Field evaluation of bauxite residue neutralization by carbon dioxide, vegetation, and organic amendments

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Abstract

The objective of this study was to investigate the mechanisms and extent of bauxite residue (red mud) neutralization at the residue surface in field impoundments as a result of long-term reaction with atmospheric CO₂ and addition of amendments to promote vegetation. The results showed that carbonation from atmospheric carbon dioxide reduces the pH of red mud from 12.5 to about pH 9.3 at the surface of storage cells, with the depth of neutralization dependent on the age of the stored residue (up to 1.2 m in 35 years). The presence of vegetation further lowered residue pH to about pH 8.5, with the depth of neutralization dependent on depth of root penetration. Sewage and yard waste amendments accelerated neutralization and the establishment of vegetation, and further lowered the residue pH to about pH 6.7, likely due to organic acid leaching. For vegetated areas, the root density (g roots/g soil) was proportional to the extent of neutralization of residue, with root density higher in near-surface residue than in deeper residue.
Introduction

The production of alumina by the Bayer process creates a slurry residue (red mud) having a pH in excess of 12.5. Approximately 3 million tons of red mud are produced in the U.S. each year and 30 million tons/yr globally (on a dry weight basis), and disposed in land-based impoundment reservoirs (Ayres et al. 2001). Stored bauxite residue represents an on-going and costly environmental liability for aluminium manufacturers. Safe storage of these materials requires engineered impoundments with leachate collection and treatment to prevent contamination of soil and groundwater. The storage impoundments typically occupy hundreds of acres of land at processing sites (Ayres et al. 2001). Usually there is no vegetation on the beds due to the high alkalinity (pH > 12) of the tailings. As dry bauxite residue is extremely friable, it can yield a significant amount of dust. Dust (predominantly Na₂CO₃) formed on the dry residue surface can pose a health risk to wildlife or humans when it is carried away from the site in air flows (Prasad et al., 1996).

To minimize dust mobilization, leachate generation, and surface erosion of stored bauxite residue, and to initiate land reclamation, it is desirable to vegetate the surface of the stored residue (Fuller et al., 1982). This can only be done if the surface material is neutralized (porewater pH is decreased) sufficiently, and if other properties of the residue can be rendered sufficiently soil-like that vegetation can be established (Woodard et al., 2008; Wehr et al., 2006).
Various laboratory studies (Khaitan et al., 2009a, 2009b, 2009c, Xenidis et al., 2005, Enick et al., 2001), as well as field studies at Alcoa’s Sherwin and Copano bauxite residue storage facilities in Texas, have been conducted to assess different approaches for neutralizing red mud and for establishing vegetation. The Sherwin and Copano facilities are co-located approximately one mile southeast of the City of Gregory, in San Patricio County, Texas. Red mud tailings produced as residue of the Bayer process for extracting alumina from bauxite ore were accumulated from the late spring of 1953 through 1967. The accumulated tailings are fairly homogeneous, both chemically and physically (Alcoa, 2002). The impoundments cover an area of 457 acres at the Sherwin storage facility (Alcoa, 2002).

According to prior observations at the impoundments, plants can grow on un-amended red mud, though high alkali content poses a challenge to establish flora and fauna on bauxite residue. Vegetation has been established on un-amended red mud, even without seeding; bermuda grass and bitter weed could effectively re-vegetate the drying beds at the Alcoa Point Comfort, TX site (Alcoa, undated).

Amendments with labile degradable organic carbon such as hay, sewage sludge, and yard waste can help increase the survivability and growth of alkaline tolerant grasses on red mud surface impoundments (Harris, 2009; Fuller et al., 1982). In a study by Hamdy and Williams (Hamdy and Williams 2001), bauxite residue was treated with hay and yard waste which supported growth of organisms like lactobacillus, micrococcus, staphylococcus, and pseudomonas and led to reduction in pH from 13 to 7. Alkali tolerant grasses, including Bermuda grass, Rhodes grass and saltbush, were planted and survived on red mud amended with hay and yard waste (Alcoa, undated; Texas A&I, 2002, un-dated).
1993). In Alcoa field studies of red mud vegetation with alkali-tolerant grasses (Alcoa, 2002; Alcoa, undated; Texas A&I, 1993; Reynolds, 1999; MFG, 2003), it was observed that vegetation survived near the edges of the cells but growth dwindled if the plants were located near the center of the cell. It was also observed that drainage was better at the edges than in the center, suggesting that drainage affected plant viability and growth on the bauxite residue as has been observed at other red mud storage sites (Woodard et al., 2008).

