EARLY WEATHERING BEHAVIOR OF PYRITIC COAL SPOIL PILES INTERSTRATIFIED WITH CHEMICAL AMENDMENTS[1]

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Abstract: An array of eleven 400-ton piles of sulfide-rich overburden rock was constructed and monitored in 1982 during the first year of leaching. Piles were constructed that had (1) no treatments, (2) layered base amendments (limestone, rock phosphate, lime), and (3) sodium lauryl sulfate (SLS). In conjunction with flow rate measurement, water samples were collected to determine major element chemistry and mass fluxes. The rate of pyrite oxidation obeyed pseudo-zero order kinetics of similar rate between piles (mean 0.0239 mol SO_4 per ton spoil per day). The ion ratio δ (dissolved SO_4 to Ca+Mg) was used as a surrogate measure of pyrite oxidation and carbonate dissolution. Observed δ was about 1.0, increasing to even higher values late in the first year in some piles; this is substantially lower than the "expected" value of 0.5 for neutralization at alkaline pH. One plausible explanation is that carbonate dissolution may be kinetically limited and exhibit different rates during the leaching period, due to more rapid dissolution of calcite than dolomite or to simple depletion of reactive calcite. Gypsum reaches saturation in mid-year and may have been a sink for Ca and SO_4, although this would not greatly alter the δ ratio. Acid produced was apparently buffered *in situ* by dissolution of natural carbonate disseminated in the spoil; most layered amendments demonstrated no unequivocal initial effectiveness. Acid conditions ensued within the first year for all non-amended and some amended piles with the ratio of neutralization potential to maximum potential acidity (NP/MPA) less than unity, but the speed and extent of acidity generation varied among these. Acidity also developed for some amended piles with NP/MPA's as high as 2.3. The layered amendments may not be as effective and rapidly available as natural carbonate disseminated throughout the spoil. More effective amendment may have been achieved had amendments been evenly distributed through the spoil.

Additional Key Words: aqueous geochemistry, acid mine drainage, coal spoil, kinetics, mineral equilibria

Introduction

Base amendments are commonly added to acidic minespoil as passive treatment agents. They are applied to supplement natural alkalinity of spoil materials in order to meet or exceed the rate of acid production from pyrite oxidation and associated reactions. Common basic amendments are crushed limestone, calcium oxyhydroxide, sodium hydroxide, and sodium carbonate. Other, non-basic amendments have been employed to slow down or prevent chemical or biological reactions leading to increased acidity or metals mobilization.

Rates and need for application of base amendments have been determined using acid-base balance of potential spoil materials. Acid-base accounting (Sobek *et al.*, 1978; Erickson and Hedin, 1988; Branham and Caruccio, 1991) uses various estimates of pyritic sulfur to calculate maximum potential acidity (MPA) in conjunction with an acid titration procedure to calculate base neutralization potential (NP). Attempts to quantitatively relate overburden acid-base balance to post-mining water quality, either *a priori* or *a posteriori*, have been only somewhat successful. DiPretoro and Rauch (1988) found poor correlation (R^2=0.16) between volume-weighted NP and alkalinity in AMD discharge from 30 West Virginia mines. While it has been noted that sulfate production of spoil correlates with pyrite sulfur content, the relationship between NP and sulfate production rates may be erratic and variable (Hedin and Erickson, 1988). Current research suggests that factors other than overburden characteristics may be important in determining post-mining water quality (Renton *et al.*, 1988; Hedin and Erickson, 1988); however, quantification of these factors is not straightforward.

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There does, however, seem to be general correlation between acid generation and NP/MPA ratio for either large excesses or deficiencies of NP. DiPretoro and Rauch (1988) found that overburden with over 3% NP (expressed in weight percent neutralization as $CaCO_3$) produced alkaline drainage while those with <1% produced acidic drainage. Erickson and Hedin (1988) observed >8% and <2% NP as the limits for alkaline and acidic drainage, respectively. Lapakko (1988) found that 3% calcium carbonate neutralized an overburden material with 1.17% sulfur. Brady and Hornberger (1989) suggested NP threshold values of >3% and sulfur <0.5% as minimum guidelines for alkaline-producing strata. Brady *et al.* (1990) concluded that, even when alkaline additions are added to spoil with insufficient natural excess overburden NP ("net neutralization potential" or NNP), AMD was formed or persisted. A common thread in these investigations is that some excess of base is required to assure neutralization of acid potential. One or more physico-chemical mechanisms for "tying up" base or making it ineffective seems to be operating. The identities of these mechanisms, however, are not clear. The problem may be kinetic in nature, related to timely delivery of base, or physical, related to the mechanical distribution of base (Brady *et al.*, 1990), or statistical, related to uncertainty in estimation of NP and MPA. It is in fact possible that all of these factors may play a role.

