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STRATEGIES FOR LIME TREATMENT OF D-AREA COAL STORAGE AREA (484-17D) VADOSE ZONE SOIL

Scope

Area Completion Projects (ACP) is developing a Removal Site Evaluation Report/Engineering Evaluation/Cost Analysis (RSER/EE/CA) for a non-time-critical removal action at the former D-Area Coal Storage Area (DCSA) to improve conditions in the D-Area Groundwater Operable Unit. In support of the RSER/EE/CA, ACP requested guidance from SRNL on the:

- Lime application rate required to raise the pH of acidic vadose zone soil in the DSCA to site background levels.
- Number of pore volumes and time required to flush acidity from vadose zone soils using pH 6.5 artesian well water.

Summary and Recommendations

Sixty years of coal storage operations in the DCSA (484-17D, Figure 1) have resulted in vadose zone soils with a total acidity level typical of acid mine drainage soils. Field measurements from June 2018 show soil pH values ranging from 3 to 4.5 to water-table depth (10 to 12 feet). Best estimates for treatment of the acidic soils with dolomitic (agricultural) limestone suggest a required application rate ranging from 8 to 10 tons per acre per foot of soil depth to raise the soil pH from 3.5 to 5.5. The model predicts a lower bound of 3 tons per acre per foot for high-quality limestone with a particle size less than 60-mesh and an upper bound of 19 tons per acre per foot for lower-quality limestone. This compares to typical residential and agricultural lime application rates of one to four tons per acre per foot of depth.

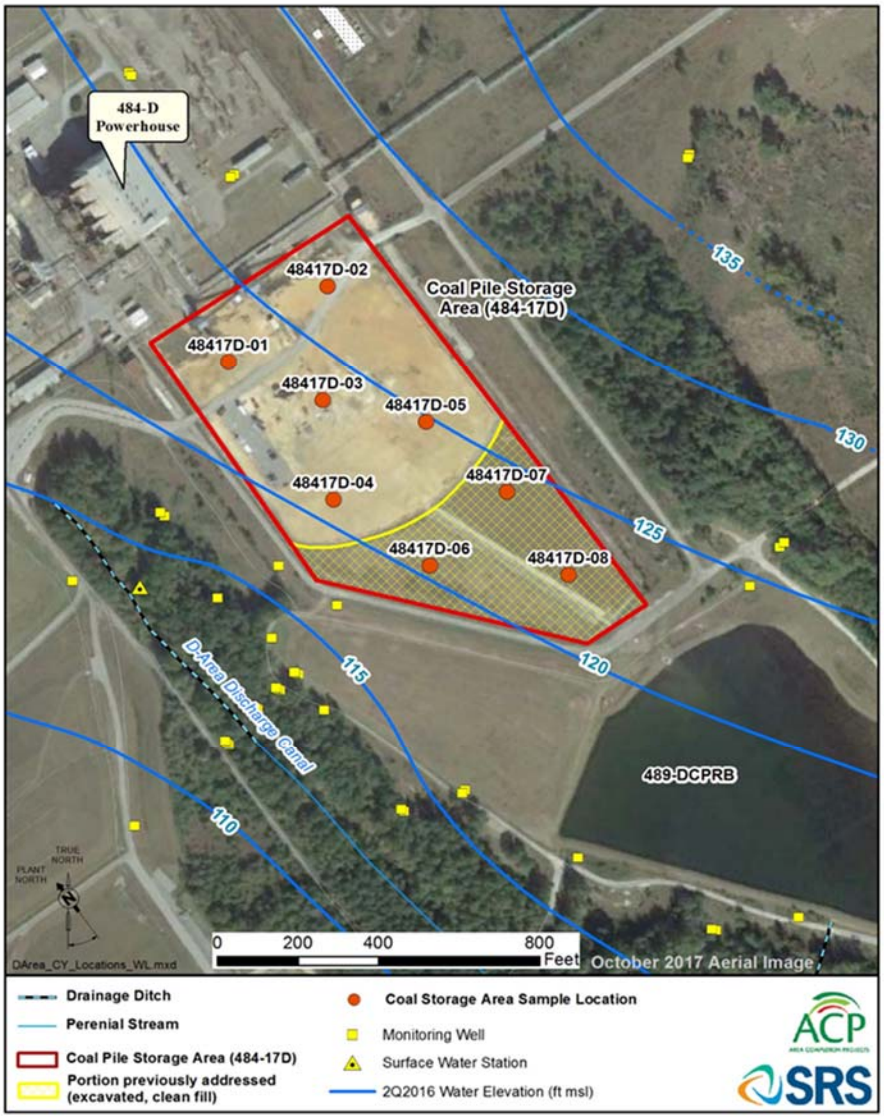

Figure 1. Location of D-Area Former Coal Storage Area (484-17D).

Bounding estimates for the soil flushing scenario indicate that injecting "neutral" artesian well water (pH 6.5) into the lower five feet of acidic (pH 3.5) vadose zone soil will require 400 to 1800 pore volumes and 25 to 100 years to leach reserve acidity and return the soil to a background pH of 5.5.

