Kinetic Testing Results of Variable Alkaline Addition Rates in Preventing Acid Generation from Pyritic Materials

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Objective:

Relay information concerning short-term effectiveness of variable rates of alkaline addition in neutralizing acidity and, importantly, in retarding the rate of acid generation.

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Background:

Highway construction projects sometimes encounter pyritic materials that leach acidic, metals-rich drainage upon exposure to oxygen and water. That drainage can result in:

- Environmental impacts to streams and wetlands
- Structural impacts to culverts, bridge abutments, etc. (concrete or metal)
- Geotechnical impacts (swelling, heating, loss of compaction)

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Background (continued):

The acid-generating oxidation process can begin essentially immediately, and lowered pH and liberated ferric iron can accelerate acid production, and even propagate continued acid production after oxygen has been excluded by encapsulation or burial. Therefore, it is important to prevent the initiation of the acid-generating process.

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Background (continued):

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).

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Abstract

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 material. Results indicate that even relatively small amounts of limestone addition can forestall acid generation during the handling, temporary storage, and fill construction process, until the material can be fully amended and capped to prevent intrusion of oxygen and water, and thereby curtail any further acid generation in the long term.

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Reason for the Kinetic Testing Program

The acid-producing material to be disposed exhibits a pyritic sulfur content that makes alkaline addition to a positive NNP value (based on the static ABA test) impracticable due to operational infeasibility, cost, and storage volume requirements. Kinetic testing of the leaching characteristics of the material with varying alkalinity applications was performed to afford better understanding of the likely drainage to result and to provide information to support potential options as to disposal design.

Methods – Leaching Columns

- 4 sample groups, each in triplicate. One group consisting of raw coal refuse material, three groups at various alkaline addition rates.

- Columns 24” long, 6” diameter
  - Samples ground to ¼” X 0 (field-collected material exhibited only 35.7% passing ¼-inch screen, and the coarsest material exhibited much higher pyritic sulfur concentrations than did the finer particles). Crushing creates increased surface area for oxidation and has the unintended but unavoidable effect of exaggerating the geochemical reactivity of pyrite in the refuse material.

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Methods – Leaching Columns

> 25-week test program duration;

> 2,000 grams of sample per column;

> Weekly leaching with 2000 mL of deionized water to replicate rainfall;

> Columns open to allow air to move into and out of the column;

> Crushing to ¼” maximum size and allowing exposure to oxygen diffusion produces over several weeks the weathering effect that would require years to occur in a fill where oxygen exposure will become limited as the fill progresses and where pore gas composition will have significant carbon dioxide to displace oxygen.

Pre-Leaching Analyses

- Particle Size Distribution
- Sulfur forms and ABA by size fraction, in triplicate (based on both total sulfur and pyritic sulfur)
- Total Metals (As, Cu, Fe, Al, Mg, Mn), by size fraction, in triplicate

Alkaline Addition Rates

- Raw material (with 7.83% average pyritic sulfur; with average inherent NP of ~26 tons/1000 tons (2.6%) as $CaCO_3$)
- 3% Limestone added (LS = 95.85% $CaCO_3$)
- Limestone added at $0.75 \times \dfrac{\text{Sul \%} \times 31.25}{0.9585}$ = 191.5 tons/1000 tons or 19.15%
- Limestone added at $1.1 \times \dfrac{\text{Sul \%} \times 31.25}{0.9585}$ = 280.8 tons/1000 tons or 28.08%
- Limestone was added to the raw acid-producing material while maintaining a constant mass of the sample. Consequently, the pyritic sulfur content (on a % 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.

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- Weekly leachate analyses were evaluated as to ratio of leaching on both a mass (mg) and mole basis, for comparison to initial values to determine 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.
  (Note: As there was an increase in the amount of sulfate-sulfur in the post-leaching residual sample due to oxidation of pyritic sulfur to sulfate, the calculated rate of sulfur release based on the cumulative dissolved, leached sulfate understates the actual amount of pyrite oxidation that occurred).

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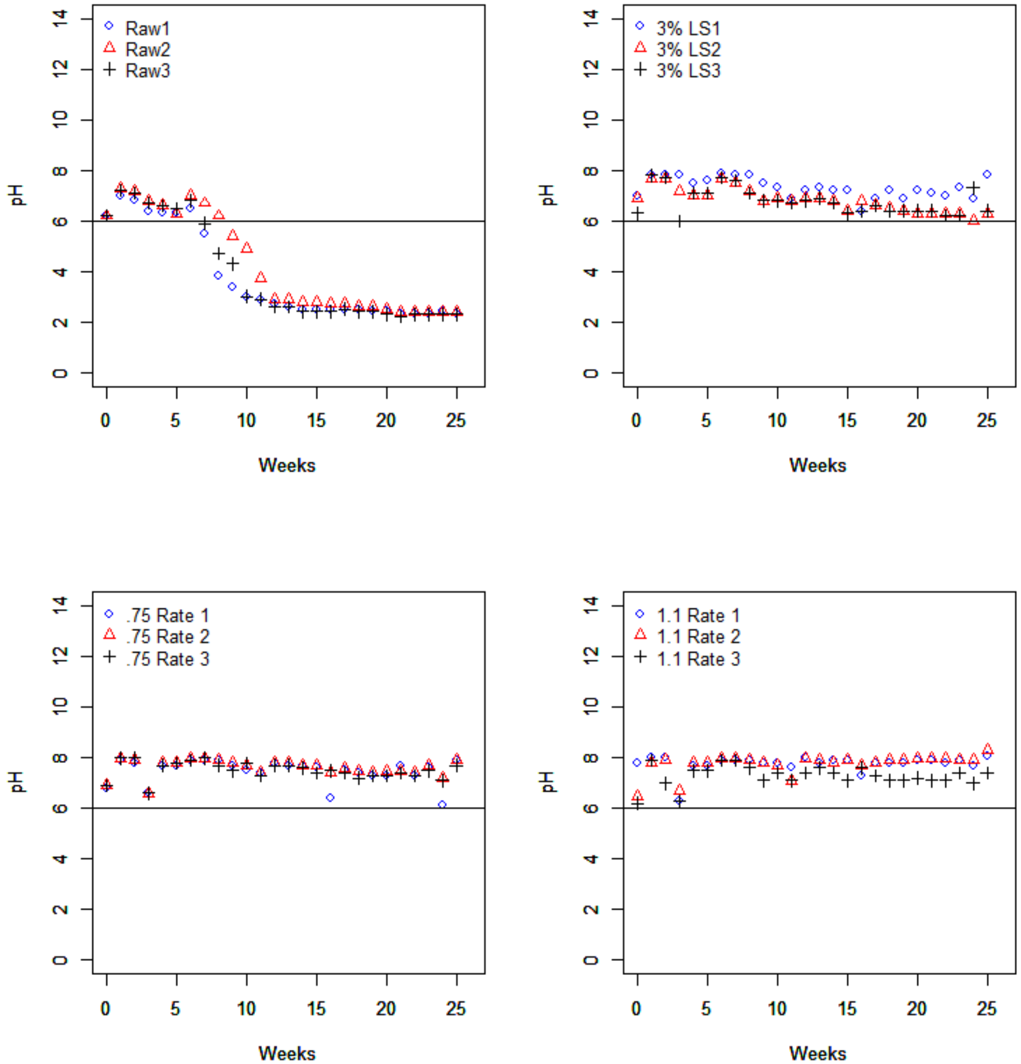
Results:
Trend in pH