In this investigation, we attempt to identify and measure mechanisms of base neutralization of acid-producing reactions. We examine short-term chemical behavior of both sulfide and carbonate reaction products in the initial phases of leaching of an acid-producing spoil pile. The dataset employed is a time series of geochemical and hydrologic measurements. The purpose is to assess (1) mechanisms of carbonate dissolution and acid production in the early phase of spoil weathering and (2) geochemical signature of early acid-pile evolution. We do not address the problem of long-term acid neutralization in the spoil, but only the issue of how piles first turn acid and what this tells us about the mechanisms and effectiveness of neutralization.

Study Area and methods

The study area is a reclaimed mine backfill in Upshur County near Buckhannon, WV, operated by Island Creek Corporation. This area has a humid climate, averaging 110 cm (45 in) of rain per year. In winter 1981-82, Island Creek personnel constructed 11 test piles with waste rock consisting of sandstone and shale overburden. The piles were flat-topped and roughly 16 x 16 m in area x 2 m high, each containing about 400 short tons of waste rock, sized to fall within the range of approximately 1 to 8 inches in diameter. Each pile was emplaced over a plastic liner for collecting basal drainage into an 8-inch-diameter perforated PVC underdrain. The underdrains discharged to a series of weirs where flow could be measured and samples of water collected.

Composition and construction methods were varied among piles. Four unamended "control" piles were used (1, 2, 3, 10), containing pure sandstone, pure shale, layered sandstone/shale/sandstone, and well-mixed sandstone and shale, respectively. Piles 6 and 7 were of shale composition, with 00.31 and 0.15 wt %, respectively, of phosphate rock amendment added in thin layers. Piles 4, 5, and 8 were of layered sandstone/shale/sandstone stratification, with additions of 0.46, 1.07, and 1.26 wt % crushed limestone, respectively, also added in thin lifts. Pile 9 was also layered sandstone/shale/sandstone, with addition of 0.15 wt % quicklime (CaO) in thin lifts. Pile 11 was composed of shale with a surface application of sodium lauryl sulfate (SLS), in addition to Microwet #2, a commercial surfactant. A summary of the materials and construction method for each pile is given in table 1. NP and MPA were determined on samples collected randomly from each truck during pile construction and batched along with the appropriate mass of amendment. The ratio NP/MPA was calculated from these values and includes both spoil material and any amendments added. Results of acid-base balance calculations are also listed in table 1.

The placement and composition of spoil materials simulated field conditions with one major difference. The screening to pass fines created a highly permeable spoil, with dominantly intergranular porosity. This material may therefore behave hydraulically quite differently from natural spoils, whose hydrogeologic characteristics have been described as dominated by highly transmissive fracture porosity (Hawkins and Aljoe, 1990). The Island Creek piles might therefore be expected to display higher recharge and fluid flow rates than natural spoils. Also, spatial variability in hydrogeologic characteristics is thought to have been largely controlled in these piles. Results, therefore, may differ from full-scale spoil piles containing more typical unscreened overburden.

Samples for water chemistry were collected at approximately 2-week intervals during the first year of the experiment. Samples were analyzed for: dissolved calcium (Ca), magnesium (Mg), and sulfate (SO_4); total recoverable (raw acidified) iron (Fe) and manganese (Mn); and pH, alkalinity, and acidity. Analytical techniques employed included atomic absorption spectroscopy for cations, spectrophotometric determination of Ba-complexed SO_4, and titrimetric alkalinity and acidity. Measurements were made on site. Using measured fluid flows, mass fluxes of ionic species were estimated for interval periods by midpoint interpolation to calculate cumulative mass fluxes. These results were compiled for the first year of pile leaching by infiltration of natural precipitation. Equilibrium calculations were made using the mineral equilibrium solver WATEQ, ignoring redox reactions because no estimates of sample Eh could be made. Equilibria and speciation were calculated following simulated addition of a balance ion (either sodium or chloride) to make up charge imbalances. Samples with >10% initial charge imbalance were not employed in equilibrium calculations.

The dataset has several limitations. No measurements were taken of ions including dissolved sodium, potassium, chloride, fluoride, silica, or aluminum. This precludes full electrochemical balance of the chemical analyses to be checked, or rigorous mineral equilibrium calculations to be performed. Na and K concentrations could be favored by ion exchange or, at lower pH than about 5.0, by hydrolysis of silicates. The extent of these processes therefore cannot be evaluated. Also, no characterization of solid-phase mineralogy, extractable ions, or geochemical composition was performed either on the spoil and amendments (before the placement of the piles) or on the altered spoil (after leaching was performed). Finally, no characterization of heterogeneity in NP or MPA within each pile was performed.

Table 1. Experimental matrix for spoil piles showing spoil composition, placement methods, amendments, and acid-base accounting, with percentages are in mass %.

