Comparative Performance of Different Alkaline Addition Rates in Kinetic Test Results

Ronald H. Mullennex, CPG, CGWP
Senior Principal – Practice Leader, Geology and Hydrogeology
Cardno, Inc.

Ankan Basu, CPG
Geologist
Cardno, Inc.

Abstract

Coal processing commonly results in concentration of pyritic sulfur into the reject fraction or refuse material from the operation. A common regulatory requirement for disposal of such material requires an alkaline addition at a rate based on the stoichiometrically-calculated acid-base balance. Implementation of the guideline has demonstrated its effectiveness in the short to medium term, but where pyritic sulfur contents are relatively high the practicability of the guideline becomes problematic from operational, volumetric, and economic standpoints.

Studies have shown the importance of carbonate in preventing acid drainage, as it not only neutralizes acid, but also inhibits acid generation. Some studies have found that as little as 2-3% neutralization potential (NP, as $CaCO_3$) significantly correlates with alkaline drainage characteristics; and that the presence of carbonates in amounts as low as 1-3% inhibits pyrite oxidation (at least for some period of time).

The subject kinetic testing program examines how alkaline (limestone) addition at different rates may affect the initiation and degree of acid generation from relatively high-sulfur-content refuse material. Results indicate that even small amounts of limestone addition can forestall acid generation for the active life of a fill, until it can be capped to prevent further intrusion of oxygen and water, and thereby curtail any further acid generation in the long term.

Introduction

Coal processing commonly results in concentration of pyritic sulfur into the reject fraction or refuse material from the operation. The West Virginia Department of Environmental Protection (WVDEP) and other regulatory agencies recognize the addition of alkaline materials to such refuse as an effective means of both retarding the acid-generation process and neutralizing acidity as it is generated. In refuse materials of moderate acid-generating potential, WVDEP's policy is to require a blended alkaline amendment equal to 0.75 times the amount needed to provide the stoichiometrically-calculated acid-base balance (the "Jenkins formula"[1]). In practice, implementation of the equation does not consider the inherent acid-neutralization potential (NP) of the material, but rather bases the calculated alkaline amendment rate on only the pyritic sulfur content of the refuse and the calcium carbonate ($CaCO_3$) equivalency of the amendment material. It has been the policy to require an increased amendment rate of 1.1 times the calculated balancing amount in the northern part of the state where pyritic sulfur concentrations are often greater than those farther south.

Implementation of the guideline has demonstrated its effectiveness in the short to medium term, but where pyritic sulfur contents are relatively high the practicability of the guideline becomes problematic from operational,

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[1] Jenkins, George T., Amending Coal Refuse with Alkaline Materials, Proceedings of the 20th Annual WVSMDTF Symposium, Morgantown, WV, 1999.

volumetric, and economic standpoints. In such circumstances, alternative or combined methods must be considered for prevention of acid generation and/or migration.

Prevention of oxidation through capping offers a potential alternative approach to achieve the goal, but a cap cannot be placed until the refuse fill structure is completed or locally-completed. During that active operational period, there is a potential for atmospheric oxidation to begin and to release dissolved ferric iron that would be capable of continuing the oxidation and acid-generating process after the cap or cover is placed and atmospheric oxygen is excluded. However, some studies have indicated that the mere presence of carbonate minerals, even in relatively small amounts, both neutralizes acid as it is formed and inhibits pyrite oxidation.[2]

The subject 25-week kinetic testing program was undertaken to examine how alkaline (limestone) addition at different rates of application may affect the initiation and degree of acid generation from relatively high-sulfur-content refuse material. The results of that testing show that limestone addition, even in amounts much lower than that required for long-term neutralization of all acid-generating potential, can forestall acid generation for the active life of a fill, until it can be capped to prevent further intrusion of oxygen and water, and thereby curtail any further acid generation in the long term.

Methods

Samples of freshly-created, raw preparation plant refuse material were collected from an adjacent refuse disposal facility. Analyses confirmed that the material there is similar to what is expected from the subject planned operation. Pre-leaching analyses included particle size distribution, sulfur forms and acid-base accounting by size fraction, and a suite of metals by size fraction, all in triplicate. Leaching tests were performed in triplicate on each of four amendment alternatives: 1) raw refuse with no alkaline amendment; 2) refuse with a 3% limestone addition (the limestone used was analyzed to be approximately 96% $CaCO_3$); 3) refuse with $CaCO_3$ applied at the rate of 3.125% per 1.0% pyritic sulfur content in the refuse, multiplied by 0.75 (the refuse pyritic sulfur was calculated by the laboratory to be 7.83%); and 4) refuse with $CaCO_3$ applied at the rate of 3.125% per 1.0% pyritic sulfur content, multiplied by 1.10. (Given the 7.83% pyritic sulfur content of the raw refuse and the 95.85% $CaCO_3$ content of the limestone, the actual rates of limestone addition to the latter two samples above were 19.48% and 28.08%, respectively.) The limestone was added while maintaining a constant mass of the sample, such that the pyritic sulfur content (on a percentage basis) varies with the amount of limestone added. The initial pyritic sulfur for each group forms the basis for subsequent calculations of percent depletion over time as leaching takes place.

Testing was performed in leaching columns 24 inches long and 6 inches in diameter. Each column was set up with 2000 grams of sample, including added limestone where applicable. The sample material was crushed to a top size of ¼-inch. (It is noteworthy that the particle size distribution of the sample material as field-collected exhibited only 35.7% passing a ¼-inch screen, such that 64.3% of the material was crushed to a smaller size than occurred in the field. This necessary crushing has the unintended but unavoidable effect of exaggerating the geochemical reactivity of the refuse by increasing the surface area available for oxidation. This effect is magnified further by the fact that the coarsest material in the sample (the > 1-inch fraction) exhibited a much higher pyritic sulfur content than that of the smaller particles. In the actual disposal structure, much of the pyrite in the coarse particles will be unavailable for reaction during the time the fill is open to atmospheric oxygen and rainfall.)

The four in-triplicate sample columns were subjected to weekly flushing with 2000 mL of deionized water to replicate rainfall diffusion. Such procedure, by intent, produces over several weeks the weathering effect that would require years to occur in the refuse fill; or may never occur within a fill where oxygen exposure becomes

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[2] Perry, Eric F., and Keith B. Brady, Influence of Neutralization Potential on Surface Mine Drainage Quality in Pennsylvania, in Proceedings, 16th Annual Surface Mine Drainage Task Force Symposium, Morgantown, WV, 1995.

limited as the fill progresses and where pore gas composition will have significant carbon dioxide to displace oxygen.

Evaluation of Data

Weekly leachate analyses were evaluated as to rates of leaching on both a mass(mg) and mole basis, for comparison to initial values to determine the amount (mg and moles) remaining at each point in time. Comparisons were made of calcium vs. sulfur moles leached and remaining, to estimate the general longevity (in the laboratory environment) of acid-generating and acid-neutralizing potential remaining at any given point in time. The relative differences in projected durations reflect expectations as to whether acid-generating and acid-neutralizing components are in balance, and, if not, the relative degree of imbalance. As expected, analyses of the solid sample materials both before and after the leaching process confirm a loss of total sulfur and of pyritic sulfur over the course of the program. However, there was also an increase in the actual amount of sulfate-sulfur in the material, due to oxidation of pyritic sulfur and some apparent retention of sulfate within the solid sample material. Consequently, the calculated rate of sulfur release based on the cumulative dissolved, leached sulfate amounts understates the actual rate of pyrite oxidation that occurred.