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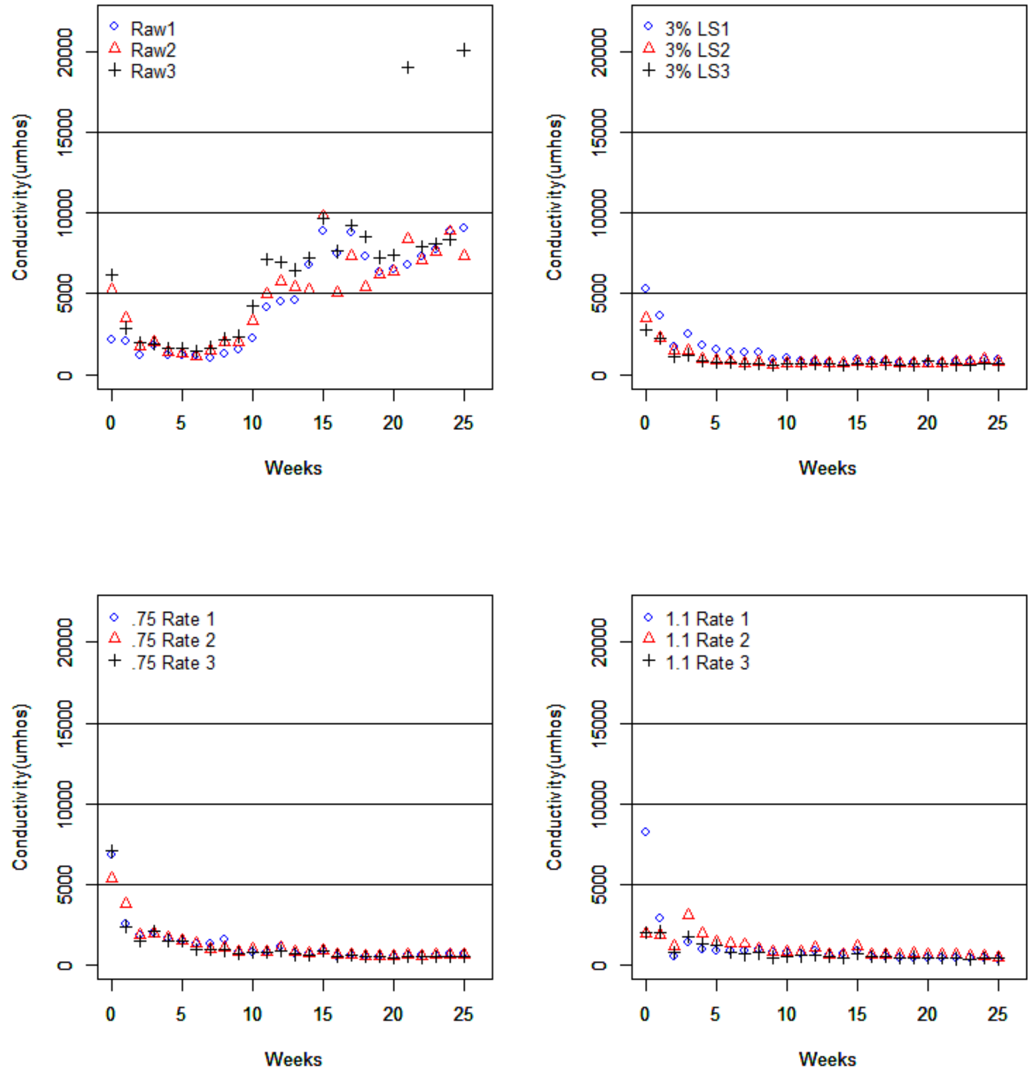
Results:
Trend in Conductivity



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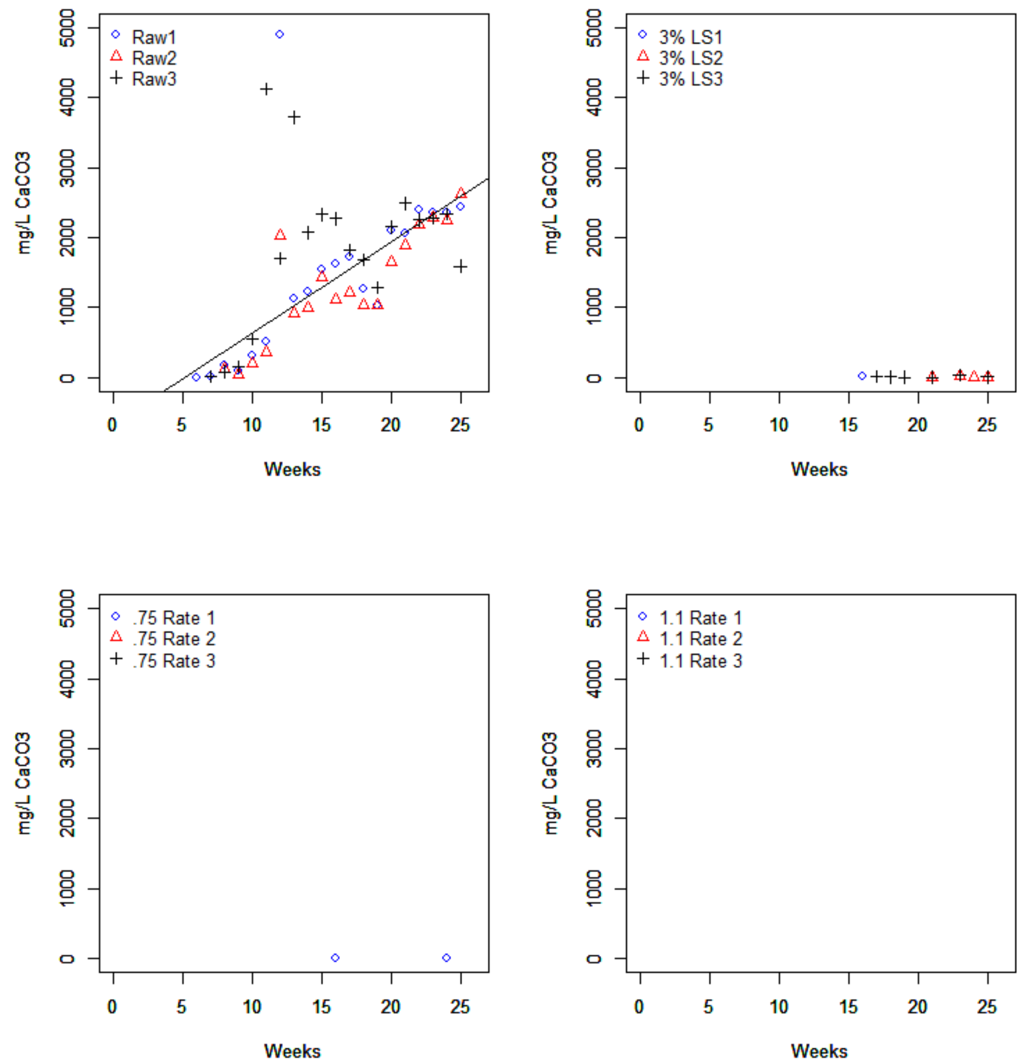
Results:
Trend in Hot Acidity