It was concluded from Alcoa’s studies (Alcoa, 2002; Alcoa, undated; Texas A&I, 1993; MFG, 2003; Reynolds, 1999) that bauxite residue had higher rates of vegetation after addition of organic amendments such as sewage sludge and yard waste. Selected species of grass, such as sacaton, Rhodes grass and Bermuda grass, showed substantial growth, but the causative factors were not studied. Further, the field investigations of bauxite residue vegetation conducted by Alcoa did not provide information on the change in stored bauxite residue properties so the causative factors supporting or suppressing vegetation are not known. The role of atmospheric carbon dioxide on red mud neutralization was investigated in the laboratory (Khaitan et al., 2009c), however, there are several open questions regarding the neutralization afforded by atmospheric carbon dioxide, various organic amendments and the vegetation itself, and the role of moisture content and soil and grain size distribution on plant survivability in field impoundments.

To examine the factors that promote or suppress vegetation of bauxite residue, additional field measurements were collected on amended and unamended residues, on vegetated and non-vegetated residues, and on aged (35 years) and younger (14 years) bauxite residue storage impoundments at the Alcoa Sherwin and Copano, TX facilities.
The research objectives were to determine 1) the extent of carbon dioxide neutralization of red mud in the field; 2) the effect of vegetation on neutralization of stored red mud in the field; 3) the effect of organic amendment on neutralization of stored red mud in the field, and 4) the effect of moisture content of the residue on its ability to vegetate.

**Methods**

**Field Sampling**

Field core samples were obtained from un-amended and amended red mud cells at the Alcoa Sherwin and Copano bauxite residue storage facilities. The size, age, and type of amendment applied to each cell are given in Table 1. A schematic of a typical bauxite residue cell at the Sherwin storage facility is shown in Figure 1. Due to topography, the center of the cell is periodically saturated with highly alkaline porewater to the point of ponding and thus cannot support vegetation, while the edges that are well drained are more neutralized than the center show higher growth of vegetation.

A sampling plan (Table 2) was devised to examine the effects of carbon dioxide, vegetation and organic amendment addition on the near surface (0.9 to 1.2 m) properties of bauxite residue, and the effect of water content on the ability to vegetate the surface. Residue cells of different age, surface amendment, and extent of vegetation at the Alcoa Sherwin facility were selected for study. The effect of carbon dioxide on residue pH was investigated by sampling from un-amended/un-vegetated residue cells at Copano and Sherwin that were of different ages (Table 1). It was expected that older cells that have had longer exposure to CO₂ will be more neutralized than younger cells. Determining the effect of vegetation and amendment on residue pH required sampling from areas that
have been vegetated and/or amended at the Sherwin bauxite residue storage facility in Texas, and comparing the results to those for un-amended cells of the same age. Lateral sampling (Figure 1) of the extent and type of vegetation across a red mud cell was done to examine the effect of moisture content on the growth of vegetation and on the neutralization of the residue. To investigate the effect of the vegetation type and the amendment type, duplicate core samples were collected to 0.9 to 1.2 m depth and at equal intervals of distance (approximately every 12 m) from the center to the edge of the cell for two types of vegetation and for two types of amendment for similar age cells.

The bauxite residue core samples were collected in 2.5 cm. diam. x 1.2 m long plastic (butyrate) tubes which were fitted inside steel Shelby-tube samplers. Undisturbed samples were obtained by pressing the Shelby tube assembly into the ground with a truck-mounded Geoprobe® sampler. The plastic tubes were removed from the sampler, and caps were applied at both ends of the tubes after collecting the cores to exclude contact with air.

Core Analysis

The collected cores were sectioned at 15 cm intervals with a hacksaw. A subsample was retrieved from each core section and was analyzed for pH, total inorganic carbon (TIC) and total organic carbon (TOC), water content and root density. pH was measured with a combined pH electrode in red mud slurry (solids plus porewater) of the material following the soil pH method specified in Methods of Soil Analysis (Page et al. 1982). The red mud TIC was measured using a solids total carbon (TC) analyzer (O-I Analytical). A measured mass (100-200 mg) of red mud was added to a quartz cup,
heated to 900°C for 10 minutes to convert all carbon to CO₂, and total carbon (TC) content was determined. Duplicate or triplicate measurements on separate subsamples were made. Reported values are the average and standard deviation of replicate analyses. For the TOC measurement, 100-400 mg of the core section subsample was transferred to a quartz cup for analysis. 200 µL of phosphoric acid (1g/L) was added to each cup and the sample was then purged with He gas at 270°C to remove the inorganic carbon. TOC was then determined by heating the sample to 900°C. TIC was calculated by difference (TIC=TC-TOC).