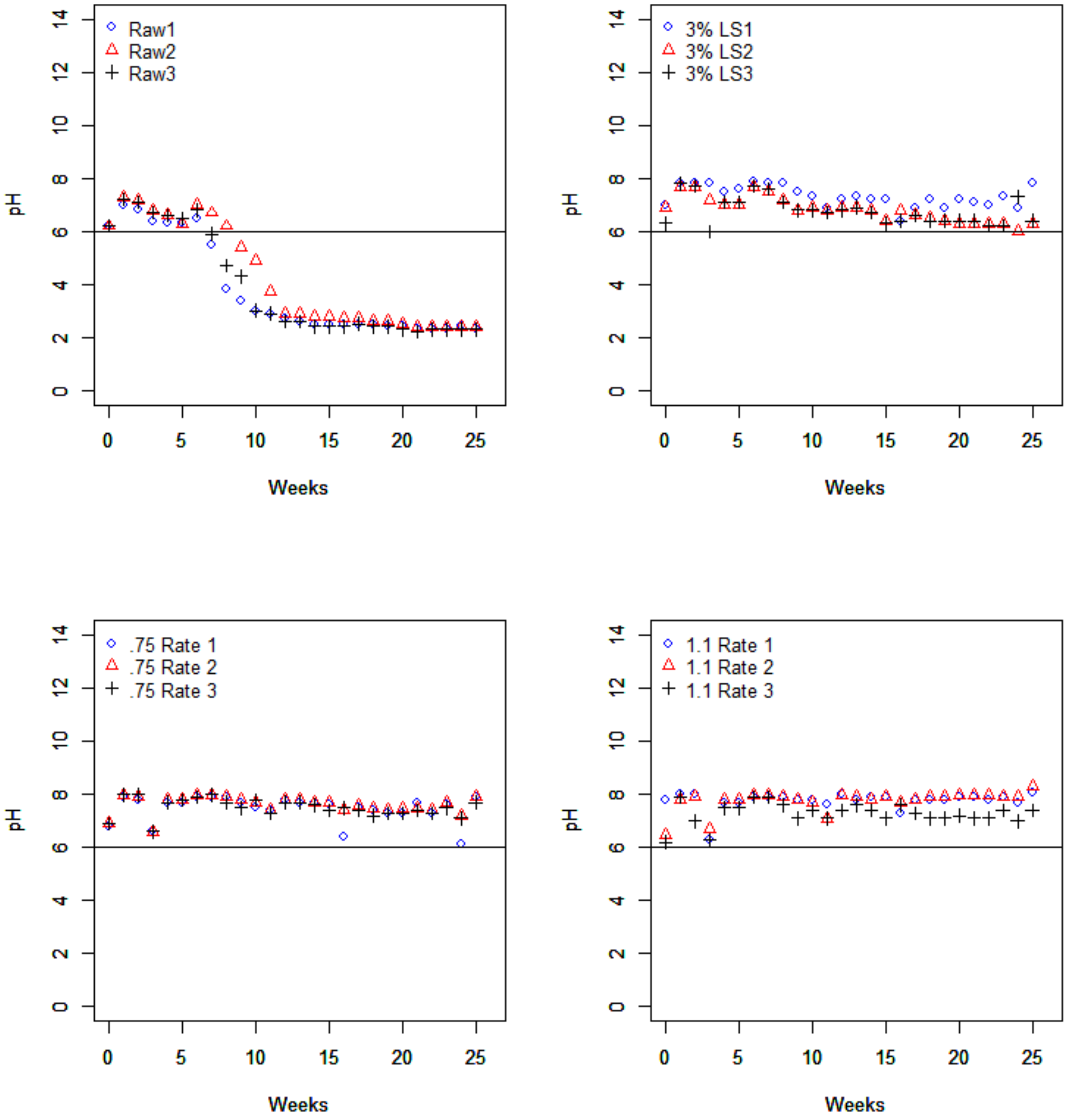
In performing calculations, the R statistical analysis programming language and its functions were used to generate tabular and graphic products for evaluation. Excel graphical tools were also utilized to generate some of the visual presentations.

Results

Effects on pH

Figure 1 below presents the trend in pH of the leachate from the four sample groups. It can be seen that low-pH conditions were encountered only for the triplicate samples of the raw refuse material, whereas the other samples, even with only the 3% limestone amendment rate, did not produce low-pH solutions over 25 weeks of the column leaching study. While the lowest observed pH among the raw refuse leaching samples was 2.2, samples with 3% limestone amendment had a minimum recorded pH of 6. Moreover, samples with much higher amendment rates followed a similar trend to that of samples with only 3% limestone addition. In other words, the experimental results suggest that, to mitigate acidic conditions resulting from pyrite oxidation, even a 3% limestone application rate is enough to prevent acid generation for many weeks under the test conditions (and much longer under actual field conditions).

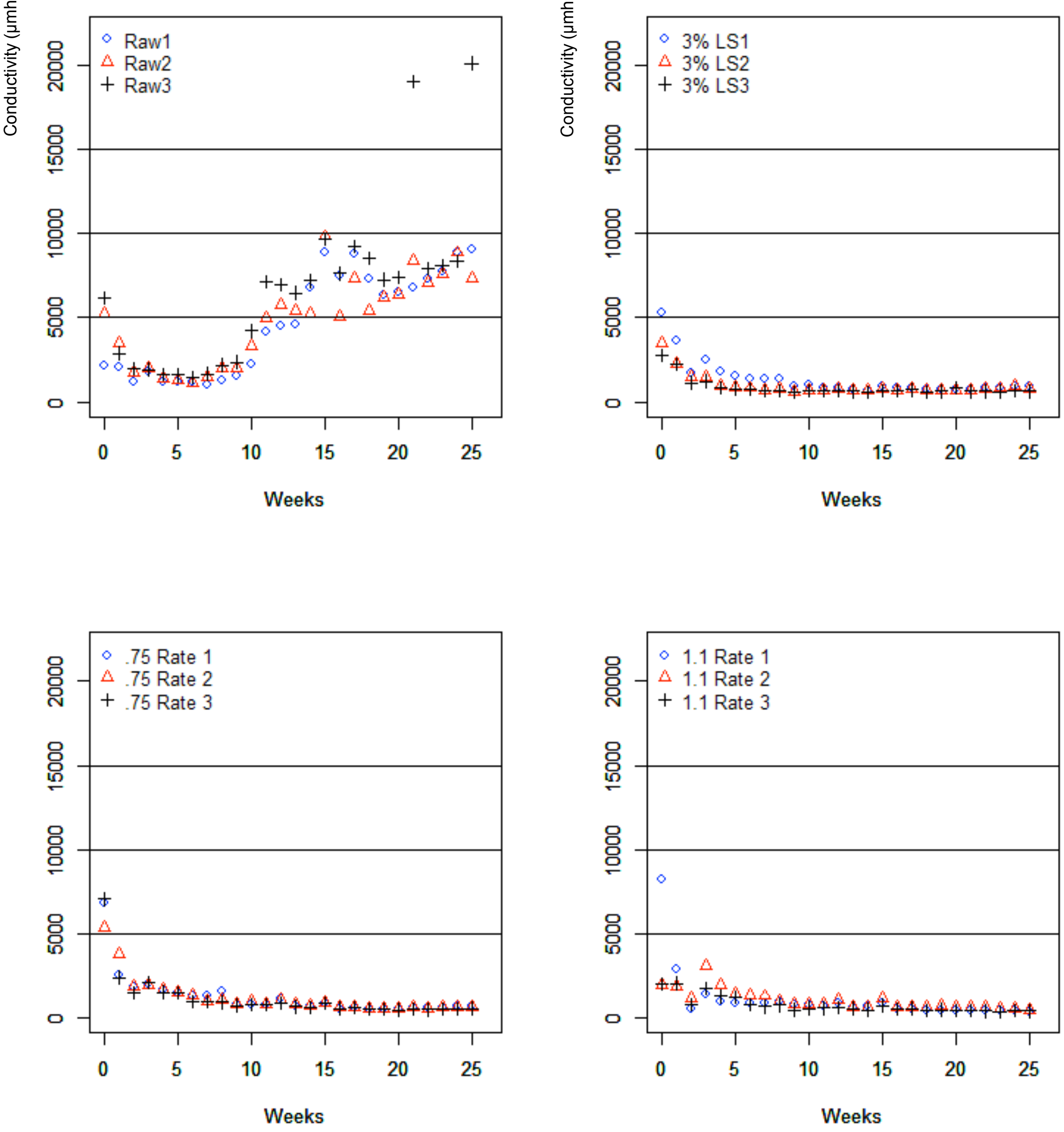
Figure 1: pH Trend in the Various Sample Groups During the Leaching Test Study