Pile	Sand-stone, %	Shale, %	Mixing method	Amendment		NP, %	MPA, %	NP/ MPA
				Type	%			
1	100	0	n/a	None	n/a	1.23	0.31	3.94
2	0	100	n/a	None	n/a	0.08	0.97	0.08
3	57	43	Layer	None	n/a	0.10	0.56	0.18
4	53	47	Layer	Ls.	1.07	1.72	1.03	1.65
5	52	48	Layer	Ls.	0.46	1.11	2.00	0.56
6	0	100	n/a	Ph.	0.31	0.08	1.88	0.04
7	0	100	n/a	Ph.	0.15	0.08	0.91	0.09
8	54	46	Layer	Ls.	1.26	1.89	0.78	2.38
9	59	41	Layer	CaO	0.15	0.89	0.50	1.73
10	44	56	Blend	None	n/a	0.58	0.91	0.63
11	0	100	n/a	SLS	30 lb.	0.08	1.28	0.06

n/a: not applicable Ls.: crushed limestone Ph.: phosphate rock

Expected Stoichiometries Of Acid Mine Drainage

AMD-producing reactions may be written as some variation of the following (Stumm and Morgan, 1981):

$$FeS_2 + \frac{7}{2}O_2 + H_2O \xrightarrow{k_1} 2SO_4^{2-} + Fe^{2+} + 2H^+, \tag{1}$$

$$Fe^{2+} + \frac{1}{4}O_2 + H^+ \xrightarrow{k_2} Fe^{3+} + \frac{1}{2}H_2O, \tag{2}$$

$$Fe^{3+} + 3H_2O \xrightarrow{k_3} Fe(OH)_3 + 3H^+, \tag{3}$$

and

$$FeS_2 + 14Fe^{3+} + 8H_2O \xrightarrow{k_4} 15Fe^{2+} + 2SO_4 + 16H^+ \tag{4}$$

Under acid pH, rate constant k_3 is the slowest of the four reactions (Garrels and Thompson, 1960) and thus may limit the rate of additional acidity production in reactions (3) and (4). Oxidation of ferrous iron proceeds most rapidly at high pH and quite slowly at pH's below about 3, where half-reaction times are on the order of 1000 days (Stumm and Morgan, 1981). Thus Fe^{2+} oxidation may be a rate-limiting step for the potential acidity from oxidation of pyrite according to reaction (1).

The stoichiometry of reactions (1) to (4) gives the expected ratio of dissolved ions in AMD effluent. For example, in the absence of Fe^{2+} oxidation, the expected molar ratio of sulfate ion to acidity evolved is 2:2. Fe^{2+} oxidation consumes one mole of this acidity, but subsequent precipitation as $Fe(OH)_3$ produces an additional 3 moles of H^+, for a net acidity of 4 moles per mole of pyrite. Thus the expected molar SO_4/acidity ratio (per mole of pyrite) is 1:2. Catalytic oxidation of pyrite by Fe^{3+} may somewhat decrease this ratio, depending on the extent of Fe^{3+} reduction by pyrite. In general, however, a sulfate/acid ratio of 1:1 would accompany lack of oxidation of ferrous iron, while a ratio of 1:2 would ensue if $Fe(OH)_3$ is actively forming. Both assume, of course, that acid is not neutralized by other reactions and that dissolved SO_4 behaves conservatively.

Dissolution of calcite by evolved acid may be written as

$$CaCO_3 + 2H^+ \longrightarrow Ca^{2+} + H_2CO_3^o \qquad (pH <\sim 5.3), \qquad (5)$$

$$CaCO_3 + H^+ + HCO_3^- \longrightarrow Ca^{2+} + 2HCO_3^- \qquad (pH >\sim 7.3), \qquad (6)$$

while similar reactions may be written for dolomite dissolution, such as

$$CaMg(CO_3)_2 + 4H^+ \longrightarrow Ca^{2+} + Mg^{2+} + 2H_2CO_3^o \qquad (pH <\sim 5.3). \qquad (7)$$

The expected stoichiometric ratio of $(Ca^{2+} + Mg^{2+})/(H^+$ neutralized) is about 1:2 at low pH (mineralization to dissolved CO_2) and 1:1 at high pH (increase in bicarbonate alkalinity). Between these two extremes, the ratio will be intermediate between 0.5 and 1. The pH governing the extent of reactions (5) to (7) will be strongly influenced by pCO_2 and the ability of carbon dioxide to exsolve to the atmosphere. Depending on which neutralization reaction dominates, we may calculate the expected stoichiometry of $SO_4/(Ca+Mg)$, using the neutralization ratios in conjunction with the 2 moles of net acidity produced per mole of sulfate. We will refer to the rate of change in this ratio of dissolved acid products to base products as

