Dust Reduction in Bauxite Waste: Role of Gypsum, Carbonation, and Microbial Decomposition

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Abstract

Producing alumina by the Bayer Process creates fine air borne red dust which devalues property and causes irritation to the human respiratory system. Aggregation of such inorganic particles was proposed as a dust-inhibiting corrective. Resistance to breakdown under simulated rain suggests a lower number of dust-size particles after rain. Samples of red mud waste (1) treated 10 years before the study at the 0-15 cm depth zone with 40 t ha⁻¹ of gypsum (2) from the subjacent 15-30 cm zone, were collected, crushed and passed through a 0.5 mm diameter sieve. Leaves from *Acacia senensis* (a legume) were finely chopped to < 1 mm and thoroughly mixed with the sieved bauxite waste at 25- and 50%, and the samples incubated for 6 weeks at ambient room temperatures, at 60% soil water-holding capacity. To determine the fraction of potential dust, the treated samples were submerged in de-ionized water for several days until there was no change in discoloration (due to clay dislocation) of the water. The samples were removed from the water and the water evaporated and the residues dried and weighed. In total, the dust-reducing capabilities of the treatments in descending order of proficiency were: 50% phytogenic > 25% phytogenic > 0-15 cm soil depth non-phytogenic > 15-30 cm-depth non-phytogenic. The 50% phytogenic-treatment reduced potential particles of fugitive dust by 70% over the untreated controls and 95% over the crushed-only (subjacent red mud; no organics added) samples. All in all, phyto-organics increased average particle size to > 100 µm by flocculation, thereby creating stable agglomerates which resisted disintegration and breakdown under simulated rain. Reducing the concentration of $< 75 \ \mu m$ particles in the air will decrease morbidity due to respiratory illnesses in surrounding populations, harmful effects on vegetation, and the defacement of buildings. This treatment promises the use of gypsum + phyto-organics for reducing the emanation of surface dust from red mud waste sites onto surrounding areas.

Keywords: aggregation, dust-amendments, organic remediation, phytogenic amendment

1. Introduction

Red mud waste (RMW) surfaces (crusts) of bauxite mine spoils are potential sources of dust emission. During storage, the surface gets dried, even though the consistency may be still liquid at a few millimeters below (Graham & Fawkes, 1992). A strong wind can then blow a red dust cloud over the surroundings at a considerable financial and environmental cost. Buildings have been defaced and vegetation damaged by dust accumulation on leaves (Graham & Fawkes, 1992).

According to the International Standardization Organization (1994), "Dust: small solid particles, conventionally taken as those particles below 75 μ m in diameter, which settle out under their own weight but which may remain suspended for some time". A Glossary of Atmospheric Chemistry Terms (IUPAC, 1990), characterizes dust as: "Small, dry, solid particles projected into the air by natural forces, such as wind, volcanic eruption, and by mechanical or man-made processes such as crushing, grinding, milling, drilling, demolition, shovelling, conveying, screening, bagging, and sweeping. Dust particles are usually in the size range from about 1 to 100 μ m in diameter, and they settle slowly under the influence of gravity." It is at the micro-aggregate size level that excess sodium from the Bayer process produces separation of clay particles. Since micro-aggregates bind < 5 μ m particles into larger entities at the < 250 μ m level, and wind-blown dust particles to form aggregates > 100 μ m should reduce the rate of wind-blown dust.

Bauxite red mud consists primarily of the insoluble fraction of the bauxite ore that remains after extraction of the aluminium-containing components (Zhang et al., 2001). Iron oxides (10-30%), titanium dioxide (2-15%), silicon oxide (5-20%) and undissolved alumina (0-20%) make up the residue (Bardossy, 1982), together with a wide range of other oxides which will vary according to the initial bauxite source (Jones & Haynes, 2011). The high concentration of iron compounds in the bauxite gives the by-product its characteristic red colour, and hence its common name "Red Mud" (AAC, 2012).

The sodium carbonate is precipitated on the surface of residue as entrained moisture evaporates (Alcoa, 2007). Therefore, dry red mud easily spreads into the air and causes dust pollution (Hai et al., 2014).

Though particle size analysis shows that Jamaican Terra Rossa bauxites contain 20% sand (O'Callaghan, 1998), it is the secondary (clay) fraction which contains the bauxite. Similar processing techniques in Jamaica (Bayer process) to that of the Weipa (West Australia) kaolinites indicate similar post-beneficiation clay particle sizes. Above 11 m s⁻¹ (40 km h⁻¹), such dust emissions from the residue area can increase rapidly and wind speeds above 14.5 m s⁻¹ (50 km h⁻¹) are predicted to be the largest source of dust (Alcoa, 2007). Attaining speeds often exceeding 13m s⁻¹ during winter months (Macpherson, 1991), unobstructed trade winds in Jamaica and the northern Caribbean should, on the above basis, normally carry fugitive dust released from the dried surface of red mud dumps.

