

PROPOSED MECHANISM FOR THE FORMATION OF DUST HORIZONS ON BAUXITE RESIDUE DISPOSAL AREAS

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Abstract

Without some form of mitigation control bauxite residue disposal areas in Mediterranean climates can be subject to large-scale dust lift-off events during summer, with significant environmental impact. Intuitively dust formation relates simply to the process of drying. However, whilst wet solids will not produce dust, the converse is not always true. Both the rate of drying and the composition of the bauxite residue are critical factors in determining whether a potential dust event will occur. In this work a dust formation mechanism is proposed in which caustic salts transport and effloresce along with a changing phase composition in the brine solids from sodium bicarbonate through to trona and then to carbonate monohydrate. The efflorescence leads to a white dust event, but the carbonate phase change and the associated reduction in sodium molar volume critically breaks inter-particulate bonding between the residue particles leading to a more severe underlying red dust event.

Introduction

In Mediterranean or warmer climates unmitigated bauxite residue disposal areas (BRDA's) can be a significant source of fugitive dust emissions. Two types of dust are recognized; an initial white dust and a secondary red dust. Although caustic migration to the surface is commonly recognized as the source of the white dust, hitherto there appears to have been no comprehensive attempt to try and understand both the nature and formation mechanism of fugitive dust from a BRDA. Dust control can be achieved with expensive water-based reticulated sprinkler systems, but this should be regarded as an approach of last resort. It is recognized that traditional binders used for mining tailings are ineffective due to the caustic and although successful polymer formulations are claimed [1] the results of tests appear not to have been published. Other references to BRDA dust are restricted to nutrient sources (fertilizers) for growth of dust control crops and native vegetation from a rehabilitation viewpoint [2, 3]. Understanding the chemistry behind the dust formation process gives the best opportunity to target appropriate lower cost mitigation strategies rather than implementing a suite of traditional binders developed for other dust sources.

In trying to understand the chemistry leading to dust formation it is necessary to manipulate the chemistry of bauxite residue and observe the effect. This is not practical on actual BRDA's due to the expense and lack of experimental control. On a smaller laboratory scale there are two obvious concerns (i) what is the minimum sample size that can give useful quantitative information and (ii) do the conditions of residue treatment lead to the same outcomes as would be expected on an actual BRDA? Anecdotal experience associates fugitive dust principally with hot, dry and windy conditions, i.e. these are invariably considered the key factors whether or not dust will form. Whilst wet solids will not produce dust (the water-solid adhesive forces exceed the water-water cohesive forces and capillary action binds the particulates) the converse is not always true, i.e. dry solids are not

necessarily sources of dust. Clearly, dry solids require a given size distribution and density and sufficient wind shear to be picked up and transported, but they also require either weak or absent inter-particulate bonding.

Although wind is a necessary condition for dust lift-off from the BRDA, initial experiment design on the basis of anecdotal experience proved to be inadequate. Freshly disposed residue is subject to two obvious processes: liquor drainage and liquor drying. In order to simulate dust formation on a laboratory scale it is a natural response to try and accelerate the process, e.g. a heated air stream across the residue surface to accelerate liquor drying. Feedback from a series of such initial design experiments unequivocally demonstrated that the process of dust formation in a test environment cannot be accelerated. Ironically the accelerated attempts to generate residue dust resulted in negligible formation. The most successful approach to dust simulation was found to be a greenhouse environment in which bauxite residue samples were allowed to dry or "age" under ambient greenhouse conditions over a period of up to 150-175 days. Two extensive greenhouse studies have been conducted over sequential summer periods, examining in all some 69 test residues, although only a subset of those tests are reported in this work.

