Development of a Rehabilitation System for the Red Mud Waste Generated at the Aughinish Alumina Bayer Plant

by

Ronan Courtney

Submitted to the Higher Education and Training Awards Council in fulfilment of the requirement for the degree Doctor of Philosophy

June 2002

Research Conducted at
School of Science,
Institute of Technology, Sligo,
Co. Sligo
and
Aughinish Alumina Ltd.,
Aughinish Island, Askeaton,
Co. Limerick

under the supervision of
Mr. J.P. Timpson and Mr. E.F. Grennan

Acknowledgements

I wish to express my gratitude to Aughinish Alumina Ltd., in particular Mr. Tom Hartney and Mr. Jerome Murphy, for their financial and technical support of this project. The financial contribution by Enterprise Ireland is also gratefully acknowledged.

The author gratefully acknowledges the support of Mr. Pat Timpson and Mr. E. Grennan of the Science Institute of Technology, Sligo under whose supervision the project was conducted.

The scientific input and encouragement of Mr. Bill Dallas and Dr. Jervis Goode of Enviroplan Services Limited is acknowledged. The assistance of the late Dick Raleigh in the implementation of trial plots is also gratefully acknowledged.

The assistance of Dr. Billy Fitzgerald and Dr. John Bartlett, the School of Science Technical Staff and the Library Staff is very much appreciated. Many, many thanks also to Deirdre and Breege (how would I have ever coped?).

I also wish to thank Dr. Alan Newman of Coventry University for his time and assistance with instrumentation.

Thanks are also extended to Swiss Combi Technology and Gypsum Industries Ireland for the *gratis* supply of thermally dried sludge and gypsum samples respectively. The assistance of the staff at Teagasc, Johnstown Castle is also acknowledged.

Members of the Research Laboratory past and present cannot be thanked enough for their continuous support and friendship through times of trouble. Drink tea, play Quake, be a PostGrad.

Lastly, I wish to extend my thanks to my parents for their continuous support over the past number of years.

DECLARATION

This thesis has not previously been submitted to this, or any other college. With acknowledged exception, it is entirely my own work.

Ronan Courtney

ABSTRACT

Aughinish Alumina Limited (AAL) have an obligation by terms of their Integrated Pollution Control Licence (IPCL) and Planning Permission to establish vegetation on the red mud stack at their plant at Aughinish, Co. Limerick. High pH and high exchangeable sodium percentage are the main known factors limiting the establishment of vegetation on red mud. Gypsum addition has been known to assist in alleviating these problems in other countries. However, there is no experience or published information on red mud rehabilitation under Irish conditions.

Red mud with organic and inorganic waste-derived ameliorants as well as selected grassland species were examined under laboratory controlled environment conditions as well as in field plot trials. Also, in order that it would be economically achievable, the research utilised locally available waste products as the organic amendments.

Screening trials found that physical constraints severely limit plant germination and growth in red mud. Gypsum addition effectively lowers pH, exchangeable sodium percentage and the availability of Al and Fe in the mud. A strong relationship between pH, ESP and Al levels was also found. Gypsum addition increased germination percentages and plant growth for all species investigated.

Greenhouse trials demonstrated that organic wastes alone did not greatly improve conditions for plant growth but when used in conjunction with gypsum plant performances for all species investigated was significantly increased. There was a high mortality rate for grasses in non-gypsum treatments. An emerging trend of preferential iron uptake and calcium deficiency in non-gypsum treatments was found at pot screening stage. Species also displayed manganese and magnesium deficiencies.

Adverse chemical conditions in field trials were significantly reduced following physical and chemical improvement of the substrate. After one year's growth in field trials at AAL, grasses had persisted in all treatments. Herbage analysis from the first years harvest showed some nutrient deficiencies and elevated sodium and iron levels, although gypsum amended plots displayed improved results. A decrease in essential elements, notably manganese, and an increase in iron and aluminium levels are attributed to the significant decrease in plant performance for all treatments in the second year's growing season.