Freisen et al. (2009) examined the associations between alumina and bauxite dust exposure and cancer incidence and circulatory and respiratory disease mortality among bauxite miners and alumina refinery workers. Their preliminary findings of the very few cases in the limited population study suggest that cumulative inhalable bauxite exposure may be associated with an excess risk of death from non-malignant respiratory disease and that cumulative inhalable alumina dust exposure may be associated with an excess risk of death from cerebrovascular disease. Nevertheless, neither exposure appeared to increase the risk of incident cancers. Further, there was no apparent danger and no association between every bauxite exposure and any of the outcomes (Freisen et al., 2009), though there was a borderline significant association between every alumina exposure and cerebrovascular disease mortality.

Wagner (1997, 2009) also found that exposures to bauxite dust, alumina dust, and caustic mist in contemporary best-practice bauxite mining and alumina refining operations have not been demonstrated to be associated with clinically significant decrements in lung function. Exposures to bauxite dust and alumina dust at such operations were also not associated with the incidence of cancer (Wagner, 1997).

Despite these favourable findings, adverse health effects of bauxite dust are possible. This is because red mud residue and sand consist primarily of alumina, silica and iron oxides (Alcoa Air Assessments, 2007) and silicosis is an irreversible condition with no cure (Wagner, 1997). Silicosis is the most common form of pneumoconiosis (lung-related diseases), which is caused by occupational exposure of free silica dust (ACGIH, 1999). Treatment options currently focus on alleviating the symptoms and preventing complications (ACGIH, 1999). According to Pattajoshi (2006), dust is inevitable in mineral industries. Also, Nouh (1989) reports that a non-occupational form of silicosis has been described that is caused by long-term exposure to sand dust in desert areas, with cases reported from the Sahara, Libyan desert and the Negev, and that the disease is caused by deposition of this dust in the lung.

Cohesiveness between clay particles can be significantly increased by inorganic cementing agents such as CaCO₃, and Fe and Al oxides (Zhang, 2015). In a study of African Ultisols and Oxisols, Ahn (1979) observed highly stable micro-aggregates not dependent upon organic matter. Therefore, binding agents need not be from organic sources. After adding gypsum to two different red-brown earths, Shanmuganathan and Oades (1984) noted a reduction in the amount of dispersible clay, an increase in the proportion of water-stable aggregates sized 50-250 µm diameter, and an increase in soil friability. Nevertheless, mechanical strength was reduced by gypsum addition (Aylmore & Sills, 1982) before strengthening by carbonation occurred.

Without dislocation there is no dust. The treatment of this study therefore aimed to "fix" the clay particles into soil aggregates. These were to bind the clay particles against dislocation by the wind. This procedure was also aimed at resisting natural field impacts such as rain and running water which dislocate fine clay particles prior to them becoming airborne dust.

2. Materials and Methods

Twenty kg of (1) gypsum-treated red mud which subsequently underwent a 10-yr lithification by atmospheric carbonation (2) red mud beneath the gypsum-treated layer (Table 1) were randomly collected from the Kirkvine Pond 6 Bauxite residue storage area in Jamaica. Whereas the gypsum-lithified red mud (G) exists in rock-hard

form in the 0-15 cm zone, the non-gypsum fraction (R) exists adjacently below 15 cm as a semi-viscous constituent, having been seemingly unaffected by the gypsum which O'Callaghan et al. (1998) had ploughed into the zone (G) directly above, in 1996. Both materials are of the same age but very different physico-chemically. The top layer is non-dispersive while the 15-30 cm layer is highly dispersive. Prior to air-dry, this 15-30 cm depth layer had the physical consistency of untreated red mud waste that supplies wind-blown dust. Samples were crushed at air-dry in a mortar and pestle and passed through a 1-mm aperture sieve. Decomposable organic material as finely chopped (< 2 mm) leaves from *Acacia senensis* ("Kasha", an invasive legume of southern Jamaica) was thoroughly mixed in with either above-mentioned bauxite waste in dry, grinded homogenous (< 1 mm) form and incubated at room temperature for 42 days at a water content of 60% of the field capacity of each soil. This "mix" is based on improved aggregation of similarly treated crushed particles at the < 2 mm diameter size by Harris (2009). Of the two crushed red muds, field capacity (water-holding capacity) was substantially higher for the gypsum-treated samples.