The project team should consider the following recommendations to minimize uncertainties and manage resources:

- Recommended lime application rates and total tonnage are high enough that uncertainties in the assumed soil chemical properties could have a substantial impact on implementation and cost. To reduce uncertainty, a limited number of soil samples should be collected below the surface to measure the CEC and buffer pH of the vadose zone soil. These are standard soil tests that can be performed by the Clemson Agricultural Service Lab (Clemson Regulatory Services, 2018).
- The fineness and quality of "lime" employed will significantly impact effectiveness. A particle size of 60-mesh (0.25 mm) and smaller and a low inert content are recommended for residential and agricultural applications to ensure high reactivity and maximum utilization. The desired fineness and quality must be weighed against practical issues such as dusting potential, exposure to rainfall, local availability, and cost. A high-quality dolomitic or calcitic limestone is recommended.
- Successive partial applications will likely be necessary to practically manage the recommended bulk volume of lime/limestone, especially if the maximum soil mixing depth is only four feet. The number of successive partial applications will depend on the tillage, excavation, or soil mixing technology chosen. Incorporating the lime/limestone amendment to a depth of 10 feet is the ideal but will require prohibitively expensive excavation or dry soil mixing technology such as that provided by Hayward Baker in Charleston, SC (https://www.haywardbaker.com/solutions/techniques/dry-soil-mixing). An alternative approach to consider if a vegetative cover is established after the first application is to mix the first lime application to depth (e.g., four feet) and then apply successive lime applications on the surface.
- Shallower depths of mixing will require the "lime" to dissolve and percolate downward through the vadose zone via infiltration. The annually averaged net infiltration rate at the Savannah River Site is approximately 15 inches per year. At this rate, it will take on the order of a decade for the neutralization front to reach the water table. Temporary irrigation would help to accelerate the downward migration of the neutralization front and to establish a vegetative cover, if desired.
- Even if a "background" soil pH is not achieved initially, raising the soil pH to 4.5, for example, will help to slow iron and aluminum oxyhydroxide dissolution and the associated release of trace metals such as chromium and lead.

Background

The vadose zone and groundwater beneath the former DCSA and the 489-D-Area Coal Pile Runoff Basin (489-DCPRB) have been impacted by low pH and dissolved metals over approximately 60 years of coal-fed power plant operations. The presence of a low-pH plume demonstrates that the buffering capacity of the sediment soil in the vadose zone and the aquifer has been consumed over the years by sulfuric acid and aluminum acidity in the leachate. The sulfuric acid and aluminum acidity have saturated the cation exchange capacity (CEC) of the soil with proton (H^+) acidity, solubilized iron, aluminum, and manganese oxide surface coatings, and changed the net surface charge of the soil from negative to positive such that dissolved metals present in the groundwater remain in solution. Saturation of the sediment CEC with H^+ ions causes the continued presence of an acid plume, and the resulting impact on downgradient groundwater and the discharge canal is estimated to persist for decades. Precipitation infiltrating the vadose zone and groundwater flowing into the acidic zone from upgradient become strongly acidic when they encounter proton and aluminum acidity in the sediments, until such time that most of the soil acidity is depleted. If the soil acidity can be largely neutralized and the pH of the aquifer raised to background levels, the metals plume surrounding the DCSA and DCPRB can be reduced or eliminated and surface water conditions in the D-Area Discharge Canal will improve.

Soil Acidity and CEC

Sawyer (2004) explains in detail the interrelationships among total, active, and reserve acidity and soil pH. Total soil acidity is the sum of active and reserve acidity. Active acidity, which consists of free [H^+] in the soil solution, comprises only a small fraction of total acidity in the soil and largely determines the reading in a soil pH test. Reserve acidity, on the other hand, represents the sum of [H^+] and [Al^{3+}] chemically bound to organic matter and clay minerals. Total soil acidity is approximately equal to the reserve acidity. Limestone and/or lime amendments added to the soil must neutralize the reserve acidity to effectively raise the soil pH.

Reserve acidity is measured by a soil buffer pH test that is tailored to geographic location and soil type. For coarse-textured sandy soils with low kaolinite clay content from the South Carolina Coastal Plain, Clemson University recommends a Moore-Sikora buffer pH test to determine the lime requirement for neutralizing total soil acidity (Huluka et al., 2014). The Moore-Sikora buffer solution (pH 8.0) was developed as an alternative to the Adams-Evans buffer solution, which contains p-nitrophenol, a listed hazardous chemical (Sikora and Moore, 2008).

A large difference between the measured soil pH and buffer pH indicates that the soil's reserve acidity is easily changed (i.e., lime requirement is low). Conversely, a small difference between the measured soil pH and buffer pH signifies that the soil's reserve acidity is difficult to neutralize (i.e., lime requirement is high). As highlighted in Table 1, a clay soil will result in a

Table 1. Impact of Soil Type on Buffer pH and Lime Recommendations (after Midwest Laboratories, 2016).

Soil Type	CEC (meq/100 g)	$[H^+]$ (meq/100 g)	Soil pH	Buffer pH *	Lime Application Rate (ton/acre) **
Sand	6	1.8	5.6	6.8	1
Silt	14	4.2	5.6	6.6	2
Clay	24	7.5	5.6	6.2	4

* Based on Shoemaker-McLean-Pratt (SMP) buffer initially at pH 7.5 for midwestern soils.