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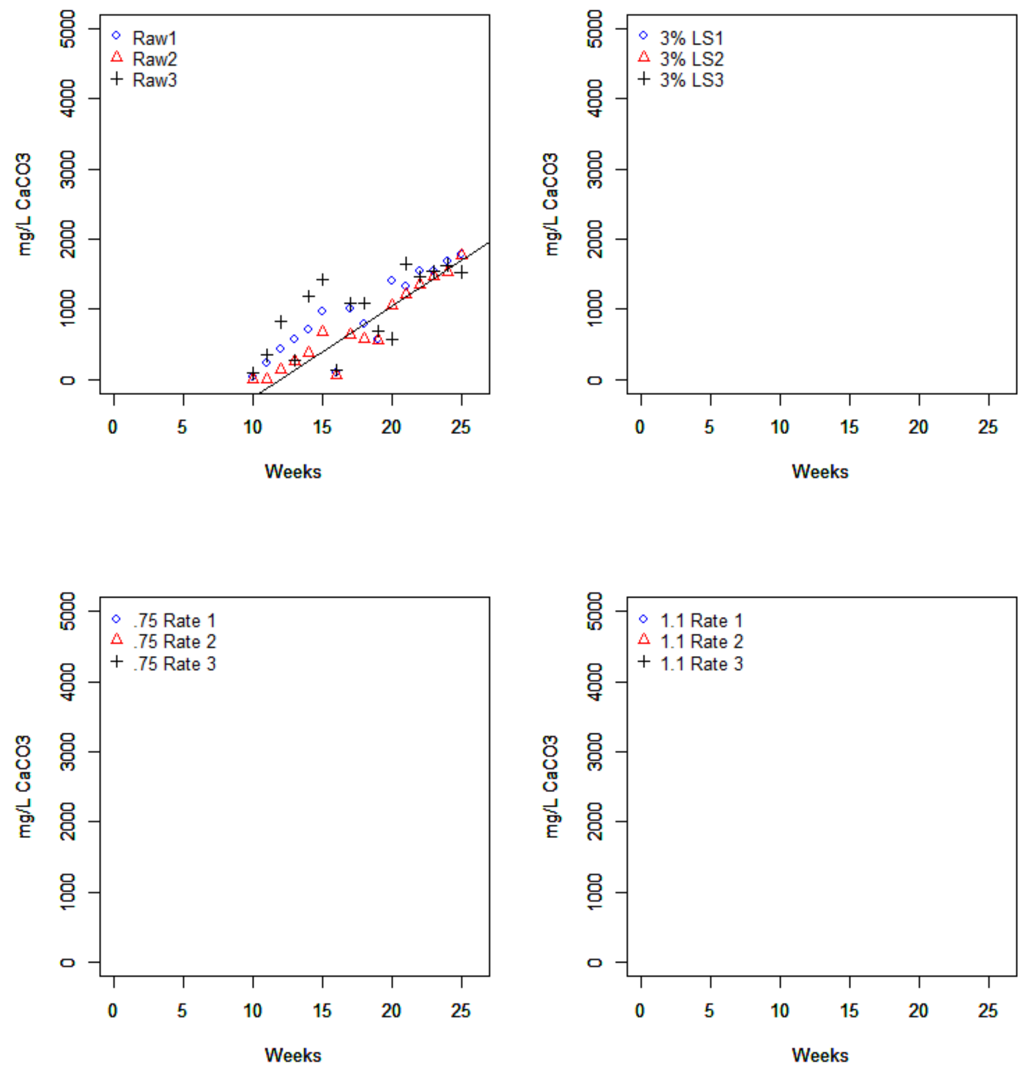
Results:
Trend in Metals Acidity



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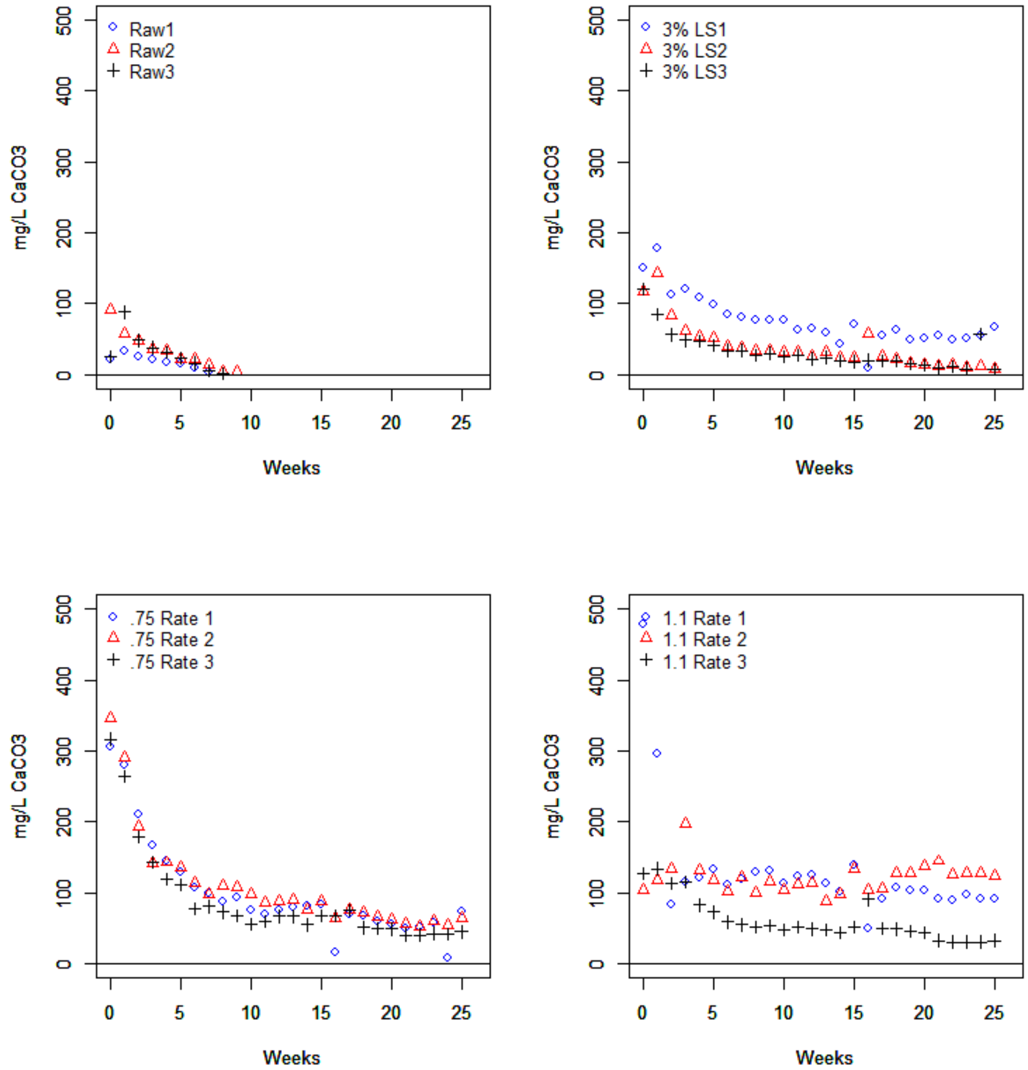
Results:
Trend in Alkalinity



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Results:
pH vs Iron Release Rate