Properties	Values	
Red mud pH (saturated extract)	12	
EC (saturated extract: dS m ⁻¹)	.25	
Organic carbon (%)	.3	
$CEC (c molc kg^{-1})$	40	
Al ₂ O ₃ (%)	16	
CaO (% w/w)	7	
Fe ₂ O ₃ (%)	47	
Na ₂ O (%)	3	
P ₂ O ₅ (%)	2	
SiO ₂ (%)	3	
TiO ₂ (%)	6	
Bound H_2O (%)	14	
Particle size	.001-mm	

Table 1. Properties of red mud subjacent (15-30 cm) to 0-15 cm depth gypsum-treated red muds

Note. There were six treatments, each having three replicates: (1) G, (2) G25 (*i.e.*, gypsum-treated red mud + 25% phyto-organics), (3) G50 (*i.e.*, gypsum-treated red mud + 50% phyto-organics) (4) R (red mud), (5) R25 (red mud + 25% phyto-organics), (6) R50 (red mud + 25% phyto-organics). Phyto-organic treatments are referred to hereafter as GP or RP.

2.1 Measuring Potential Wind-Blown Dust

Clay dislocation: 1st submergence

After incubation for six weeks, the samples at air dry were subjected to submergence in de-ionized water which simulated rain water. Deionized water was included because Khattab and Othman (2013) noted a general reduction of strength of rocks with an increase in the number of wet-dry cycles when using distilled water. Replicates of treated aggregates having a diameter of approximately one cm were each placed in a watch glass, after which water was slowly added because the weak structure of bauxite waste is subject to breakdown by electrolytes. The relative rates of clay dislocation from the aggregates signified the amount of dust particles which would have emerged on drying. Without clay dislocating forces on the aggregates there would be no potential dust. The extent of clay particle dislocation from the aggregates was determined by measuring the weight of the dislocated particles. The clay dislocation process was monitored for the ensuing days until no further change was observed. At air dry, aggregates were removed from the watch glasses and the masses of air-dry residues of fine dust weighed.

Clay dislocation: 2nd submergence

After clay removal from watch glasses at air-dry, the clay dislocation procedure was repeated. Each aggregate was then mechanically agitated in an end-over-end shaker for a pre-determined time period. At air-dry, all particles were again weighed. The separated fractions were air-dried. They were weighed after sieving on a nest of three sieves: 2 mm-, 500μ m-, and 100μ m-diameter.

3. Results

Table 2 shows that after incubation plus air-dry and 5 days of submergence in deionized water, relatively little observable clay particle dislocation occurred from any of the non-phyto-organic treatments as compared to that of the phyto-organic treatments (Table 2, Figure 1). The R50 (R samples are from 15-30 cm depth) dislocated 29% of the mass of the sample as clay, and the R25 dislocated 33% of the sample mass for an average of 31% dislocation by the subjacent phyto-treated samples. The R50 dislocated less clay than did the R25. This was expected because these soil particles were considered bound by organic matter due to the treatment.

Further, it can be seen that the quantity of clay dislocated was much greater from the 15-30 cm depth compared with the 0-15 cm depth, *i.e.*, in a ratio approximating 15:1 (Table 3). For the 0-15 cm depth the samples containing 25% phyto-organics dislocated no clay, while the samples containing 50% phyto-organics produced a 4% w/w rate of clay dislocation. Thus for the 0-15 cm depth, rate of phyto-organics determined effectiveness to suppress clay dislocation in deionized water. Similarly, at the 15-30 cm depth (Table 3), where the 25% phyto-organics treatment dislocated less clay than the 50% phyto-organic treatment. This was surprising. Clearly, the factor which produced the initial dislocation in deionized water existed in the phyto- samples, and the greater concentration of phyto- material the lesser was the clay dislocation. This pattern is examined later.

After 8 days of submergence in deionized water, non-phyto-organic treatments from all samples dislocated very little clay above the level of detection (Table 3, Figure 1).



Figure 1A. Clay dislocation in deionized water for remolded aggregate samples from the 15-30 cm depth in carbonated red mud

Note. At extreme left are the R50 (phytogenic-treated) samples; second from left are the R25 (phytogenic) samples with less clay dispersion depicted by the lighter colour.



Figure 1B. Dried samples of dislocated clay from the 15-30 cm depth after aggregates were removed from deionized water

Note. R50 = 50% decomposable phyto-organics R25 = 25% phyto-organics, RC = no phyto-organics. Each small circle in background paper is 1-mm in diameter.

