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**CHARACTERISTICS OF GYPSUM AND
DI-AMMONIUM PHOSPHATE FERTILISER USED IN
RESIDUE REHABILITATION**

**I. R. Phillips
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SUMMARY

Improving rehabilitation protocols at Alcoa's residue storage areas (RSAs) is an on-going process. Gypsum incorporation to achieve pH reduction is one of the fundamental steps in the rehabilitation process of residue sand embankments. This report outlines a range of experiments aimed at investigating the characteristics of gypsum and di-ammonium based inorganic fertiliser used in Alcoa's residue rehabilitation program. Gypsum was found to effectively reduce the pH of residue sand, but its effect was limited by the low solubility of gypsum (about 0.2 g per 100 mL of water). Gypsum did however provide additional benefits, which include improved flocculation of colloidal material, decreased exchangeable sodium ratio, and a supply of essential plant nutrients such as phosphorus, potassium and zinc. It is recommended that gypsum remains an integral component of the residue rehabilitation operational protocol.

Application of 2.71 t/ha of di-ammonium phosphate-based inorganic fertiliser was found to supply most nutrients at levels exceeding or at least similar to those measured in natural systems (i.e. coastal dune systems developed on limestone and unamended topsoil surrounding the Kwinana RSA). Nitrogen (N) management in alkaline residue sand represents a major area of residue rehabilitation research. It is possible that a major proportion of applied N (as NH_4) is lost through volatilisation as NH_3 ($\text{NH}_{4(\text{aq})} \rightarrow \text{NH}_{3(\text{g})}$ $\text{pK}_a = 9.2$) in a relatively short time after application. If volatilisation is a major N loss mechanism, then continued use of DAP may be ineffective as a means of supplying plant available N, and should be regarded as inefficient from a cost perspective. Therefore, a better understanding of N dynamics in residue sand is required, and other forms of N addition (e.g. nitrate, sulphur-coated N) will need to be identified.

INTRODUCTION

Residue sand represents that fraction of bauxite-processing residue with a nominal particle size greater than 150 μm . This material can exhibit a $\text{pH} > 11$, and an electrical conductivity (EC) > 2 dS/m. Because of its greater particle size, hence lower reactive surface, and lower quantities of residual alkalinity, pH reduction is often more efficient in residue sand than in residue mud. For this reason, residue sand has a beneficial re-use in the construction and rehabilitation of Alcoa of Australia (Alcoa) bauxite-processing residue storage areas (RSAs). However, given its poor nutrient status and poor water-retention properties, use of residue sand as a suitable plant growth media poses many challenges to successful rehabilitation. Some initial properties of residue sand are: (1) very low concentrations of P (5 mg/kg), K (15 mg/kg), organic carbon (0.07 %) and trace elements (Cu, Zn and Mn); (2) highly

alkaline ($\text{pH}_{1:5} > 10.5$) and saline ($\text{EC}_{1:5} = 2 \text{ dS/m}$); and (3) is dominated by Na in the exchange complex (5.6 cmol/kg and $\text{ESP} > 90\%$) (Thiyagarajan *et al.* 2009; Chen *et al.* 2009a,b; Phillips and Chen 2010; Banning *et al.* 2010; Jones *et al.* 2010a,b).

Two of the fundamental steps in Alcoa's residue rehabilitation protocol are (1) the incorporation of gypsum for reducing alkalinity and ESP levels of residue sand prior to vegetation establishment, and (2) the addition 2.71 t/ha of a di-ammonium phosphate (DAP) based fertiliser. Alcoa obtains its gypsum from CSBP Wesfarmers at Kwinana WA, and is a by-product from the manufacture of concentrated phosphate fertilisers. Gypsum incorporation rates (50 to 225 t/ha) and depths (0.3 to 1.5 m) have varied over the 1990's through to 2003 to accommodate changes in vegetation cover, to encourage plant root distribution to greater depths, and to remain cost-effective. Phillips (2010) compared the current and alternative methods for gypsum incorporation, and identified some of the issues associated with gypsum solubility. Importantly, field observations revealed undissolved gypsum was still present within the residue sand profiles after 3 years. It is uncertain from existing data whether this slow dissolution of gypsum under field conditions was of benefit or detriment to plant growth, and whether gypsum movement throughout the profile through advection (leaching) and diffusion occurs over an extended timeframe. With continuing refinement of the operational rehabilitation protocol at Alcoa residue storage areas (RSAs), a better understanding of the characteristics of gypsum, and how these characteristics affect residue rehabilitation, is required.

Di-ammonium phosphate (DAP) based fertiliser is initially surface-applied at a rate of 2.71 t/ha, and then disc-harrowed into the residue sand profile to a depth of about 0.2 m. Although inorganic nitrogen (N) can be present initially in the residue sand, very little of this element can be observed at later times. The likely loss mechanisms of fertiliser N from residue rehabilitated areas include leaching, plant uptake, microbial uptake and volatilisation. The primary mechanism responsible for loss of inorganic N (predominantly as ammonium (NH_4)) and alternative fertiliser sources (e.g. nitrate (NO_3)-based) are the focus of future research activities. In this report, only the composition of the DAP-based fertiliser will be presented.

The primary aim of this report is to provide some fundamental characteristics of gypsum used for pH reduction in Alcoa's RSAs as part of the current operational residue rehabilitation program. The specific objectives of this report are to (1) compare the solubility of gypsum in the absence and presence of residue sand; (2) compare gypsum-amended residue sand EC and pH under leaching and static flow conditions; (3) undertake preliminary modelling of geochemical speciation of gypsum

using PHREEQC, and (4) to provide the chemical composition of gypsum and DAP-based fertiliser used in residue rehabilitation operations.

MATERIALS AND METHODS

All laboratory-based experiments were undertaken using samples of gypsum and fertiliser collected from stockpiles at the Kwinana (KW) and Pinjarra (PJ) RSAs during July 2006. Approximately 500 g of each material were collected randomly from various locations within the stockpiles to obtain a representative sample.

A sample of residue sand was obtained from the KW RSA (July 2006), with approximately 1 kg of this material being collected from the stockpile at the end of the sand slurry pumping pipe located at Area F.

Chemical Composition of Gypsum

The chemical composition of gypsum was determined using two approaches. The first approach involved dissolving 0.2 g of gypsum in 100 mL of Milli-Q water¹, with the filtrate (< 0.45 µm) being analysed for sodium (Na), magnesium (Mg), aluminium (Al), phosphorus (P), sulphate (SO₄), potassium (K), calcium (Ca), iron (Fe), ammonium (NH₄), nitrate (NO₃), electrical conductivity (EC), pH, bicarbonate (HCO₃), carbonate (CO₃), boron (B), manganese (Mn), copper (Cu) and zinc (Zn).

The second approach used aqua regia as the extracting solution to dissolve (0.2 g) gypsum into its individual components (Rayment and Higginson 1992). Aqua regia (3:1, v/v, 12M HCl to 15M HNO₃) is a digestion procedure considered adequate for analysing total-recoverable metals, and is used to estimate the maximum element availability to plants (Chen and Ma 2001). The resulting solution was analysed for sodium (Na), magnesium (Mg), aluminium (Al), phosphorus (P), sulphate (SO₄), potassium (K), calcium (Ca), iron (Fe), boron (B), manganese (Mn), copper (Cu), zinc (Zn), silica (Si), cobalt (Co), selenium (Se) and molybdenum (Mo). All analyses were performed by CSBP Ltd.

Gypsum Solubility in the Absence and Presence of Residue Sand

In the absence of residue sand, gypsum was added in varying amounts to 100 mL of deionised (reverse osmosis) water. The amounts of gypsum added per 100 mL of water were 0, 0.01, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, 1 and 10.2 g.

¹ The solubility of gypsum in water is 0.24 g per 100 mL of cold water (Lide 1992)

In the presence of residue sand, gypsum was added in varying amounts to 20 g of residue sand and 100 mL of deionised (reverse osmosis) water. The amounts of gypsum added were 0, 0.02, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 1, 2.5, 5 and 10. On a percent basis (mass of gypsum per 20 g of residue sand), these amounts of gypsum were equivalent to 0, 0.1, 0.25, 0.50, 0.75, 1, 1.25, 1.5, 2, 5, 12.5, 25 and 50 % (w/w basis).

Each sample was shaken over a 72-hour period, with pH and EC measurements taken after 2, 18, 24, 40, 56 and 72 h. For the samples with residue sand, after the initial 72-hour shaking period, the suspension was allowed to stand until the supernatant was clear. After this time, the supernatant was removed and the equivalent mass of deionised water added to replace the supernatant. The suspension was then shaken for various time periods with sequential removal of the supernatant and replacement with deionised water. Prior to removal of the supernatant, the pH and EC was recorded. The supernatant was replaced after 66, 84, 108, 132, 228, 252, 276, 300, 372, 396, 420, 444, 516, 564, 608, 616, 784, 792, 840, 848 and 896 h.

The saturation index of gypsum was simulated using PHREEQC (pH Redox Equilibrium), a chemical speciation and reaction path program developed by the US Geological Survey (Parkhurst and Appello 1999). PHREEQC uses the C language and is capable of performing speciation and solubility, reaction path, inverse mass balance modelling, and 1-dimensional advective-dispersive-reactive transport calculations. A detailed description of geochemical speciation models such as PHREEQC and its application to environmental chemistry is provided in Zhu and Anderson (2002).

Effect of Gypsum on Leachate pH and EC

Small-scale leaching experiments were conducted to compare the pH and EC of leachate from unamended and gypsum-amended (equivalent to 1% gypsum) residue sand. The gypsum rate of 1% (w/w basis) was selected as this was the standard used for Alcoa's 2006 residue rehabilitation operations. Approximately 30 g of residue sand were packed into a 60 mL polypropylene syringe barrel and intermittently leached with 20 mL of deionised water. One pore volume (equivalent to the volume of pore space) for the residue sand was estimated to be 9.4 mL. Therefore, each leaching event represented the addition of about 2 pore volumes. The leaching experiment was conducted over a period of 1124 h, with 93 pore volumes of water passing through the residue sand material. The pH and EC of the leachate were determined after each leaching event.

Effect of Gypsum on Pore-Water pH and EC Under Static Conditions

Unamended and gypsum-amended (1% gypsum) residue sand was placed into a 100 mL glass beaker and wetted with deionised water to achieve a saturated paste ($\theta_g \approx 0.3$). The pH and EC of the saturated paste were determined intermittently over a period of 1124 h using the same time intervals as for the leaching study (see above).