Trials show that the establishment of vegetation directly on red mud is achievable when inhibitive parameters, notably pH and ESP levels, are sufficiently reduced and organic amendments added. However, a period of monitoring is recommended to assess if sustainable growth of herbage on the stacks is achievable.

TABLE OF CONTENTS

List of Tables

List of Charts

List of Figures

List of Schematics

List of Plates

List of Appendices

1.0 INTRODUCTION

1.1 Bauxite Ore & Alumina Extraction

The only current commercial route for aluminium production involves the extraction of alumina (Al_2O_3) from bauxite ore by caustic digestion (Bayer Process) followed by the molten salt electrolysis of alumina dissolved in a cryolite bath (Hall-Heroult Process) (Prasad *et al.*, 1996). Bauxite ore ($Al_2O_3.xH_2O$) always has silica, iron oxide, titanium oxide and other minor and trace impurities associated with it. Bauxite is, therefore, an impure mixture of aluminous minerals, in particular the trihydrite gibbsite $Al(OH)_3$ and the monohydrates diaspore and boehmite (Schaffer, 1983; Smurthwaite, 1990).

The percentage of the various hydrated alumina compounds in the ore will determine production costs with regard to the amount of sodium hydroxide (NaOH) required in the process and the digestion temperature. Gibbsitic bauxite, which is digested at ~145°C (Table 1.1), is the most easily processed hydrated alumina, followed by the boehmitic bauxites. Most commercial bauxites have a minimum Al_2O_3 content of 50-55% (Harben and Bates, 1990).

	Hydrated Alumina Compound	**Percent Al_2O_3**	**Specific Gravity**	**Digestion Temp. (°C)**
Gibbsite	$Al_2O_3.3H_2O$	65.35	2.3-2.4	135-145
Boehmite	$Al_2O_3.H_2O$	84.97	3.01-3.06	205-245
Diaspore	$Al_2O_3.H_2O$	84.98	3.3-3.5	340-350

Table 1.1: Properties of Bauxite (after Patterson, 1984; Harben and Bates, 1990).

The first commercial extraction of alumina from bauxite is attributed to Henri Saint Claire Deville in about 1854. In the 1880s Karl Joseph Bayer developed a method for extracting alumina from bauxite by treating it with caustic soda.

The entire process, which is named after Bayer, is illustrated in Figure 1.1.