Table 2. Clay (% of mass) dislocated after incubation treatments and submergence in de-ionized water for 8 days

Red mud (depth in cm)	0 % phyto-organics	25% phyto-	50% phyto-	Average
0-15	0	0	4	2
15-30	0.01	29	33	31



Figure 2A. Post-incubation gypsum-treated samples in distilled water after 1st submergence

Note. GC = 0.15 cm and no phto-organics; G50 = 0.15 cm + 50% organics. No discoloration suggests effective flocculation of red mud individual particles.



Figure 2B. Post-incubation gypsum-treated samples in non-deionized water after 1st submergence, in contrast to the reaction with deionized water (Figure 2A) where the colorless water indicated no clay dislocation

Non-de-ionized water also dislocated clay from the samples but there were minor but important differences. Firstly, the total mass of clay dislocated was higher for the deionized water (Table 3), where the 15-30 cm level dislocated almost twice as much clay under the deionized water compared to the non-deionized water. On the other hand, for the 0-15 cm level, the non-deionized water caused a 4-fold increase in clay dislocation compared to the deionized water. Again, only the phyto- treatments caused substantial clay dislocations.

Red mud (depth in cm)	0 % phyto-organics (controls)	25% phyto-organics	50% phyto-organics	Average
0-15 (G)	0	8	8	8
15-30 (R)	0	16	16	16





Figure 3. Mass of clay dislocated after incubation and soaking in de-ionized water for 8 days



Figure 4. Post-incubation gypsum-treated samples in non-distilled water after the 1st submergence

Note. Dislocated clay particles can be observed from the 50% phyto- treatment at left (G50). Stippled background contains 1-mm diameter circles.

For the G samples (no phyto-), submergence in non-deionized water produced small, barely visible levels of clay dislocation (Table 4, Figures 3 and 4). This nevertheless was greater than that for de-ionized water, where no dispersion appeared from any of the non-phyto samples. Similarly, from the 0-15 cm depth, GP25 samples increased clay dislocation up to half the level of the RP samples (*i.e.*, RP25 or RP50). Of all the phyto-organic treatments, GP samples treated with 50% phyto-organics exhibited the lowest levels of clay dislocation from the aggregates (Table 4, Figures 1 and 5). The possible reasons are discussed later.



Figure 5. G50 (50% phytogenic additive) dislocated very little clay even in non-de-ionized water

The clay dislocations in deionized water were less severe for the G samples. Only 2% of the GP mine-waste dispersed, whereas 29% of the R samples dislocated in the form of clay particles. This is almost a 15-fold difference. As electrical stresses on soil aggregates vary directly with purity of water, a high concentration of electrolytes (*i.e.*, > EC) in a soil should increase clay dislocation in deionized water. Thus the R samples, with a higher electrical conductivity than the G samples, released more clay particles in deionized water than in non-deionized water.

The relative rates of clay dislocation from the aggregates signified the amount of dust particles which would have emerged on drying. After incubation for 6 weeks, the result for either the G or R samples was that little or no observable clay dislocation occurred in deionized or non-deionized water.

In deionized water, gypsum-treated bauxite waste without phyto-organics (GC) showed no dispersion of clay-particles at the microstructural level (< 100 μ m diameter) for the 0-15 cm-depth. For samples taken from the subjacent level, a very slight clay dislocation effect was visible. This was below the detection level of the weighing equipment (Figure 3). However for the RP samples a large amount of dust averaging 25% w/w would

have been generated by phyto-organic treatments. This was unexpected. This is discussed later. Based on these results, the GP samples were overwhelmingly less dispersive than the RP samples.

After removal from Petri dishes at air-dry, and after the second episode of clay dislocation in water the remolded aggregate masses were weighed and measured. Even after the 2^{nd} submergence, the phyto-organically treated samples in general retained stability in water to a far greater degree than that of the 1^{st} submergence. Clay dislocation procedure was repeated on the aggregates. The results show that no dislocation occurred at all from any sample. It can be seen that the 2^{nd} submergence produced no dislocation of clay particles (Table 4), because the total mass for each sample submerged was zero.

Red mud (depth in cm)	0 % phyto-organics (controls)	All phyto-organics	Total mass
0-15	0	0	0
15-30	0	0	0

Table 4. Mass of clay (grams) dislocated from aggregates after2nd submergence for 8 days

In comparison to the low levels of dislocation observed from the G, R, and G50 treatments, the level of clay dislocation exhibited by all RP treatments was more than 10 times as high. However, for all phyto-organic treatments, especially in the case of the RP, the second submergence produced far less clay dislocation (> 10-fold decrease) than the first submergence (Table 4). On the established fact that totally untreated Bayer red muds are (1) totally dispersive (AAC, 2012) and (2) hence totally disaggregated (Bardossy, 1982), clay dispersion would therefore have been far greater in such totally untreated red muds than had occurred with the treatments of this study. Overall, greater clay dislocation was more evident from the de-ionized samples, especially from the R and RP samples.