$$\delta = \frac{d\{SO_4^{2-}\}}{d\{Ca^{2+} + Mg^{2+}\}} \qquad (8)$$

The index δ will have an expected value ranging from 0.5 (high pH) to 1.0 (low pH), with values between 0.5 and 1.0 at intermediate pH. δ values of less than the expected value under prevailing pH might indicate either (1) slower pyrite oxidation than base dissolution, (2) depletion of pyrite, or (3) neutralization by hydrolysis of Ca- or Mg-aluminosilicate minerals, such as clays or feldspars. A value of δ greater than expected could, on the other hand, suggest (1) slower carbonate dissolution than pyrite oxidation, (2) incomplete oxidation of ferrous iron resulting in less acid production, (3) ion exchange reactions transferring dissolved Ca or Mg to clays, or (4) depletion of carbonate minerals. Values of δ exactly equal to the expected value would suggest that reactions 1 through 7 are appropriate, i.e. acid is produced by both sulfide oxidation and metal-hydroxide formation and consumed by carbonate dissolution. The index δ thus provides a means to infer mechanisms of carbonate buffering within AMD-generating spoil. The sum of Ca + Mg is employed rather than Ca^{2+} alone because many natural carbonate rocks contain minerals of both calcitic (pure or magnesian) and of dolomitic composition. An inherent assumption in use of δ is that there is no source or sink for either sulfate or alkaline-earth cations (for example, acid sulfate salts, gypsum, sulfate reduction) not accounted for in reactions 1 through 7. Under specific conditions, this geochemical assumption may be reasonable.

Results

Plotted in figures 1-4 are the cumulative {SO_4} and {Ca+Mg} fluxes for groundwater effluent during the first year after placement of the piles. Also plotted is discharge pH. The results are grouped accorded to treatment types: control (no amendments: piles 1, 2, 3, and 10); limestone-amended (piles 4,5, and 8); phosphate rock-amended (piles 6 and 7); quicklime-amended (pile 9); and SLS-amended (pile 11). Table 1 details variations in the observed spoil materials composition and in their placement.

Figure 1 shows comparative results for the control piles. The NP for piles 2 and 3 are 0.08% and 0.10%, values typical for native carbonate composition in most of the unamended spoils. However, piles 1 and 10 had 1.23% and 0.58%, respectively, rather anomalously high values. The reason for the high "background" carbonate compositions in these latter two piles is unknown, but could be related to natural variability or to sampling error. All except pile 1 would be expected to be net acid producers based on the low values of NP/MPA observed (<0.65). Inspection of Figure 1 shows that all (including pile 1) did in fact at least start to turn acid, with the slowest rate of acid production coming from pile 10, the well-blended but unamended spoil pile. Pile 1 (unamended) gave the most rapid rate of acid evolution, with pH dropping below 5 within about four months. Near the end of year 1, pH in water from pile 1 appeared to be rising somewhat, but remained acid. For all four piles, the cumulative SO_4 and {Ca + Mg} fluxes show quite similar patterns, as do in fact nearly all of the piles.

