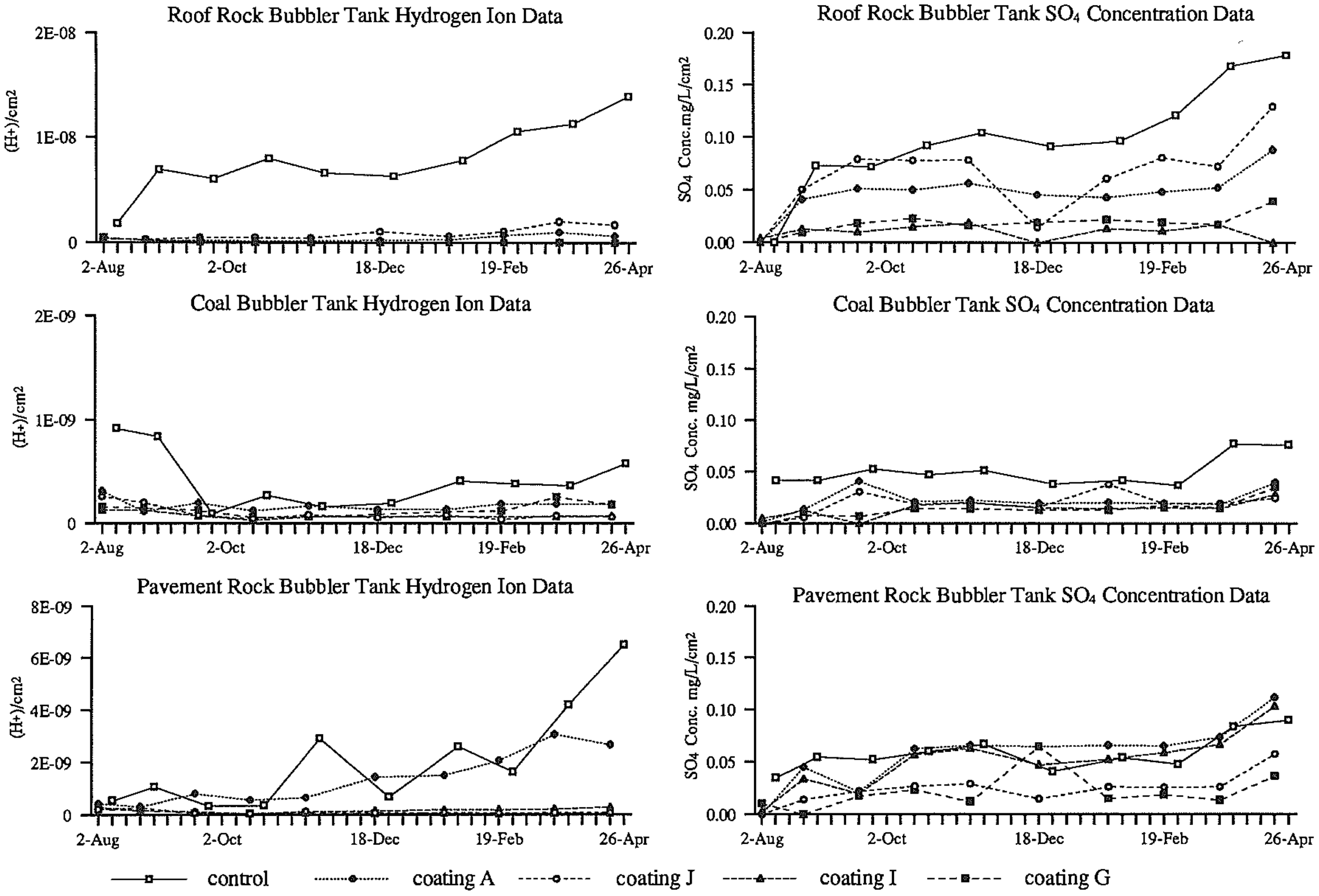

Figure 1. Graphs of water quality data for bubbler tank experiments performed on mine roof, coal, and pavement rock samples treated with various coating chemicals mixed with apatite dust. Hydrogen ion activity (H+) and sulfate (SO_4) concentration are reported in ratios to their respective rock sample surface areas. Control test bubbler tanks were started 1 week after all of the coating test bubbler tanks. The first water samples were taken prior to rock sample submersion.