** Unless stated otherwise, lime application rates for residential and agricultural applications are based on an assumed soil treatment depth of six inches.

lower buffer pH and, therefore, a higher lime application rate than both silt and sandy soil types with the same soil pH because of its greater CEC (Midwest Laboratories, 2016).

Past geological and soil surveys and geochemical studies at the Savannah River Site (SRS) were reviewed to generate an expected range for the CEC of DCSA vadose-zone soil. A general soil map of the SRS area developed by Rogers (1990) indicates that the upper five to seven feet of native, undisturbed soil in D-Area is predominantly of the Fuquay-Blanton-Dothan Association. Rogers (1990) also provides a much more detailed soil survey map of D-Area showing that the soils within and surrounding the DCSA are Udorthents, which consist of mostly well-drained soils that formed during excavations and major construction operations (i.e., the soil material has been removed, mixed, and moved). Because Udorthents occur in such irregular patterns on the landscape, classification is impractical. For this evaluation, the assumption is made that Udorthents consist of an unknown blend of the Blanton/Troup, Fuquay/Dothan, Vaucluse, and Orangeburg soil series, which comprise two-thirds of the soil series at SRS (Looney et al., 1990).

Previously reported values for the CEC of SRS upland soils include:

- Goto et al. (2014) compiled a summary for SRS upland soils from the Fuquay (2.0-2.2 meq/100 g), Orangeburg (1.7 meq/100 g), and Lakeland, Blanton, and Vaucluse (0.5 meq/100 g) soil series.
- Martin and Kaplan (1998) measured CECs ranging from 2.1 to 3.8 meq/100 g for SRS soil samples from the Orangeburg soil series.
- Siple (1967) reports CECs on the order of only 3 meq/100 g for surface clay and sand from the Hawthorn Formation (red, white, and purple sandy clays) at SRS.

Looney et al. (1990) reported that the clay mineral fraction in SRS soils is less than ten percent with the primary and secondary clay minerals being kaolinite (83.5 average weight percent) and vermiculite (14.9 average weight percent), respectively. Kaolinite and vermiculite have CECs ranging from 3 to 15 meq/100 g (Hillel et al., 1980) and 10 to 200 meq/100 g (Sparks, 2003), respectively. Based on these data, a soil CEC of 1 to 5 meq/100 g would be expected, which agrees well with the published CEC data for SRS upland soils.

No reported values of total acidity and buffer pH were found for SRS soils; however, based on 2018 soil and groundwater pH measurements (pH 3.0 to 4.5), it is likely that soil beneath the former DCSA is saturated with respect to both [H^+] and [Al^{3+}] acidity to water-table depth (approximately 10 to 12 feet).

Parameters affecting Lime Application Rates

The required lime application rate will be a function of the soil CEC, current soil pH, target soil pH, lime effectiveness, and treatment depth. Field and laboratory measurements from June 2018 show a soil pH ranging from 3.0 to 4.5 across the 15-acre former DCSA to the depth of the water table. Looney et al. (1990) reported soil pH values for 25 SRS upland soils ranging from 4.4 to 6.1. A target soil pH of 5.5 following lime treatment is reasonable.

Lime effectiveness, which is usually expressed as effective calcium carbonate equivalent (ECCE), depends on fineness efficiency (particle size), $CaCO_3$ equivalent (function of inert fraction and chemical form), and moisture content (Sawyer, 2004). Table 2 displays the calculated ECCE for several different hypothetical lime/limestone scenarios. ECCE can range from well below 100% to well above 100%. Best practice in agricultural and residential applications is to use a lime product with a particle size smaller than 60-mesh (< 0.25 mm).

Table 2. Calculated ECCE for Several Different Hypothetical Lime Sources.

Case	Lime Source	Moisture Content (%)	Fineness Efficiency (%) *	$CaCO_3$ Equivalent (%)	ECCE (%)
1	Calcite	0.2	45	77	35
2	Dolomite	1	70	110	76
3	Hydrated Lime	2	100	135	132

* When 100% of the particles pass a 60-mesh screen, total fineness efficiency will equal 100%.

Published lime application rates for residential and agricultural applications are usually based on an assumed soil treatment depth of six to eight inches which is the assumed depth of the root zone. For the former DCSA, the required treatment depth is four to ten feet; therefore, lime application rates will be a minimum of eight to twenty times higher than agricultural practices simply due to the increased treatment depth.

Estimating Lime Application Rates

In the absence of total soil acidity measurements (e.g., Moore-Sikora buffer pH) for the DCSA soil, recommended lime application rates for the 15-acre area were estimated in three ways:

1. Set total acidity equal to 100 percent of the soil CEC.
2. Extrapolate Moore-Sikora buffer pH test data for different soil types (sand, silt, and clay) published by Clemson Regulatory Services (2018) to current DCSA soil conditions.
3. Use results for pyritic mine soils and coal mine waste reported by Cagnetta and Jencks (1990) and Yang et al. (2006), respectively.

For estimation techniques 1 and 2 above, optimistic, best estimate, and pessimistic cases were considered to bracket uncertainties. Calculations were performed using Microsoft Excel and the assumptions shown in Figure 2.