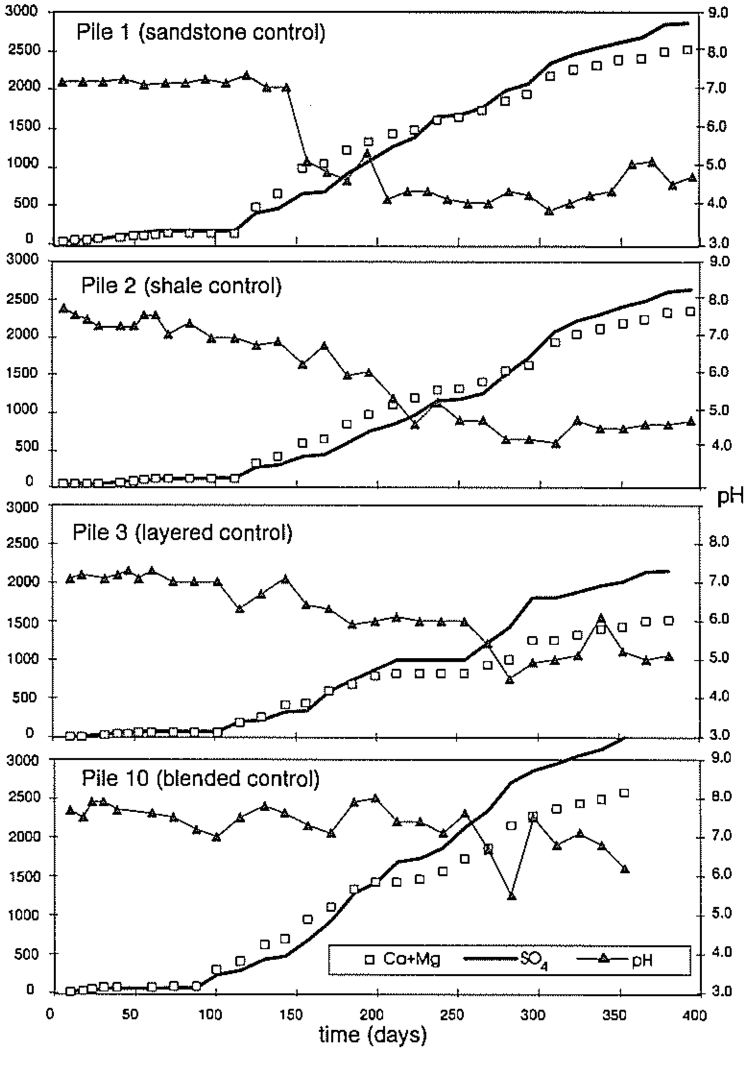

Figure 1. pH (right axis) and cumulative SO_4 and {Ca+Mg} fluxes (left axis, in mol) for leachate from unamended piles..

Figure 2 shows the flux data for the limestone-amended piles, all composed of three horizontal layers of sandstone/shale/sandstone lithology. For these three, pile 5 (0.46% limestone, NP=1.11) shows a gradual decline to pH levels just above 5, while pile 8 (1.26% limestone, NP=1.89) dropped below pH 5 within 70 days. Pile 4 (1.07% limestone, NP=1.72) showed little variation in pH during this year.

Figure 3 shows the piles treated with rock phosphate from Florida deposits. This amendment consists largely of the minerals apatite ($CaPO_4$) as well as calcite ($CaCO_3$), a common impurity within phosphate deposits. Pile 7 (0.15% phosphate, NP=0.08) failed to turn acid, while pile 6 (0.31% phosphate, NP=0.08) turned acid near the end of the sampling period.

Figure 4 shows piles treated with quicklime (pile 9, CaO=0.15%, NP=0.89%) and SLS (pile 11; NP=0.08%). The former became acid within 5 months; the latter failed to turn acid and displayed relatively slow SO_4-production.

Figure 5 shows time versus pH (right axis) and molar Ca/Mg ratio, pCO_2 (atmospheres), and saturation indices for selected mineral phases (calcite, gypsum) in the leachate for pile 3, the unamended layered mixture of sandstone and shale. Saturation index as used here is defined as SI = log [ion activity product/equilibrium constant]. A value of zero for SI indicates saturation with respect with the mineral phase. pH gradually declined in this pile to about 5, while Ca/Mg rose to a mid-year peak of about 4, dropping to about 2 in the latter half of the year. Gypsum reached saturation in mid-year, at about the same time Ca/Mg peaked. Calcite increased to about 3 to 4 orders of magnitude undersaturation by 300 days elapsed due to acid production in the pile. All other mineral phases of possible importance to the geological setting were also highly undersaturated.

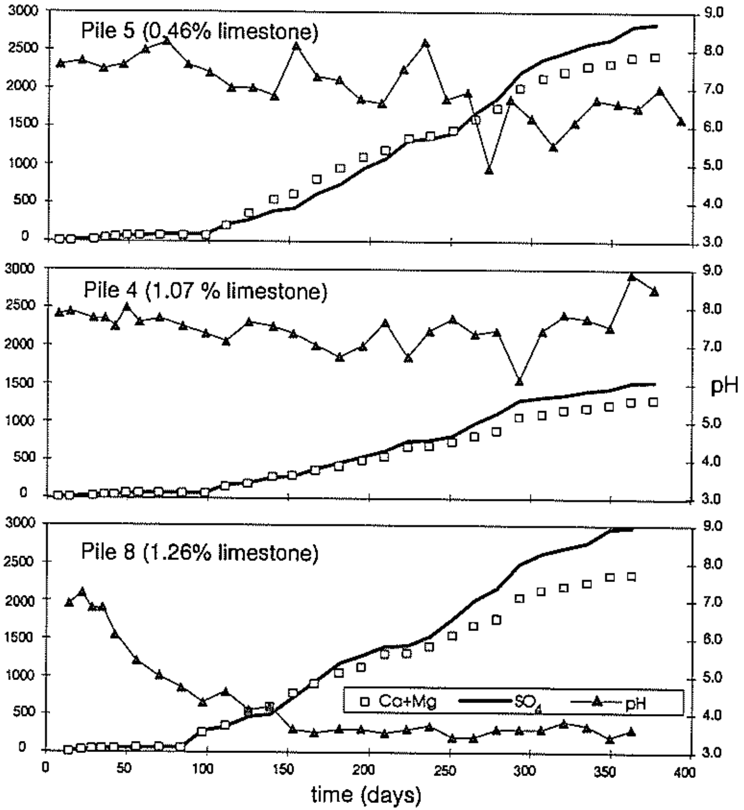

Figure 2. pH (right axis) and cumulative SO_4 and {Ca+Mg} fluxes (left axis, in mol) for leachate from limestone-amended piles, layered sandstone/shale/sandstone.