Experimental

The bauxite residue used for this project was from a Darling Range (Western Australia) refinery and contained 62.8% solids by mass slurried in a dilute Bayer liquor. This is referred to in this work as normal residue so as to distinguish it from modified residue. A quantity of residue was washed with de-ionized water to produce nominal levels of caustic compared to normal of 60%, 30% and ~0%. The slow dissolution of solid alkali makes a true zero caustic residue difficult on the scale required and the ~0% residue continued to release caustic. For a non-caustic dissolved salts comparison NaCl was added to the "zero" caustic residue to produce samples with equivalent sodium loadings to the 30%, 60% and 100% caustic residues. All samples were adjusted to a starting solids level of 62wt%. In all this made 7 distinct residue sample types. Comparing the behaviour of the two variations in residue chemistry compared to normal proved to be the key to the understanding of the residue dust formation mechanism. These residues were placed in a simple tunnel greenhouse using low gain 180 µm thermal plastic. Excessive temperature variations were controlled in a simple fashion via a thermostatically controlled extraction fan set to a temperature of 30°C allowing a gentle ingress of cooler outside air and also using partial shade-cloth cover. In all other respects the greenhouse conditions of temperature and humidity were allowed the full range of day-night variation as would be expected for an actual BRDA.

The residue sample containers were polypropylene cubes with side bracing of internal box dimensions of 330x330x275 mm (LxWxD). The maximum capacity of a box was 29 L so at the initial 62wt% solids a full residue box weighed ~55 kg. A Microlog temperature and relative humidity data logger (Model

EC650, Fourier Systems) was used to record the ambient conditions in the greenhouse of air temperature, relative humidity plus an internal residue temperature for one unmodified sacrificial residue (probe in box centre at an ~80 mm depth).

Each residue sample sat on an individual balance (Adam Equipment Model #CPWplus75, 75 kg capacity, a readability of 20 g and a platform size of 300x300mm) and the drying progress of all test residues was followed by nett mass logged twice daily which was then converted to weight percent solids. A sub-set of replicate residue boxes were allowed free drainage via an array of drain holes in the bottom covered by a polypropylene felt filter cloth, but the majority were undrained. Photographs of the residue surface were also taken at least daily in order to track the general morphology and appearance of the residue surface during the 0 to 150-175 day time period. During the initial ageing period (first 6 days) when residue solids were settling pooled surface liquor was decanted off by vacuum aspiration to simulate surface liquor draining in a BRDA situation. Total liquor recovery from the normal (undrained) residues averaged 2008±191 g, a range of 1258-2633 g was observed for the caustic reduced residues and the NaCl substituted residues averaged 1314 g.

The absence of close artificial greenhouse control proved not to be a problem as evidenced by a close correlation of outcomes for the two sequential summer periods, both for internal conditions and dust outcomes. Table I gives the greenhouse averages for the two summer seasons. The temperature was elevated above ambient by an average of 11.5±3.2°C and 10.6±2.7°C for the two sequential seasons. As would be expected residue temperatures lagged air temperatures, cycling half a “wavelength” out of phase and peaking ~6 hours after the air temperature peaked. Moreover the residue temperature variation damped with ageing. As the residues became drier and thermal conductivity of the residue mass decreased the peak-to-peak temperature variation of the residue decreased. As a consequence the temperature frequency distribution for the residues was narrower than the air temperature with the residue core temperature typically ~26°C (Figure 1). Note also that nightly temperature drops, combined with any associated surface condensation, would play a part in surface salt transport and crystal growth and hence a part in dust formation.

At appropriate points during the ageing of the bauxite residue samples quantitative dust harvesting was undertaken using a vacuum horn apparatus. This involved a square pyramidal horn, with an aperture of 170x170 mm, that acted as collector when placed on the surface of the residue and represented 26.5% of the available residue surface area. Two modes of collection were employed, a normal mode (vacuum only) and a high shear mode in which a compressed air vortex was injected into the skirt of the horn.

Table I. Average inside greenhouse conditions for the two summer seasons. BOM - Bureau of Meteorology air T.