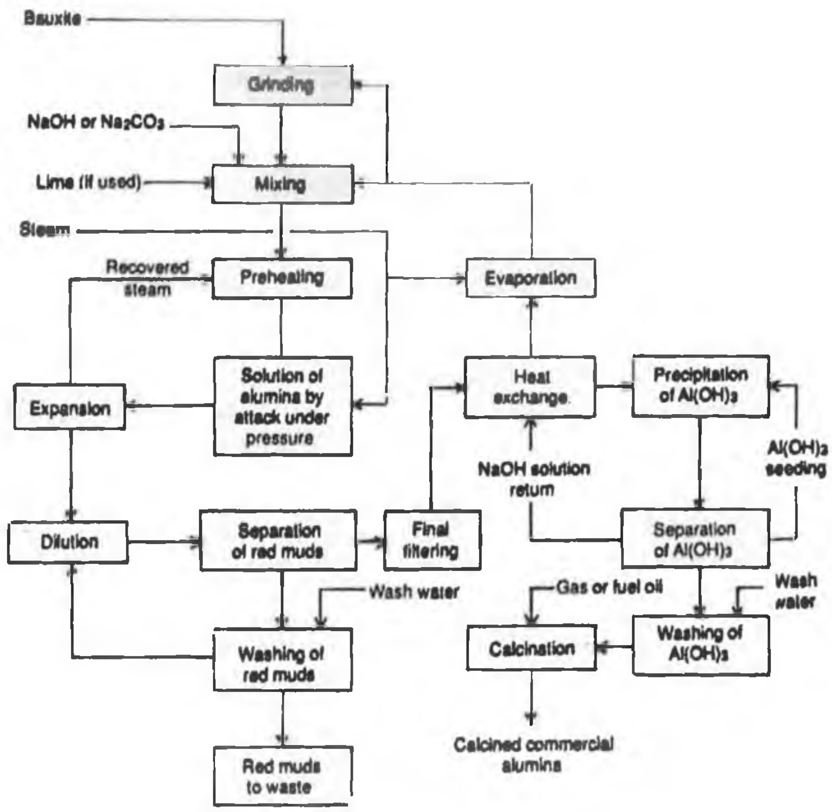


Figure 1.1: Bayer Process for the Production of Alumina (from:- Thakur and Das, 1994)

1.2 Aughinish Alumina Limited (AAL)

Aughinish Alumina Limited (AAL) operates a Bayer Plant at Aughinish Island on the Shannon Estuary, Co. Limerick in south west Ireland, producing approximately 1.5 million tonnes of alumina and over 1.05 million tonnes of residue per annum from imported bauxite.

The plant has been in operation since 1983 and was designed with an original operating output of 0.8 M tonnes of alumina per annum. Planning permission was obtained in 1990 to expand production. An Integrated Pollution Control Licence (IPCL) granted by the Irish Environmental Protection Agency (EPA) in 1998 is based on an anticipated operating plant production of 1.75 M tonnes of alumina per annum.

The plant extracts and refines alumina from boehmite bauxite imported by sea from the Boké mine, Guinea, West Africa. The plant is a high temperature caustic soda digestion process, treating bauxite ore to make metallurgical grade alumina. The insoluble constituents of the bauxite, mainly sand (5%) and the finer mud (20%) are separated from the 'pregnant solution[1]' by settling, and filtered before being transferred to a constructed mudstack for storage. Alumina is precipitated as a slurry of white aluminium hydrate ($Al_2O_3.3H_2O$) which is then heated in fluid bed calciners at 1000°C. A fine white powder of anhydrous alumina (Al_2O_3) is formed. This final product is cooled and stored in silos prior to ship-loading. The total product from the Aughinish operation is exported, principally to aluminium smelters for conversion to aluminium metal.

1.3 Bayer Process at Aughinish

Bauxite ore is ground to a fine powder and mixed with hot sodium hydroxide (caustic soda). The powdered bauxite and caustic soda are pumped to large digesters and heated to 250°C under 47 atmospheric pressure. The alumina in the bauxite dissolves to give sodium aluminate.

[1] "Pregnant Solution" - Solution from the ore recovery process containing hydrated aluminium oxides removed from the bauxite

$Al_2O_3.3H_2O(s) + 2NaOH \longrightarrow 2NaAlO_2 (aq) + 4H_2O$ + residues

At the classification stage the solid impurities (red mud/sand) are removed. Sodium aluminate, in solution, is cooled and a flocculant (flour) is added. The residue, mainly oxides of iron, silicon and titanium, settle out in tanks and are washed to remove excess caustic before being discharged to the mudstack storage area. The aluminate solution overflows the settling tanks and is pumped to precipitator tanks. Alumina trihydrate is added and the mixture agitated. Alumina hydrate crystals form through the following chemical process.

$2NaAlO_2 (aq) + 4H_2O \longrightarrow Al_2O_3.3H_2O (s) + 2NaOH (aq)$

The sodium aluminate crystals are thickened in a primary clarification tank and transferred to the calcination stage. The material at this stage is a cream coloured paste.

During calcination flue gases are used to dry and heat up the hydrate. The hydrate, now partially converted to boehmite is calcined in the main furnace at 1000°C for approximately one minute. A fine white powder of anhydrous alumina is formed (Al_2O_3). This final product is cooled and stored prior to export to smelters.