Effect of Atmospheric Carbonation on Residue Sand pH and EC and Other Chemical Parameters

Carbonation is a proven technology for reducing the soluble and residual alkalinity of residue sand (and mud). However, this process can occur to a limited extent at any stage the residue materials are in contact with atmospheric carbon dioxide (CO₂). For example, carbonation may be expected on the outer surface of residue sand stockpiles and the surface layer of residue mud drying areas. To better understand the effect of atmospheric CO₂ on the pH and EC of residue sand, a small-scale laboratory study was undertaken. Approximately 500 g of residue sand were spread onto a tray to a depth of < 10 mm. The residue sand was exposed to the atmosphere for a period of 405 h. Over this period, the pH and EC (1:5 sand to water ratio; Rayment and Higginson 1992) were measured on a daily basis. Testing was terminated once the difference in pH between 3-successive readings was negligible.

A field sample of carbonated residue sand was also obtained from KW RSA, and analysed for a range of water-soluble and solid-phase parameters by CSBP Ltd.

RESULTS AND DISCUSSION

Gypsum Studies

Chemical Composition of Gypsum

The water-soluble composition of gypsum was found to be dominated by Ca and SO₄, with lesser amounts of Na and HCO₃ (Table 1). Also present in measurable concentrations were other essential plant nutrients such as Mg, P, K, Mn and Zn. By converting these concentrations into field concentrations equivalent to a “ha per 1.5 m depth” basis, then the incorporation of 225 t/ha of gypsum per 1.5 m depth provides about 2400 mg Ca/kg, 1600 mg SO₄/kg, 14 kg Na/kg, 7 kg K/kg and 3 kg P/kg. This calculation assumes however that all of the applied gypsum is solubilised, which is often not the case (at least in the short-term). Thus, the low solubility of gypsum (0.2 g/100 mL of water) could in fact act as a slow-release fertiliser.

Extraction using aqua-regia produced markedly different results to those obtained by water-extraction. In particular, much greater concentrations of Al, P, K and Fe were extracted under acid conditions,

with lower concentrations of Na, Mg, Ca, Cu and Zn relative to the water-extraction. The increased solubility of Al and Fe with increasing acidity is well-documented (e.g. Langmuir 1997), and it is possible that the concomitant increased P solubility may be through dissolution of Al- and/or Fe-phosphate minerals present within the gypsum sample. The reason for less Na, Mg, Ca, Cu and Zn in aqua regia relative to the water-extraction is uncertain and may be related to reduced metal solubility in the presence of acid-soluble Si (Table 1; as H_4SiO_4) and to a lesser extent P (Lide 1992; Langmuir 1997). However, to investigate the cause for reduced metal solubility in gypsum under acid conditions would require comprehensive geochemical modelling (e.g. PHREEQC).

Despite the discrepancy between the two datasets, the water-soluble concentrations are considered to be most-representative of ion compositions and concentrations following gypsum incorporation due to the inherent long-term, highly alkaline nature of residue sand.

Gypsum Solubility in the Absence and Presence of Residue Sand

In the absence of residue sand, addition of 0.01, 0.05, 0.1, 0.15, 0.2 and 0.25 g of gypsum resulted in a water pH of 4.88, 4.99, 5.10, 5.19, 5.23 and 5.26, respectively after a 72-hour shaking period (Figure 1a). For gypsum additions greater than 0.25 g/100 mL, a relatively constant pH of 5.3 was found. Similar trends were observed in the EC readings; addition of 0.01, 0.05, 0.1, 0.15, 0.2 and 0.25 g of gypsum resulted in a water EC of 16, 46, 81, 110, 139 and 168 mS/m, respectively (Figure 1b). For gypsum additions greater than 0.25 g/100 mL, a relatively constant EC of 190 mS/m was found.

Throughout this experiment, gypsum was visually observed to fully-dissolve in all samples receiving less than 0.25 g of gypsum per 100 mL, whereas, gypsum was observed to only partially-dissolve at additions greater than 0.25 g/100 mL. The dissolution of gypsum is described as:



The solubility product (K_{sp}) for pure gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is about 0.24 g/100 mL (Zhu and Anderson 2002). The geochemical speciation model PHREEQC predicted that 0.222 g of gypsum per 100 mL of water is required to achieve a saturation index of 0 (Figure 1c). This implies that for gypsum additions < 0.22 g/100 mL, complete dissolution of gypsum should occur, whereas additions > 0.22 g/100 mL will result in only partial-dissolution of gypsum. This was observed in the study reported here.

In the presence of residue sand, addition of 0, 0.02, 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 1, 2.5, 5 and 10 g of gypsum resulted in a water pH of 11.73, 11.60, 11.43, 11.12, 10.79, 10.55, 10.42, 10.33, 10.26, 10.19, 9.70, 9.23 and 8.59, respectively after a 72-hour shaking period (Figure 1a). Thus, as the quantity of added gypsum increased, the corresponding pH decreased. However, the time to attain a relatively steady pH exceeded 24 hours for all treatments, being more pronounced (> 40 h) at the higher rates of gypsum addition (Figure 2a).

The EC of the residue sand/gypsum suspension increased with increasing gypsum addition up to and including an addition of 0.4 g/100 mL (from 103 – 217 mS/m; Figure 1b). For gypsum additions greater than 0.4 g/100 mL (i.e. 1 – 10 g/100 mL), the EC remained relatively constant at 265 mS/m, and in these samples, undissolved gypsum was observed. Interestingly, the EC for all samples did not remain relatively constant until after 24 h of shaking (Figure 2b), whereas in the absence of residue sand, steady EC values were observed within 2 hours.

The greater timeframe to achieve a relatively constant pH and EC following adding gypsum to residue sand suggests that interactions with residue sand has affected the extent and rate of gypsum dissolution. Gypsum (CaSO_4) is considered to reduce the pH of residue materials through the reaction of Ca^{2+} ions with carbonate (CO_3^{2-}) to form weakly-soluble CaCO_3 (Barrow 1982):



The smaller K_{sp} for CaCO_3 compared to Na_2SO_4 results in CaCO_3 being precipitated within the residue material, with the more soluble Na_2SO_4 being leached from the material with drainage water. However, in the presence of residue sand, the opportunity for Na:Ca cation exchange reactions must also be considered. Residue sand has a cation exchange capacity (CEC) of about 5 cmol/kg, and this is initially dominated by exchangeable Na. The dissolution of gypsum (Eqn 1) provides Ca in the water phase which can subsequently displace Na from the exchange sites according to:



where X refers to exchangeable cation and Sol refers to solution cation.

As solution Ca concentrations decrease due to precipitation (Eqn 2) and cation exchange (Eqn 3), this would stimulate further dissolution of gypsum to until the saturation index became zero, after which the Ca, SO_4 , Na, pH and EC of the solution phase would remain relatively constant.

To evaluate the impact of cation exchange on gypsum dissolution, PHREEQC was run for the two conditions: no Ca:Na exchange and with Ca:Na exchange. Figure 3 demonstrates that in the presence of cation exchange, solution Na and SO₄ concentrations are greater, and solution Ca is lower, relative to when Ca:Na exchange is ignored. The displacement of resident Na by gypsum-Ca, coupled with enhanced gypsum dissolution to produce elevated SO₄, is supported by PHREEQC simulations.

Of the various reactions occurring between gypsum and the residue sand, PHREEQC demonstrates that Ca preferentially reacts with CO₃ (Eqn 1) prior to undergoing cation exchange. Calcium sorption involves both adsorption and precipitation reactions but the relative importance of these two mechanisms in removing solution Ca was not studied in this experiment. Wong and Ho (1995) reported that Na was preferentially adsorbed by residue mud relative to Ca at solution cation fractions > 10%, and that Ca rarely exceeded 20% of the exchange phase. This cation exchange behaviour may be attributed to the presence of zeolitic-type minerals grouped as desilication product (DSP; Wong and Ho 1995). Desilication product (DSP) is formed by the reaction of soda and alumina with reactive silica during the Bayer process. Residue mud contains about 11% DSP, whereas residue sand contains about 1% DSP. Simplified calculations (Appendix A) estimated that DSP may account for up to 3 cmol/kg of charge, or ≈ 40% of the overall CEC. This implies that a significant proportion of the CEC of residue sand may exhibit a relatively low affinity for Ca (particularly at high solution Ca fractions) and this would encourage Ca to remain in solution and be preferentially lost via precipitation as CaCO₃.

Effects of Dilution of Gypsum Concentration on Residue Sand pH and EC

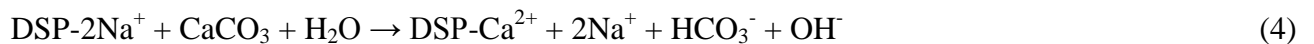
Replacement of the bulk solution with deionised water (after 72-hours reaction time) caused sequential reduction in suspension pH and EC until all of the soluble gypsum had been removed. After this time, the pH and EC of individual treatments remained relatively constant (Figure 4). These findings are not unexpected and result from serial removal of readily-soluble alkaline salts in the supernatant. The rate at which the pH and EC are observed to decline would be directly related to the removal of alkaline salts.

It was generally observed that suspensions with an EC of < 10 mS/m in conjunction with a pH > 10 remained cloudy with sediment. However with successive removal of the supernatant the quantity of suspended sediment declined until the supernatant eventually remained clear after a short (1-hour) settling period. These results suggest that under field conditions, appreciable amounts of colloidal

material may be able to be mobilized during initial leaching of recently-placed residue sand during residue rehabilitation.

Effect of Gypsum on Leachate pH and EC

Leaching unamended (0% gypsum) residue sand with about 70 pore volumes of water resulted in a steady decline in pH from about pH 12 to pH 9.5, after which the pH remained relatively constant (Figure 5a). The incorporation of 1% gypsum reduced the initial leachate pH from about pH 12 (0% gypsum) to about pH 9.5 (Figure 5a). Leachate pH from the 1% gypsum treatment tended to continue to decline to pH 8 to 8.5 over the initial 20 pore volumes of drainage, after which it increased slightly to about pH 9 and remained relatively steady over the remaining leaching period. It is unknown whether the initial decline in pH is a significant effect or whether it is simply inherent variability in the leachate composition. If this effect is “real”, then it may be explained in a two-stage process. First, gypsum reacts with soluble alkalinity to reduce pH according to Eqn (2). Second, after the gypsum has been dissolved and consumed, dissolution of mineral phases containing residual alkalinity (e.g. DSP) may produce an increase in pH. Alkalinity due to NaOH, Na₂CO₃, NaHCO₃ and NaAlO₂ could be regarded as actual (or readily-soluble) alkalinity, while DSP could be regarded as potential (or residual) alkalinity. Consequently, while actual alkalinity may be removed relatively quickly by leaching the residue material, DSP can result in sustained elevated pH values due to continued dissolution of these products over time. The release of alkalinity from DSP is believed to follow the double decomposition reaction proposed by Cruz-Romero and Coleman (1974) (Hossner *et al.* 1986):



The EC of both unamended (0% gypsum) and amended (1% gypsum) residue sand samples decreased markedly over the initial 35 pore volumes of leachate, after which the EC of both treatments remained relatively steady (Figure 5b). Interestingly, the EC of the gypsum-amended sample was consistently greater than the unamended sample (presumably due to the contribution of gypsum dissolution), although there was a trend for increasing EC for the unamended treatment during the later stage of leaching. Whether or not these effects are “real” (due to possible dissolution of DSP) or simply “background noise” cannot be determined from the limited data. To quantify any increase in EC via dissolution, the ionic composition of the leachate is required. Unfortunately this data was not determined.