Interpretations

Shape of the ion flux time series

Cumulative SO_4 and {Ca + Mg} fluxes display grossly a similar pattern for all piles, irrespective of lithology, construction method, amendment, NP, and MPA. Several flux time-series show three characteristic features:

1. An initially flat curve for both fluxes, of 50-100 day duration
2. A slightly steeper slope of Ca+Mg flux than that for SO_4 between 100-300 days ($\delta<1$).
3. A later period of slower Ca+Mg flux ($\delta>1$) after about day 250, developing a gap for several piles between cumulative SO_4 and {Ca+Mg} fluxes.

The initial flat portion of the leaching curve (period 1) is interpreted as a period of saturation of the spoil with water and humidity, during which pyrite oxidation is incipient. The lag time may represent passage of the first pore volume through the piles.

The early Ca + Mg "bulge" (period 2) appears to reflect a transition from early base dissolution behavior, at the expected low ratio of $\delta\cong0.5$, to the later period (period 3) where δ rises to and exceeds unity. The Ca/Mg molar ratio of in period 2 rises to above 3.0, higher than the ratio of 1.5 to 2.5 observed later in the year (fig. 5). This behavior was general to all the spoil piles and not related to any particular base amendment; it occurs for control piles also. The late decrease in Ca/Mg ratio suggests that a carbonate phase of approximately equal mass of dolomite and calcite may have been dissolving in this period, if the assumption is valid that all Mg is derived from carbonates as opposed to hydrolysis and ion exchange. During the earlier bulge period, the calcite percentage leached was likely >75%.

The unexpectedly high values of δ observed late in the year (period 3) may be interpreted in several ways, none of which may be unambiguously validated with available data. One possibility is that carbonate dissolution is kinetically slowed, due either to a net decrease in the ratio of calcite vs. dolomite or to a net decrease in surface area of the carbonate fraction. Another possibility is that the "effective" carbonate is simply near depletion, with some or much of the amendments added being hydraulically isolated from the leachate, as by ferric hydroxide armoring. The SO_4-Ca/Mg gap correlates with development of low pH in at least two of the piles, although this relationship is not consistently observed. In several piles with low naturally-occurring carbonate NP (on the order of 0.1%, or about 2600-3600 moles of carbonate as $CaCO_3$ in various piles), cumulative carbonate flux approaches 80% or more of the available carbonate by the end of the sampling period.

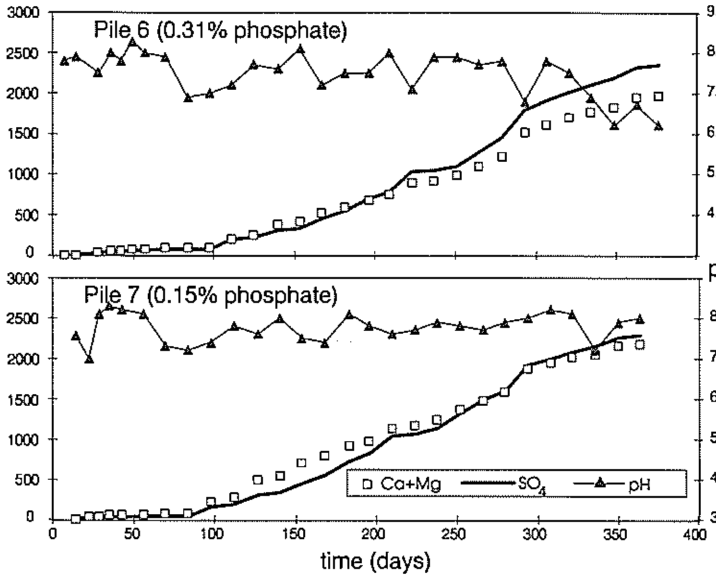

Figure 3. pH (right axis) and cumulative SO_4 and {Ca+Mg} fluxes (left axis, in mol) for leachate from phosphate-amended piles, all of uniform shale.

Another possibility is transfer of Ca and/or Mg to other solid phases. Mineral equilibria indicate that no Ca- or Mg-bearing minerals are at or above saturation except gypsum, which reaches slight supersaturation for most of the piles following mid-year. Gypsum precipitation and ion exchange of Ca or Mg onto clays are both feasible reactions, but have not been confirmed by examination of reacted spoil. Gypsum precipitation would not by itself explain the anomalously-high δ values, although δ would vary somewhat under gypsum saturation.

The notable similarity between flux curves from different piles (both amended and unamended) suggests that base consumed in the first year of leaching was primarily native carbonate disseminated in spoil. The layered amendments cannot be demonstrated as ineffective but do not control flux behavior in early stage leaching.