The total product from the Aughinish operation is exported, approximately 97% of it to aluminium smelters for conversion to aluminium metal. The balance is sold as hydrate of alumina for use in water treatment and other chemical and filler applications.

Bayer plants are custom designed to handle one generic bauxite ore and it is usually difficult to interchange to an alternative bauxite without substantial and expensive process and equipment modifications.

1.4 Residue Processing and Storage

Residues are separated at the clarification stage and can be differentiated into two fractions, fine 'red mud' and a coarse fraction of 'process sand'. The principal residue, the red mud, is produced at Aughinish at a rate of approximately 1.5 million tonnes per annum. It is thickened by vacuum filtration and pumped to a mudstack, located one kilometre southwest of the alumina plant (Schematic 1.1).

About 0.15 million tonnes of process sand waste is also produced. After separation it is washed to remove excess caustic, dewatered and trucked to the mud stack.

	Tonnes
Red Mud (Wet Basis)	1,590,431
Process Sand (Wet Basis)	471,185

Table 1.2: Quantities of the two residues fractions produced in 1997 at AAL

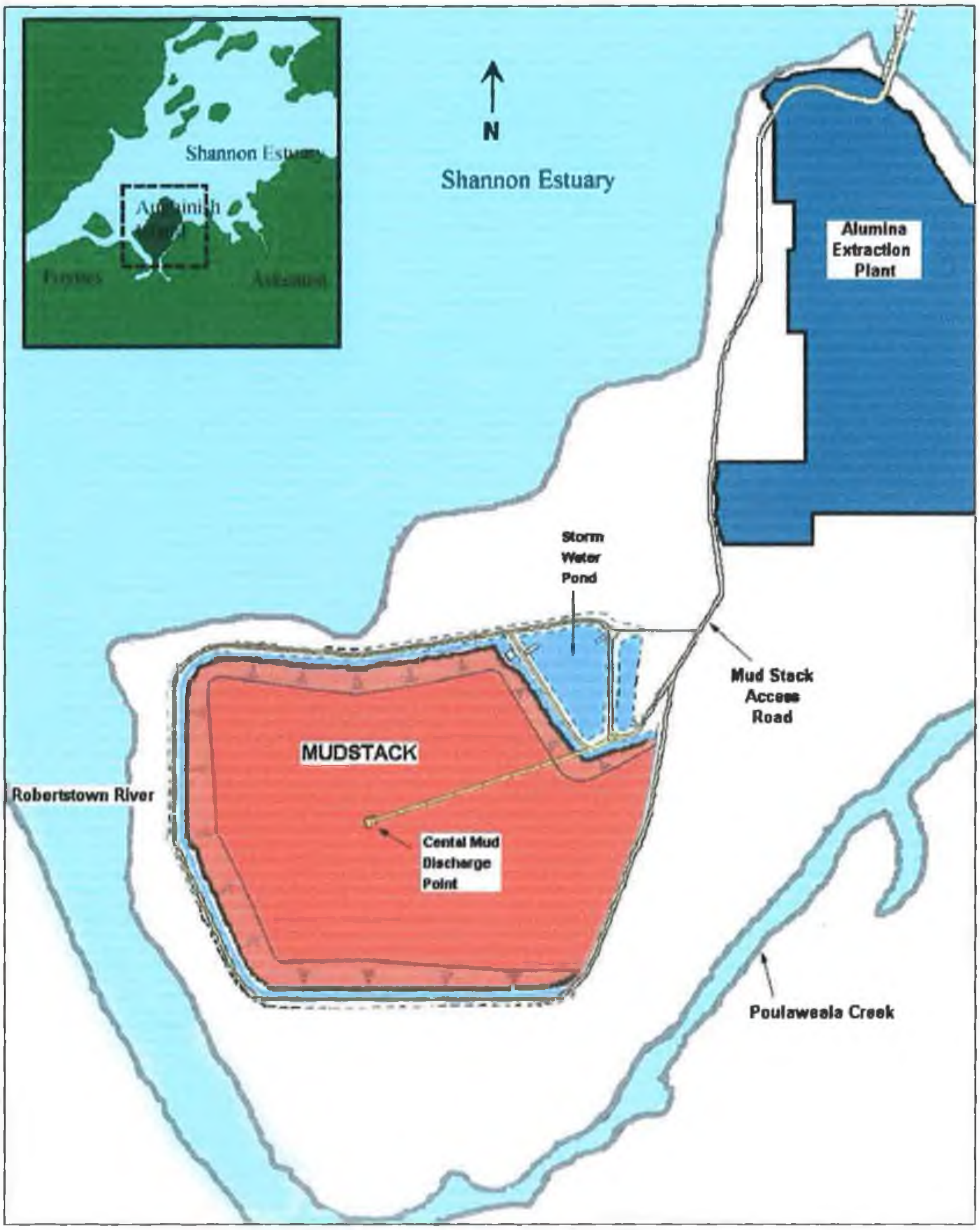
Red mud has 90% of its particles smaller than 35 microns and 35% are finer than 2 microns. As a result, permeability of the mud is low and is in the range 1×10^{-8} to 1×10^{-9} m/sec. Process sand has 90% of particles smaller than 500 microns and 10% smalller than 100 microns (Arup *et al.*, 1993).