	2005-06	2006-07
Max air T	37.4°C	39.2°C
Min air T	17.4°C	20.1°C
Max residue T	28.6°C	30.4°C
Min residue T	20.3°C	24.4°C
Max RH	69.0%	62.6%
Min RH	18.0%	17.7°C
Increased T over BOM	11.5±3.2°C	10.6±2.7°C

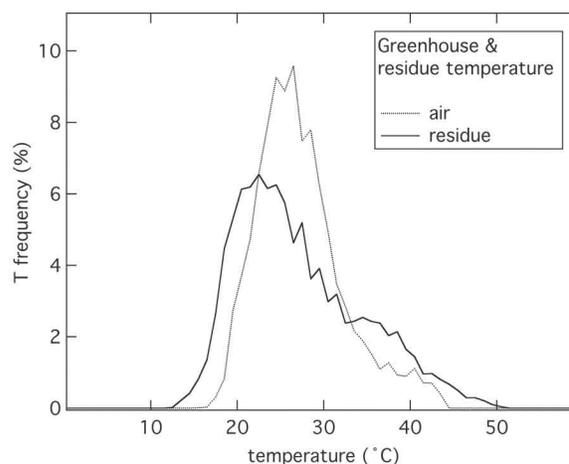


Figure 1. Frequency distribution for the greenhouse air and a “typical” residue temperature over 176 days.

The dust samples were analysed using powder-XRD, particle size distribution (PSD) in n-hexane and XRF analysis measured the SiO₂, Al₂O₃, CaO, Na₂O, K₂O, MgO, P₂O₅, SO₃, TiO₂, MnO, Fe₂O₃, Cr₂O₃, ZrO₂, BaO and V₂O₅ composition of the samples. In addition the samples were subjected to thermal gravimetric analysis (TGA) and a small subset to TGA-MS in which the off-gases were analysed with mass spectrometry. Both TGA-DTA and TGA-DSC were employed. Although the powder XRD only yields the ordered phases present, a simplifying assumption was made that they represented both the ordered and disordered phases present. Using the quantitative elemental composition and loss on ignition (LOI) from the XRD and the identifiable CO₂ and H₂O mass losses in the TGA data it is possible to solve for the most likely phase composition of the harvested dusts. Note that this is not strictly an over-determined set, but the results are nonetheless informative. The comprehensive dust phase analyses are not reported here but were determined not only over the variation in residue chemistry but also as a function of ageing and for both the white and red dust phases.

Results and Discussion

Following the bauxite residue ageing process by virtue of the drying curve behaviour, the photographic sequence for the surface morphology, the quantity and composition of the dusts harvested at particular points on the weight percent solids curves and how these responses varied with deliberate changes in bauxite residue chemistry enabled a robust model to be developed for dust formation. Weight percent solids drying curves are shown in Figures 2 and 3 for the caustic variation residues and the NaCl replacement residues over the first 90 days. Note that the residue labelled as “100% caustic” is a normal residue. These investigations were part of a larger scope and the influence of rainfall (as an example) was also investigated, so the discontinuities in Figure 2 represent simulated rainfall events and hence a sharp fall in percent solids.

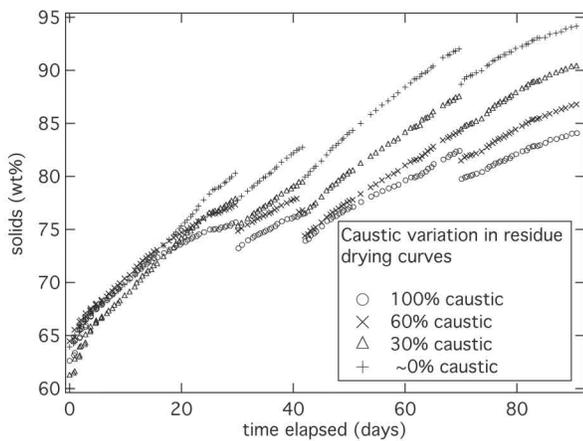


Figure 2. Ninety day drying curve behaviour for caustic reduced residues, the lower the caustic level the more rapidly the residue dried.

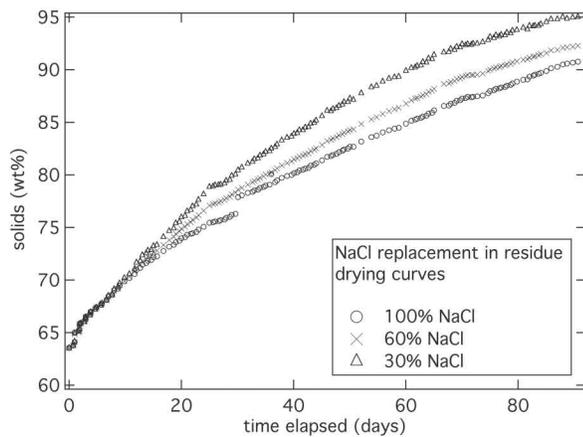


Figure 3. Ninety day drying curve behaviour for NaCl replacement residues, the lower the NaCl level the more rapidly the residue dried.