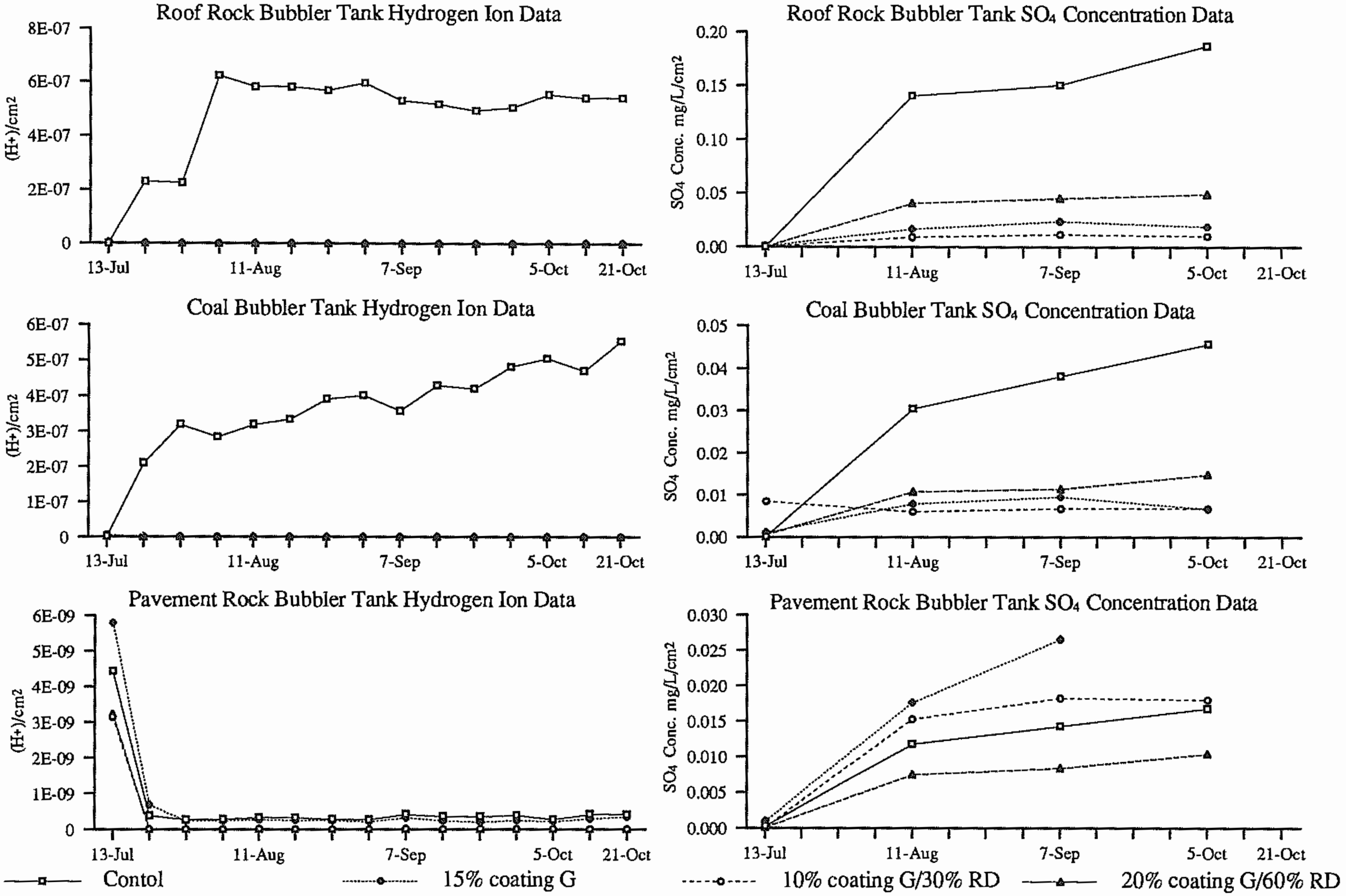

Figure 2. Graphs of water quality data for bubbler tank experiments performed on mine roof, coal, and pavement rock samples treated with mixtures of coating G and limestone rock dust (RD). Hydrogen ion activity (H+) and sulfate (SO_4) concentration are reported in ratios to their respective rock sample surface areas. The hydrogen ion activity ratio is shown for each week, while the sulfate ratio is shown for each month. The first water samples were taken prior to rock sample submersion.