Effect of Gypsum on Residue Sand pH Under Static Conditions

Under static conditions (i.e. no leaching) the pH of unamended (0% gypsum) residue sand was reduced from pH 12 to pH 10.8 over the initial 72-hour period. After this time, the pH remained relatively steady at about pH 10.5 (Figure 6). The addition of gypsum reduced the residue sand pH from 12 to pH 10 within the initial few hours, and after this time the pH remained relatively steady between pH 9 to 9.5 (Figure 6). For the gypsum-amended treatment, the range of pH values attained under static conditions was similar to those observed in the leaching experiment (Figure 5). This suggests that the pH of the pore-water of gypsum-amended residue sand under rehabilitation will fall within the range of pH 9 to 9.5 for an extended period of time in the absence of any other acidifying processes (e.g. organic acid formation, nitrification, etc.). However, to achieve reduction in the pH of residue sand that has not been treated with gypsum, significant leaching with rainwater (approximately > 30 years) will be required.

Effect of Carbonation on Residue Sand Characteristics

Carbonation is the addition of gaseous CO₂ to residue material to reduce the amounts of alkaline components within the soluble, adsorbed and solid phases. The primary sources of alkalinity in residue sand are considered to be soluble NaOH, Na₂CO₃ and NaHCO₃, and DSP, and the addition of CO₂ can remove alkalinity via the following reactions:

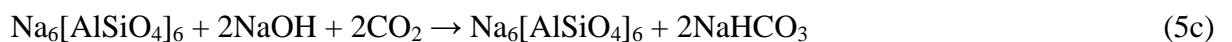
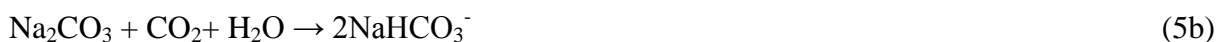


Figure 7 shows that exposing residue sand to atmospheric CO₂ reduced pH from about pH 11.8 to pH 10.5 within 24 hours. However, longer periods of exposure did not produce any additional reduction. Similar trends were observed for the EC, decreasing from about 100 mS/m to about 70 mS/m. The decrease in EC associated with carbonation may be due to the lower solubility of NaHCO₃ (6.9 g/100 mL) relative to NaOH (42 g/100 mL) as shown in Eqn 5a-c (Lide 1992).

The chemical composition of carbonated residue sand compared with (unamended) residue sand and gypsum + DAP amended residue sand is provided in Table 3. The main effects of carbonation on residue sand composition includes: (1) decreases in water-soluble Al (> 20 to 4 mg/L), water-soluble Na (2700 to 780 mg/L), pH (pH 10.6 to 9.6), water-soluble CO₃ (> 30,000 to 2,800 mg/L), EDTA-Fe (79 to 10 mg/kg) and exchangeable Na (8.4 to 3.5 cmol/kg), and (2) increases in EC (190 to 400

mS/m), water-soluble Fe (0.04 to > 5 mg/L), water-soluble HCO₃ (1 to 3200 mg/L), oxalate-extractable Fe (< 4700 to 7700 mg/kg) and Total P (26 to 43 mg/kg). Overall, these results clearly indicate that the most beneficial effect of carbonation is through the reduction of carbonate into more-soluble HCO₃, hence a reduction in alkalinity (Equation 5b). This process provides little nutritional benefit except through the reduction of Na and Al(OH)₄⁻. Interestingly, carbonation was found to increase EC (Table 3) however direct exposure to atmospheric CO₂ produced a reduction in EC (Figure 7). The reason for this discrepancy is unclear, but may be related to the different pH values for the two systems, whereby the higher pH of the atmosphere carbonated sample may have retained chemical species as low solubility carbonates. The lower the solubility the less chemical that is released into solution, hence the lower the EC.

General Findings From Gypsum Study

The main findings from this laboratory-scale study were:

- In addition to Ca and S, CSBP-gypsum contains other essential plant nutrients (K, Mg and P). Due to its low water-solubility, gypsum may also act as a slow-release fertiliser.
- Increasing amounts of gypsum reduced the pH of residue sand. The final pH was limited by gypsum solubility.
- The presence of residue sand appeared to encourage gypsum dissolution due to cation (Na:Ca) exchange.
- Gypsum reduced suspended colloidal material. This may be attributed to changes in surface chemistry (diffuse double layer theory) due to Na:Ca cation exchange and/or increased EC. Subsequent reductions in EC caused re-suspension of colloidal material, suggesting EC may play a more-dominant role in reducing suspended sediment loading.
- Leaching gypsum-amended residue sand with water reduced leachate pH to pH 9.5. However, significant volumes of water (> 20 pore volumes) will be required to induce major pH reduction in non-amended residue sand.
- Carbonation via atmospheric CO₂ reduced residue sand pH to pH 10.5 within 24 hours reaction time. However this method of carbonation is much less efficient compared to that within Alcoa's carbonation plant.

Fertiliser Composition

Rehabilitation of residue sand embankments includes a single application of 2.7 t/ha of a di-ammonium phosphate (DAP) based inorganic fertiliser. The concentrations of the major constituents of the fertiliser are presented in this section of the report. Also, an estimation of the expected nutrient profiles (assuming homogeneous mixing of gypsum and DAP throughout the residue sand) immediately after gypsum and DAP incorporation is provided.

Sample Collection and Chemical Analysis

Samples ($n = 2$) of fertiliser were obtained directly from the stockpile at the KW and PJ RSAs in July 2006. The chemical composition of the DAP fertiliser was determined using aqua regia as the extracting solution (Rayment and Higginson 1992). The resulting solution was analysed for sodium (Na), magnesium (Mg), phosphorus (P), sulfur (S), potassium (K), calcium (Ca), iron (Fe), manganese (Mn), copper (Cu) and zinc (Zn). Total N was determined by combustion (950°C in oxygen as the carrier gas) using a LECO FP- 428 Nitrogen Analyser. All analyses were performed by CSBP Ltd.

Fertiliser Composition

The dominant constituents of DAP fertiliser were N, P, K and S, with lesser amounts of Ca, Mg and Na (Table 2). Di-ammonium phosphate fertiliser is incorporated into the 0 – 0.3 m depth interval by disc-harrowing at a rate of 2.71 t/ha. On a “kg per ha” basis, the concentrations reported in Table 2 are equivalent to 271 kg N/ha, 328 kg P/ha, 297 kg K/ha, 222 kg S/ha, 29 kg Ca/ha, 27 kg Mg/ha, 6 kg Na/ha, 2 kg Cu/ha, 2 kg Mn/ha, 3 kg Zn/ha, and 3 kg Fe/ha. This rate of N is about 2-times that applied in agricultural practices (≈ 150 kg/ha), whereas the P rate is about 6- times that applied in agriculture (≈ 50 kg/ha) (Tisdale *et al.* 1993).

Estimation of Initial Nutrient Distributions in Residue Sand Profile

Estimated nutrient concentrations due to gypsum were calculated using a gypsum application rate of 225 t/ha, an incorporation depth of 1.5 m, and a residue sand bulk density of 1400 kg/m³ (Appendix B). The expected concentrations were estimated by calculating each chemical’s concentration due to 100% dissolution of gypsum (in water) and adding this to the concentration initially present in the residue sand, for each nutrient (Appendix B). For Na, Mg, Al, P, SO₄, Cl, K, Ca, Fe, N, HCO₃, B, Mn, Cu and Zn, the expected concentrations were 934, 6.7, 4.9, 8.6, 1643, 1.1, 10.7, 2313, 8.7, 4.8, 147, 0.7, 1.3, 0.8 and 1.3 mg/kg, respectively.

Estimated concentrations due to fertiliser and gypsum incorporation

Estimated nutrient concentrations due to DAP were calculated using a fertiliser application rate of 2.71 t/ha, an incorporation depth of 0.3 m, and a residue sand bulk density of 1400 kg/m³ (Appendix B). The expected concentrations were estimated by calculating each chemical's concentration due to 100% dissolution of fertiliser, and adding this to the concentration present in the residue sand after gypsum incorporation, for each nutrient (Appendix B). For Na, Mg, Al, P, SO₄, Cl, K, Ca, Fe, N, HCO₃, B, Mn, Cu and Zn, the expected concentrations were 935, 13.2, 4.9, 86.4, 1696, 1.1, 81.0, 2320, 9.5, 69, 147, 0.7, 1.9, 1.3 and 2.0 mg/kg, respectively.

Comparison of estimated and measured nutrient profiles

Typical nutrient concentrations in residue sand embankments immediately following gypsum and fertiliser incorporation were obtained from recent rehabilitation trials. Only concentration profiles for P, N, S and K are presented (Figure 9) as these are the major components of DAP (Table 2). Total and available forms of each nutrient were used for comparison with estimated concentrations, where possible, to identify potential fractions these nutrients are associated with, hence their availability in residue sand for plant uptake.

Estimated and measured (actual) Total P concentrations in the surface 40 cm depth were relatively similar, and could be reasonably well described using a power function ($r^2 > 0.9$). Inorganic P concentrations however, were consistently less than the “estimated” and Total concentrations. This suggests that a significant proportion of the added P was present in non-plant available fractions, at least in the short-term following gypsum and DAP incorporation into residue sand.

Measured N (Total and inorganic) was consistently well-below the estimated N concentrations. The measured data are less-reliable than the estimated data since all the measured N data were at or below the analytical detection limit of the instrument. Despite this, the lack of measurable N immediately following incorporation represents a serious management issue in the use of ammonium-based forms of N in highly-alkaline residue sand. Fundamental research into N dynamics in alkaline residue sand is necessary to develop more effective means of supplying N to plants within residue rehabilitation (e.g. organic N or NO₃-based fertiliser).