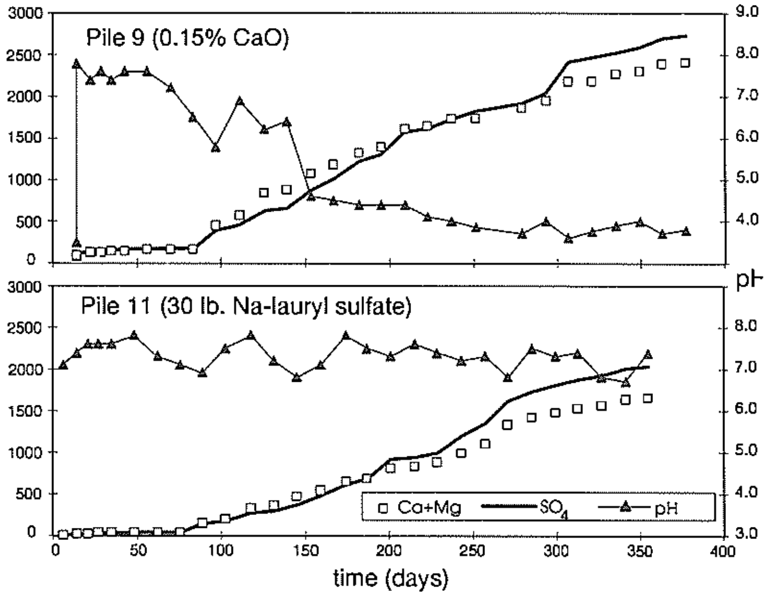

Figure 4. pH (right axis) and cumulative SO_4 and {Ca+Mg} fluxes (left axis, in mol) for leachate from CaO--and sodium lauryl sulfate-amended piles.

Effect of amendments

No clear relationship is indicated between presence/amount of base amendment and prevention of acid leachate. For example, all of the uniform or stratified control piles (pile 1, 2, 3) developed acid conditions readily, and the blended control pile 10 was on the verge of going acid near the end of the first year. On the other hand, one limestone-amended piles (pile 8, 1.25% limestone) and one apatite-treated piles (pile 6, 0.3% phosphate) went acid as well. These suggest that the initiation of acid conditions in these experiments was not strictly limited by the amendments and may have been influenced by the balance between pyrite oxidation and naturally-occurring carbonate. There appears to be enough variation in NP/MPA values (mean 1.04, standard deviation 1.28) to account for the observed variation in rate of acid generation. No data are available describing inter-pile heterogeneity of NP and MPA or the precision with which these were sampled and estimated.

The effect of differing spoil lithologies was not examined in these experiments due to the small number of piles examined. Only for the shale lithology (4 pure samples, piles 2, 6, 7, and 11) may natural variability be described. Shale (NP mean 0.08±0.003; MPA mean 1.26±0.44) exhibited almost no variance in NP and a coefficient of variation of about 0.35 in MPA. Higher NP values were observed in unamended piles containing sandstone, pile 1 (100%

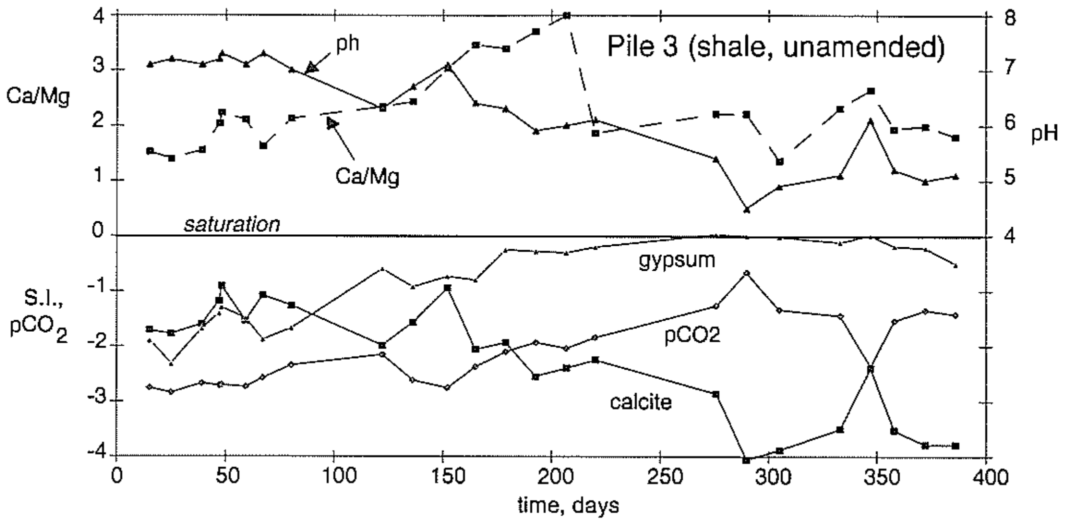

Figure 5. Leachate pH (right axis) and saturation indices, pCO$_2$, and molar Ca/Mg ratio (right axis).

sandstone) and pile 10 (44% sandstone), suggesting that sandstone contained higher NP than shale. From the limited data available, the shale had lower NP (<0.1%) and higher MPA (1.3%) than the sandstone (1.2% NP with MPA <0.5%).