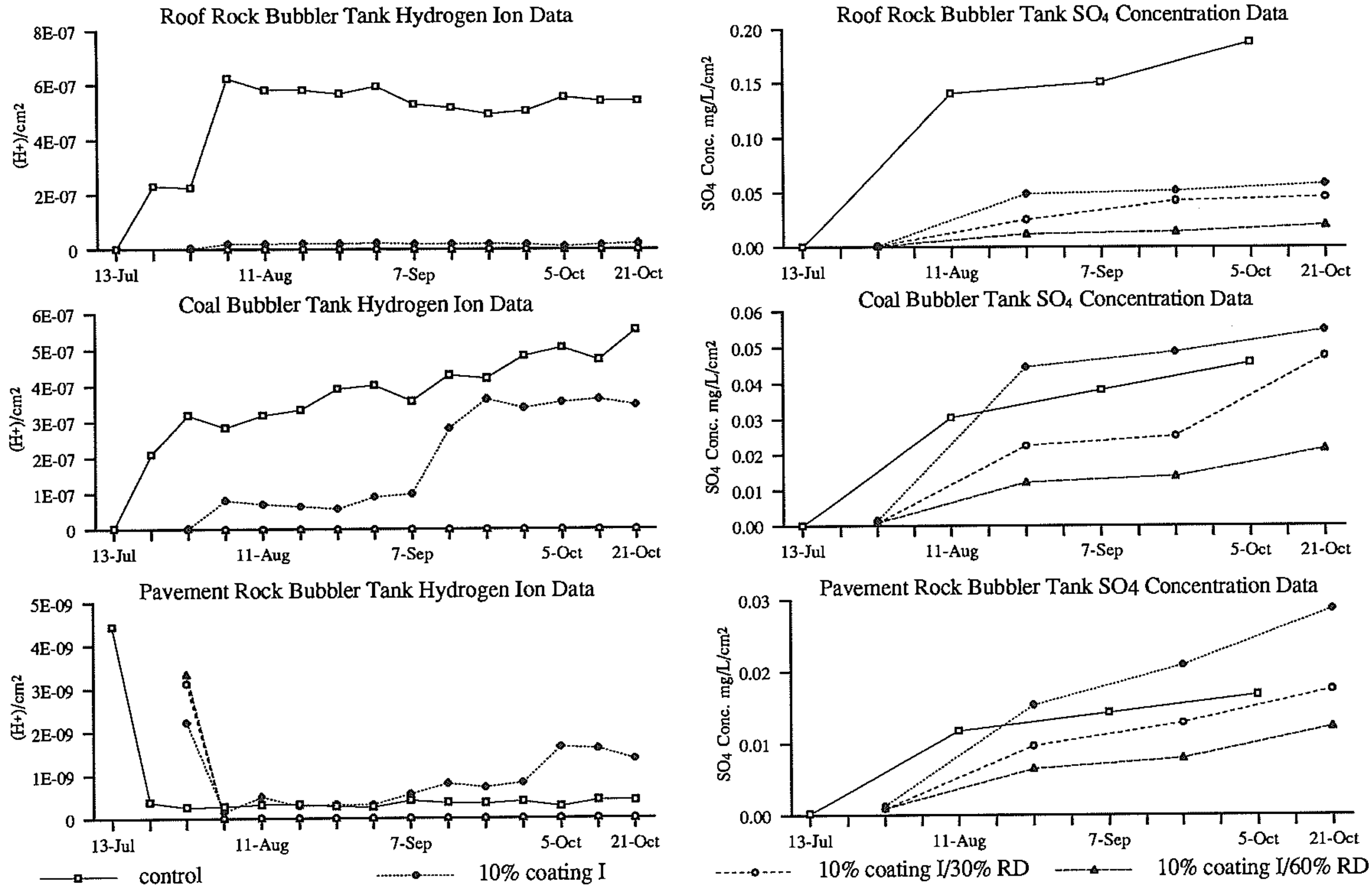

Figure 3. Graphs of water quality data for bubbler tank experiments performed on mine roof, coal, and pavement rock samples treated with mixtures of coating I and limestone rock dust (RD). Hydrogen ion activity (H+) and sulfate (SO4) concentration are reported in ratios to their respective rock sample surface areas. The hydrogen ion activity ratio is shown for each week, while the sulfate ratio is shown for each month. Coating I bubbler tanks were started 2 weeks after the control bubbler tanks. The first water samples were taken prior to rock sample submersion.