Measured S concentrations were well-below the estimated S concentrations at all depths (Figure 9c). This finding was not unexpected as much of the measured S represent available forms (water-soluble

and KCl-extractable), and would not include S in undissolved gypsum. A more-representative comparison would require analysis of residue sand for Total S, but this data currently is not available.

Estimated and measured available-K concentrations were quite similar within the incorporation depth (Figure 9d), and the measured K was adequately-described using a power regression function ($r^2 > 0.9$). These data suggest that much of the applied K was present in readily-available forms for plant uptake, at least in the short-term.

Estimated and measured concentrations for selected chemical parameters at selected depths were compared with concentrations measured in native Banksia woodland and coastal analogue soils (Table 4). Compared with native soils, amended (gypsum plus fertilizer) residue sand exhibited higher pH and EC values, and greater concentrations of exchangeable Na, Al, K and Ca, Total and available- P, available-SO₄, and CO₃. Total and inorganic- N concentrations tended to be similar to slightly higher in native soils relative to amended residue sand. More information is required to determine if these nutrients are in adequate supply for the native coastal vegetation currently used in residue rehabilitation, and whether the residue sand can supply these nutrients at the required level in the long term.

General Findings From Fertiliser Study

The main findings from these analyses were:

- Estimates of nutrient concentrations in amended (gypsum plus fertiliser) residue sand were similar to those measured *in-situ*.
- More fundamental information on nitrogen dynamics in alkaline residue sand is required, and alternative forms of N-based fertiliser is required to improve plant-residue sand-nitrogen relationships (Chen *et al.* 2009a,b).
- Concentrations of many essential plant nutrients in amended residue sand were at concentrations similar to or greater than those measured in natural soil ecosystems.
- More information on the ability of residue sand to supply essential plant nutrients in the long term is required.

CONCLUSIONS AND RECOMMENDATIONS

The limited studies described in this report have provided fundamental information on the composition of gypsum and di-ammonium (DAP) fertiliser used in rehabilitation operations at Alcoa's RSAs. Gypsum effectively reduced residue sand pH from about pH 12 to about pH 9, with the final pH controlled by gypsum dissolution. Since water contents are often very low in residue sand for much of the year ($\theta_g \approx 0.06$ g/g), the rate of *in-situ* gypsum dissolution will be slow. This may explain why significant quantities of gypsum remain within residue rehabilitated areas for many years after incorporation. Although final pH reduction was restricted by low gypsum solubility, cation exchange may assist gypsum dissolution due to removal of soluble Ca. Leaching with water alone does not represent an effective method of removal of alkalinity.

The benefits of gypsum on residue sand characteristics include:

- Reduced colloidal material: Flocculation of colloidal material (due to changes in surface electrochemistry) could reduce colloidal transport and consequently movement of nutrients (e.g. P) and contaminants (e.g. metals) sorbed to these mobile colloids, and clogging of water-conducting pores.
- Act as a slow-release fertiliser: Gypsum sourced from CSBP Ltd contains a range of essential plant nutrients other than CaSO₄ (e.g. P, K, Mg and Zn). The slow dissolution rate of gypsum under field conditions may therefore provide a long term supply of these nutrients over a number of years. Field evidence shows gypsum persists in the rehabilitated residue sand embankments for many years (> 5 years at least).
- Reduced exchangeable sodium percentage (ESP): The release of soluble Ca causes cation exchange and the replacement of resident pore-water and exchangeable Na with (gypsum) Ca. This affects both the ESP and sodium adsorption ratio (SAR) of the solution phase, hence colloidal dispersion.

Di-ammonium based inorganic fertiliser provides many of the nutrients essential for plant growth. Estimates of nutrient concentrations in amended (gypsum plus fertiliser) residue sand were similar to those measured *in-situ* immediately following gypsum and fertiliser incorporation. The low nitrogen concentration in fertilised rehabilitated areas shortly after incorporation requires more investigation into N dynamics under alkaline conditions. Importantly, the addition of N in the NH₄ form may not be

cost-effective due to rapid loss by volatilisation rather than being available for plant uptake, and other forms of N fertiliser may be necessary in future residue rehabilitation operations.

It is recommended that:

- Gypsum incorporation continues to play an important role in residue rehabilitation operations. This will be expected irrespective of changes in residue sand characteristics due to improved plant operations such as carbonation.
- More detailed information on nitrogen dynamics be undertaken to quantify the effectiveness of DAP-based fertiliser for supplying nitrogen for plant uptake in residue rehabilitation operations.

REFERENCES

- Alcoa World Alumina (2003) “Characterisation of AWA bauxite and residue mud and sand”. Unpublished Report, Fundamental residue properties AWA 07.06. (Technology Delivery Group: Perth)
- Banning NC, Phillips IR, Jones DL, Murphy DV (2010) Development of microbial diversity and functional potential in bauxite residue sand under rehabilitation. *Restoration Ecology* Published online doi: 10.1111/j.1526-100.2009.00637.x
- Barrow NJ (1982) Possibility of using caustic residue from bauxite for improving the chemical and physical properties of sandy soils. *Australian Journal of Agricultural Research* **33**, 275-285
- Chen M, Ma LQ (2001) Comparison of three aqua regia digestion methods for twenty Florida soils. *Soil Science Society of America Journal* **65**, 491-499
- Chen CR, Phillips IR, Wei LL, Xu ZH (2009a). Behaviour and dynamics of di-ammonium phosphate in bauxite processing residue sand in Western Australia – I. NH₃ volatilisation and residual nitrogen availability. *Environmental Science and Pollution Research* Published online DOI 10.1007/s11356-009-0267-5
- Chen CR, Phillips IR, Wei LL, Xu ZH (2009b) Behaviour and dynamics of di-ammonium phosphate in bauxite processing residue sand in Western Australia – II. Phosphorus fractions and availability. *Environmental Science and Pollution Research* Published online DOI 10.1007/s11356-009-0267-5
- Cruz-Romero G, Coleman N (1974) Reactions among calcium carbonate, carbon dioxide, and sodium absorbents. *Soil Science Society of America Proceedings* **38**, 738-742

- Hossner L, Loeppert R, Woodard H, Moore T, Thompson T (1986) Reclamation and vegetation of bauxite residues. (Texas A and M University: Texas, USA)
- Jones BEH, Haynes RJ, Phillips IR (2010a). Effect of amendment of bauxite processing sand with organic materials on its chemical, physical and microbial properties. *Journal of Environmental Management* Published online doi: 10.1016/j.jenvman.2010.06.013
- Jones BEH, Haynes RJ, Phillips IR (2010b) Influence of organic waste and residue mud additions on chemical, physical and microbial properties of bauxite residue sand. *Environmental Science and Pollution Research* Published online doi: 10.1007/s11356-010-0364-5
- Langmuir D (1997) “Aqueous environmental geochemistry”. 602 pp. (Prentice-Hall Inc: USA)
- Lide DR (1992) “Handbook of chemistry and physics. 72nd edition”. (CRC Press: Boston USA)
- Parkhurst DL, Appelo AAJ (1999) “User’s guide to PHREEQC (version 2) – A computer program for speciation, batch-reaction, one dimensional transport, and inverse geochemical modelling”. (U.S. Geological Survey: USA)
- Phillips IR (2010) Comparing techniques for incorporating gypsum into residue sand embankments at Alcoa’s Residue Disposal Areas. Mining Environmental Research Bulletin 32 (Alcoa of Australia: Perth)
- Phillips IR, Chen C (2010) Surface charge characteristics and sorption properties of bauxite-processing residue sand. *Australian Journal of Soil Research* **48**, 77-87
- Rayment GE and Higginson FR (1992) “Australian Laboratory Handbook of Soil and Water Chemical Methods”. (Inkata Press: Melbourne)
- Thiyagarajan C, Phillips I, Dell B, Bell RW (2009) Micronutrient fractionation and plant availability in bauxite-processing residue sand. *Australian Journal of Soil Research* **47**, 518-528
- Tisdale SL, Nelson WL, Beaton JD, Havlin JL (1993) “Soil Fertility and Fertilizers 5th edition”. 634 pp. (MacMillan Publishing Company: Sydney)
- Wong JWC, Ho GE (1995) Cation exchange behaviour of bauxite refining residues from Western Australia. *Journal of Environmental Quality* **24**, 461-466
- Zhu C, Anderson G (2002) “Environmental applications of geochemical modelling”. (Cambridge University Press: Melbourne, Australia)

Table 1. Chemical composition of gypsum following dissolving 0.2 g in 100 mL of water, and in aqua-regia

<i>Parameter</i>	<i>Water-Soluble</i>				<i>Aqua-Regia</i>
	Average (mg/L)	SD (mg/L)	Average (mg/kg)	SD (mg/kg)	
Na	22.23	16.94	11116	8469	490
Mg	1.21	1.02	606	511	38
Al	0.92	0.66	461	331	1419
P	0.29	0.30	143	152	636
SO ₄ -S	296	4	148002	2015	121720
Cl	0.21	0.34	103	169	nd
K	1.25	0.17	625	85	1532
Ca	431	14	215683	6962	103880
Fe	0.09	0.14	45	69	317
NH ₄ -N	0.09	0.03	43	14	nd
NO ₃ -N	0.01	0.00	5	1	nd
EC	224	3	-	-	nd
pH	6.60	0.13	-	-	nd
HCO ₃	27.44	1.32	13720	658	nd
CO ₃	0.01	0.00	5	1	nd
B	0.13	0.02	66	8	33.08
Mn	0.25	0.01	125	15	0.14
Cu	0.15	0.02	74	9	1.38
Zn	0.25	0.01	125	11	10.64
Si	nd	nd	nd	nd	1477
Co	nd	nd	nd	nd	0.40
Se	nd	nd	nd	nd	2.86
Mo	nd	nd	nd	nd	0.42

Table 2. Mean ($n = 2$) chemical composition of di-ammonium based fertilizer (DAP) in aqua-regia

<i>Parameter</i>	<i>Unit</i>	<i>Concentration</i>	<i>SD</i>
<u>Macro-nutrients</u>			
Total (LECO)			
N	(%)	9.98	0.10
P	(%)	12.10	0.28
K	(%)	10.95	2.05
S	(%)	8.20	1.13
Ca	(%)	1.07	0.63
Mg	(%)	1.02	0.59
Na	(%)	0.21	0.01
<u>Trace-nutrients</u>			
Cu	(mg/kg)	750	354
Mn	(mg/kg)	850	354
Zn	(mg/kg)	1000	90
Fe	(mg/kg)	1150	71