Root density was measured on core section samples in terms of root mass per unit mass of soil (g/g), and in terms of specific root length (SRL; m/g) (Jones, 1998). SRL is the ratio of the root length to the total root mass and therefore integrates root length and thickness (Atkinson 2000). Though root mass/soil mass is not a standard plant literature unit for root density, it proved to be useful measure in this study to compare the growth of root mass at various sections of a cell. The following procedure was used to determine root mass per unit mass of soil (g/g) and SRL. A sample containing both soil and roots was washed with water to separate the soil and roots. The soil was then dried at 105°C for 24 hours. The soil and roots were weighed to obtain the mass of roots per unit mass of soil. The washed roots were separated by hand and spread on a white absorbent paper. The root length and diameter were measured by taking an image of the roots using a flat bed scanner, and obtaining the root length with use of Win-Rhizotron image analysis software (Regent Instruments Inc., Canada).

**Solid Phase Mineral Analysis**
X-Ray diffraction (XRD) was performed to identify the dominant solid phases present in the red mud. The samples B1-Top (surface) and B4-Bottom (1.2 m below ground surface) (Table 2) from Copano were dried and crushed to powder using a mortar-pestle. A Rigaku instrument (Geigerflex Theta-Theta, Texas, US) was used to perform the XRD analyses. The solid phases were determined with XRD using a scan from 10 to 60 degrees 2θ, a step size of 0.05 deg and a 6 sec dwell time. Peak identification was done using Philips X’pert graphics and identifier software (Version 1.2b, Netherlands).

**Moisture Content Measurement**

Bauxite residue water content was determined gravimetrically (Brady and Well 2002). A sample of moist residue was weighed and then dried in an oven at a temperature of 105° C for about 24 hours, and weighed again. This process was repeated until the soil reached a constant weight. The weight loss represented the soil moisture.

**Particle Size Distribution**

The standard test method (ASTM D 422-63) was used to determine the grain size distribution of bauxite residue. Standard sieves (#10, #40, #60, #100, #140, #200, and #400) were used to classify the residue among common soil particle size ranges including gravel, sand, silt and clay. A measured dry mass of 50-100 grams of residue from sample locations of A1-Bottom, A4-Top and Bottom, and B1-Top and Bottom (Table 2) was added to the top sieve. The whole assembly was placed on a shaker for 10 minutes. The residue retained on each sieve was transferred to an aluminum foil dish and weighed using a balance.
Results and Discussion

Bauxite residue neutralization by carbon dioxide in the field

Bauxite residue neutralization by carbon dioxide in the field was investigated for two un-amended storage cells at the Alcoa Sherwin and Copano, TX sites. The extent of neutralization via carbonation observed at the older Sherwin cell (35 years) was higher than that at the younger Copano cell (14 years). The measured pH and total inorganic carbon content as a function of depth are plotted in Figures 2a and 2b and Figures 3a and 3b, respectively. Note that total carbon equaled total inorganic carbon in these unvegetated cells, i.e. organic carbon was below detection. The (older) Sherwin cell had a lower pH than for the (younger) Copano cell at all depths. The surface neutralization was also higher for the Sherwin cell (pH=9.5) than for the Copano cell (pH=10.5). Since no amendments were applied to either site, and no vegetation was present, the resulting neutralization and increase in inorganic carbon is attributable to slow carbonation from atmospheric CO2. The pH varies with depth in the Copano (younger) pond indicating that neutralization by atmospheric CO2 is probably limited by the availability of carbon dioxide to the residue. The inorganic carbon content was higher in the older Sherwin residue and at a greater depth as compared to that in the younger Copano residue. The differences in the extent and depth of neutralization between older and younger cells imply that carbonation of bauxite residue by exposure to atmospheric CO2 is a slow process. It should be noted that the water content, i.e. degree of saturation, could affect the rate of CO2 flux into the residue. The moisture content was similar in each cell at the time of measurement as discussed later.
X-ray diffraction analysis was performed on select samples (B4-Bottom and B1-Top; Table 2) from the Copano cell. In a study conducted by Khaitan et al. (2009b), it was found that carbon dioxide neutralization decreases the tri-calcium aluminate content in the residue and increases the calcite content. The key controlling reactions for long term carbonation of bauxite residue in the field include dissolution of C3A (eqn 1),