The lack of dislodged clay particles from the 2nd submergence could have meant that all the dispersible clay had been released at the first submergence (Table 4). To test this assumption, the aggregates were again air-dried and subjected to dry sieving in a shaker where the aggregates were rolled and bounce on a sieve having a 100 micron aperture (the diameter of micro-aggregates). Each aggregate was then mechanically agitated in an end-over-end shaker for a pre-determined time period. At air-dry, all particles were again weighed.

In the rating scheme for this study, the clay dislocation ratio for the RP as compared with the GP samples was > 10:2.6. Nevertheless, the aggregates of this study, which were: (1) totally suffused with the water and (2) 1-cm diameter sub-rounded spheres had a much larger surface area than the same volume in field conditions (where there is just a sub-aerial surface of exposure from which dust could have potentially emanated).

Therefore, as the 2^{nd} submergence of this study caused no observable clay dislocation, the maximum total potential dust for any treatment remained at 29% w/w. After the 2^{nd} submergence, samples were air-dried and shaken in a sieve having apertures 100 µm in diameter. Results are shown in Table 5.

Red mud (depth in cm)	0 % phyto-organics (controls)	25% phyto-organics	50% phyto-organics	Total
0-15 (G)	4	2	1	7
15-30 (R)	60	2	0	62

Table 5. Proportion of < 125 μ m particles after dry-sieving of aggregates following two submergences in water for a total of 15 days after incubation

It can be seen that, whereas the phyto-treatments continued to dislocate very little clay even during dry sieving, the non-phyto- treatments dislocated at least twice as much clay as the least efficient phyto-treatment, during this procedure. In fact, R samples (non-phytogenic-) dropped 60% of their mass from the dry-sieve as dislocated < 100 μ m clay particles (Table 5). As noted in section 1.0 above, among the world's bauxite ores Jamaican bauxite texturally contains by far the largest clay fraction at 75% (Wehr et al., 2006). Therefore, had this been a field study, it is reasonable to assume that the R (non-phyto-organic) samples would have potentially released 42% of its mass as wind-blown clay. Again, as stated above, several variables determine the actual concentration of wind-blown dust at any given location. Therefore no attempt is made here to quantify the potential rate of wind-blown dust. Nevertheless, it can be seen that despite being by far the least effective treatment of this study,

the R (non-phyto-) samples reduced potential wind-blown dust by 33% (*i.e.*, 75 - 42 = 33). Using Tables 2-5, similar calculations estimate the potential dust reduction by other treatments as follows:

 $\begin{array}{l} G50 = 75 - (4 + 8 + 0 + 1) = 67\% \\ G25 = 75 - (8 + 0 + 2 + 3) = 67\% \\ R50 = 75 - (16 + 0 + 0 + 13) = 56\% \\ R25 = 75 - (16 + 0 + 2 + 3) = 54\% \\ G = 75 - (0 + 0 + 0 + 4) = 71\% \\ R = 75 - (.01 + 0 + 0 + 60) = 14.99\% \end{array}$

Prior to the test of aggregate stability, the leading treatment for dust reduction here is still gypsum (71%), with gypsum + phytogenic being second at 67%. Predictably, without gypsum, incubation yielded only 15% dust reduction for non-gypsum treatments (R samples).

In a physical sense, resistance to shattering impacts reduces dust production. After 15 days, the samples were subjected to falling drops of water which simulated raindrops from a pre-determined height. The results showed that the phyto-organically treated samples at 50% from either the 0-15 cm depth or the subjacent red mud withstood more than twice as many impacts before shattering, as each of the non-phyto-organically treated samples (Table 6). Additionally, the G50- proved substantially more resilient in this respect than the R50 samples (Table 6). Without organics, the G aggregates withstood three times as many raindrop impacts as the R aggregates. The overall G treatment produced 50% greater resiliency under simulated raindrop impacts than the R treatments (Table 7). However, the CND resistance of the R25 exceeded that of the G25 samples by 50%. This apparent anomaly is discussed later.

Table 6. Impact of large falling water drops on remolded aggregates (days) after incubation and submergence in water for 15 days as depicted by the counted number of drops (CND) before shattering

Red mud (depth in cm)	0 % phyto-organics	25% phyto-organics	50% phyto-organics	Total
0-15	150	30	430	670
15-30	50	70	330	450

Aggregates treated with 50% phyto-organics were the most resilient in still water for 15 days (Table 7, Figure 6).