Table 3. Mean ($n = 2$) chemical composition of native topsoil (Banksia woodland from outside KW RDA), unamended residue sand, gypsum+fertilizer amended residue sand, and carbonated residue sand. * all units in “mg/L” unless stated, ** all units in “mg/kg” unless stated

<i>Parameter</i>	<i>Native Topsoil</i>	<i>Residue Sand</i>	<i>Amended Residue Sand</i>	<i>Carbonated Residue Sand</i>
<i>Water-Soluble Fraction (Saturated paste analysis)</i>				
Na	34	2843	2708	784
Mg	6.52	1.98	0.39	1.71
Al	50.15	18.48	29.59	3.66
P	0.47	2.83	10.29	0.18
SO ₄	8.65	121.60	109.70	38.00
Cl	58.10	158.10	17.53	157.98
K	4.96	13.79	13.12	5.19
Ca	18.45	6.82	<0.01	1.32
Fe	20.45	0.04	7.98	5.50
NH ₄ -N	4.06	1.00	0.21	0.05
NO ₃ -N	<0.01	1.00	0.60	0.05
EC (mS/m)	410	191	116	400
pH	6.12	10.58	9.82	9.68
HCO ₃	373	<1	589	3209
CO ₃	<0.01	30458	18380	2848
<i>Exchangeable or Available Fraction (after water-extraction)</i>				
NO ₃ -N	5.00	1.00	3.00	1.00
NH ₄ -N	<0.01	1.00	1.00	1.00
Available-P	2.11	3.20	4.00	2.00
Available-K	37.34	11.70	nd	15.00
Available-S	4.67	14.12	24.30	15.00
Organic C (%)	1.21	0.13	0.10	0.17
Oxalate-Fe	96	4690	2350	7745
Oxalate-Al	33	90	871	??
EDTA_Cu	nd	0.27	nd	0.22
EDTA_Zn	nd	0.03	nd	0.19
EDTA_Mn	nd	0.77	nd	0.33
EDTA_Fe	nd	78.83	nd	10.38
Exchangeable Ca (cmol/kg)	3.35	3.29	3.63	1.68
Exchangeable Mg (cmol/kg)	0.48	0.12	0.08	0.05
Exchangeable Na (cmol/kg)	0.11	8.42	5.53	3.52
Exchangeable K (cmol/kg)	0.04	0.02	0.06	0.07
Exchangeable Al (cmol/kg)	0.01	0.02	0.02	0.01
Exchangeable Fe (cmol/kg)	1.94	0.56	10.71	nd
ECEC (cmol/kg)	5.93	12.43	20.03	5.33
PBI (L/kg)	nd	565	nd	594
Total N (%)	0.02	0.03	0.02	0.03
Total Al	nd	44660	nd	nd
Total Fe	nd	243700	nd	nd
Total P	28.39	26.25	27.00	42.50

Table 4. Nutrient composition of native topsoil and coastal analogue (3 depths) communities, and expected (2 depths) and measured (4 depths) concentrations in gypsum+fertilizer amended residue sand. all units in “mg/kg” unless stated

Parameter	Native Banksia Woodland (KW)	Coastal Analogue (0-0.1m)	Coastal Analogue (0.5-0.7m)	Coastal Analogue (1.3 to 1.5m)	Expected Nutrient Concentration in Amended Residue Sand (0 to 0.3m)	Expected Nutrient Concentration in Amended Residue Sand (0.3 to 1.5m)	Measured Nutrient Concentration in Amended Residue Sand (0-0.1m)	Measured Nutrient Concentration in Amended Residue Sand (0.1-0.2m)	Measured Nutrient Concentration in Amended Residue Sand (0.2-0.3m)	Measured Nutrient Concentration in Amended Residue Sand (0.3-0.4m)
Exchangeable Na	25.46	21.40	14.63	21.40	935.25	933.90	1360.10	1430.35	1513.00	1615.75
Exchangeable Mg	57.52	145.20	45.87	42.49	13.24	6.68	10.20	10.20	10.20	10.80
Exchangeable Al	1.02	nd	nd	nd	4.94	4.94	126.13	269.47	295.77	269.08
Total P	28.39	nd	nd	nd	86.40	8.61	113.00	57.00	49.50	54.50
Available P	2.10	8.64	5.11	4.65	61.33	8.61	46.00	19.50	15.50	9.50
Available SO4	4.67	5.87	4.25	4.19	1695.66	1642.94	567.95	1185.55	595.50	766.20
Water-soluble Cl	17.43	nd	nd	nd	1.10	1.10	10.14	7.35	9.80	11.36
Exchangeable K	37.00	24.58	18.11	18.38	81.04	10.65	123.57	56.47	56.23	45.29
Exchangeable Ca	669.20	2634.39	1371.00	1230.76	2319.59	2312.71	835.67	884.72	844.65	959.40
Oxalate-Fe	96.00	130.19	116.75	92.41	4690.00	4370.00	2233.00	2456.00	2355.00	2406.00
Total N	200.00	nd	nd	nd	68.91	4.75	100.00	100.00	100.00	100.00
Inorganic N	5.33	7.58	2.47	2.18	4.75	4.75	2.00	1.50	1.30	1.40
HCO3	111.96	140.41	67.13	101.93	147.00	147.00	205.98	248.81	276.03	214.37
CO3	0.00	6.48	4.00	4.18	0.05	0.05	43.66	71.50	91.01	116.79
pH	6.12	8.31	8.54	8.81	nd	nd	9.01	9.25	9.35	9.13
EC (mS/m)	410	9	7	7	nd	nd	9000	7825	8870	10590

Figure 1. Effect of gypsum on (a) pH and (b) EC in the presence and absence of residue sand, (c) saturation index (SI), and (d) comparison between the effects of gypsum on pH observed by Alcoa (2003). Line fitted to saturation index data had the form: $\text{Gypsum Added} = 0.222 e^{(1.632 \text{ SI})}$ $r^2 = 0.995$

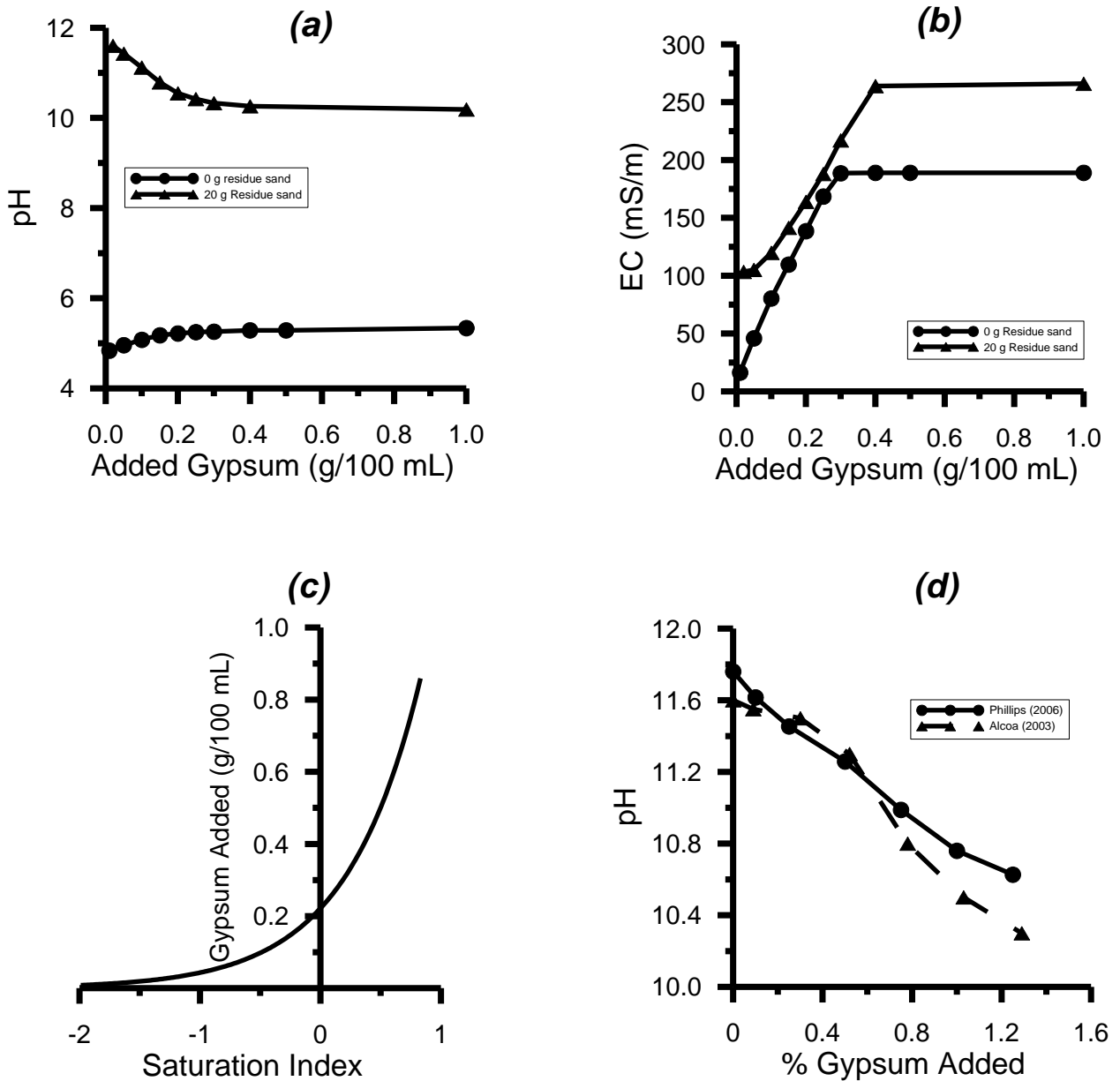


Figure 2. Changes in (a) pH and (b) EC of residue sand following gypsum addition over the initial 72-hour reaction time. (solid line) ● 0, ▲ 0.1, ■ 0.25, + 0.5, × 0.75, ○ 1, △ 1.25, and □ 1.5 % gypsum, and (dashed line) ● 2, ▲ 5, ■ 12.5, + 25, and × 50 % gypsum