The mud is red in appearance due to the presence of iron oxide (Fe_2O_3). The principal constituents of red mud as produced at AAL are shown below in Table 1.3.

Ferric Oxide (Fe_2O_3)	46.18 %
Aluminium Oxide (Al_2O_3)	16.5%
Titanium Oxide (TiO_2)	9.93%
Silica (SiO_2)	8.11%
Sodium Oxide (Na_2O)	4.39%
Calcium Oxide (CaO)	4.41%

Table 1.3: Principal Constituents in Red Mud (reported as oxides) as produced AAL

The mud is discharged from a series of spigots along the central spine of the mudstack. It flows to the perimeter rockfill dyke which contains the stack and subsequently rests at a slope angle of approximately 2.5%. This is governed by the viscosity or mobilised shearing strength of the slurry. The end product is an irregular cone-shaped mound below the discharge points (Robinsky, 1986; Hartney & Courtney, 1998).



Schematic 1.1. Location of Aughinish Alumina Ltd. and Plant Layout

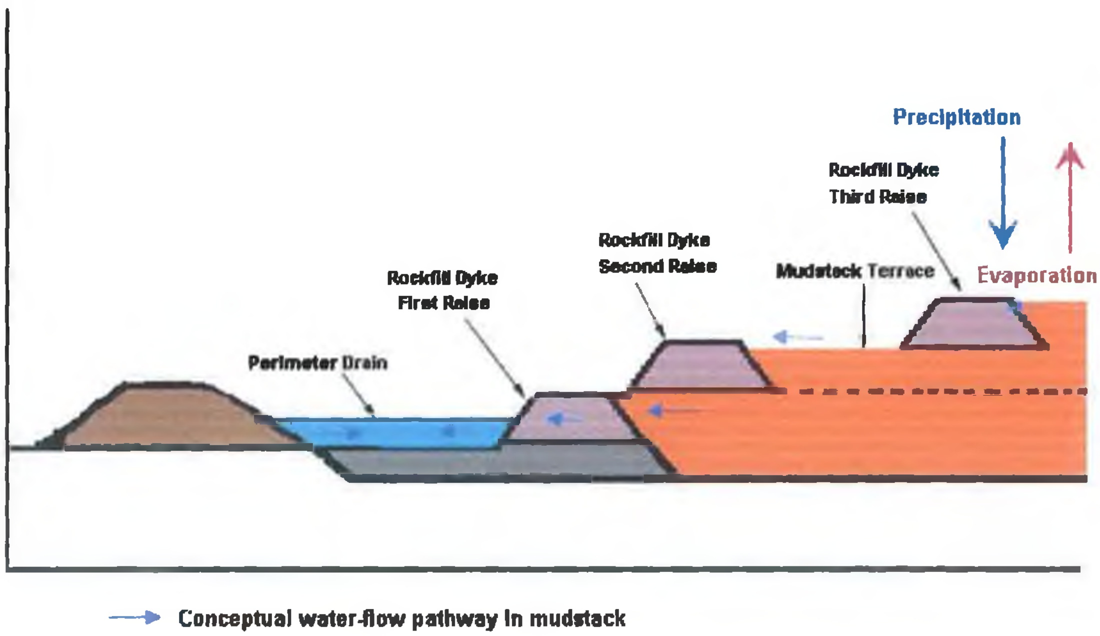
1.5 Mud Stack Construction

The original mud stack area covered an area of 71.5 ha. A second stage Planning Permission, obtained in 1993, increased the area to 103.5 ha giving a total storage volume of 13.1 million m^3 which is sufficient to allow deposition until the end of the year 2010 at annual production rates anticipated in1993. Construction of the additional storage facility was completed in 1998. Plate 1.1 illustrates a view of the red mud stack prior to any management to abate dust generation. Drying and cracking of the mud can be seen with the 'mosaic' type formation in Plate 1.1.

Plate 1.1. View of section of red mud stack showing mosaic cracking of surface

The original mudstack is located on reclaimed and very impermeable estuarine soil deposits and the recently commissioned extension is lined with a flexible membrane. Mud deposits are contained by a series of 2m high rockfill dykes underlain by separation/filter layer of process sand (Schematic 1.2). By 2010 seven of these raises will give the stack a maximum height of 26 metres from ground level. At plant closure the final shape of the mudstack will be an irregular circular mound with a gentle sloping crown.