Effect on Conductivity

Conductivity is a measure of total ions in solution. Conductivity was measured on a weekly basis for all samples during the column leaching study. *Figure 2* below presents the trend in conductivity recorded in the four groups of samples. While there was a general increase in conductivity for the raw refuse samples, those groups with limestone addition underwent an initial decrease in conductivity, then general stability of that metric over the remainder of the test period. The trend in conductivity complements the pH condition, where the acidic conditions of the raw samples led to accelerated metals release. While the maximum recorded conductivity for the raw sample group was 20,100 µmhos/cm, the maximum observed conductivity for the samples with 3% limestone application was only 5,340 µmhos/cm.

Figure -2: Conductivity Trend in the Various Sample Groups During the Leaching Test Study



Effect on Acidity and Metals Acidity

The column leaching study also evaluated the potential acidity from the sulfide-rich samples over the 25-week period. Generation of acidity is directly related to the pH and metals mobility from the samples. *Figure 3* below presents the trend in hot acidity generation due to sulfide oxidation from the four sets of samples. The trends correspond well with those in pH and conductivity; that is, only the raw sample group produced significant amounts of acidity over time due to pyrite oxidation, whereas the addition of as little as 3% limestone greatly inhibited significant acidity generation for the duration of the study. No acidity generation was observed for samples with the higher limestone amendment rates. While the maximum acidity seen within the raw sample group was 4,900 mg/L of $CaCO_3$, for the 3% limestone amendment sample group, the maximum observed acidity was only 38 mg/L of $CaCO_3$.

Metals acidity usually comes from dissolved concentrations of iron, aluminum, and manganese in solution. Similar to total acidity, metals acidity showed a similar trend, and was observed only in the raw samples. *Figure*

4 below presents the trends in metals acidity during the leaching test study. As total aluminum was insignificant, most metals acidity resulted from the release of iron due to pyrite oxidation.

Figure 3: Acidity Trend in the Various Sample Groups During the Leaching Test Study