$$\text{Ca}_3\text{Al}_2\text{O}_6(s) + 12\text{H}^+ = 3\text{Ca}^{2+} + 2\text{Al}^{3+} + 6\text{H}_2\text{O}$$  \hspace{1cm} (1)

and precipitation of calcite (eqn 2).

$$\text{Ca}^{2+} + \text{CO}_3^{2-} = \text{CaCO}_3(s)$$  \hspace{1cm} (2)

The XRD results in Figure 4 show an increase in the height of calcite peaks and decrease in tri-calcium aluminate (C3A) for the surface residue compared to the deeper residue at Copano. Also, the surface residue had a lower pH of 10.4 compared to the deeper residue which had a higher pH of 12.1. Thus, the data indicate that carbon dioxide neutralization occurs more slowly for the deeper residue than for the surface, likely limited by the rate of transport of CO₂ to depth, and possibly also by the rate of C3A dissolution in the residue (Khaitan et al., 2009b).

**Vegetation effect on neutralization of Red Mud cell in the field**

The growth of vegetation and the associated increase of root mass on the surface of a bauxite residue cell appear to lower the pH and further neutralize the residue compared to the un-amended cases. As shown in Figures 5a and 5b, the pH of the vegetated residue was lower than the pH measured in un-amended cells (Figures 2a and 2b). This suggests that vegetation contributed to neutralization in addition to the carbonation effect on the vegetated cells. Further, the pH is generally highest for positions near the center with no vegetation and lowest near the edge of the cell where
maximum growth of vegetation was observed (Figures 5a and 5b). The root mass density in g/g increased (indicated on Figures 5a and 5b) as core sampling positions moved near the edge where vegetation was present in greatest abundance.

Thus, the vegetation existing on the bauxite residue appears to neutralize the residue, possibly due to the growth of roots that produce organic acids. Grasses and similar plants are known to produce organic acids at their root tips (Brady and Well 2002). The accumulation of organic matter also helps to acidify the soil. First, organic matter forms soluble complexes with cations such as Ca\(^{2+}\) and Mg\(^{2+}\), thus facilitating the reduction of OH\(^-\) by the corresponding electroneutrality adjustment. Second, organic matter is a source of H\(^+\) ions because it contains numerous acid functional groups from which these ions can dissociate. Organic acids reported to be present in plant roots include lactate, acetate, oxalate, succinate, fumarate, malate, citrate, isocitrate and aconitate (Jones 1998, Dennis et al. 1990, Marschner 1995). The release of organic acids from roots was studied extensively by Jones (1998) and was found to occur by multiple mechanisms in response to a number of well-defined environmental stresses (e.g. Al, P and Fe concentrations in the dissolved and precipitated phase). Particular responses were specific to the plant species under investigation.

Bermuda grass and bitter weed vegetation were observed to reduce the pH of the residue further below the pH of the carbonated residue in un-amended cells, and lower than the pH 10.5 expected for neutralization by atmospheric CO\(_2\) alone (Dennis et al. 1990; Khaitan et al., 2009c). In the absence of sewage sludge application, root mass density in (g/g) was found to be proportional to the extent of neutralization, as shown in Figure 6, suggesting an effect of vegetation on neutralization. The root mass dwindled to
zero at the center of the cell (Bed #1 and Sherwin, Table 1) where SRL measurements could not be obtained due to the very low root masses.

The total carbon contents measured for the core samples from the vegetated cells are shown in Figures 7a and 7b. A significantly higher total carbon content (mostly due to a higher organic carbon content) was observed at the surface and up to a depth of 15 to 25 cm in the amended, vegetated cells relative to the carbon content in the un-amended, un-vegetated cells (Figures 3a and 3b). This is due to the root mass produced by the bermuda grass and bitter weed plants. Higher carbon content was observed at the surface for bitter weed than for bermuda grass, due to higher root mass values of bitter weed. The carbon contents for the deeper core sections at 25 cm or more were similar to the values for the un-amended cells. Bermuda grass shows higher carbon content than that of bitter weed at a depth of 15 cm, due to deeper root penetration by bermuda grass.