Red mud (depth in cm)	0 % phyto-organics (controls)	25% phyto-organics	50% phyto-organics	Total
0-15	2	3	13	21
15-30	12	3	13	28

Table 7. Longevity of remolded aggregates (days) after incubation and submergence in water for 15 days



Figure 6. Longevity of remolded aggregates from two depths after incubation and soaking for 15 days

A vast difference of water-stable longevity amongst treated samples can be seen, because samples from the 15-30 cm depth with either 50% phyto-organics (R50) or without phyto-organics (R only) are by at least a 5-fold margin the most resilient under wet sieving (Figure 7, Table 8). Aggregates subjected to wet-sieving maintained their integrity in the following order of decreasing longevity: R50 > R > G > R25 > G25 = G50 (Figure 7, Table 8).



Figure 7. Stability of remolded aggregates from two depths after incubation and soaking

Red mud (depth in cm)	0 % phyto-organics	25% phyto-organics	50% phyto-organics	Total
0-15	11	2	2	15
15-30	12	3	13	28

Table 8. Aggregate longevity in minutes of stability during wet-sieving after incubation treatments

4. Discussion

As dust results from dislocated clay, and contact with water weakens soil aggregates and dislocates clay (Rengasamy et al., 1984), the most resilient aggregates are the lowest potential producers of dust. It can be seen that despite being submerged in still water for 15 days, the phyto-organic (P) samples outlasted all others. In fact, before the end of day 1, several non-P samples had already disintegrated (Table 7), some having done so within a few minutes of submergence.

For aggregates without phyto-organics from the 0-15 cm previously gypsum-treated layer, relatively few measurable clay particles (potential dust) were dislocated during submergence in water for several days. At the end of day 2 of submergence, those samples incubated from the 15-30 cm layer (*i.e.*, under the gypsum-treated layer, without phyto-organics) released no visible clay particles. Wind power increases exponentially with wind speed such that the power of the wind varies as the cube of its speed (Jackson & Hunt, 1975). Thus an increase of even two or three km hr⁻¹ is a significant increase in terms of energy expended and hence the amount of dust removable from a surface. As adsorbed Na⁺ causes mutual repulsion among clay particles, and the 15-30 cm depth contained Na⁺ far in excess of the surface layer, the low level of clay dislocation from that depth was unexpected. This is further discussed later.

In the first submergence, the gypsum plus phyto-organics treatment dislocated > 5-times the amount of fine clay particles (potential dust) compared to the amount from the gypsum-only treatments. This also was against expectations because applying similar treatments to sodic (Na⁺-rich or high ESP) subsoils, Harris and Rengasamy (2004) used sub-micron particle analysis to show that phyto-organics with gypsum substantially flocculated (agglutinated) clay particles. Thus by increasing the mass sizes, they decreased the release of individual clay particles. Further, for the first submergence of this study, the greatest reduction of potential dust occurred as follows in descending order of efficiency: G > R > G50 > G25 > R50 = R25.

Decomposable phyto-organics have been shown to bind sodic clay particles (Harris & Rengasamy, 2004) and inorganic particles in bauxite waste (Harris, 2009), and as discussed later, wet-sieving results showed that strong binding of inorganic particles also occurred in this study. Yet, for the ultra-fine (highest dust-potential) inorganic

colloids, such a binding force from phyto-organics proved, particularly at the lower phyto-organic rates, ineffective initially in this study. Isomorphic atomic substitution causes the negative charge exhibited by all clay particles. Muneer and Oades (1989) noted an increased number of negatively charged particles formed as decomposition and breakdown of phyto-organics advances in remolded aggregates. They concluded that small negative charges from organic colloids which were the same approximate length as clay particles were dispersing the clay particles. In this study, it can be seen that, compared with non-phyto-organic-treatments, it was the phyto-organic samples that produced more clay dislocation in the 1st submergence, especially the phyto-organics at the lower rate (R25, and to a lesser extent, the G25). On the other hand, though they readily broke down even in still water, non-phyto- treated macro-aggregate samples from the 0-15 cm depth (G) did not dislocate ultra-fine clay particles when those macro-aggregates were submerged in water (Table 2). Furthermore, the following observations were made:

- ▶ No clay dislocation from the G50 or G25 samples occurred in deionized water;
- ▶ Between G50 & G25 samples, clay dislocation in non-deionized water was greater from G25.