In the course of both extended greenhouse studies each residue sample surface was photographed approximately 250 times and assembled as time-lapse movie clips. These clips gave the best indication of morphological behaviour but cannot be reproduced within the paper. Figures 4 through 6 show individual stills in three (*) of the seven residue variants (i.e. 100%*, 60%, 30%, ~0%* caustic and NaCl replacement to 30%, 60% and 100%*) at 1, 2 4 and 16 weeks. These are B&W in the printed version but in colour in the electronic version. In terms of morphological changes for a normal residue the general ageing sequence was residue settling (accompanied by liquor decant), drying/drainage to an increasing solids level, white salts efflorescence (white dust), marked horizontal residue shrinkage causing cracks and movement away from the residue container sides and finally formation of a friable red dust phase. This second dust phase was particularly evident in the time-lapse movie clips as the dried residue acts as a fluidized powder and slowly cascaded into the newly formed perimeter gap. In general terms the process was simply one of capillary transport of dissolved salts toward the surface of the residue profile with the salts crystallizing as the water component of the liquor evaporated. This is a conventional salt transport process and exactly parallels that of salt damp in

masonry structures. The role of the capillary transport is important; in earlier forced-air drying experiments the rapid drying was found to shut down the capillary transport at the surface and stop the efflorescence. The ability of the increasingly dry residue mass to plastically deform stopped at some critical point so the residue ceased slumping to a lower level and exhibited its higher solids by horizontal shrinkage, mainly at the perimeter, but also through fissures within the main residue body.

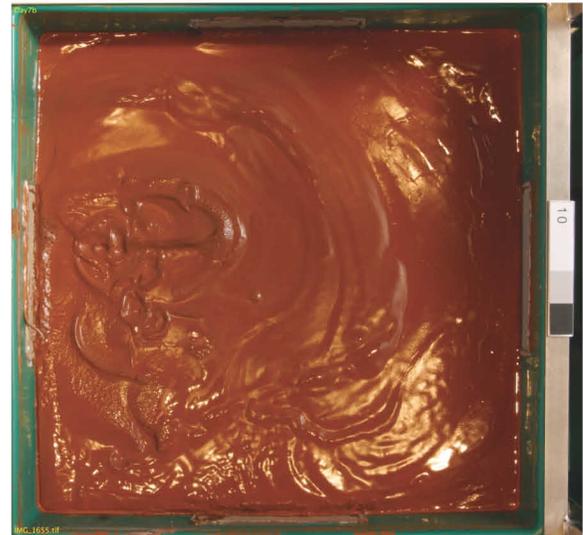


Figure 4(a). 100% caustic residue at 1 week.



Figure 4(b). 100% caustic residue at 2 weeks.



Figure 4(c). 100% caustic residue at 4 weeks.



Figure 5(b). Reduced caustic (~0%) residue at 2 weeks.



Figure 4(d). 100% caustic residue at 16 weeks with white dust overlayer removed revealing friable red dust.



Figure 5(c). Reduced caustic (~0%) residue at 4 weeks.



Figure 5(a). Reduced caustic (~0%) residue at 1 week.