Assumptions		
Total Impacted Area	15	acre
Depth of Treatment	10	feet
Bulk Density Soil	112.4	lb/ft3
Bulk Density Limestone	60.0	lb/ft3
Current Soil pH	3.5	
Cation Exchange Capacity Soil		
Optimistic	2.5	meq/100 g
Best Estimate	5	meq/100 g
Pessimistic	10	meq/100 g
"Lime" Effectiveness (ECCE) Factor		
Optimistic (high-quality limestone)	95	%
Best Estimate (medium-quality Limestone)	80	%
Pessimistic (low-quality Limestone)	65	%

Figure 2. Assumptions used to Estimate Limestone Application Rates for DCSA Soil.

Soil CEC Basis

This estimation approach assumes that 100 percent of the CEC is saturated with $[H^{+}]$ acidity but excludes any reserve acidity contributed by $[Al^{3+}]$. Table 3 summarizes results for the optimistic, best estimate, and pessimistic cases. The highlighted column displays the calcitic/dolomitic limestone dose in units of ton per acre per foot of depth, while the last column gives the total mass of limestone required for a 15-acre area and ten-foot soil depth. Incremental limestone required to neutralize latent acidity associated with an eight-inch thick residual coal fragments layer covering five acres in the southern portion of the 15-acre former DCSA is not included in the lime application rates reported in Table 3. The incremental lime dose needed to treat the coal fragments layer is calculated separately below. Figure 3 is an extension of Table 3 and allows for interpolation and extrapolation to other values for soil CEC.

Table 3. Calculated Lime Application Rates based on an Estimated Soil CEC.

Case	Soil CEC (meq/100 g)	Mass CaCO3 100% Eff. (ton/acre/ft depth)	Mass Limestone* Actual Eff. (ton/acre/ft depth)	Total Mass Limestone* Required Soil (ton)
Optimistic	2.5	3.1	3	483
Best Estimate	5	6.1	8	1148
Pessimistic	10	12.2	19	2825

* Limestone refers to high-quality calcitic or dolomitic limestone with particle size under 60-mesh for the optimistic case. The best estimate and pessimistic cases assume a calcitic/dolomitic limestone of lower quality (more inerts) and larger particle size (> 60-mesh).

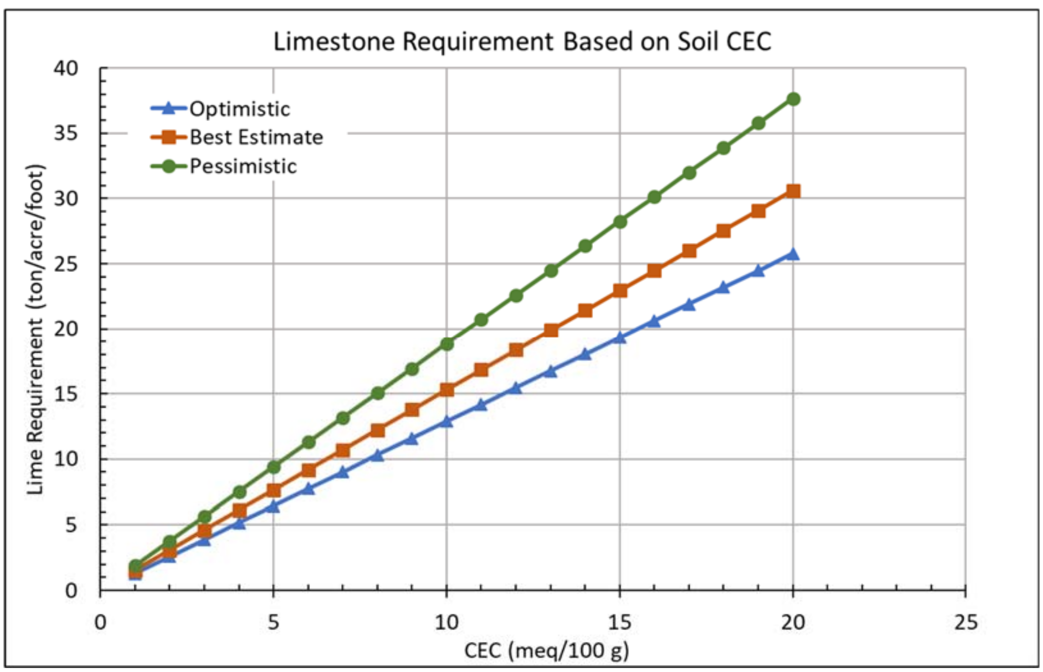

Figure 3. Limestone Requirement based on the Soil CEC.

Buffer pH Basis

Clemson Regulatory Services (2018) provides tables of recommended ground, agricultural limestone application rates to raise the soil pH of the surface eight inches to a target pH as a function of the current soil pH, target soil pH, and Moore-Sikora buffer pH. Table 4 displays the recommended agricultural limestone application rates for a target pH of 5.5 (Clemson Regulatory Services, 2018). Data in Table 4 were normalized to a soil depth of one foot, rather than eight inches, and were then linearly extrapolated to soil pH 3.5 as shown in Figure 4.

Table 5 summarizes the estimated limestone application rates required to raise DCSA soil from pH 3.5 to a target soil pH of 5.5 for the optimistic, best estimate, and pessimistic cases when based on hypothetical Moore-Sikora buffer pH test results. The optimistic, best estimate, and pessimistic cases in Table 5 assume a buffer pH equal to 7.6, 7.3, and 7.0, respectively. The highlighted column in Table 5 displays the limestone dose in units of ton per acre per foot of depth, while the last column reports the total mass of limestone required for a 15-acre area and ten-foot soil depth. Incremental limestone required to neutralize latent acidity associated with an eight-inch thick residual coal fragments layer covering five acres in the southern portion of the 15-acre former DCSA is not included in the lime application rates reported in Table 5. The incremental lime dose needed to treat the coal fragments layer is calculated separately below.