Effect of amendment on neutralization of stored bauxite residue in the field

The surface residue amendments examined in this study - sewage sludge and yard waste – appeared to enhance residue neutralization. The neutralization occurred at the surface and deeper residue of the amended, non-vegetated sections, likely due to acid leaching from the sludge and yard waste. The amendments also enhanced vegetation which further neutralized the residue.

The amendment effect - probably acid leaching – was significantly greater than the vegetation effect for the selected amendments in this work. Core sample pH and total carbon content vs. depth are shown in Figures 8a-8d for the two amendments examined in this study. The observed pH values for amended, un-vegetated residue in Figures 8a
and 8b were lower than those of the un-amended and vegetated residue (Figure 5a and 5b). The sewage sludge amendment alone (no vegetation) produced the lowest pH (Figure 8a) among all the conditions studied.

Sewage sludge amendment provided significant neutralization, but did not produce a significant amount of root mass in g/g in comparison to the yard waste (Figure 8). The change in pH for sewage sludge did not correlate with the root mass increase, suggesting that the neutralization caused by sewage sludge had minimal contribution from vegetation. The increase in root mass produced by the yard waste decreased the pH more than cases where vegetation was established without amending with yard waste (Figure 5).

In Figures 8c and 8d, the total carbon content was higher for the core samples from the sewage sludge amended residue than for the yard waste amended residue, which correlates with the lower pH values for sludge amendment. The higher total carbon content in the sewage-sludge amended residue was due to the organic amendment itself rather than from the vegetation, considering the low root mass measured for the core samples in the sludge amended cell. The carbon content was highest in the top 6 inches as shown in Figures 8c and 8d, and decreased to lower values at depths greater than 6 inches, indicating that no deep mixing of amendment and residue occurred. The carbon contents at depths greater than 6 inches were comparable to those in un-amended cells (Figures 3a and 3b), implying that the higher carbon content at the surface was in fact due to the amendment.

**Variation in Moisture Content**

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Moisture content can affect the rate of neutralization by atmospheric CO\textsubscript{2} and prevent growth of vegetation if the pore water has high alkalinity. Moisture content varied with lateral distance across the red mud cells and with depth. The moisture content was higher towards the center of the cells and increased with depths at individual locations. The moisture content vs. depth for un-amended, vegetated and amended locations is shown in Figures 9a-9d.

The variation in moisture content with lateral distance and depth for the un-amended Sherwin and Copano cells is illustrated in Figures 9a and 9b. The moisture content at the center of Sherwin cell was found to be higher than that in Copano cell, which implied that the Copano cell had better drainage and a lower level of water saturation in the cell. As the particle size distribution for the residue in both the cells showed similar results (Figure 10), the water holding capacity for both the cells appeared to be about the same.

The variation in moisture content for the vegetated Sherwin cells is shown in Figures 9c and 9d. The moisture content was lowest near the edges of the vegetated cells, probably reflecting better drainage near the edges due to topography. The growth of vegetation was negatively correlated to the moisture content in Figures 9c and 9d, as higher moisture content at the center does not support vegetation on the surface of the cell due to the highly alkaline nature of the porewater. Comparing the moisture content of un-amended cells without vegetation (Figure 9a) to vegetated cells (Figures 9c and 9d), indicates that moisture contents in vegetated locations were similar to those in the un-amended un-vegetated locations, and implies that evapotranspiration from vegetation did not significantly affect moisture content.
Summary and Conclusions

The neutralization of the surface (approximately the top meter of residue) of impounded bauxite residue by contact with atmospheric carbon dioxide, addition of organic amendment such as sewage sludge or yard waste, and/or vegetation with grasses was studied at two Alcoa bauxite residue (red mud) storage cells near Gregory, TX. Core samples were acquired from various storage cells in Sherwin and Copano, TX that contained residue of different age, different types of surface amendments, and different kinds of vegetation. Locations with no amendments and no vegetation were studied as controls. Atmospheric carbon dioxide neutralized the bauxite residue to a pH=9.4 at a depth of at least 3 ft over a period of 35 years. The older cell (35 years) at Sherwin was neutralized to a greater extent and greater depth than the younger one (14 years) at Copano. At all locations, inorganic carbon was higher at the surface (2-3 mg TIC/g residue) than at depth due to surface carbonation by atmospheric CO₂.