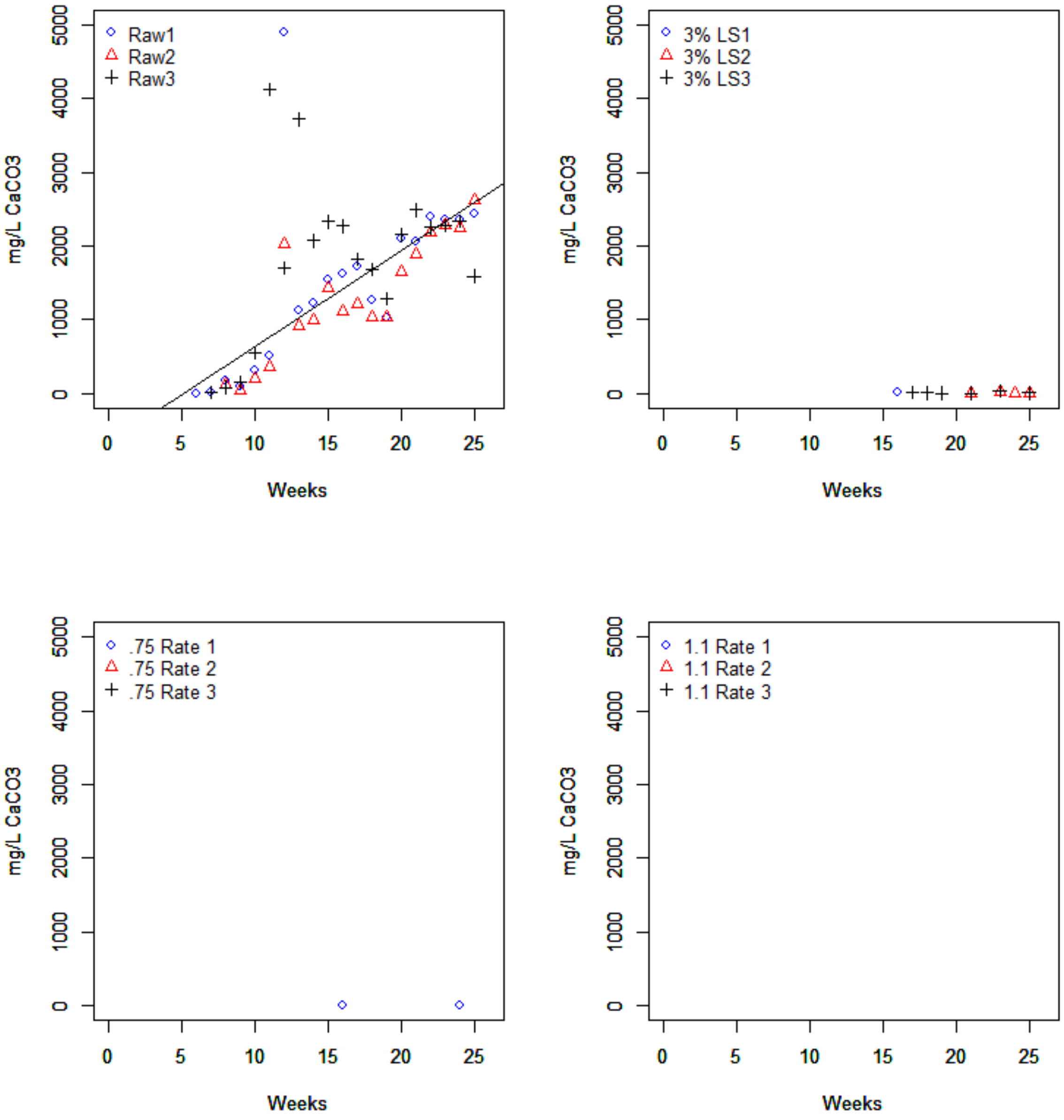
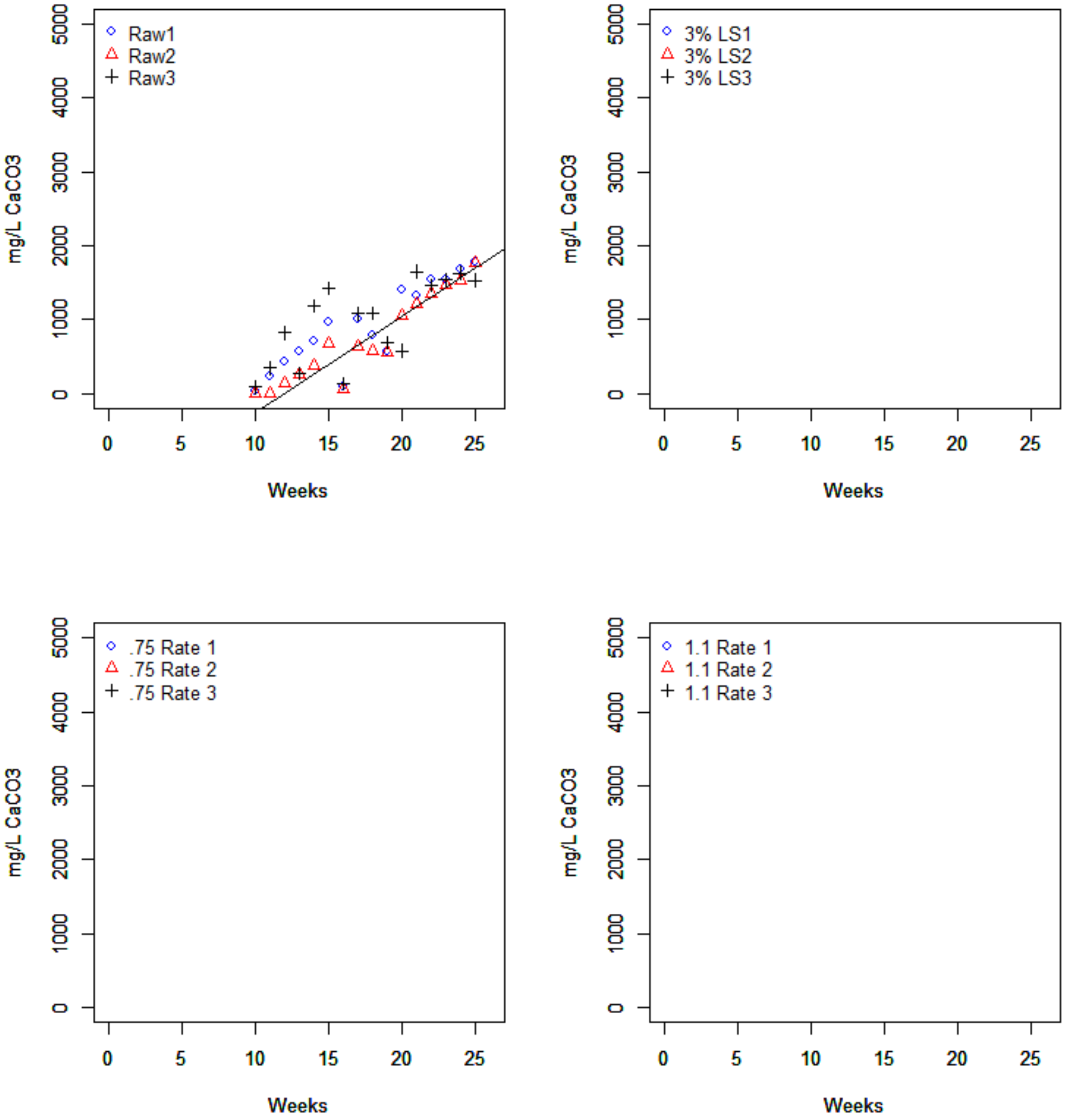


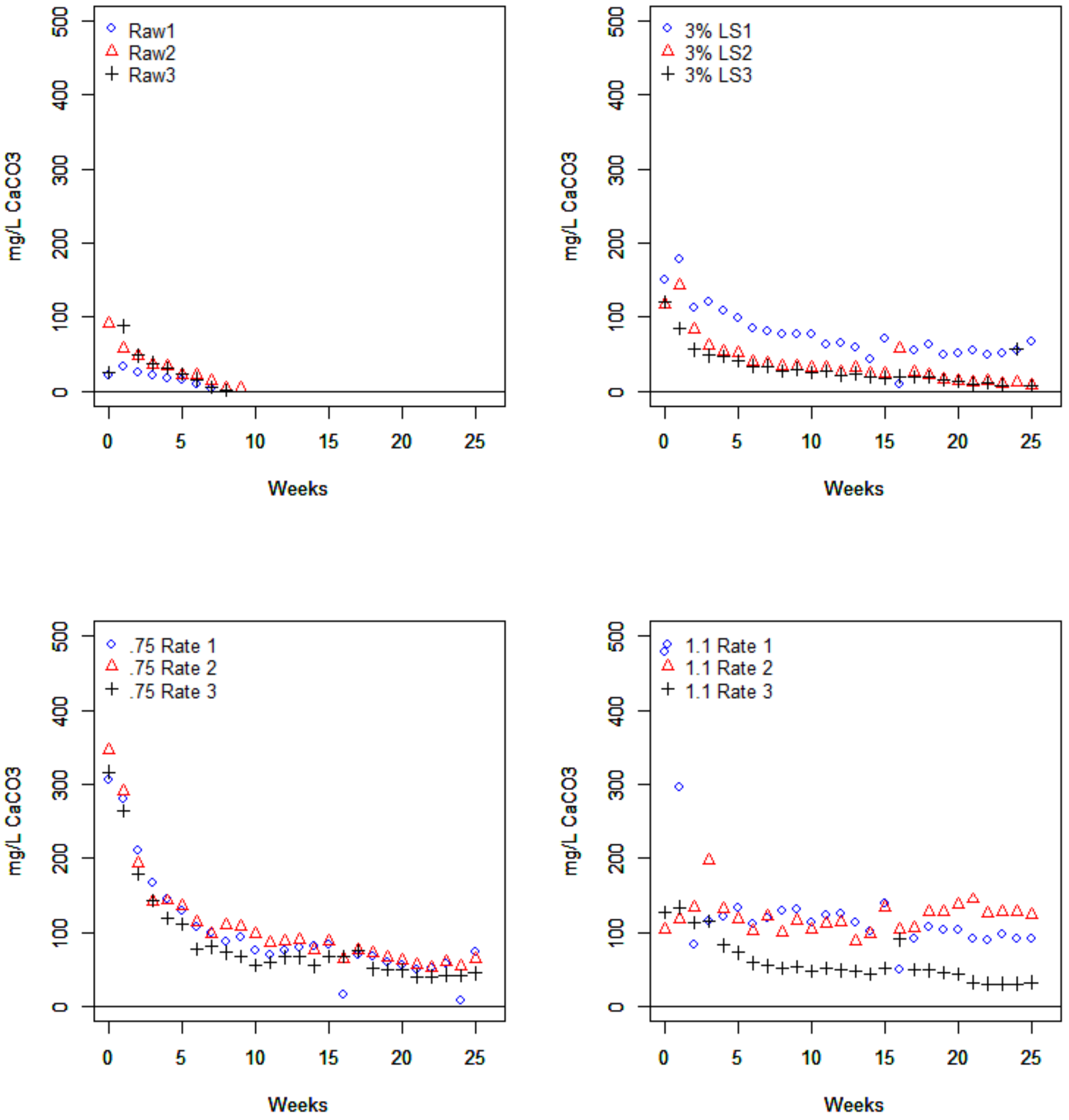
Figure 4: Metals Acidity Trend in the Various Sample Groups During the Leaching Test Study