Table 4. Agricultural Limestone Requirement (ton/acre/foot depth) for Target pH 5.5 based on Moore-Sikora Buffer pH Test (Clemson Regulatory Services, 2018).

Buffer pH	Soil pH											Extrapolated
	5.4	5.3	5.2	5.1	5	4.9	4.8	4.7	4.6	4.5	4.4	3.5
7.95	-	0.08	0.08	0.15	0.15	0.15	0.23	0.23	0.23	0.30	0.30	
7.9	0.08	0.15	0.23	0.23	0.30	0.38	0.45	0.45	0.53	0.60	0.68	
7.85	0.08	0.23	0.30	0.38	0.45	0.53	0.60	0.68	0.75	0.90	0.98	
7.8	0.15	0.30	0.38	0.53	0.60	0.75	0.83	0.90	1.05	1.13	1.35	
7.75	0.15	0.30	0.53	0.60	0.75	0.90	1.05	1.13	1.28	1.43	1.65	
7.7	0.23	0.38	0.60	0.75	0.90	1.05	1.28	1.43	1.58	1.73	2.03	
7.65	0.23	0.45	0.68	0.90	1.05	1.28	1.43	1.65	1.80	2.03	2.33	
7.6	0.30	0.53	0.75	1.05	1.20	1.43	1.65	1.88	2.10	2.33	2.70	4.67
7.55	0.30	0.60	0.90	1.13	1.35	1.65	1.88	2.10	2.33	2.63	3.00	
7.5	0.38	0.68	0.98	1.28	1.58	1.80	2.10	2.33	2.55	2.85	3.38	
7.45	0.38	0.75	1.05	1.43	1.73	1.95	2.25	2.55	2.85	3.15	3.68	
7.4	0.45	0.83	1.20	1.50	1.88	2.18	2.48	2.78	3.08	3.45	4.05	
7.35	0.45	0.90	1.28	1.65	2.03	2.33	2.70	3.00	3.38	3.75	4.35	
7.3	0.45	0.98	1.35	1.80	2.18	2.55	2.93	3.23	3.60	4.05	4.73	8.13
7.25	0.53	0.98	1.50	1.88	2.33	2.70	3.08	3.45	3.90	4.35	5.03	
7.2	0.53	1.05	1.58	2.03	2.48	2.93	3.30	3.75	4.13	4.58	5.33	
7.15	0.60	1.13	1.65	2.18	2.63	3.08	3.53	3.98	4.43	4.88	5.70	
7.1	0.60	1.20	1.73	2.25	2.78	3.23	3.75	4.20	4.65	5.18	6.00	
7.05	0.68	1.28	1.88	2.40	2.93	3.45	3.90	4.43	4.95	5.48	6.38	
7	0.68	1.35	1.95	2.55	3.08	3.60	4.13	4.65	5.18	5.78	6.68	11.57

Table 5. Calculated Lime Application Rates based on a Moore-Sikora Buffer pH Test.

Case	Target Soil pH	Assumed Moore-Sikora Buffer pH	Moore-Sikora Lime Dose (ton/acre/foot depth) #	Mass Limestone* Actual Eff. (ton/acre/ft depth)	Total Mass Limestone* Required Soil (ton)
Optimistic ("Sand")	5.5	7.6	4.7	5	738
Best Estimate ("Silt")	5.5	7.3	8.1	10	1525
Pessimistic ("Clay")	5.5	7	11.6	18	2670

Clemson Agricultural Service Lab limestone requirements were linearly extrapolated to lower soil pH and adjusted for a one-foot depth vs. an eight-inch depth.

* Limestone refers to high-quality calcitic or dolomitic limestone with particle size under 60-mesh for the optimistic case. The best estimate and pessimistic cases assume a calcitic/dolomitic limestone of lower quality (more inerts) and larger particle size (> 60-mesh).