Clay dislocation by the G25 & G50 in the non-deionized water could have been due to a greater number of negatively charged colloids (organic and/or inorganic) intrinsic to that water as compared to the deionized (less contaminated) type. Indeed, the pH of the non-deionized water had a value of 7.8-8.0. The total mass of negative charges/colloids would be greater in the non-deionized system. The G25, with less microbial substrates than the G50 and hence with more competition among microbial decomposers, would have been expected to have undergone more advanced breakdown of organic matter, thereby presenting smaller colloids to the system. As noted earlier, highly comminuted negative colloids of similar sizes mutually repel. It is thus more likely that of the two treatments, the G25 would have been more likely to contain organic colloids fine enough to repel clay particles of similar sizes. Such electronic forces could have dislocated the clay particles at a higher rate from the G25 than from the G50 aggregates.

For similar reasons, in a study incubating gypsum with sodic sub-soils, Harris and Rengasamy (2004) observed no stable macro-aggregates (*i.e.*, > 250 μ m) at any stage of incubation. They concluded that gypsum alone cannot produce stable macro-aggregates, though stabilization occurred at the < 250 μ m size level. They also reported that phyto-organic additions caused a slight increasing trend.

The ability of negatively charged clay colloids to disperse clay particles is illustrated by the immediate settling out by flocculation of clay colloids or organic colloids whenever small amounts of multivalent cations from $Al_2(SO4)_3$ (alum) are added to such suspensions. It is very likely that after the first submergence, most or all of the organic colloids became trapped in the dried residue. This may explain why, after dislocating such high levels of clay in the first submergence, at submergence #2, the phyto treatments failed to dislocate any clay at all.

The natural flushing by rainfall for more than a decade (Harris, 2009) would have removed much sodium sulfate in the 0-15 cm layer. This relative increase in the ratio of Ca^{2+} to Na^+ ions promoted the binding action among clay particles. However, annual rainfall also subsequently depleted the unprotected Ca^{2+} ions in the upper (0-15 cm) layer. It was expected that phyto-organic gums from the decomposing phyto-organics, would have induced stable aggregation among the G25 and G50 samples. This did not occur. On the other hand, with the same levels of gypsum in the same bauxite waste, Harris (2009) observed stabilization of macro-aggregates. The explanation may be that Harris (2009) incubated the samples for a much longer period of time (more than 24 weeks) compared to the 6-week incubation of the present study. With more advanced levels of decomposition, stronger binding between inorganic particles may have occurred in that earlier study.

Yet, paradoxically, in this same study of just six weeks, underneath the surface, the 15-30 cm layer, despite having massively accumulated Na⁺ ions from the prolonged eluviation from the 0-15 cm layer plus residual Na⁺ from the Bayer Process, produced stable macro-aggregates of 6-fold the longevity under wet-sieving than those produced by the Na⁺-deficient 0-15 (surface) layer. Moreover, as stated above, Harris and Rengasamy (2004) concluded that with or without gypsum applications, phyto-organics cannot macro-aggregate sodic clays to a level of water-stability, though stable micro-aggregation (< 250 μ m) can be achieved. The objective of flushing is to remove the Na⁺ in the form of Na₂SO₄ from the exchange reaction with CaSO₄ to provide greater opportunities for the adsorption of Ca²⁺ onto clay particles. Yet despite the obvious absence of flushing at the 15-30 cm level (indicated by high Na⁺ levels), strong Ca²⁺ adsorption as proven by high aggregate stability, had clearly occurred subsequently (*i.e.*, after gypsum addition to the superjacent layer). The explanation may be that with such unusually high levels of Ca²⁺ in the 15-30 cm level, exchange sites became dominated by the more strongly bound Ca²⁺. Purely from the standpoint of stability, this nullified the need for Na₂SO₄ flushing. Interestingly, as stated above, the R25 samples dislocated more clay than all other treatments. It is therefore

unsurprising that the R25, perhaps for reasons stated above, exhibited also the least resistance to wet sieving (Table 8).

On the other hand, the lower resistance to wet-sieving of the 0-15-cm gypsum-treated phytogenic macro-aggregates suggests an inactivation by carbonation to $CaCO_3$ of a substantial quantity of the Ca^{2+} released in the early stages of the gypsum treatment applied several years before this study. Being exposed sub-aerially, greater atmospheric CO^2 would have been available in the 0-15 cm depth compared to the subjacent layer.

Another possible explanation for the longevity of the R samples to wet sieving entails thixotropically affected entities, referred to by Coughlan et al. (1979) as "fortuitous agglomerates." These fortuitous agglomerates survive wet-sieving but are not true aggregates, being case-hardened during storage possibly in this case by oxidation of iron oxides (Ly, 2001; Zhang, 2015).