Effect on Alkalinity

Alkalinity is a measure of the capacity of water or any solution to neutralize or buffer acids. For the raw refuse samples, all of the inherent alkalinity or buffering capacity was used up within the first 8 weeks of the leaching study, which resulted in a steep lowering of pH and increased generation of acidity. For the remainder of the samples, alkalinity was never exhausted during the period of study. *Figure 5* below presents the trend in alkalinity as observed during the program, from which it can be seen that all samples with limestone addition had retained buffering capacity at the end of the study period.

Figure 5: Alkalinity Trend in the Various Sample Groups During the Leaching Test Study



Effect on Metals Release

Iron is the metal of principal concern resulting from pyrite oxidation. *Table 1* below presents the rate of iron release from each of the four sample groups (represented by the No. 2 sample from each group). The rate of iron release, as would be expected, is correlative with the pH value of the leachate, which is also shown on *Table 1*. As can readily be seen, the native alkalinity of the raw material was exhausted within several weeks, leading to a rapid drop in pH and consequent increase in the rate of iron release. In contrast, even as little as a 3% limestone amendment greatly retarded pyrite oxidation, kept the pH level at 6.0 or greater for the duration of the testing program, and kept the rate of iron release minimal.

pH Value	Iron Release Rate (mg/Kg/wk)
>6	<1
5 - 6	1 - 10
4 - 5	10 - 100
3 - 4	100 - 500
<3	>500

Table 1: pH vs. Iron Release Rate

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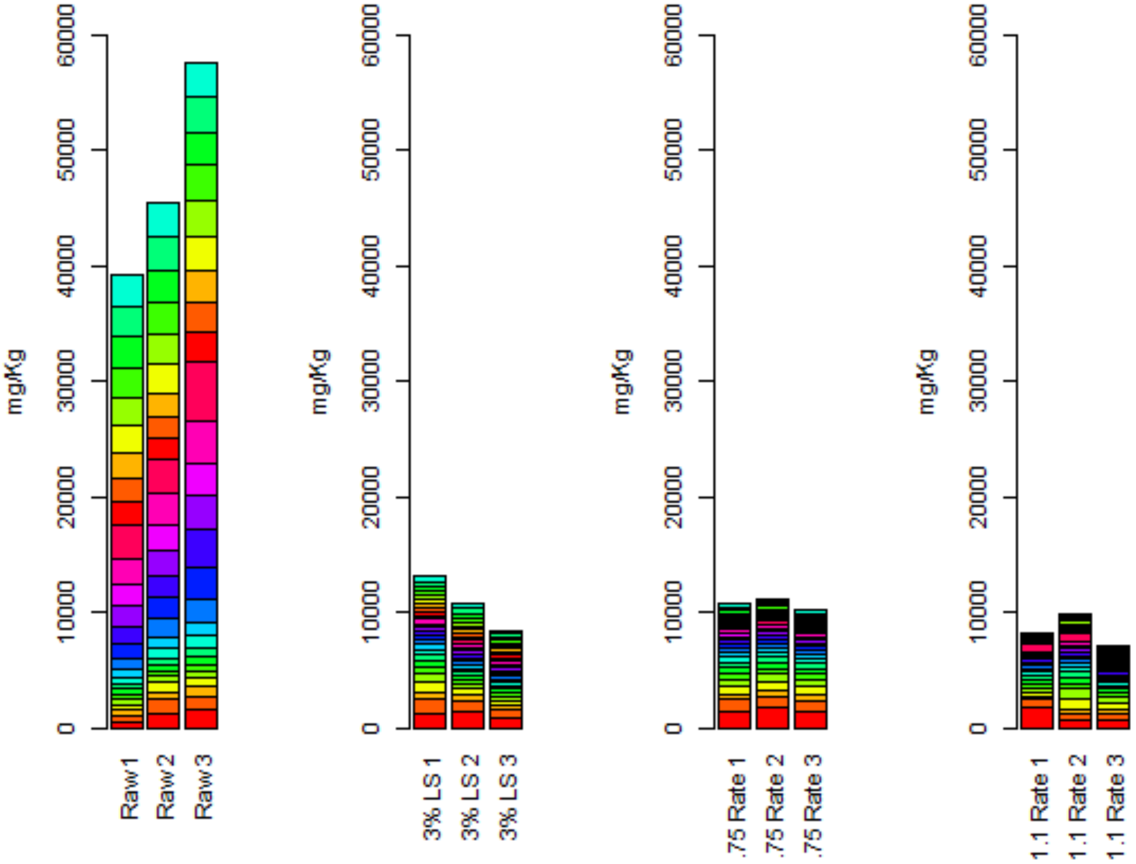
	Raw 2		3% LS2		0.75-Rate 2		1.1-Rate 2	
	pH	T. Fe	pH	T. Fe	pH	T. Fe	pH	T. Fe
Week	s.u.	mg/Kg/Wk	s.u.	mg/Kg/Wk	s.u.	mg/Kg/Wk	s.u.	mg/Kg/Wk
0	6.2	29.75	6.9	0.37	6.9	0.15	6.5	0.05
1	7.3	0.09	7.7	0.11	8.0	0.10	7.8	0.10
2	7.2	0.10	7.7	0.09	7.9	0.10	7.9	0.08
3	6.8	0.03	7.2	0.03	6.6	0.01	6.7	0.02
4	6.6	0.15	7.0	0.18	7.8	0.14	7.8	0.16
5	6.3	0.02	7.0	0.01	7.8	0.01	7.8	0.06
6	7.0	0.22	7.7	0.03	8.0	0.20	8.0	0.02
7	6.7	1.33	7.5	0.07	8.0	0.09	8.0	0.05
8	6.2	4.08	7.2	0.09	7.9	0.06	7.9	0.05
9	5.4	9.14	6.8	0.17	7.8	0.20	7.8	0.20
10	4.9	52.73	6.9	0.09	7.7	0.08	7.7	0.07
11	3.7	89.39	6.8	0.01	7.4	0.01	7.1	0.01
12	2.9	150.66	6.9	0.10	7.8	0.08	8.0	0.06
13	2.9	238.76	6.9	0.06	7.8	0.05	7.9	0.03
14	2.8	285.12	6.8	0.04	7.7	0.01	7.8	0.02
15	2.8	472.88	6.4	0.03	7.7	0.01	7.9	0.01
16	2.7	341.89	6.8	0.10	7.4	0.01	7.7	0.01
17	2.7	373.44	6.6	0.05	7.6	0.01	7.8	0.01
18	2.6	504.00	6.5	0.10	7.5	0.01	7.9	0.01
19	2.6	540.54	6.4	0.18	7.4	0.01	7.9	0.01
20	2.5	710.64	6.3	0.14	7.5	0.02	8.0	0.01
21	2.4	835.05	6.3	0.46	7.5	0.01	8.0	0.01
22	2.4	885.48	6.3	0.31	7.4	0.01	8.0	0.01
23	2.4	920.00	6.3	0.68	7.7	0.01	7.9	0.01
24	2.4	893.86	6.0	1.38	7.2	0.07	7.9	0.01
25	2.4	852.39	6.3	1.80	7.9	0.01	8.3	0.01

Pyrite Oxidation and Sulfate Depletion

The raw material used for the study had a pyritic sulfur content of 7.8309%. The column leaching tests were performed to simulate, at a greatly accelerated rate, natural weathering whereby pyrite is oxidized to form sulfuric acid.