Vegetation and organic amendments further neutralized the surface residue. Vegetation further lowered residue pH compared to the un-vegetated and un-amended (but carbonated) cells. The root penetration and root mass lowered the pH of the residue due to organic acid produced by the growth of plant roots. Organic amendments neutralized the red mud likely by acid leaching. Amending with sewage sludge lowered pH more than amending with yard waste. Yard waste produced more vegetation root mass than the sewage sludge amendment, and this vegetation further neutralized the residue. The root mass produced by the vegetation on the yard-waste-amended residue correlated with the pH of the residue, except in the case of sewage sludge amendment.
which provided significant neutralization without an associated increase in root mass indicating that organic acids in sewage sludge provided neutralization.

Moisture content was higher in the center of the cells, and at depth. Higher moisture content leads to higher pH in the residue cells due to excess base in the porewater. Vegetation was negatively correlated with the moisture content. Moisture content was comparable for the un-amended cells and the vegetated cells indicating that vegetation did not significantly affect the moisture content through evapotranspiration.

Overall, this field study of bauxite residue neutralization found that (1) residue pH may be lowered to pH = 9.5 by reaction with atmospheric carbon dioxide with the depth of neutralization increasing to approximately 1 m over 35 years; (2) specific varieties of vegetation, namely bermuda grass and bitter weed, grow well on the red mud without seeding and enhances neutralization to pH of 9 (and reduces dust from the residue cells); and (3) residue pH may be lowered further, to approximately 8.0, by addition of organic amendment such as sewage sludge or yard waste which likely release organic acids.

Acknowledgements

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References


<table>
<thead>
<tr>
<th>Type of Cell</th>
<th>Bed #</th>
<th>Location (Texas)</th>
<th>Area (m²)</th>
<th>Age (Years)</th>
<th>Dimensions (m x m)</th>
<th>Depth (m)</th>
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<tbody>
<tr>
<td>Un-amended Sherwin cell</td>
<td>3</td>
<td>Sherwin, TX</td>
<td>84,000</td>
<td>35&lt;sup&gt;a&lt;/sup&gt;</td>
<td>275x305</td>
<td>5.5</td>
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<td>Sherwin, TX</td>
<td>75,000</td>
<td>35&lt;sup&gt;a&lt;/sup&gt;</td>
<td>245x305</td>
<td>5.5</td>
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<td>14&lt;sup&gt;b&lt;/sup&gt;</td>
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<tr>
<td>Yard Waste Cell</td>
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<td>5.5</td>
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<td>75,000</td>
<td>14&lt;sup&gt;a&lt;/sup&gt;</td>
<td>245x305</td>
<td>5.5</td>
</tr>
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</table>

<sup>a</sup>Age of upper most residue in cell
<sup>b</sup>Age when amendment was applied on the surface of the residue
Table 2. Sampling plan for bauxite residue cells at Sherwin and Copano, TX.

<table>
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<th>Objective No.</th>
<th>Treatment</th>
<th>Number of Cores</th>
<th>Comments</th>
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<td>1</td>
<td>No Vegetation/Amendment</td>
<td></td>
<td>Selected one bed at each location. Collected four samples starting from near edge to center at equidistant locations.</td>
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<td></td>
<td></td>
<td>Sherwin: 4</td>
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<tr>
<td></td>
<td></td>
<td>(A1-Center A2, A3 A4-Edge)</td>
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<tr>
<td></td>
<td></td>
<td>Copano: 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(B1-Edge B2, B3 B4-Center)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Vegetation Type</td>
<td>Bermuda: 4</td>
<td>Sampled from vegetated, non-amended locations. Transect sampling as above.</td>
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<tr>
<td></td>
<td></td>
<td>(C1-Center C2, C3 C4-Edge)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bitter Weed: 4</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(D1-Center D2, D3 D4-Edge)</td>
<td></td>
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<tr>
<td>3</td>
<td>Amendment Type</td>
<td>Sludge: 4</td>
<td>Sampled from areas where sludge or yard waste was previously applied but not actively seeded or vegetated. Transect sampling as above.</td>
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<td>(E1-Edge E2, E3 E4-Edge)</td>
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<td>Yard Waste: 4</td>
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<td>(F1, F2, F3, F4)</td>
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<td>TOTAL NUMBER OF CORES: 24</td>
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Figure Captions

Figure 1. Schematic (cross section) of the neutralization processes for a bauxite residue storage cell.