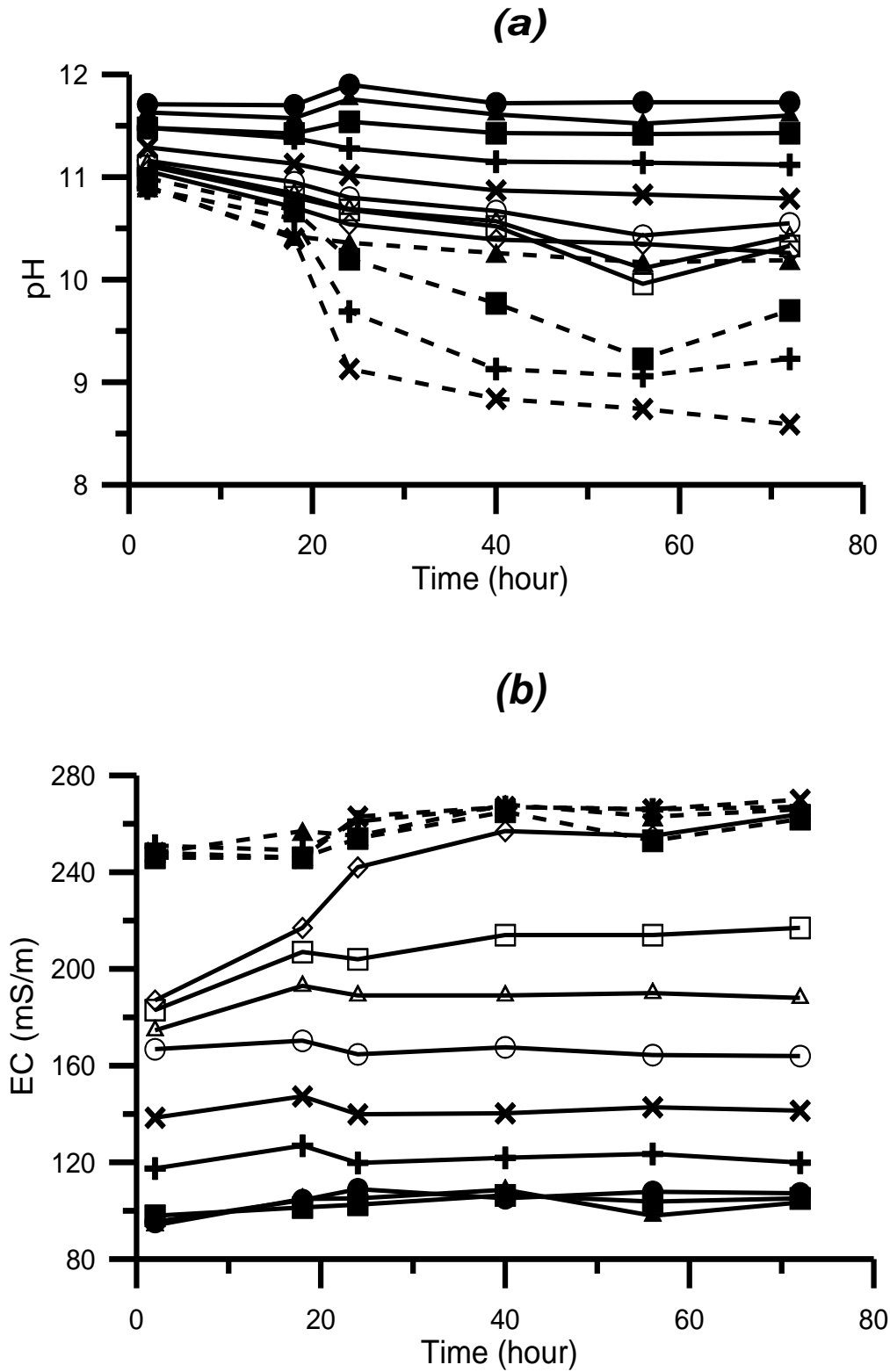


Figure 3. Simulated (PHREEQC) changes in water-soluble (a) Na, (b) Ca, (c) SO₄ and (d) CO₃ concentrations following gypsum addition to residue sand in the absence and presence of cation (Na:Ca) exchange

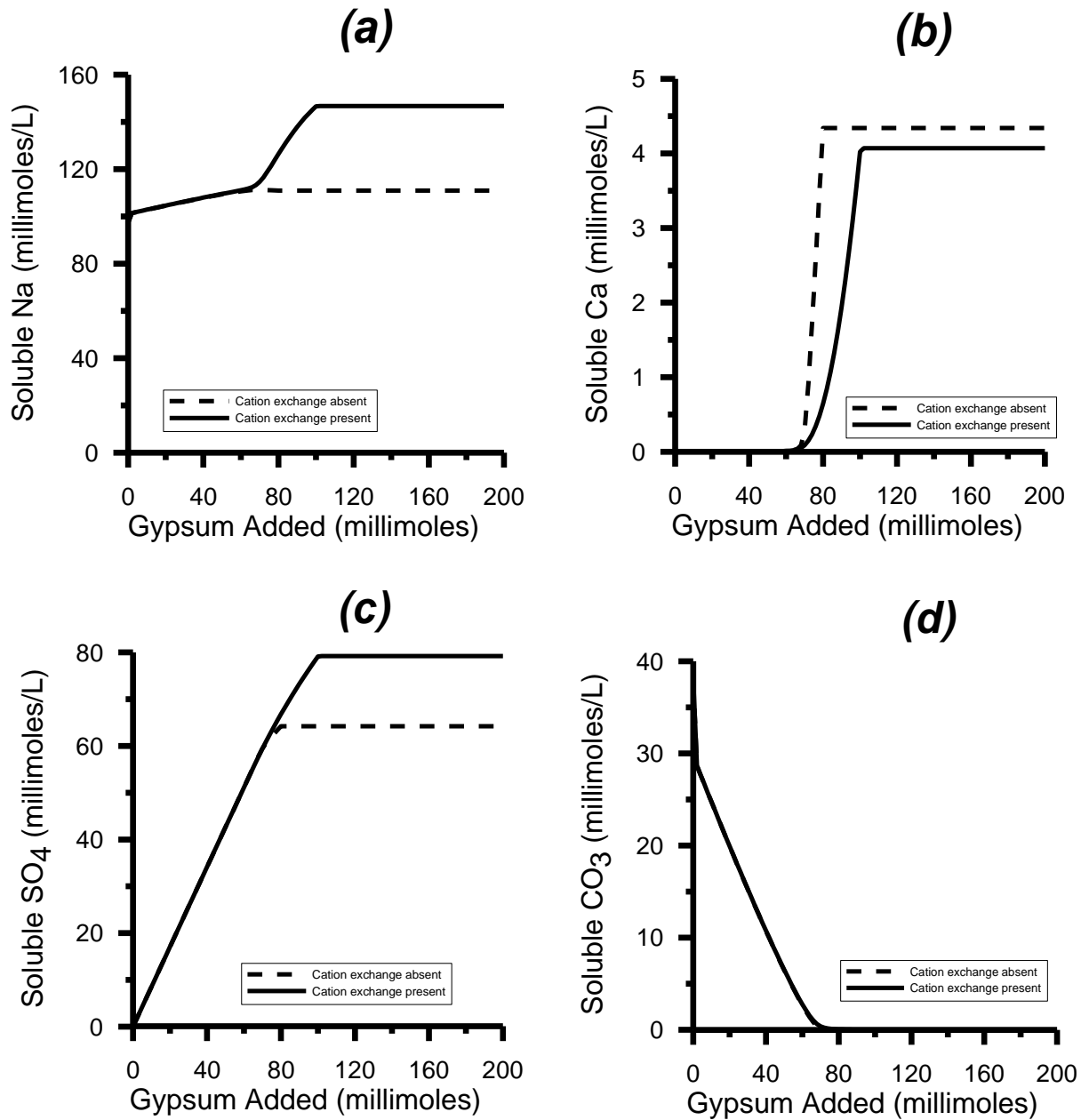


Figure 4. Changes in (a) pH and (b) EC of residue sand following gypsum addition over the 72 – 996 hour reaction time. (solid line) ● 0, ▲ 0.1, ■ 0.25, + 0.5, × 0.75, ○ 1, Δ 1.25, and □ 1.5 % gypsum, and (dashed line) ● 2, ▲ 5, ■ 12.5, + 25, and × 50 % gypsum

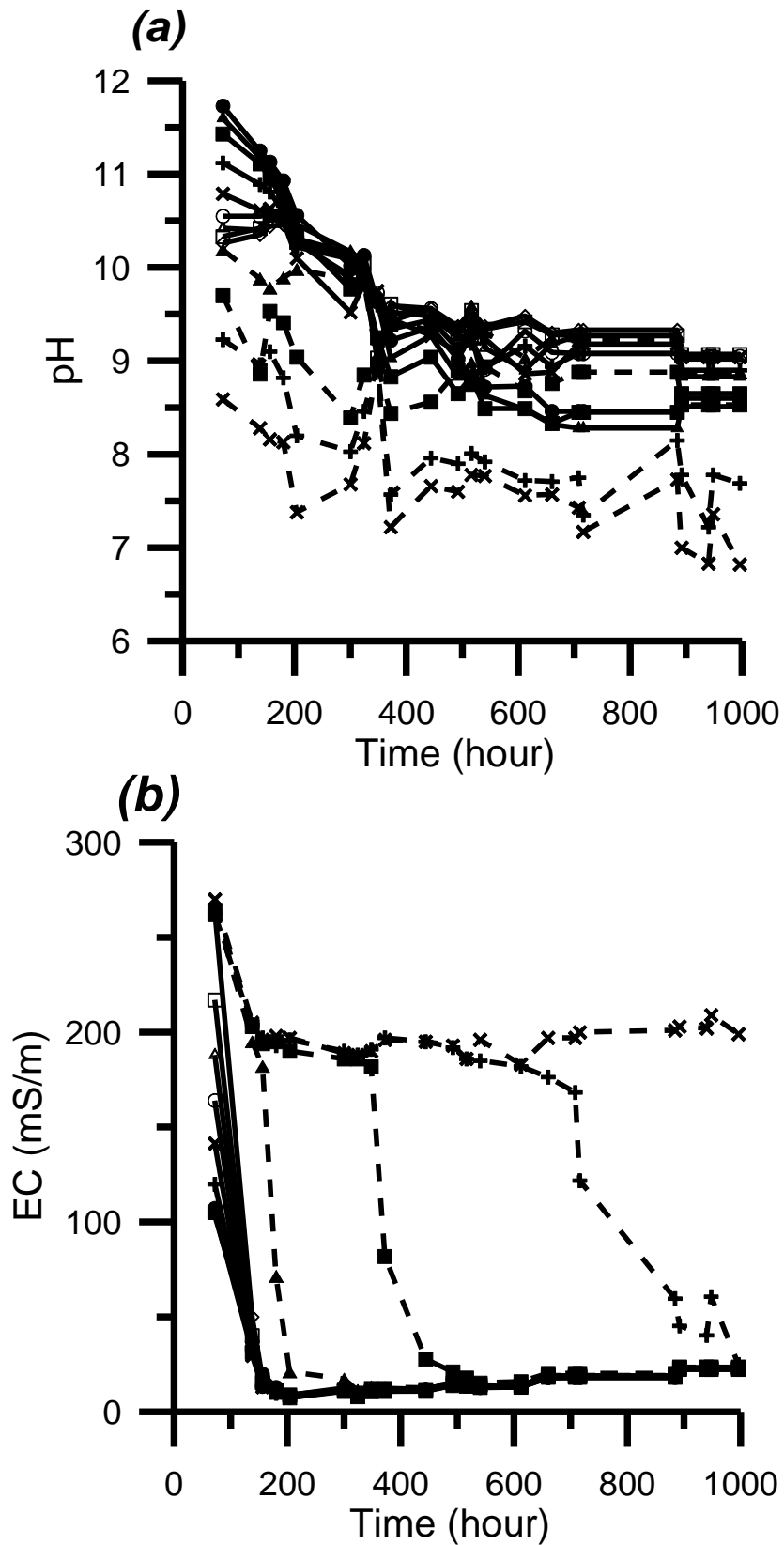


Figure 5. Changes in leachate (a) pH and (b) EC of gypsum-amended (1% gypsum) and unamended (0% gypsum) residue sand. ● 0% gypsum, ▲ 1% gypsum