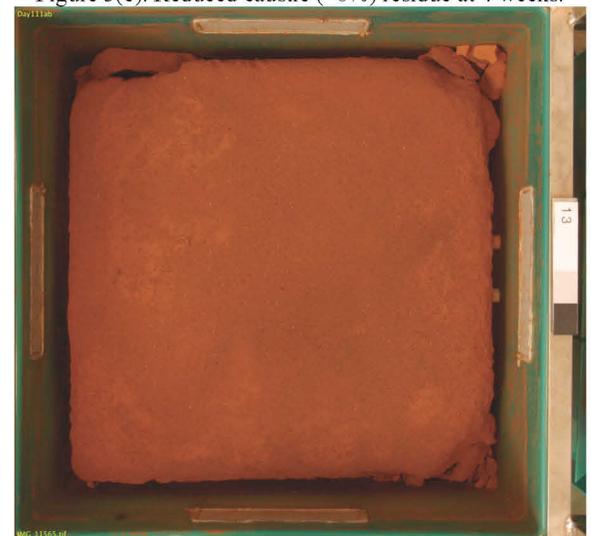


Figure 5(d). Reduced caustic (~0%) residue at 16 weeks. Prior to 16 weeks some surface detail lost due to rain events, but no friable red dust had formed at this point.



Figure 6(a). NaCl replaced (100%) residue surface at 1 week.



Figure 6(b). NaCl replaced (100%) residue surface at 2 weeks.



Figure 6(c). NaCl replaced (100%) residue surface at 4 weeks.



Figure 6(d). NaCl replaced (100%) residue surface at 16 weeks. NaCl efflorescence was strongly adherent and no friable red dust formed.

Residue ageing was clearly a function of a number of parameters: air T, relative humidity, residue T; hygroscopic salts content; capillary permeability of water pathway; thermal conductivity to residue core; available surface area; extent of liquor drainage. All played a role in the observed residue ageing, though in the absence of drainage, hygroscopic salts content and the consequential impact upon water activity in the residue liquor was the single most important factor in the rate of drying. The lower the caustic or the salt and the more rapidly the residue dried. Moreover, in terms of dust formation, it was the nature of the residue dissolved salts, in particular their alkalinity, that was the controlling factor.

As might be expected primary white salt efflorescence was directly related to caustic salt content; the higher the caustic level the greater the degree of white dust. Dissolved salts alone were insufficient to generate the high efflorescence levels as observed in normal residue as shown by the 100% NaCl replacement case. The secondary red friable zone also required caustic salt to form. In the ~0% caustic case and all the NaCl replacement cases the early red friable zone failed to form. Indeed the NaCl replacement cases aged to a very hard coherent solid and produced negligible dust. The key was salt alkalinity – even small residual levels in the absence of added NaCl would cause some red friable dust if drying were taken to very high solids levels, as for the nominal ~0% caustic case. Quantitative dust yields (estimates of tonnes per hectare) are determinable with this approach but are not reported. Harvest determinations at 75wt%, 80wt%, 85wt% and 90wt% solids indicated a rise in harvested dust yields with normal residue. Comparing (for example) harvest quantities at 75wt% solids showed that normal residue could yield ~800X the dust of ~0% caustic residue and ~270X the dust of 100% NaCl at high wind shear and respectively ~15X and ~75X the dust at low wind shear. These figures change with harvest point, i.e. overall residue solids level. Interestingly the 30% NaCl residue gave consistently the lowest dust for both shear regions.

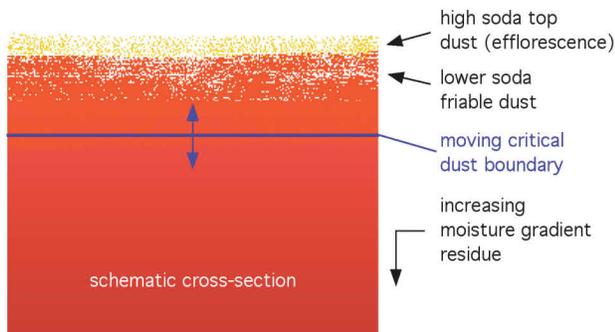


Figure 7. Schematic cross-section of ageing residue illustrating the two dust zones and the (water dependent) moving dust boundary.