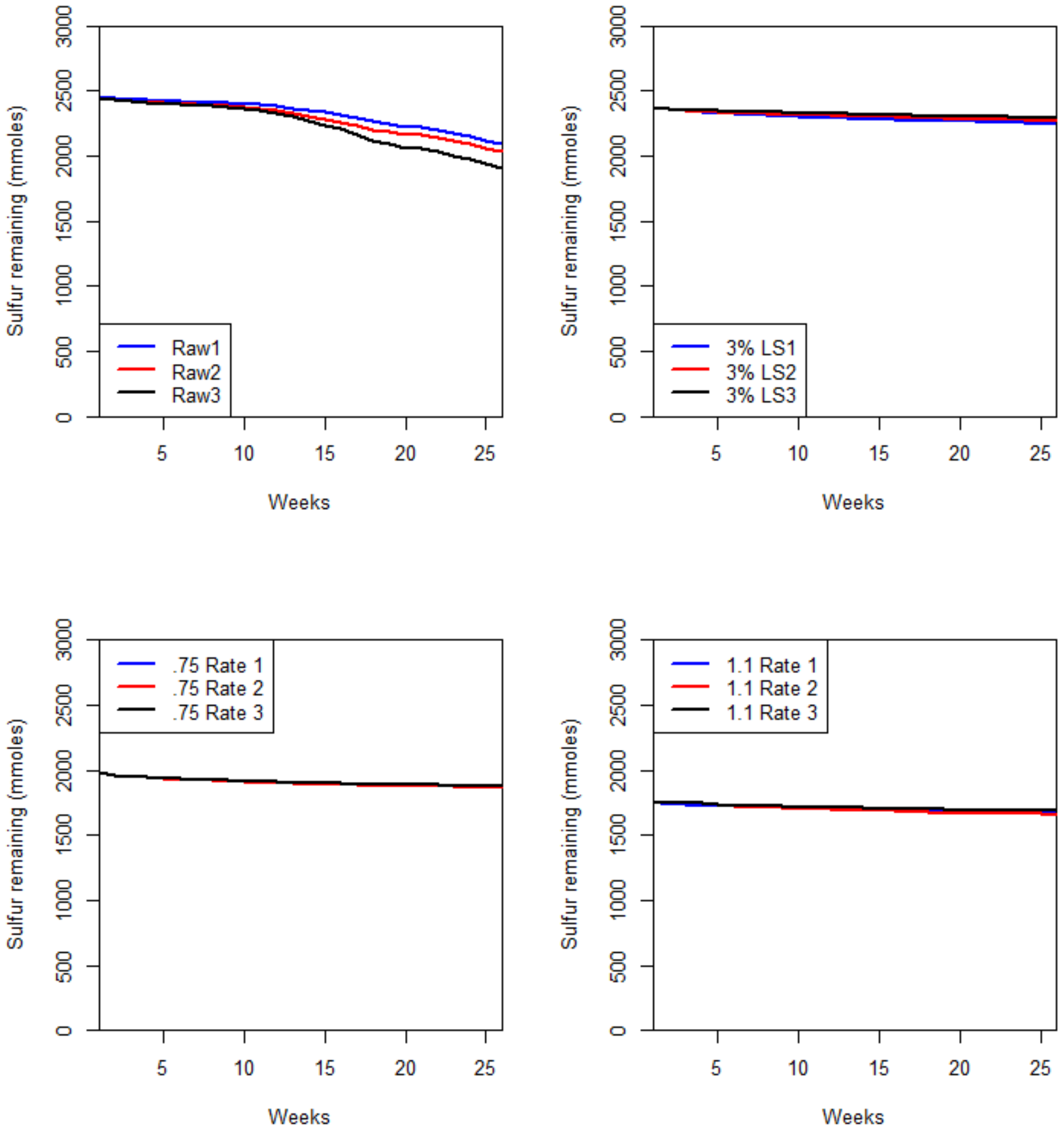
The rate of sulfate release by pyrite oxidation was calculated from the lab results and is presented in *Figure 6* below. The raw refuse sample group displayed the highest rate of sulfate release, indicating the fastest rate of pyrite oxidation from the samples. Notably, the groups with alkaline addition behave very similarly to each other, and the rate of decay is generally comparable regardless of the rate of limestone addition. This phenomenon is well-complemented by the trends in pH, acidity, and alkalinity. Once again, the data indicate that even a small addition of limestone is capable of retarding the rate of pyrite oxidation to a significant degree.

Figure 6: Cumulative Sulfate Release Over First 25 Weeks
(mg/Kg/week and cumulative)



In a further review of the sulfate release rate, *Figure 7* displays remaining moles of pyritic sulfur in the samples over time. While the raw sample group clearly exhibits a relatively rapid decline in pyritic sulfur content, other sample groups (those with alkaline addition) follow a much flatter trend, indicating a much slower rate of pyrite oxidation.