	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

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

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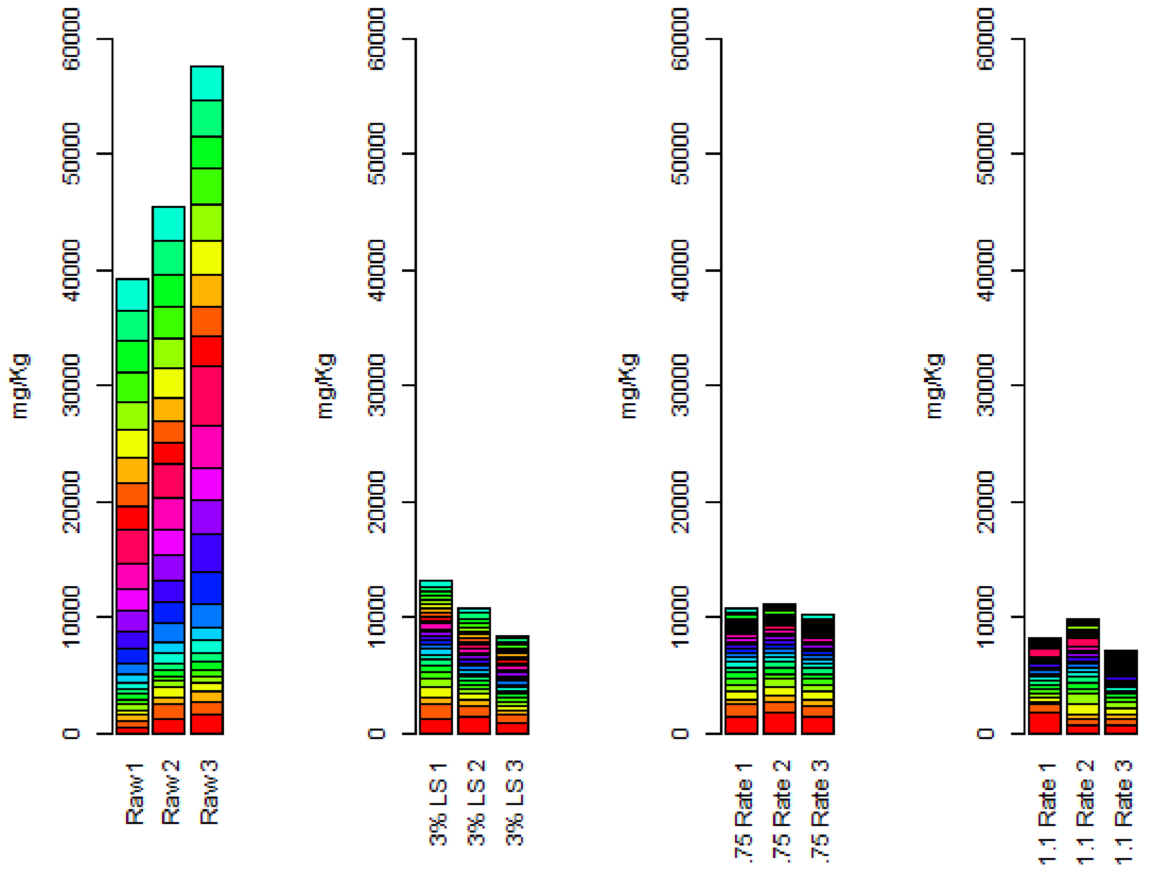
Results:
Cumulative Sulfate Release Over First 25 Weeks



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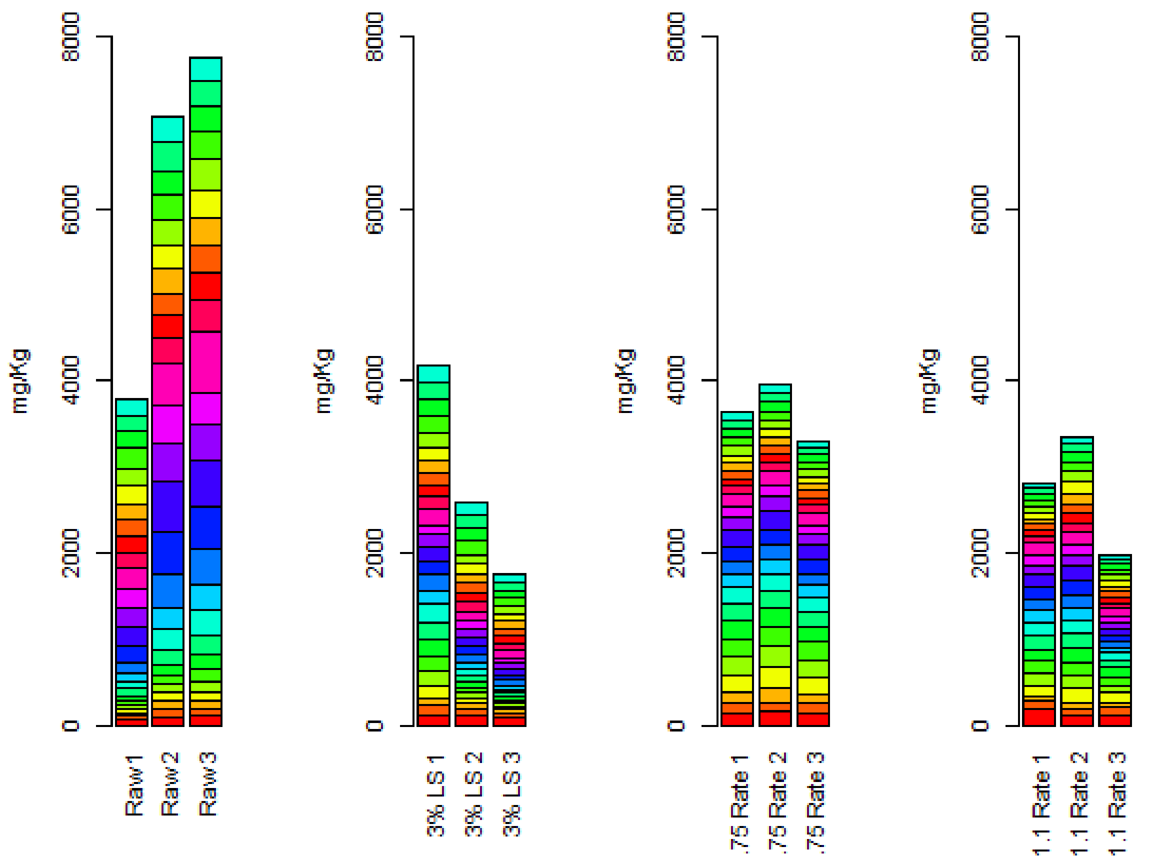
Results:
Cumulative Calcium Release Over First 25 Weeks