Iron and manganese oxidation

Total recoverable iron concentrations were low in the great majority of effluent samples, exceeding 1 mg/L for only a very few. Manganese concentrations were somewhat higher (2 to 5 mg/L) for most piles and in the vicinity of 10 to 50 mg/L for piles 8 and 9, whose pH reached to below 4. It may be inferred that ferrous iron oxidation was rapid and led to precipitation of hydroxides in all piles. On the other hand, formation of manganese oxides may have become inhibited at lower pH. The ferrous/ferric redox couple was not analyzed, and so no estimates of oxidation potential could be made and mineral equilibria are not calculated for iron- and manganese-species.

Pyrite oxidation kinetics

Cumulative sulfate flux is nearly linear with respect to time after the first 100 days or so; that is, dissolution of pyrite apparently obeys a pseudo-zero-order rate law. The mean rate is 0.0239 moles SO_4 per ton spoil per day, with rather small variance and narrow confidence limits (table 2). This low variance is striking considering the broad range of NP, MPA, amendments, lithologies, and construction methods employed. It appears that pyrite oxidation causes a uniform flux of dissolved sulfate, with rate controlled by oxygen availability, surface area of spoil fragments, pyrite reaction rind thickness, and other factors prominent in pyrite oxidation kinetics (Cathles and Apps, 1975). Hydraulic and transport factors may well be also important, but were not studied in this investigation.

Table 2. Zero-order pseudo-rate constants (mol SO_4/ton/day) based on sulfate fluxes. Confidence intervals based on T-distribution, $\alpha=0.05$, 10 degrees of freedom.

Pile	Rate constant
1	0.0284
2	0.0259
3	0.0189
4	0.0150
5	0.0239
6	0.0230
7	0.0247
8	0.0239
9	0.0223
10	0.0358
11	0.0207
Mean	0.0239
Std. dev.	0.0053
Conf. limits	$0.0203<\mu<0.0275$

Mineral Equilibria

pCO_2 values rise in groundwater within the pile from near-atmospheric levels at the onset of leaching to about 10^{-1} atm as carbonate dissolution begins. While some values of pH seem anomalously low with respect to measured alkalinities and may represent field errors and overestimation of pCO_2, high CO_2 pressures are nonetheless indicated by the data. Calcite (and dolomite, not shown) is at no point after mid-year less than 2 orders of magnitude undersaturated. Only gypsum approaches saturation, after about 200 days of leaching. SI_{gyp} reaches an apparent plateau that would be consistent with gypsum precipitation, although no x-ray observations of gypsum reaction products have been made to determine whether gypsum was in fact being formed. The observed decrease in Ca/Mg ratio late in the first year is consistent with gypsum formation.

Conclusions

Leachate samples collected during the first year of weathering of a large-scale field experiment yield insights into mechanisms of development of acid conditions in sandstone and shale spoil materials. Major conclusions are:

1. Dissolution of pyrite obeys a pseudo-zero-order kinetic rate law over a broad range of lithologies, NP, MPA, amendments, and pile construction. The mean rate constant is 0.0239 ± 0.0036 moles SO_4 per ton spoil per day.

2. SO_4 and {Ca+Mg} flux time series indicate that naturally-occurring carbonate disseminated through the spoil rocks neutralizes early acidity generated by acid reactions. Carbonate mineralogy (calcite, magnesian calcite, dolomite) may influence neutralization rates.

3. Amendments studied had no pronounced impact on early AMD evolution and were in some cases ineffective at preventing AMD for NP/MPA ratios as high as 2.3. One the other hand, in all cases for which NP/MPA was less than unity, acid leachate was generated within the year of study. Response in pH and acidity varies more between piles than SO_4 or {Ca+Mg} flux.

4. Layered base amendments appeared to have had no clear effect on leachate during the period of study. This may relate due to their inhomogeneous distribution, to heterogeneity in NP or MPA within the piles, to hydroxide armoring of amendment layers, or to time lag in their reaching the outflow.

5. Equilibrium calculations using WATEQ for a time series of samples from a typical pile indicate that gypsum reached a saturation plateau after about 200 days of leaching. Mineral equilibria support that gypsum or some calcium sulfate polymorph could precipitate in these piles. Calculated pCO_2 values ranged from an initial 10^{-3} atm to as high as about 10^{-1} atmospheres late in the year. Calcite ranged from 2 to 4 orders as acid production ensued in the first year of leaching.

Sampling of these piles was discontinued for a 10-year period following the first year; samples were not again collected until 1993. Current work on this site is focusing on the long-term impacts and success of the amendments on mitigating spoil-pile discharge, and on examination of the reacted spoil to determine mineralogical and chemical changes since mining.

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