Figure 7 shows a schematic illustration of the residue ageing process. Of particular interest in this model is not the appearance of the initial white dust but what mechanism is at play in causing the underlying friable red dust zone. The key factor appears to be trona brine chemistry. Figure 8 below (redrawn from Haynes 2003 [4]) shows the trona-phase equilibrium phase diagram for the low temperature region covering in particular the sodium bicarbonate, trona and sodium carbonate monohydrate phases. For normal residue the total soda level *S* of ~35 g/L equivalent Na_2CO_3 equates to a molality of 0.33, i.e. on the leftmost end of the abscissa. In the 20-40°C range for the residue the liquor brine would start out dominated by bicarbonate as the solid phase component of the brine. As the residue ages and the liquor loses water *S* would continue to increase (especially at the residue surface). The stable brine solid would then convert from bicarbonate through to trona (sodium sesquicarbonate $\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$) and with further ageing to sodium carbonate monohydrate. In all of the harvested dusts trona and the monohydrate were the dominant soda phases found. What is significant with the brine crystallization transformation of bicarbonate \rightarrow trona \rightarrow monohydrate is that it represents a sequence of *reducing* molar sodium volumes (see Table II) as not only water is lost from the liquor but CO_2 .

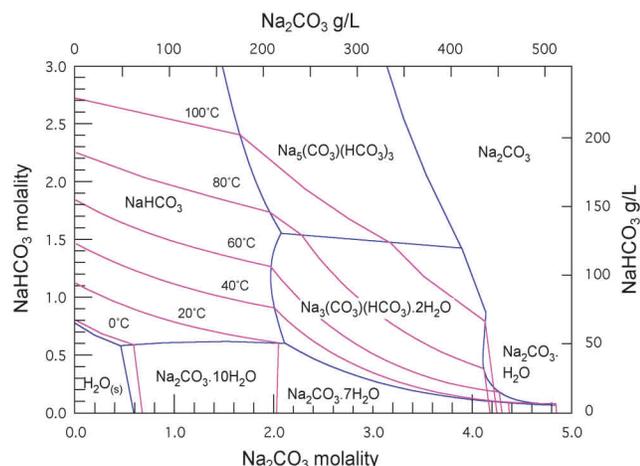


Figure 8. Haynes [4] trona phase equilibrium diagram (redrawn).

For comparison the sodium molar volume for NaCl is 27.0 cm³. When the NaCl substituted residues dry out and the efflorescent

salt crystallizes the residue particulates remain physically adhered to the salt. In the case of the actual caustic residues this adherence is only initially true for the bicarbonate precipitates, the eventual conversion to the favoured monohydrate causes an overall 30% volume reduction in the precipitated salts. It is proposed that this shrinkage fractures whatever original cementing may have occurred, thereby causing the friable zone. This breakdown of the residue structure is a consequence of drying and de-carbonation and is unrelated to any shear forces that may accompany wind events.

Table II. Sodium molar volumes for the trona brine solid phases.

Phase	formula	volume	$\text{CO}_3^{2-}:\text{Na}^+$
nahcolite	NaHCO_3	38.9 cm ³	1
trona	$\text{Na}_3(\text{CO}_3)(\text{HCO}_3) \cdot 2\text{H}_2\text{O}$	35.7 cm ³	0.67
monohydrate	$\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$	27.6 cm ³	0.5

Conclusions

The key factors for dust formation with conventional bauxite residue are capillary salt transport, the deposition (efflorescence) and decomposition of caustic salts (dehydration and de-carbonation) and the commensurate reduction of sodium molar volumes leading to a breakdown of inter-particle bonding between residue solids. This model explains the formation of both the white and red dust phases. It also predicts the likely dust response of modified residues such as carbonation [5, 6] as a neutralization strategy. Carbonation will drive toward the monohydrate carbonate prior to disposal, i.e. the sodium molar volume will already be at the minimum so the residue should not physically breakdown in the BRDA, i.e. it is “pre-aged”. Interestingly in an environment of increased concern over greenhouse gas emissions wet residue disposal would sequester twice the tonnage of CO_2 compared to direct residue carbonation due to retention of the bicarbonate.

One of the curious findings is that although a complete removal of caustic would eliminate dust, solid alkali reversion makes this very difficult and even a small residual amount of caustic will result in some dust production. This also means that after a dust lift-off event on a BRDA, sufficient summer rainfall would be expected to re-initiate subsequent dust events. If, however, the low (but non-zero) caustic residue is treated with NaCl the tendency to dust becomes negligible.

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