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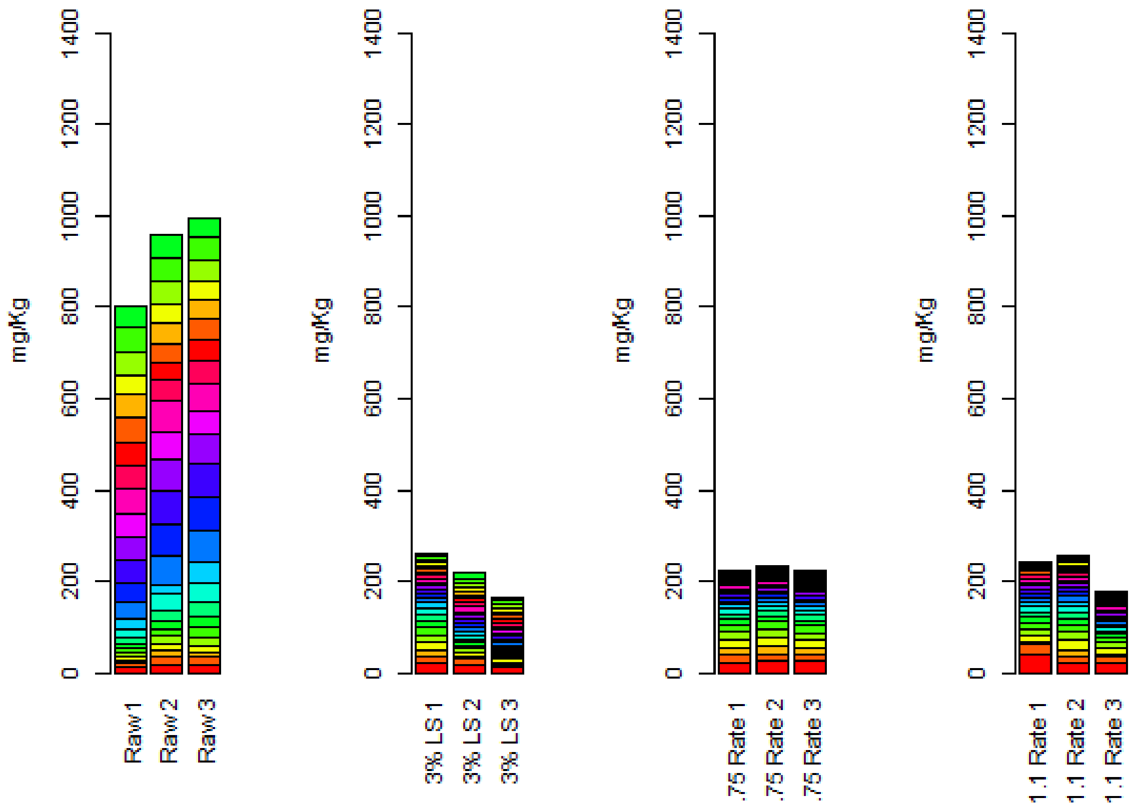
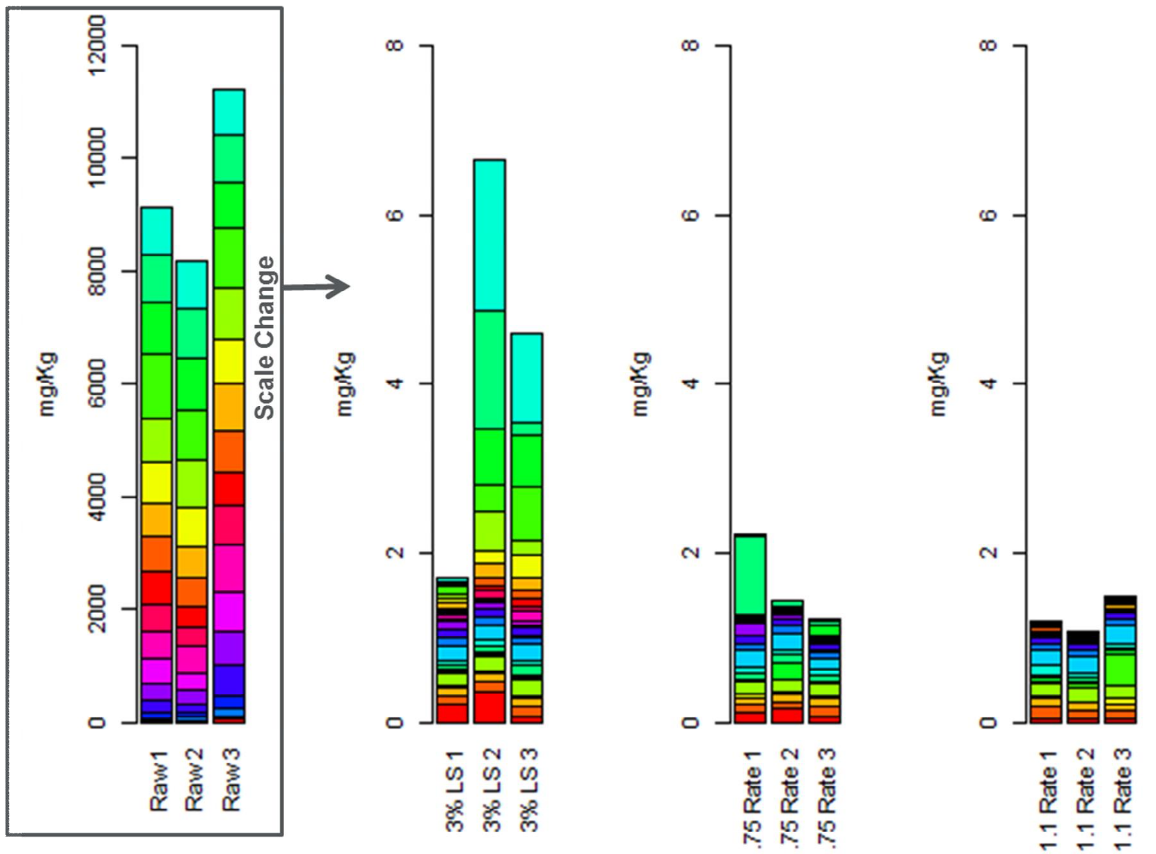
Results:
Cumulative Magnesium Release Over First 25 Weeks



Results:
Cumulative Iron Release Over First 25 Weeks



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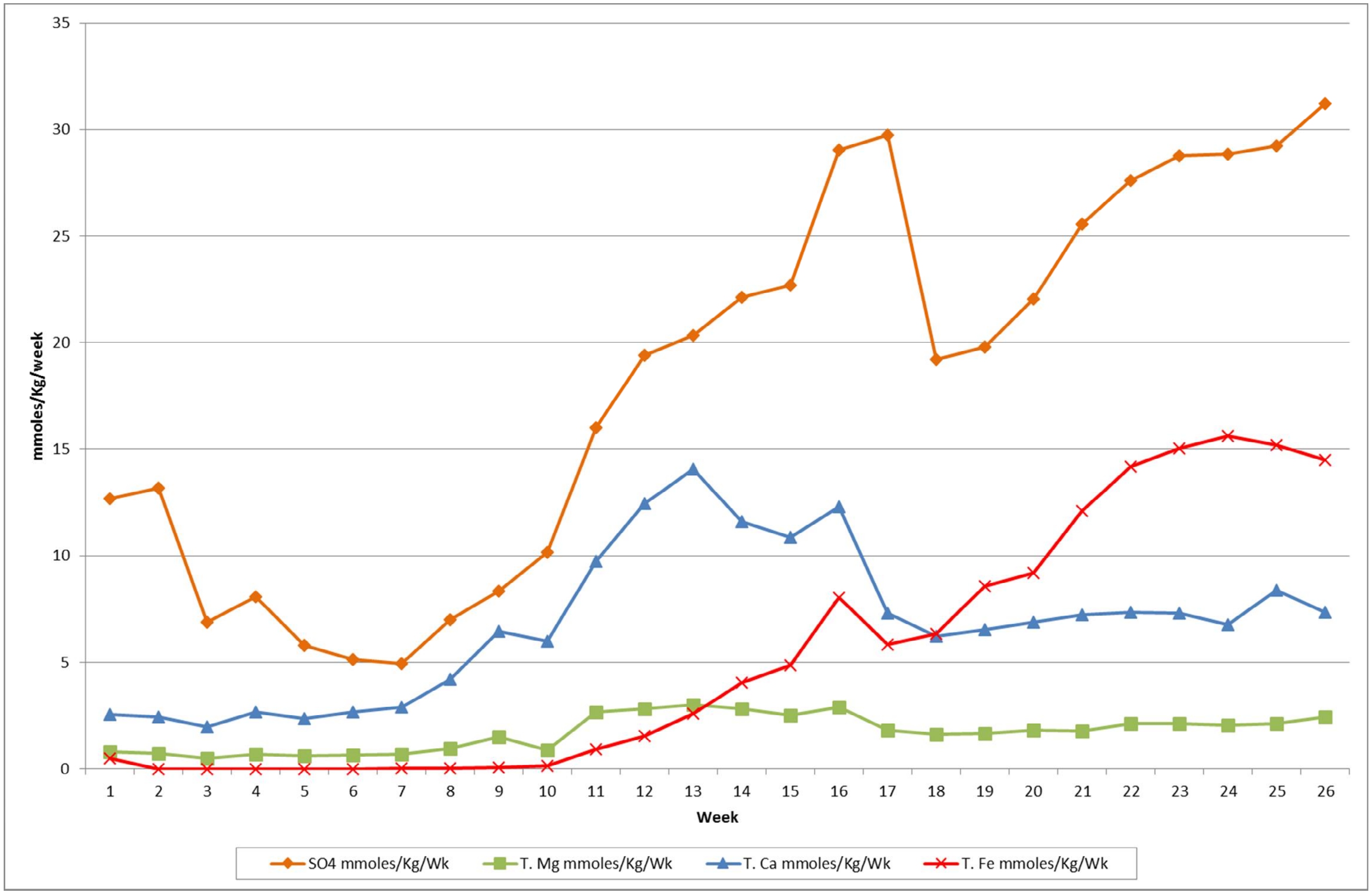
Results:
Rate of Release Over Time – Raw 2