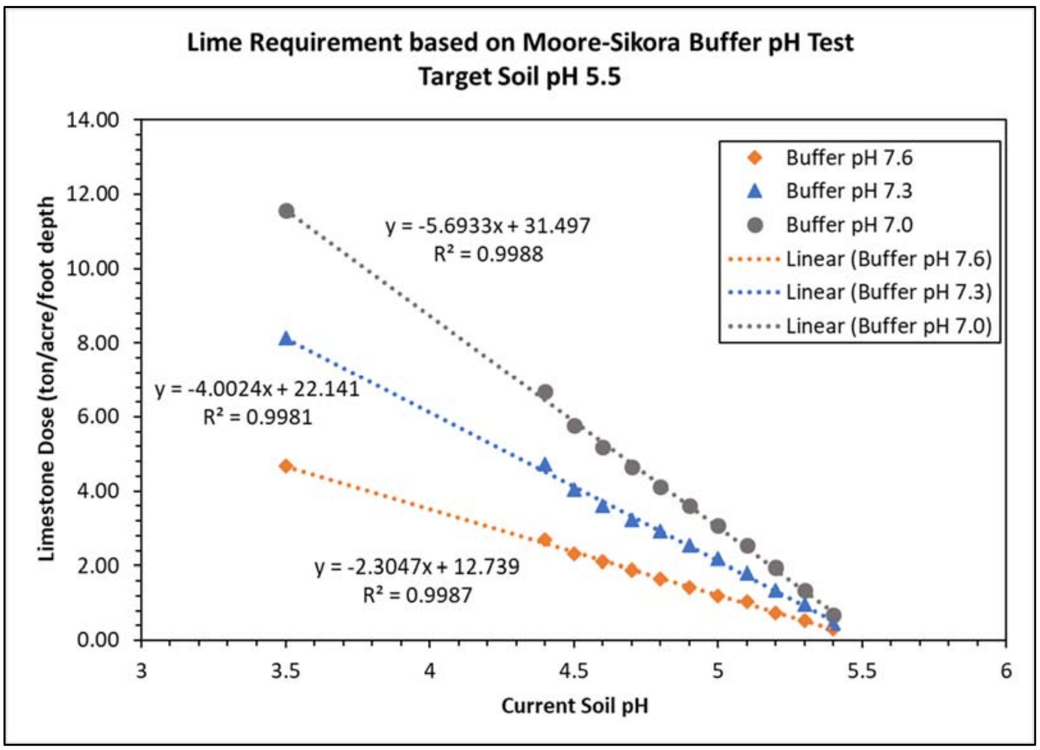

Figure 4. Extrapolation of Lime Requirements based on the Moore-Sikora Buffer pH Test to pH 3.5 (Target pH = 5.5).

Published Data for Pyritic Mine Soil and Coal Mine Waste

Cagnetta and Jencks (1990) conducted long-term incubation tests with mine soils and limestone having an ECCE equal to 96 percent. Mine soil samples 2, 3, and 4 in Tables 1 and 2 of their report appear to be most representative of the D-Area soil, although the mine soil clay content is much higher. Assuming a more conservative ECCE of 85 percent, the calculated lime application rate for mine soils 2, 3, and 4 ranges from 12 to 25 ton per acre per foot of depth, which is more in line with the pessimistic projections in Table 3 and Table 5.

Yang et al. (2006) applied 7.5 tons of wet lime cake per acre to test plots overlaying the surface of coal waste. The lime cake was sandwiched between top soil and coal waste or mixed with topsoil. Grasses were then grown on the topsoil. Although not stated in the paper, the assumed depth of treatment was six inches to one foot, and the assumed ECCE was 100%. Assuming a more conservative ECCE of 85 percent, the calculated lime application rate ranges from 8.8 to 17.6 ton per acre per foot of depth, which falls within the range of the best estimate to pessimistic projections in Table 3 and Table 5.

Incremental Lime Requirements for Residual Coal Fragments Layer

During soil coring in June 2018, an approximately eight-inch thick residual coal fragments layer was discovered beneath the topsoil and grass cover in the southern five acres of the 15-acre former DCSA. The origin and age of the coal fragments are unknown; therefore, the fragments are conservatively assumed to be fresh bituminous coal that has undergone negligible oxidation of included pyrite (FeS_2).

Oxidation of pyrite generates [H^+] acidity and can occur via the following abiotic and biotic pathways:

Abiotic (slow)

$$2FeS_2\ (s) + 7O_2 + 2H_2O = 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

Biotic (fast)

$4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$	(oxidation of ferrous iron to ferric)
$FeS_2\ (s) + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$	(oxidation of pyritic sulfur to sulfate)
$Fe^{3+} + 3H_2O = Fe(OH)_3\ (s) + 3H^+$	(hydrolysis/precipitation of ferric iron)
$FeS_2\ (s) + 3.75O_2 + 3.5H_2O = Fe(OH)_3\ (s) + 2SO_4^{2-} + 4H^+$	(overall biotic oxidation reaction)

Limestone neutralization reaction (fast)

$$CaCO_3\ (s) + 2H^+ = Ca^{2+} + H_2O + CO_2\ (g)$$

Total acidity generated by the oxidation of FeS_2 in the coal fragments layer will be bracketed on the low end by the abiotic pathway (4 moles H^+ per 2 moles FeS_2 = 1 mole H^+ per mole S) and on the high end by the biotic pathway (4 moles H^+ per 1 mole FeS_2 = 2 moles H^+ per mole S). The incremental lime dose required to treat the coal layer, therefore, will equal the total limestone required to neutralize 100% of the acidity generated by the coal fragments assuming a total pyritic sulfur content of one to two weight percent minus the lime dose that would have been applied if the coal layer was composed of acidic soil instead (from Table 3 and Table 5). Calculations were performed using Microsoft Excel and the assumptions shown in Figure 5 below. An example calculation is included in Appendix A.

Total Impacted Area	5	acre
Coal Layer Depth	8	inches
Bulk Density Bituminous Coal	52	lb/ft3
Oxidizable Sulfur Content Coal		
Optimistic	1	%
Best Estimate	1.5	%
Pessimistic	2	%
Mole H+ per mole sulfur		
Optimistic (abiotic oxidation rxn.)	1	mole/mole
Best Estimate (50% abiotic, 50% biotic)	1.5	mole/mole
Pessimistic (biotic oxidation rxn.)	2	mole/mole
"Lime" Effectiveness (ECCE) Factor		
Optimistic (high-quality limestone)	95	%
Best Estimate (medium-quality limestone)	80	%
Pessimistic (low-quality limestone)	65	%

Figure 5. Assumptions used to Calculate the Incremental Limestone Required to Treat the Coal Fragments Layer.