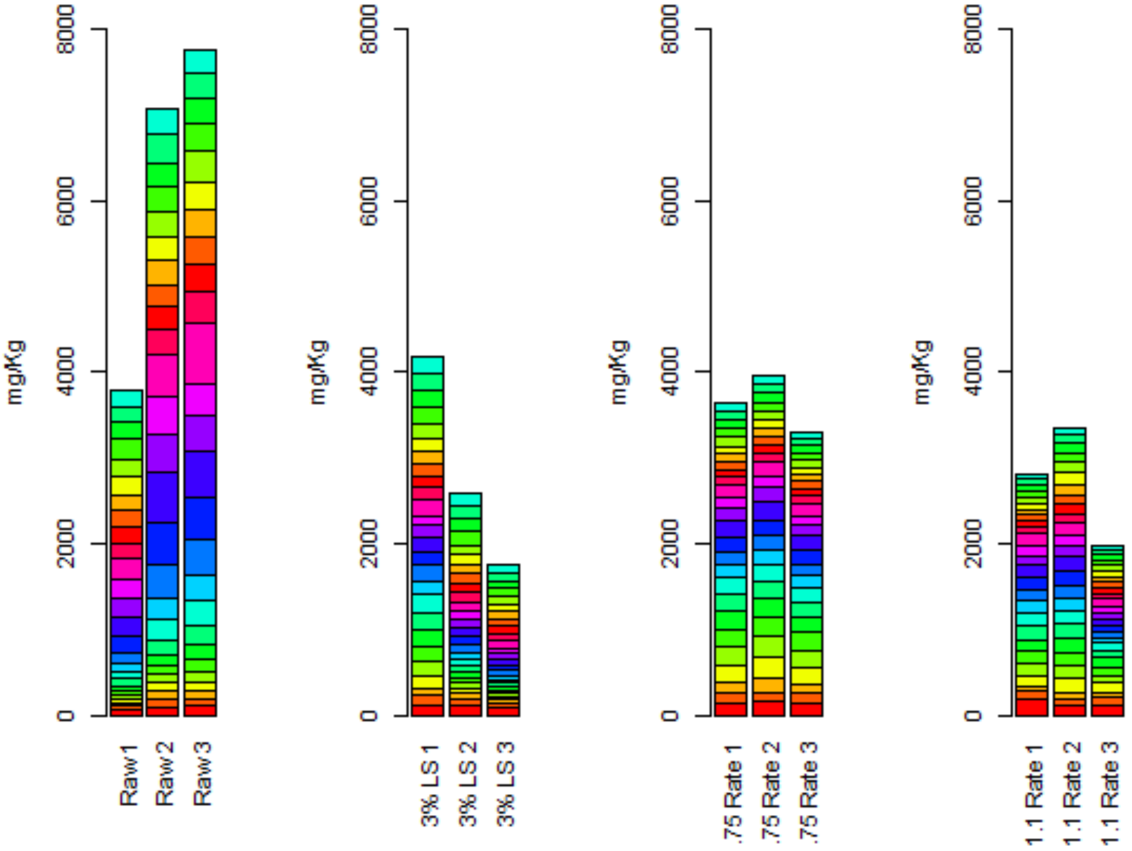
Figure 7: Remaining Moles of Pyritic Sulfur in the Sample Over Time



Calcium Depletion

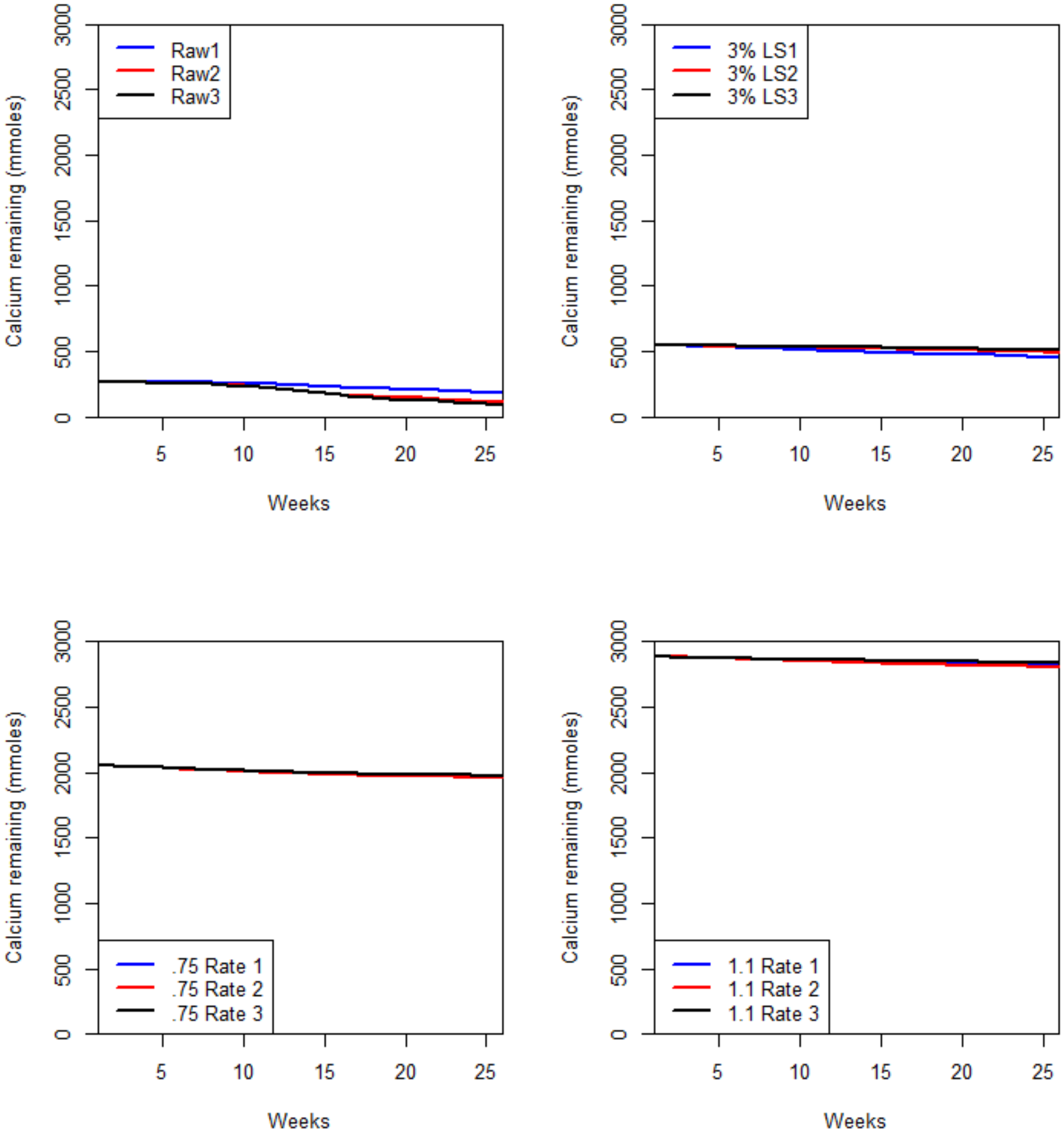
Dissolved calcium was also monitored during the study, for comparison to sulfur trends. The raw refuse materials had some inherent calcium (approximately 1.08%). Calcium carbonate ($CaCO_3$) was added to each of the other three groups, at varying rates of addition. When calcium carbonate dissolves, it produces alkalinity and dissolved calcium ion, and the resulting alkalinity buffers the pH of the resulting solution. *Figure 8* below shows the rate of calcium release over 25 weeks of leaching. The calcium release rate showed a similar trend to that observed for other metals such as iron and magnesium, whereby the most acid-producing sample group exhibited the highest rate of metals leaching.

Figure 8: Cumulative Calcium Release Over First 25 Weeks (mg/Kg/week and cumulative)



Similar to the trend in remaining sulfur, remaining moles of calcium in the raw refuse samples showed a steep declining trend after the first 8 weeks (when the pH began to drop below about 6), but only a very gradual decline was seen where limestone was added (*see Figure 9)*.

Figure 9: Remaining Moles of Calcium in the Sample Over Time



Short-Term Performance

The results of the study show that without any limestone amendment, the refuse material generated acid drainage conditions within about two months under the lab conditions. The inherent alkalinity was lost within the first 8 weeks, promoting generation of acidity, which in turn accelerated pyrite oxidation and metal leaching as evidenced by iron and other metals. However, the other samples with varying amounts of added limestone showed pyrite oxidation rates that were very similar to each other, and much suppressed as compared to the raw samples over the 25-week test period (*see Table 2*). Such period in the lab would equate to many years in the field conditions of progressing fill construction. For example, the three replicates with 3% limestone added are projected to maintain $CaCO_3$ presence for another 1.7 to 4.3 years (88 – 224 flushes) at the final rate of leaching attained over the 25 weeks (total of 113 – 249 flushes) in the lab protocol of weekly flushing and ready availability of oxygen. Within an actively-operated fill, it is expected that the leaching process would be substantially less aggressive and retention of $CaCO_3$ would continue for a much longer period.