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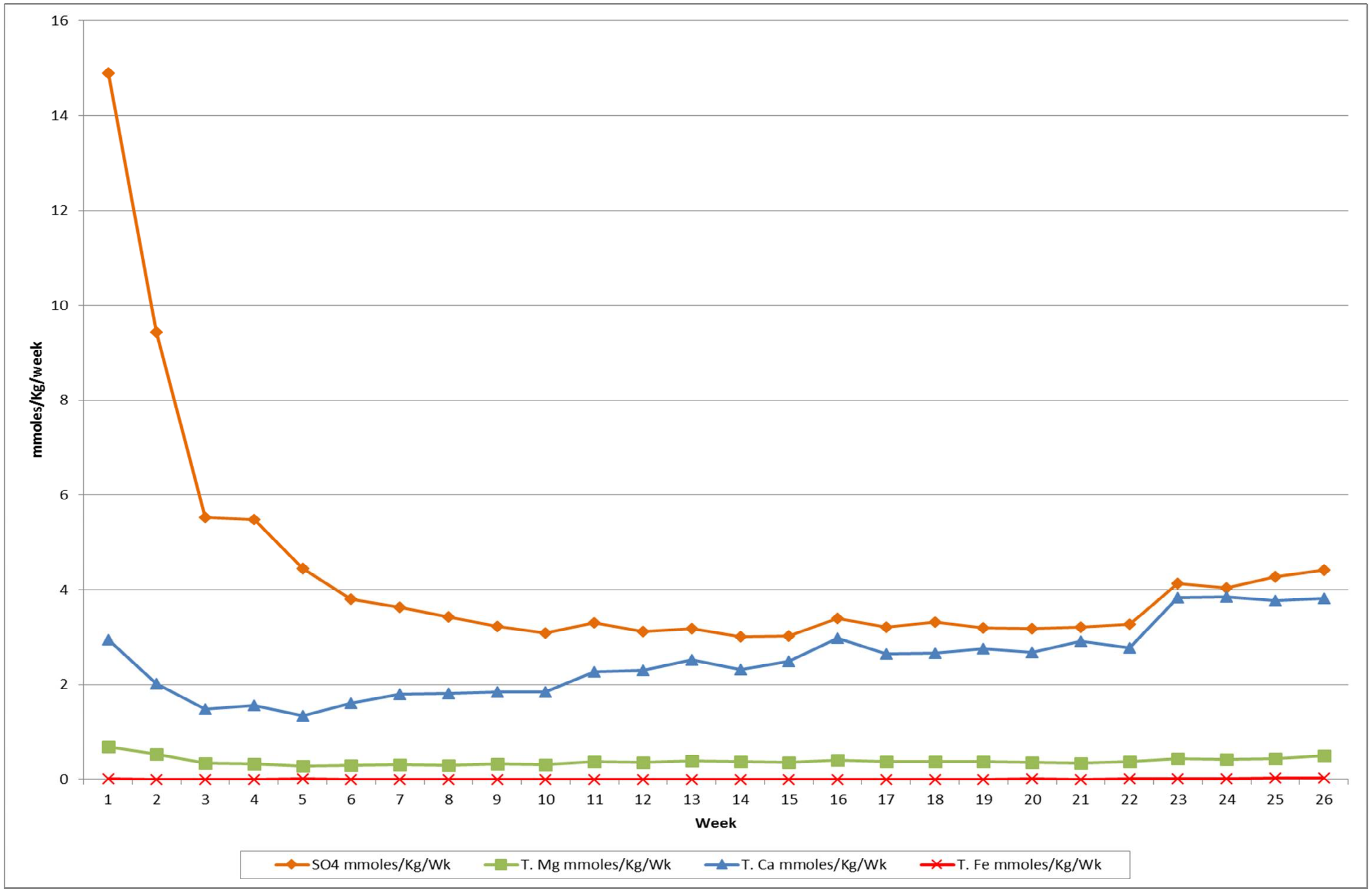
Results:
Rate of Release Over Time – 3% Grey Limestone 2



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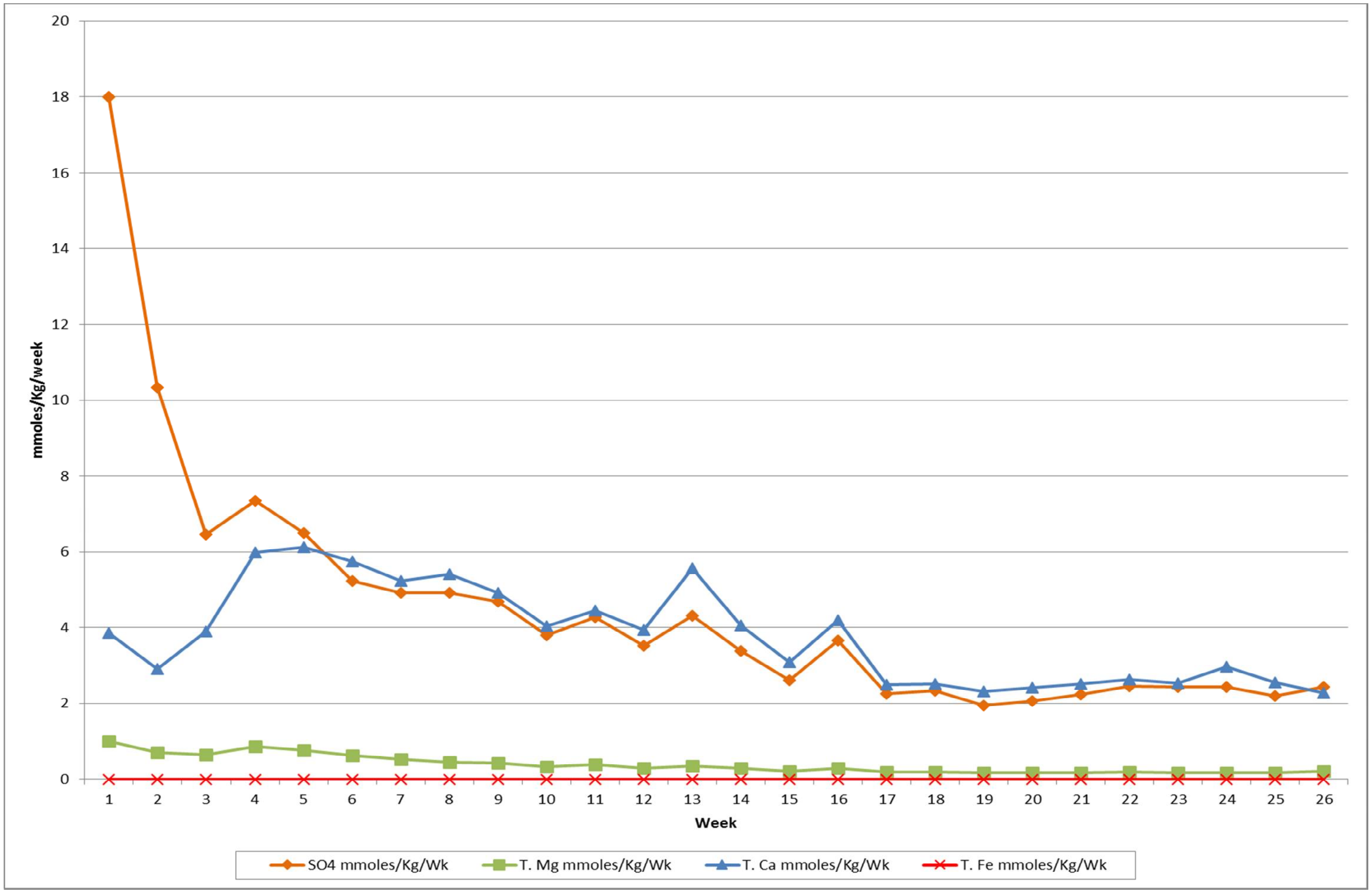
Results:
Rate of Release Over Time – 0.75 Amendment Rate 2