Surface runoff and leachate from the mudstack percolates through the rockfill embankments and eventually into a perimeter drain at the toe of the first raise. The perimeter drainage flows to a sump from where it is pumped to the adjacent storm water pond. The storm water pond contents are pumped back to the plant and directed to the industrial effluent treatment plant or used as wash water within the process plant as required.



Schematic 1.2. Cross section of mudstack showing first three raises

1.6 Mud Stack Environmental Management

1.6.1 Dust Suppression

The erodibility of a soil by wind depends primarily on the structure of the soil in a dry condition. This structure is governed by a number of factors including the soil texture, or the relative proportion of sand, silt and clay (Chepil, 1953) and is further addressed in Section 2.3.2.1.

Despite the compact nature of the mud it can be a significant source of dust generation and given its composition, effective control is a strict operating requirement being governed primarily by Integrated Pollution Control Licence (IPCL) conditions. Measures to prevent mud dusting are employed when weather is warm and dry with light winds, weather is very cold with dry and moderate winds or where the mud surface is dry or semi-dry.

The deposition of dust from such an operation is a major public concern and the Irish Institute for Industrial Research and Standards indicates that average deposition rates greater than 200 mg/m^2/day are likely to cause a significant nuisance. For a dust with a greater colour contrast to background, a deposition rate of 80 mg/m^2/day is likely to give rise to complaints (Bate and Coppin, 1991).

Following a fugitive dust incident in 1987 (Arup *et al.*, 1993) AAL has investigated a number of dust control measures on the stack, including water spraying of the stack, the use of chemical stabilisers, windbreaks, and the application of shredded straw or low quality hay as a thatch (See Plate 1.2). Since 1989 Aughinish has adopted the application of thatch as the most practical and cost effective method. Typically, the operation is a biannual event involving a shredder mounted behind a low pressure tractor and costs approximately €100,000 per annum. Degradation of the thatch normally occurs within 15 months.