Table 6 and Table 7 summarize results of the limestone application rate calculations for the optimistic, best estimate, and pessimistic coal-fragment cases. In Table 6, the incremental limestone application rate for the coal layer is calculated assuming a soil-only limestone application rate based on the CEC of DCSA soil (Table 3). Table 7, on the other hand, assumes a soil-only limestone application rate based on the Moore-Sikora buffer pH of DCSA soil (Table 5). In all cases for both scenarios, the incremental mass of limestone required to treat the coal fragments layer ranges between five and ten percent of the limestone required to treat the soil itself. For this reason, in situ treatment of the coal fragments layer is recommended over excavation and disposal.

Table 6. Incremental Limestone Required to Treat Coal Fragments Layer – Soil Limestone Application Rate based on CEC of DCSA Soil.

Case	Volume Coal (ft3/acre)	Mass Coal (lb/acre)	Mass Sulfur (lb/acre)	Mass CaCO3 100% Eff. (ton/acre)	Mass Limestone* Actual Eff. (ton/acre/ft)	Total Mass Limestone* Required (ton)	Incremental Mass Limestone* Required for Coal** (ton)
Optimistic	29040	1510080	15101	11.8	19	62	51
Best Estimate	29040	1510080	22651	26.5	50	166	140
Pessimistic	29040	1510080	30202	47.2	109	363	300

* Limestone refers to high-quality calcitic or dolomitic limestone with particle size under 60-mesh for the optimistic case. The best estimate and pessimistic cases assume a calcitic/dolomitic limestone of lower quality (more inerts) and larger particle size (> 60-mesh).

** Incremental mass of limestone required for coal fragments layer equals the total mass of limestone required for neutralization of the coal fragments layer less the mass of limestone that would have been applied if the coal layer was composed of acidic soil instead.

Table 7. Incremental Limestone Required to Treat Coal Fragments Layer – Soil Limestone Application Rate based on Moore-Sikora Buffer pH.

Case	Volume Coal (ft3/acre)	Mass Coal (lb/acre)	Mass Sulfur (lb/acre)	Mass CaCO3 100% Eff. (ton/acre)	Mass Limestone* Actual Eff. (ton/acre/ft)	Total Mass Limestone* Required (ton)	Incremental Mass Limestone* Required for Coal** (ton)
Optimistic	29040	1510080	15101	11.8	19	62	46
Best Estimate	29040	1510080	22651	26.5	50	166	132
Pessimistic	29040	1510080	30202	47.2	109	363	304

* Limestone refers to high-quality calcitic or dolomitic limestone with particle size under 60-mesh for the optimistic case. The best estimate and pessimistic cases assume a calcitic/dolomitic limestone of lower quality (more inerts) and larger particle size (> 60-mesh).

** Incremental mass of limestone required for coal fragments layer equals the total mass of limestone required for neutralization of the coal fragments layer less the mass of limestone that would have been applied if the coal layer was composed of acidic soil instead.

<u>Total Lime Requirements</u>

Table 8 displays the total mass and bulk volume of lime required across the 15-acre former DCSA to treat both the acid soil and the coal fragments for both the soil CEC and SMP-buffer-pH scenarios. The bulk volume was calculated using the bulk densities reported for hydrated lime and limestone in Figure 2.

Table 8. Total Mass and Bulk Volume of Lime Required to Treat both Acid Soil and Coal Fragments Layer (15 acres and 10-foot treatment depth).

Basis: 100% of the Soil CEC			
Case	**Soil CEC (meq/100 g)**	**Total Mass Limestone* Required for Soil + Coal Layer (ton)**	**Volume Limestone* Required (cu. yd.)**
Optimistic	2.5	**535**	660
Best Estimate	5	**1288**	1590
Pessimistic	10	**3125**	3858
Basis: Moore-Sikora Buffer pH (Target pH 5.5)			
Case	**Assumed Buffer pH**	**Total Mass Limestone* Required for Soil + Coal Layer (ton)**	**Volume Limestone* Required (cu. yd.)**
Optimistic ("Sand")	7.6	**783**	967
Best Estimate ("Silt")	7.3	**1657**	2046
Pessimistic ("Clay")	7	**2974**	3671

* Limestone refers to high-quality calcitic or dolomitic limestone with particle size under 60-mesh for the optimistic case. The best estimate and pessimistic cases assume a calcitic/dolomitic limestone of lower quality (more inerts) and larger particle size (> 60-mesh).

Vadose Zone Flushing

A simple mass balance model was developed using Microsoft Excel to estimate the volume of pH 6.5 artesian well water and associated pumping time required to simply flush/leach reserve acidity from the lower vadose zone (five to ten feet below ground surface) within the 15-acre former DCSA. Figure 6 displays a screen capture of the model where optimistic, best estimate, and pessimistic cases were considered. The optimistic and pessimistic bounding cases are based on the minimum (2.5 meq/100 g) and maximum (10 meq/100 g) CECs reported in Table 3. The best-estimate case is based upon an equivalent CEC (6 meq/100 g) back-calculated from the lime application rate (10 ton/acre/foot depth) for the best-estimate “silt” case in Table 5. No credit is taken for neutralization of acidity by carbonate alkalinity in the artesian well water.