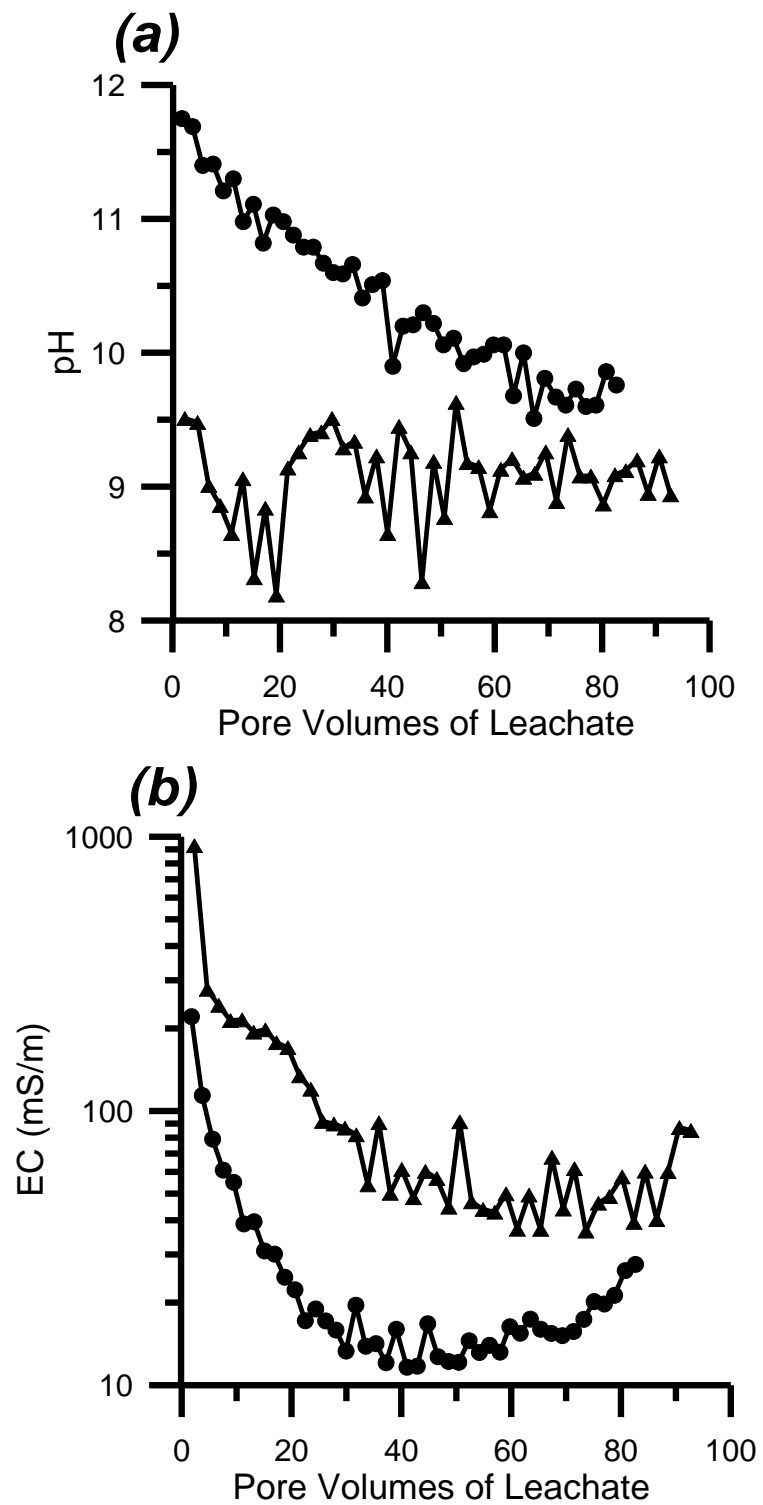


Figure 6. Changes in pH of gypsum-amended (1% gypsum) and unamended (0% gypsum) residue sand under static conditions. ● 0% gypsum, ▲ 1% gypsum

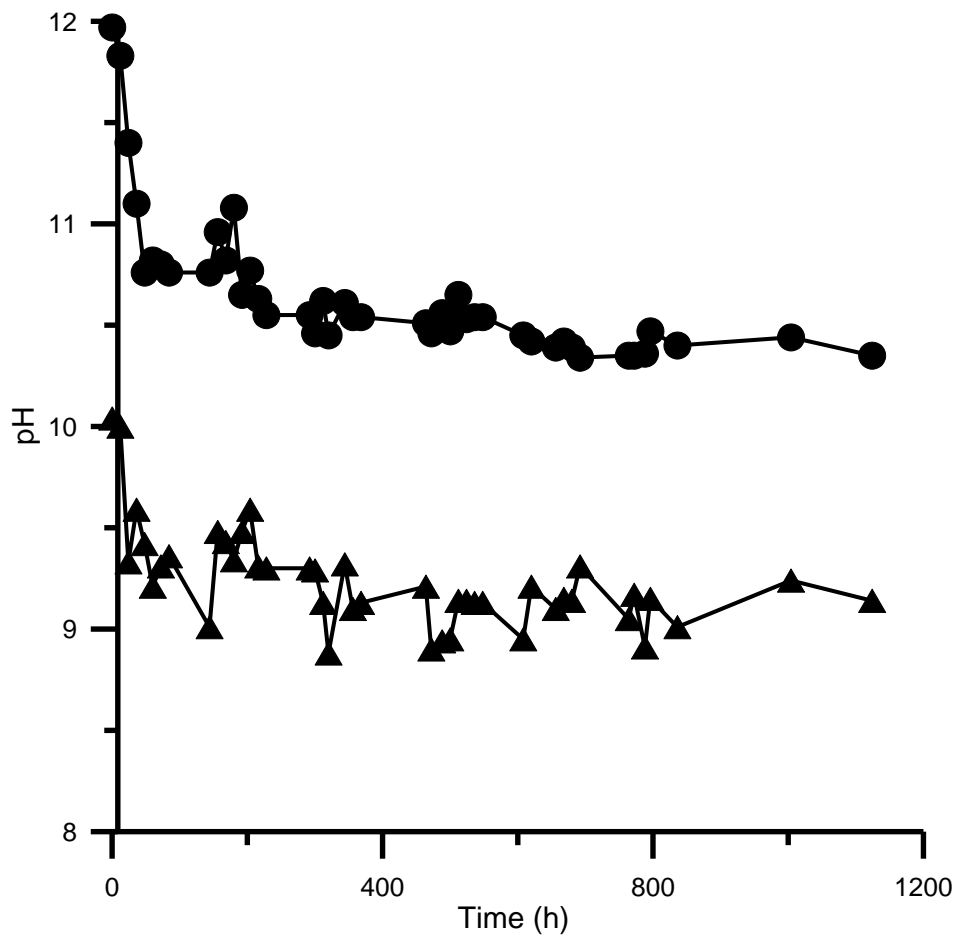


Figure 7. Changes in (a) pH and (b) EC of unamended (0% gypsum) residue sand with time of exposure to atmospheric CO₂. • 0% gypsum