Notwithstanding all of the above, the rehabilitation of the red mud stack by the development of a vegetation system thereon is another desirable option for reducing the potential impacts on the surrounding environment. The establishment of vegetation on the red mud will improve its physical stability, reduce erosion and also the dispersion of dust on the surrounding environment. In addition, it mitigates the visual impact and will facilitate a beneficial post closure after-use of the stack.

However, given the nature of the substrate the creation of a vegetation cover is not a straightforward process in locations such as AAL (Section 2.4). Whilst workers in other countries and climates have demonstrated that establishing vegetation in red mud is possible, the available literature has shown that, in the majority of cases, this is achieved with grasses typical of alkaline and sodium rich substrates. Also, much of the published data only concerns growth of grasses at pot trial stage. There is limited information on the suitability of temperate grassland species as candidate grasses in developing rehabilitation systems for red mud.

Plate 1.2. View of section of mud stack shortly after application of straw thatch to suppress dust.

1.6.2 Legislative Implications in the Environmental Management and Storage of Wastes

The need to employ measures to control dusting and other environmental implications and, in general, adopt good management practices in the management and storage of wastes is governed by certain legislation.

The Waste Framework Directive 75/442/EEC and 91/156/EEC states that the operator
"take the necessary measures to ensure waste is disposed of without endangering human health and without harming the environment"

The Council Directive on the Landfill of Waste 99/31/EEC stipulates that
"measures should be taken to minimise nuisances and hazards arising from the landfill through emissions of odours and dust" and that the site be "adequately monitored and managed to prevent or reduce potential adverse effects on the environment and risks to human health"

In addition, in the Proposed Directive on Civil Liability for Damage Caused by Waste COM (89) 282 and COM (91) 282 it is stated that "Liability primarily rests with the producer of the waste for damage to property or any significant physical, chemical or biological deterioration of the environment".

The Proposal for a Directive on The Management of Waste Resulting for Prospecting, Extracting, Treatment and Storage of Minerals states in Article 12 - *Prevention of Water and Soil Pollution from Disposal Facilites* that the operator take appropriate measures in order to " prevent surface water and/or ground water being contaminated by the waste" and "prevent leachate generation as far as technically achievable". Preventative measures may include, unless the competent authority decides otherwise, a combination of a geological barrier and, if necessary, an artificial barrier.

The regulatory authorities associated with mudstack operations at AAL are the Environmental Protection Agency (EPA) and to a lesser extent the local planning authority, the Limerick County Council (LCC). Actual management is based on an in-house operational manual which is a requirement of the company's Integrated Pollution Control Licence (IPCL) issued by the EPA in 1998.

1.6.3 Legal Requirements to Rehabilitate

The conditions of the original planning permission, granted to AAL in September, 1974 (Planning Register reference number: 74/8580), require that AAL is obliged to rehabilitate the mud stack area when deposition of red mud finally ceases and also require that the stack is grassed in order to provide total coverage.

(Condition 9) "During the 'life' of the mud stack trials shall be conducted to determine a suitable grass which will establish itself permanently on the stack."

(Condition 10e) "The developer shall keep records of all trials carried out for the establishment of a planting/landscaping scheme for the rockfill dykes and for the grassing of the surface of the mud stack. These records shall be made available to the Planning Authority on request."

In June 1995, AAL submitted an application for an IPCL under the requirements of the Environmental Protection Agency Act 1992. The licence was granted in May 1998 (Licence Register Number 35).

IPCL Conditions relevant to rehabilitation are:

- all tailings capping containment engineering works must be agreed with the EPA and include a Construction Quality Assurance Plan for their implementation.

- AAL must draft and submit to the Environment Protection Agency (EPA) by January 1999 a Landfill Operational Plan covering all operational, technical, geotechnical stability, storage development, environmental protection and monitoring as well as restoration and aftercare management. The Landfill Operational Plan applies to both closed and currently active areas of the mudstack.

- AAL shall compile and submit to the EPA a fully costed Closure Plan which should include a scope statement, criteria for successful decommissioning with minimum environmental impact.