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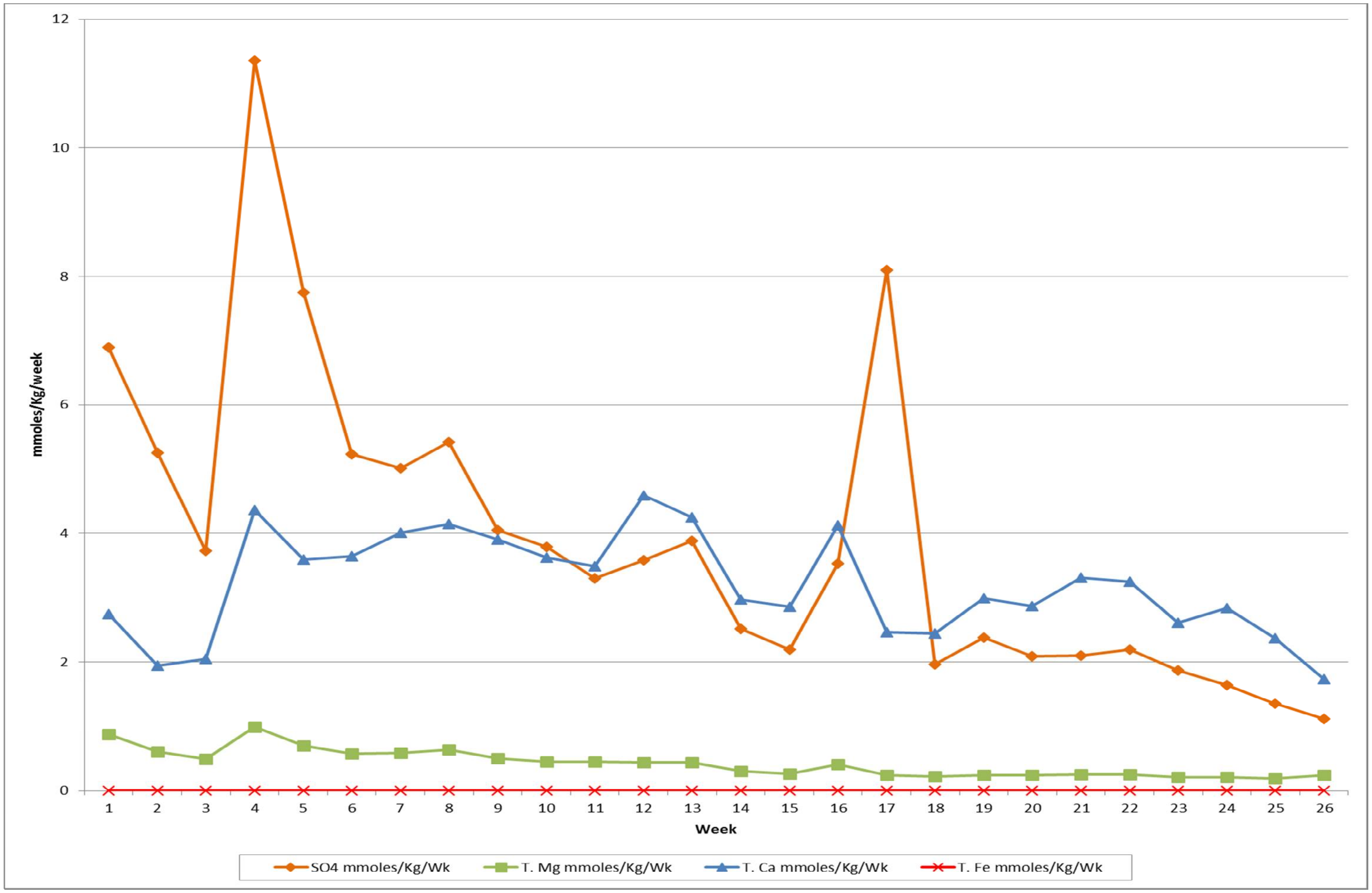
Results:
Rate of Release Over Time – 1.1 Amendment Rate 2



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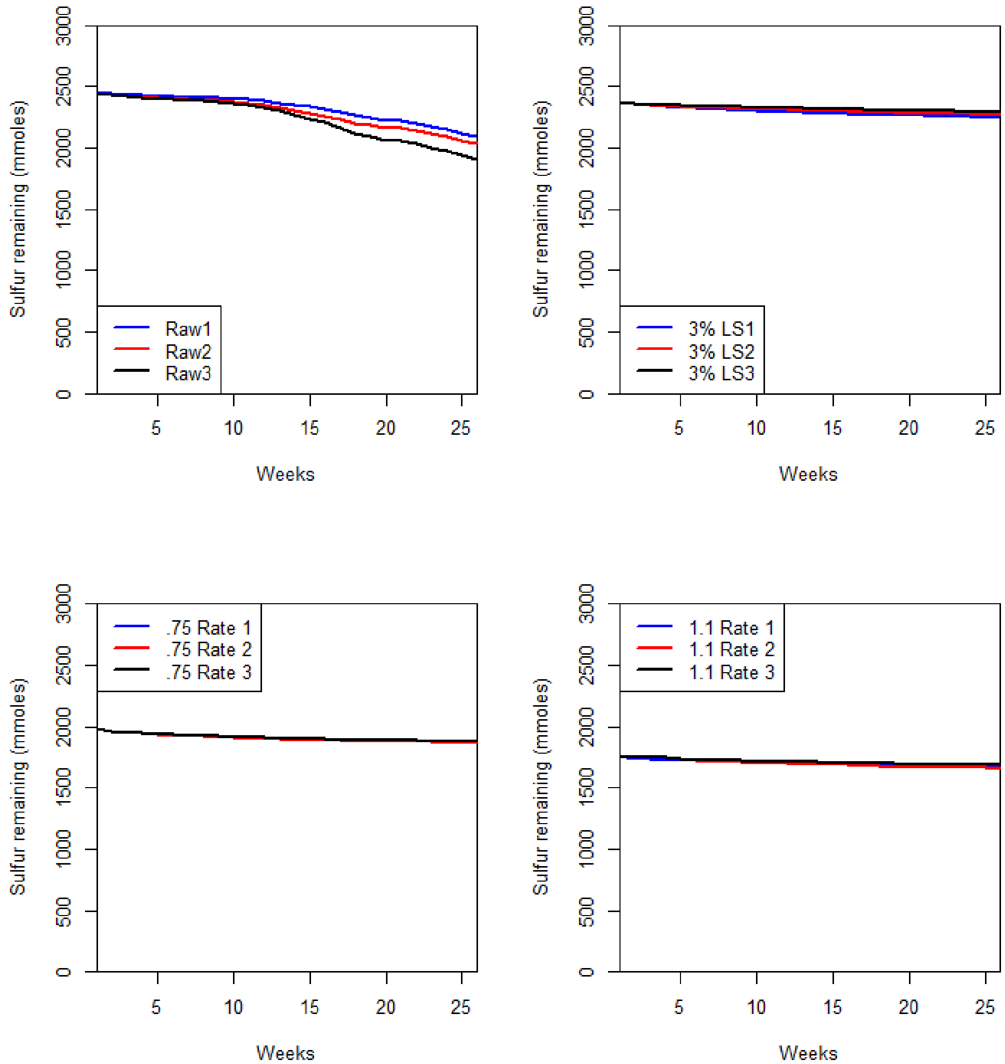
Results:
Remaining Moles of Pyritic Sulfur Over Time