Table 2: Summary of Calcium and Sulfur Release Rates (through Week 25)

	Initial % Pyritic S	Initial % Ca	Cumulative % Pyritic S Reduction over 25 wks	Cumulative % Ca Reduction over 25 wks	Remaining % Pyritic S (25 wks)	Remaining % Ca (25 wks)	*Years to deplete if most current release rate remains constant**	
							Years to deplete Pyritic S	Years to deplete Ca
Raw 1	7.83	1.08	16.74	35.11	6.52	0.70	1.36	0.70
Raw 2	7.83	1.08	19.36	65.48	6.32	0.37	1.22	0.24
Raw 3	7.83	1.08	24.48	71.78	5.91	0.30	1.15	0.22
3% Grey Limestone 1	7.60	2.20	5.77	19.01	7.16	1.78	8.64	1.71
3% Grey Limestone 2	7.60	2.20	4.73	11.80	7.24	1.94	9.85	2.44
3% Grey Limestone 3	7.60	2.20	3.71	8.01	7.31	2.02	13.84	4.28
0.75 Amendment Rate 1	6.33	8.23	5.64	4.43	5.97	7.86	13.93	14.39
0.75 Amendment Rate 2	6.33	8.23	5.90	4.81	5.96	7.83	14.71	16.43
0.75 Amendment Rate 3	6.33	8.23	5.34	4.02	5.99	7.90	16.06	19.44
1.1 Amendment Rate 1	5.63	11.57	4.84	2.43	5.36	11.28	34.99	42.15
1.1 Amendment Rate 2	5.63	11.57	5.81	2.88	5.30	11.23	28.61	31.01
1.1 Amendment Rate 3	5.63	11.57	4.21	1.71	5.39	11.37	21.73	43.45

** Calculated times pertain to leaching column environment. Actual time in field fill conditions will be much longer.*

Long-Term Performance

Addition of limestone at a 3% rate, while it forestalled acid generation throughout the 25-week test period in the lab, would likely not prevent acid generation in perpetuity. As can be seen on *Figure 10*, there is considerably more pyritic sulfur than calcium in that scenario. As is shown on *Table 2*, the estimated time required to deplete the acid-generating sulfur far exceeds that of the acid-neutralizing calcium under the 3% limestone addition scenario, under laboratory conditions of aggressive leaching and availability of oxygen. In the long term, exclusion of oxygen and/or of flushing mechanisms is needed in order to prevent acidic drainage.

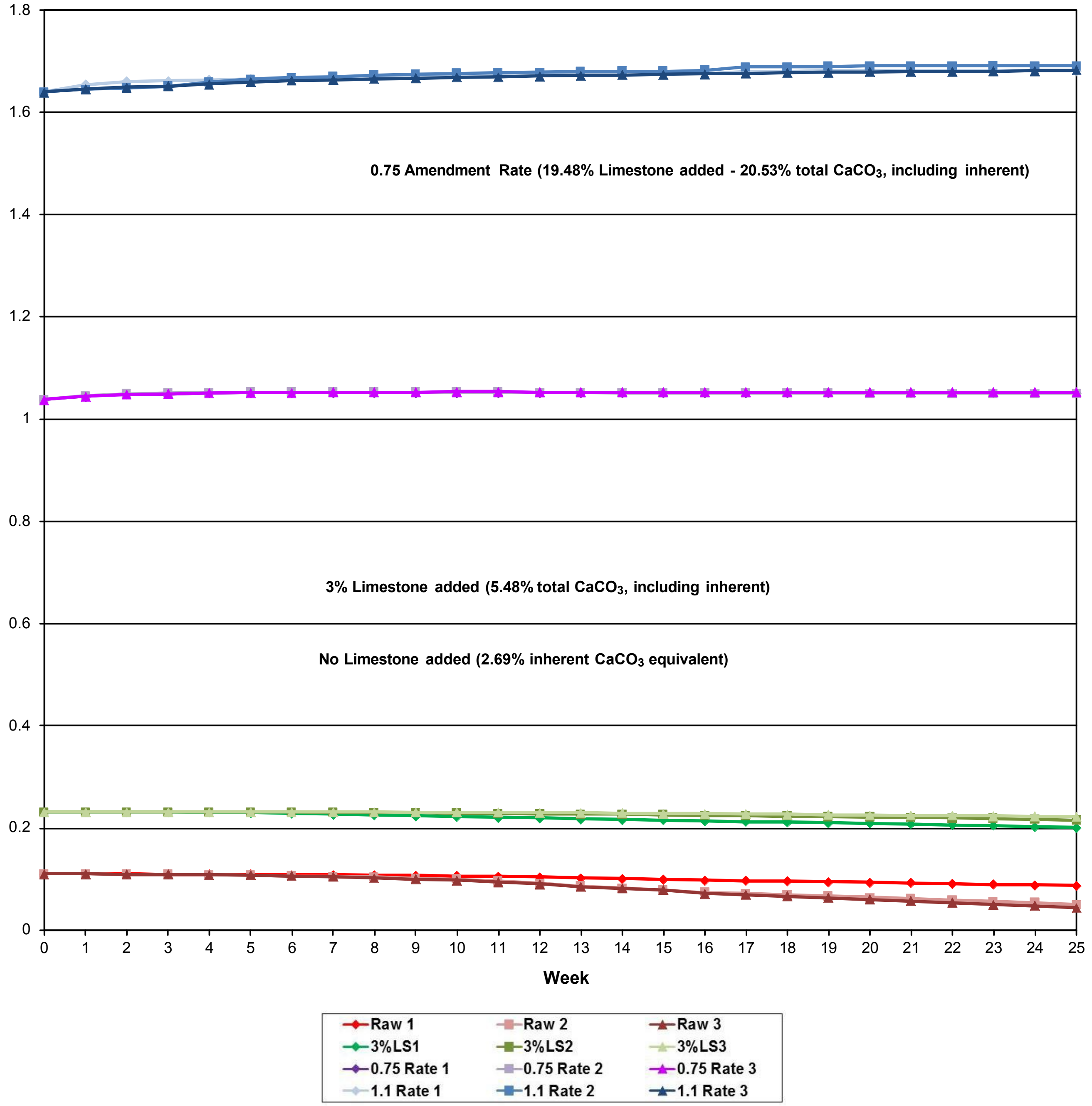
Summary

In short, the test program results indicate that addition of even a relatively small amount of alkalinity forestalls the onset of acid generation. This finding is consistent with observations of others published in relevant literature that presence of alkalinity is a more dominant control upon acid generation than that of sulfur for some initial weathering period. Of course, assuming continued weathering and reactivity of the material over the long term, the alkalinity would eventually be consumed and acid generation would accelerate, but the forestalling of that process by a small alkaline addition during fill construction provides operational options for employment of long-term solutions such as capping/encapsulation measures that can be implemented upon fill completion.

mmoles/Kg/we

1.1 Amendment Rate (28.08% Limestone added - 28.85% total $CaCO_3$, including inherent)

Figure 10: Ca/S Mole Ratio



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