Figure 2. Bauxite residue pH with lateral location and depth for un-amended cell at a) Sherwin, TX, b) Copano, TX.

Figure 3. Total carbon measured in bauxite residue as a function of lateral location and depth for un-amended cell at a) Sherwin, TX, and b) Copano, TX.

Figure 4. Comparison of bauxite residue mineral analysis from the surface (0 to 15 cm) (B4-Top) and at a depth of 100 to 120 cm (B1-Bottom) for the Copano cell.

Figure 5. Bauxite residue pH with lateral location and depth for residue vegetated with a) Bermuda Grass, and b) Bitter Weed at Sherwin, TX bed #1.

Figure 6. Bauxite residue surface pH vs. root mass at Sherwin, TX bed #1.

Figure 7. Total carbon measured in bauxite residue with lateral location and depth for residue vegetated with a) Bermuda Grass, and b) Bitter Weed at Sherwin, TX bed #1.

Figure 8. Bauxite residue pH with lateral location and depth for Sherwin, TX residue amended with a) sludge (bed #21), b) yard waste (bed #5). Total carbon measured in bauxite residue with lateral location and depth for Sherwin, TX residue amended with c) sludge (bed #21), and d) yard waste (bed #5).

Figure 9. Moisture content measured in bauxite residue with lateral location and depth for a) un-amended residue at Sherwin, TX (bed #3), b) un-amended residue at Copano, TX (bed #1), c) residue vegetated with Bermuda Grass at Sherwin, TX (bed #1), and d) vegetated with Bitter Weed at Sherwin, TX (bed #1).

Figure 10. Particle size distribution of bauxite residue from different locations of Sherwin, TX and Copano, TX residue cells.
Saturated Zone

Vegetation survives near drained edges

Decreasing vegetation and root mass

Increasing moisture content and pH

No vegetation near water table

Atmospheric CO₂

Sewage Sludge or Yard Waste

Vegetation survives near drained edges

Organic acid leaching

Increasing pH with depth

Pore Water Neutralization

\[
\begin{align*}
\text{Al(OH)}_4^{\text{aq}} + \text{H}^+ &= \text{Al(OH)}_3^{\text{aq}} + \text{H}_2\text{O} \\
\text{NaOH}^{\text{aq}} + \text{H}^+ &= \text{Na}^+ + \text{H}_2\text{O} \\
\text{NaCO}_3^{\text{aq}} + \text{H}^+ &= \text{Na}^+ + \text{HCO}_3^{-}
\end{align*}
\]

Solid Phase Neutralization

\[
\begin{align*}
\text{Ca}_3\text{Al}_2\text{O}_6^{\text{solid}} + 12\text{H}^+ &= 3\text{Ca}^{2+} + 2\text{Al}^{3+} + 6\text{H}_2\text{O} \\
\text{Ca}^{2+} + \text{CO}_3^{2-} &= \text{CaCO}_3^{\text{solid}}
\end{align*}
\]

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Figure 2a
Figure 2b


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Figure 3b
Figure 4
Figure 6

The figure shows a graph plotting the pH of different materials against the ratio of groot/gsoil. The materials include Bermuda Grass, Bitterweed, yard waste, and Sewage Sludge. The pH values range from 6.5 to 9.5, and the ratio of groot/gsoil ranges from 0 to 250.
Figure 7a

The graph shows the distribution of total carbon (mg/g) with depth in centimeters. The data points are labeled as follows:

- C1 = Center
- C4 = Edge
- C3
- C2

The graph indicates that total carbon content decreases with increasing depth, especially evident near the surface. The data points are plotted against depth (cm) on the y-axis and total carbon content (mg/g) on the x-axis.
Figure 7b

A graph showing the relationship between total carbon (mg/g) and depth (cm) at various locations labeled D1-Center, D2, D3, and D4-Edge. The graph indicates a decrease in total carbon with increasing depth, with the surface receiving the highest values and depths below 20 cm showing lower concentrations.
Figure 8a
Figure 9a

Diagram showing the relationship between depth (cm) and moisture content (wt%) with different symbols for A1-Center, A2, A3, and A4-Edge.