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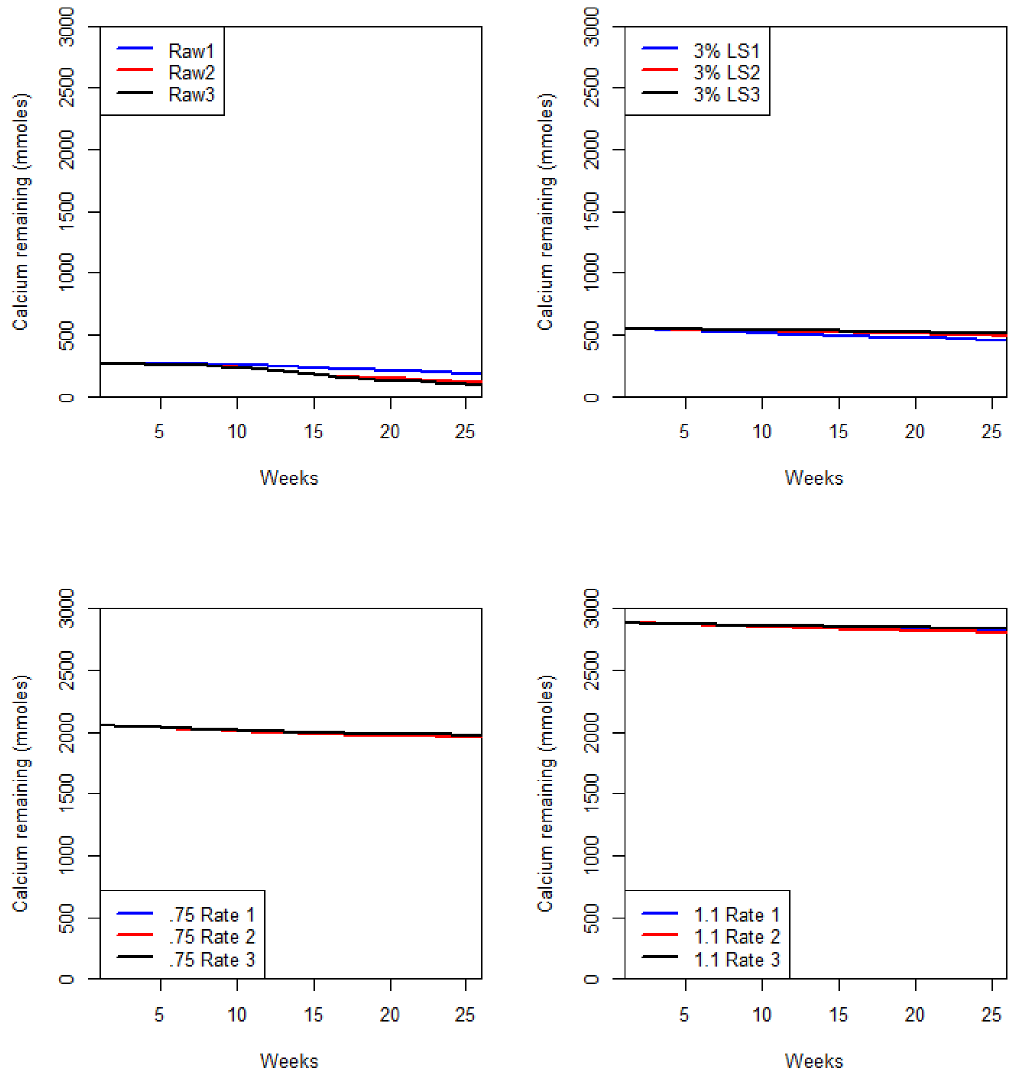
Results:
Remaining Moles of Calcium Over Time



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Results: Short-Term Performance

> Without any limestone amendment, the raw material generated acidic drainage within about 2 months, under the lab conditions. The inherent alkalinity was consumed by then, generating acid and accelerating pyrite oxidation and metal leaching.

> Samples with limestone added showed mutually-similar pyrite oxidation rates. Addition rates of 3%, 19%, or 28% all showed fairly similar suppressed rates of pyrite decay over the 25-week test period, as compared to the “raw” samples.

> Even at the lowest addition rate (3%), the rates of sulfate and acid generation were effectively retarded throughout the test period. Iron release was well-suppressed for the first 20 weeks.

> The effectiveness in the laboratory tests reflects thorough blending achieved there. Field applications may be challenged to achieve that degree of uniform blending and may therefore require a factor of safety consideration in application rate.

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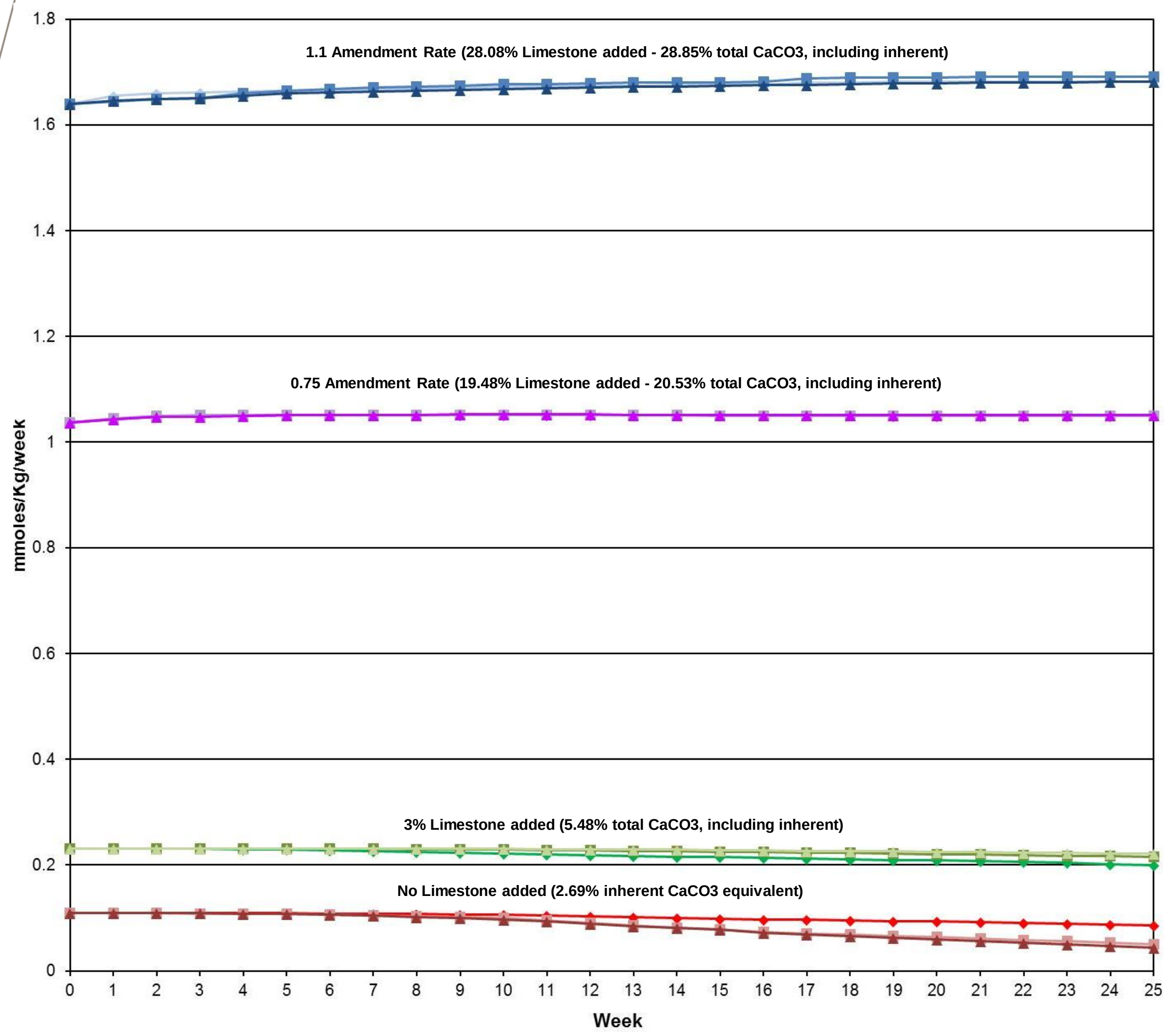
Ca / S Mole Ratio in Sample Material, Over Time



Results: Long-Term Performance

- Ultimately, the stoichiometrically-predicted equal balance of acid and base components is required, to prevent eventually acid generation:
  - Unless the process is curtailed by:
    - Exclusion of oxidizers (oxygen, ferric iron)
    - Removal of percolating water for transport of acid salts.

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 conditions will be much longer

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