As stated above (section 1.2), based on Wehr (2006), the total clay fraction for the Jamaica bauxite waste is 75%. On the assumption that all clay particles are $< 100 \mu m$ in diameter, potential dust in Jamaica bauxite waste, according to his table, is at least 84% w/w. As the best treatments of this study increased more than 95% of the particle size of the bauxite waste to well over the $< 100 \mu m$ - diameter threshold after submergence in de-ionized water, it is concluded that the phyto-organic treatments substantially decreased potential dust not just from Jamaica bauxite wastes, but potentially for all other wastes listed above. This includes red muds from St. Croix (Virgin Islands), Guyana, and Haiti.

The relatively high level of aggregate stability under wet-sieving observed for the crushed G (no phyto-organics) samples in this study was not expected because an opposing result occurred in a study of the same lithified red mud waste by Harris (2009). In yet another study, Harris and Rengasamy (2004) also found that no macro-aggregate stability in a sodic sub-soil when treated with gypsum. However, in both of those studies, they used < 2 mm particle sizes, whereas in the current study the particle size used was < 1 mm. Particles must be fine enough to provide a sufficient reactive surface area for the solid-state chemical reactions (Mehta & Monteiro, 1993; Malhorta & Mehta, 1996). It is thus postulated that the larger surface area (more than twice as large) of the smaller particles of this study afforded far greater opportunities for cohesive forces of the Ca²⁺ ions among inorganic particles.

It is the binding action of organic cements and electronic attraction of cations that produce aggregation and, by extension, can reduce dust formation in sodic soils and spoil heaps. It is interesting that both the mine tailings of the present study and the soil studied by of Harris and Rengasamy (2004) reacted similarly to phyto-organic additives. Neither sodic entity was influenced by phyto-organics acting alone. In other words, without gypsum, sodic clays do not react significantly with phyto-organics to form stable macro-aggregates. This is primarily because organic colloids and sodic clays are mutually repulsive, being both negatively charged. Without multi-valent cations there are few positive charges to link the clay particles. Harris and Rengasamy (2004) found that the role of gypsum is to flocculate the clay particles, as has been found by Baldock and others (1994); and Muneer and Oades (1989), where Ca^{2+} in soil solution did not improve macro-aggregation. In this study, however, gypsum acting alone stabilized macro-aggregates from finer inorganic particles.

Applying similar treatments to sodic subsoils, Harris and Rengasamy (2004) found that clay particles had been aggregated by decomposing phyto-organics into a size range not exceeding 30 µm. In this study, agglomerates from the RM + phyto-organics treatment remained stable under physical pressure, and did not release dust particles. Yet, these agglomerates of varying sizes up to 4 mm from the RM + phyto-organics treatments were readily unstable under wet-sieving (Table 3), as was the case for those produced in an experiment conducted by Harris and Rengasamy (2004). The implications here are that under field conditions, such stability would be destroyed during the first rain shower, and that dust would be produced on drying of the crumbled masses. However, destruction of unstable macro-aggregates produce progressively smaller aggregates with an inverse change in soil strength (Dexter, 1988) caused by stronger inter-particle binding mechanisms (Seguel et al., 2006). Thus below a particular wind speed, micro-aggregates above dust-size produce less dust per volume than macro-aggregates. As reported above, dust particles of up to 100 µm can be airborne. As soil micro-aggregates range up to 250 µm (diameter), an appreciable proportion can be airborne. Though micro-aggregate size was not measured in this study, Harris and Rengasamy (2004) found that micro-aggregates which formed under similar conditions had an average size of 30 µm (diameter). It is therefore reasonable to conclude that although dust was reduced in this study by creation of aggregates exceeding 100 µm, a proportion of micro-aggregates created would be below 100 µm, and hence susceptible to creating dust hazards.

Based on the above, it is clear that (1) the water-stability of red mud waste with or without added phyto-organics varies directly with addition of gypsum (2) water-stability of red mud waste determines dust production levels.

Under specific conditions of this study, water-stability was achieved not only during wet-sieving trials, but prior to that, during two episodes of several days of submergence.

5. Conclusions

Gypsum treatment decreased dust-sized clay particles by > 80%. At a rate of 7% CaO and 3% Na₂O (Table 1), average dust particle sizes of < 100 μ m in original samples aggregated to larger particles and showed a > 4-fold increase in resistance to clay dislocation over that of the controls. Tuffour et al. (2015) found that finer particles were highly effective in altering soil properties even at low concentrations. Therefore, decreasing the original particle size of the remolded aggregates from < 2 mm in previous studies to < 1mm of this study is also likely to have increased stability of aggregates against clay dislocation. The size of dislocated particles was < 100 μ m. Under the influence of simulated de-ionized water, decomposable phyto-organic additives initially increased small quantities of the finest clay particles. Nevertheless, increasing the size of particle clusters in this study potentially produced greater resistance against wind saltation and airborne movements than that which occurs for individual clay particles, or sub-100 μ m domains.

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