To leach reserve acidity from the pH 3.5 soil within the vadose zone and return the soil to background pH (5.5), the model predicts that 400 to 1800 pore volumes of flush water will be required (Step 4 in Figure 6). The number of pore volumes required will be less if carbonate alkalinity is present in the artesian well water. The corresponding time required to flush reserve acidity from a 15-acre by five-foot-thick section of the vadose zone assuming a 250 gallon per minute pumping rate will range from 25 to 100 years (Step 5 in Figure 6).

Assumptions

Basis for Pore Volume Calculation	1	cu yd soil	
Total Impacted Area	15	acre	
Thickness of Soil Flushed	5	feet	
Bulk Density Soil	112.4	lb/ft3	Clay-Sand
Mineral Density Soil	166.7	lb/ft3	
Current Soil Water pH	3.5		
Artesian Well Water pH	6.5		
Injection Rate	250.0	gpm	
Total Acidity in Soil			
Optimistic	2.5	meq/100 g	
Best Estimate	6	meq/100 g	
Pessimistic	10	meq/100 g	

Conversion Factors

Grams to Pounds	453.592	g/lb
Cubic Feet to Cubic Yards	27	ft3/yd3
Liters to Cubic Feet	28.317	L/ft3
Gallons to Liters	0.264	Gal/L
Square Feet to Acre	43560	ft2/acre
Minutes to Years	525600	min./yr
Equivalents per mole H+	1	equiv/mole

1. Calculate Pore Volume of Soil

Calculated Porosity	0.326	ft3 pores/ft3 total
Volume of pore space	249.0	L/pore volume

2. Calculate Acid Capacity of One Pore Volume of Flush Water

[H+] at pH soil water	3.162E-04	moles/L
[H+] at pH flush water	3.162E-07	moles/L
Acid Capacity of Flush Water	3.159E-04	moles/L
Acid Capacity of One Pore Volume	7.868E-02	moles H+/pore volume

3. Calculate Total Reserve Acidity in Soil

Optimistic Case	34.41	moles H+
Best Estimate Case	82.59	moles H+
Pessimistic Case	137.66	moles H+

Figure 6. Vadose Zone Flushing Model for DCSA.

4. Calculate Required Number of Pore Volumes of Flush Water

Optimistic Case	437	Pore Volumes
Best Estimate Case	1050	Pore Volumes
Pessimistic Case	1750	Pore Volumes

5. Calculate Time Required to Flush Acidity

Total volume soil flushed	121000	yd3
Optimistic Case	28778	gallons flush water/yd3 soil
Best Estimate Case	69066	gallons flush water/yd3 soil
Pessimistic Case	115110	gallons flush water/yd3 soil
Optimistic Case	3.48E+09	Total gallons flush water
Best Estimate Case	8.36E+09	Total gallons flush water
Pessimistic Case	1.39E+10	Total gallons flush water
Optimistic Case	26	Total flush time (years)
Best Estimate Case	64	Total flush time (years)
Pessimistic Case	106	Total flush time (years)

Figure 6 (cont'd). Vadose Zone Flushing Model for DCSA.

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Appendix A. Sample Calculation of Lime Requirement for Coal Fragments Layer

Abiotic (slow)

$2FeS_2$ (s) + $7O_2$ + $2H_2O$ = $2Fe^{2+}$ + $4SO_4^{2-}$ + $4H^+$

Biotic (fast)

FeS_2 (s) + $3.75O_2$ + $3.5H_2O$ = $Fe(OH)_3$ (s) + $2SO_4^{2-}$ + $4H^+$

Limestone neutralization reaction (fast)

$CaCO_3$ (s) + $2H^+$ = Ca^{2+} + H_2O + CO_2 (g)

The abiotic oxidation reaction generates 4 moles H^+ acidity per 4 moles reduced S (2 moles FeS_2 x 2 moles S/mole FeS_2 = 4 moles S).

The biotic oxidation reaction generates 4 moles H^+ acidity per 2 moles S (1 mole FeS_2 x 2 moles S/mole FeS_2 = 2 moles S).

The neutralization reaction consumes 1 mole $CaCO_3$ per 2 moles H^+ acidity.

Mass of Limestone Required at 100% ECCE

<u>Optimistic Case, CEC of Soil Basis (Table 6)</u>

Mass $CaCO_3$ (ton/acre) = (43,560 ft^2 coal layer/acre) x (8/12 ft thick coal layer) x (52.0 lb coal/ft^3) x (0.01 lb S/lb coal) x (453.59 g/lb) x (mole S/32 g S) x (1 mole H^+/mole S) x (1 mole $CaCO_3$/2 mole H^+) x (100 g $CaCO_3$/mole $CaCO_3$) x (1 lb/453.59 g) x (1 ton/2000 lb) =

<u>11.8 tons $CaCO_3$/acre</u>

where

lb = pound mass
g = gram mass
ft = feet
ft^2 = square feet
ft^3 = cubic feet

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