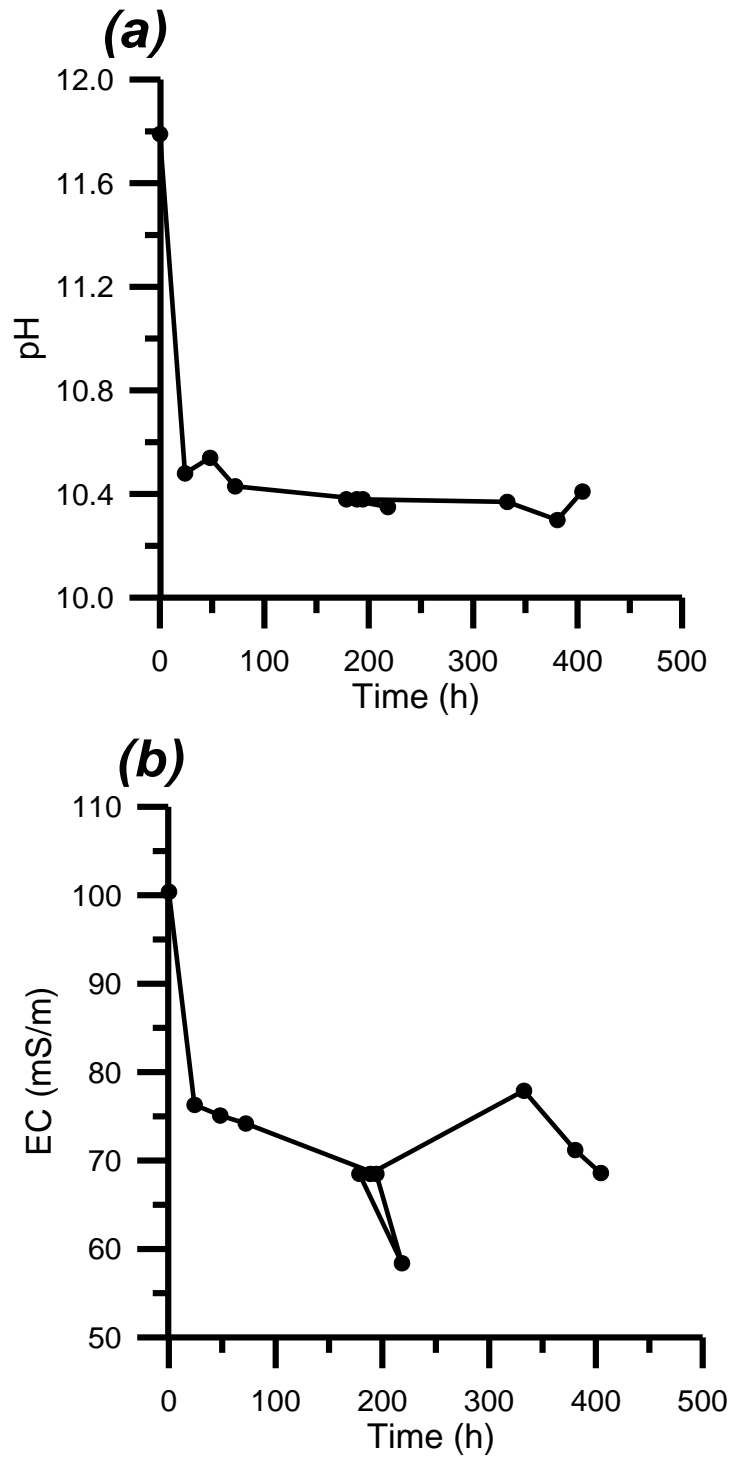
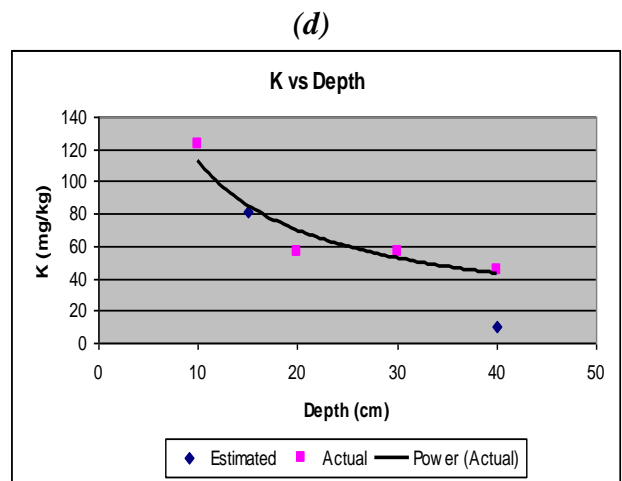
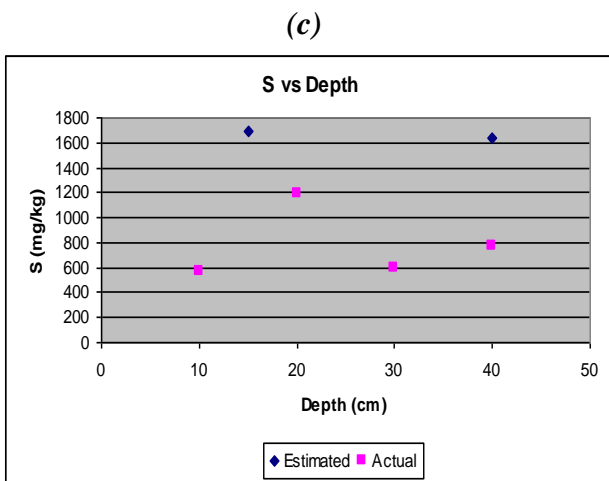
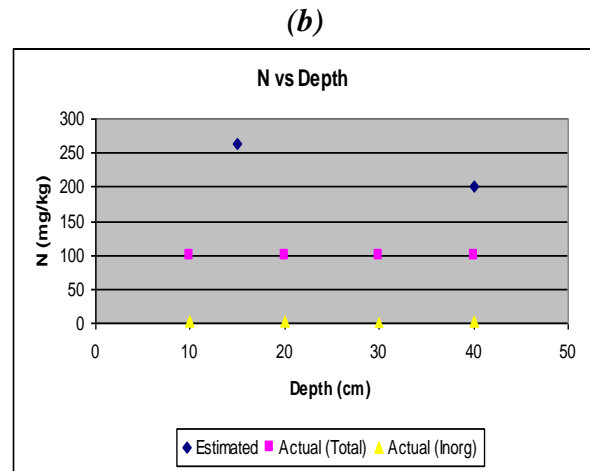
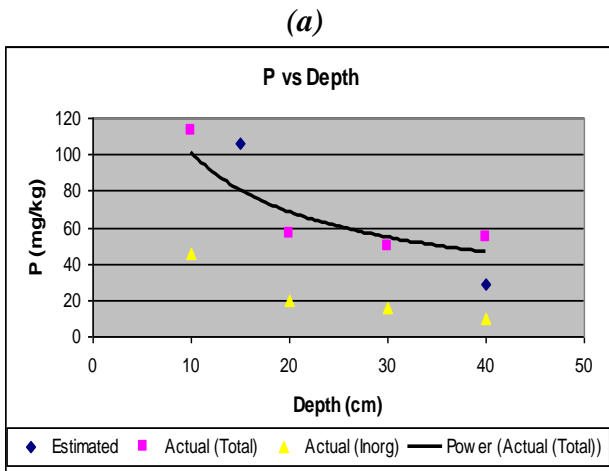


Figure 8. Effects of gypsum on suspended sediment. The residue sand on the left received no gypsum, and maintained a high concentration of suspended sediment



Figure 9. Estimated and actual (measured) nutrient distributions with depth for residue sand after gypsum and DAP fertilizer incorporation. (a) P, (b) N, (c) S and (d) K (A “power function” was fitted to the Total P and Available K data for comparison with “estimated” concentration)



APPENDIX A

Estimation of DSP Contribution to CEC of Residue Sand Based on Wong and Ho (1995)

1. Exchangeable Na in residue mud was about 60 cmol/kg
2. CEC based on exchangeable Ca was about 28 cmol/kg
3. Residue mud contains about 11% DSP.
4. Thus, 11% DSP may represent about 32 cmol/kg of charge (ie. $60 - 28$ cmol/kg).
5. Residue sand has a DSP content of 1% which represents about 3 cmol/kg of charge.
6. Residue sand has a CEC of about 5 cmol/kg based on exchangeable Ca concentrations, so overall CEC may be about 8 cmol/kg (ie. $5 + 3$ cmol/kg).
7. Of this 8 cmol/kg, about 40% is due to DSP.
8. Interestingly pH Leach tests using residue sand displayed a maximum release of Na around pH 5 which is the pH at which DSP dissolution occurs. The release of Na was about 850 mg/kg between pH 12 and pH 5, which equates to 3.7 cmol/kg.

APPENDIX B

Estimation of Nutrient Concentrations Due to Gypsum, DAP Fertiliser and Gypsum+DAP in Residue Sand Profile. Assume gypsum and fertiliser application rates of 225 and 2.71 t/ha respectively, incorporation depths of 1.5 and 3 m respectively, and a residue sand bulk density of 1400 kg/m³. All units are in “mg/kg”.

			Expected Nutrient Concentration on over Incorporation Depth	Expected Nutrient Concentration After Gypsum and DAP Incorporation In 0- 0.3m Interval	Expected Nutrient Concentration After Gypsum and DAP Incorporation In 0.3- 1.5m Interval	Initial Nutrient Concentrations in Unamended Residue sand	Combined Nutrient Concentration After Gypsum and DAP Incorporation In 0- 0.3m Interval	Combined Nutrient Concentration After Gypsum and DAP Incorporation In 0.3- 1.5m Interval	Measured Data 0-10 cm	Measured Data 10-20 cm	Measured Data 20-30 cm	Measured Data 30-40 cm
	(mg/kg)	(kg/ha)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)	(mg/kg)
<u>Gypsum</u>												
<u>m</u>												
Na	11116	2501	119.10	120.45	119.10	814.80	935.25	933.90	1360.10	1430.35	1513.00	1615.75
Mg	606	136	6.50	13.06	6.50	0.18	13.24	6.68	10.20	10.20	10.20	10.80
Al	461	104	4.94	4.94	4.94	0.00	4.94	4.94	126.13 (Avail) 47.59 (Total)	269.47	295.77	269.08
P	143 14800	32	1.53	79.31	1.53	7.09	86.40	8.61	113.00	57.00	49.50	54.50
SO ₄	2	33300	1585.73	1638.45	1585.73	57.21	1695.66	1642.94	567.95	1185.55	595.50	766.20
Cl	103	23	1.10	1.10	1.10	0.00	1.10	1.10				
K	625 21568	141	6.69	77.09	6.69	3.95	81.04	10.65	123.57	56.47	56.23	45.29
Ca	3	48529	2310.89	2317.77	2310.89	1.82	2319.59	2312.71	835.67	884.72	844.65	959.40
Fe	45	10	0.48	1.22	0.48	8.24	9.46	8.72	8.78 (Inorg) 1.99 (Total) 100	11.93	10.66	10.13
N	48	11	0.51	64.67	0.51	4.24	68.91	4.75		1.42	1.42	1.35
HCO ₃	13720	3087	147.00	147.00	147.00	0.00	147.00	147.00		100	100	100
CO ₃	5	1	0.05	0.05	0.05	0.00	0.05	0.05				
B	66	15	0.71	0.71	0.71	0.00	0.71	0.71				
Mn	125	28	1.34	1.89	1.34	0.00	1.89	1.34				

Cu	74	17	0.79	1.27	0.79	0.00	1.27	0.79
Zn	125	28	1.34	1.98	1.34	0.00	1.98	1.34
Si	1477	332	15.83	15.83	15.83	0.00	15.83	15.83
Co	0.40	0	0.00	0.00	0.00	0.00	0.00	0.00
Se	2.86	1	0.03	0.03	0.03	0.00	0.03	0.03
Mo	0.42	0	0.00	0.00	0.00	0.00	0.00	0.00
<u>DAP</u>								
Na	2100	6	1.35					
Mg	10200	28	6.56					
Al	0	0	0.00					
	12100							
P	0	327	77.79					
SO4	82000	221	52.71					
Cl	0	0	0.00					
	10950							
K	0	296	70.39					
Ca	10700	29	6.88					
Fe	1150	3	0.74					
N	99800	269	64.16					
HCO3	0	0	0.00					
CO3	0	0	0.00					
B	0	0	0.00					
Mn	850	2	0.55					
Cu	750	2	0.48					
Zn	1000	3	0.64					
Si	0	0	0.00					
Co	0	0	0.00					
Se	0	0	0.00					
Mo	0	0	0.00					