2.0 LITERATURE REVIEW

2.1 Bauxite Residue Production

Red mud production can range from 0.5 to 2.5 tonnes per tonne alumina produced (Zambo, 1979; Thakur and Das, 1994; Prasad *et al.*, 1996; Nguyen and Boger, 1998). Characteristics of red mud are determined by the chemical and mineralogical composition of the processed bauxite and by the applied variant of the Bayer process (Solymar and Bujdoso, 1993; Thakur and Das, 1994; Prasad and Subramanian, 1997).

Red muds contain varying proportions of Fe_2O_3, Al_2O_3, TiO_2, SiO_2, CaO, and Na_2O as chief constituents and numerous minor/trace constituents (Prasad and Subramanian, 1997). Red muds of similar composition may create different types of pollution under different environmental conditions e.g. sunshine, rainfall, wind velocity and soil permeability (Thakur and Das, 1994).

Red mud slurries are alkaline (pH 11-13), contain 10-30% solids, are extremely fine sized (over 60% less than 10 microns) and possess inherently poor settling properties. In addition, they are also thixotropic and exhibit poor soil-mechanical properties (Prasad *et al.*, 1996).

At present there are 84 alumina producers in the world with a current production capacity of 60 M tons alumina and 70 M tons of red mud per year (Prasad *et al*, 1996). Appendix 1 illustrates the main producers of red mud on a global scale.

2.2 Research and Development

The disposal of the wastes adds up to 2-5% of the production costs (Thakur and Das, 1994). Over the past four decades several efforts have been made to utilise the red mud.

A wide variety of applications for red mud utilisation have been found and these can be grouped into five categories.

- Production of building/construction materials

- Raw material to make ceramic/refractory products
- Metallurgical raw material
- Absorbent for waste gases/liquid effluents
- Miscellaneous uses

However, thus far there are no appropriate technologies for the bulk utilisation of these bauxite tailings. It is recognised that disposal and utilisation are interrelated aspects and that the technologies are plant specific depending on the quantity, composition and the diverse physiochemical as well as soil-mechanical properties of the red mud (Thakur and Das, 1994; Prasad *et al.*, 1996; Prasad and Subramanian, 1997).

2.3 Environmental Impact of Red Mud Storage

Disposal options are normally designed to conform to particular national as well as corporate environmental standards but can also be decided by economic and weather factors. Red mud disposal is usually on land (impoundments in natural basins or artificial lakes) but in some cases discharge to sea is employed. This latter approach has been adopted in France and Japan. The conventional landfill disposal approach or Closed Cycle Disposal (CCD) is the cheapest in capital and operating costs. In this method, washed red mud slurry containing 10-30% solids is pumped to an impoundment area. When the mud has settled the supernatant liquor is recycled back to the plant. Inherent contamination of groundwater due to leakage of the alkaline supernatant could be a problem and the surrounding areas are at risk to spillage of red mud due to overflow or failure of containment dams. A vast area of land is consumed for the mud disposal and containment and this reduces availability of usuable land. Not only is this aesthetically damaging to the landscape, but air pollution by red mud dust generated from any dried surface of the containment area may be a problem (Salopek and Strazisar, 1992; Hartney, 1993; Prasad *et al.*, 1996; Li, 1998).

With thickened tailings technology, such as that employed at AAL, the red mud is washed in a series of washing tanks, resulting in a slurry of 25-35% solids, before undergoing thickening by vacuum filtration. Flocculants are also usually added to promote sedimentation of the solids, this allows for production of thicker, compacted muds and clearer overflows. At AAL two types of flocculent are used, the first type is made from flour and the second is synfloc (i.e. synthetic flocculent). Following thickening, the solids content is increased from c.30% to 50-60% (Nguyen and Boger, 1998).

The advantages of this approach are a stable residue deposit that requires less space than conventional methods (about one third to one fifth). There is also a reduction in soluble caustic losses as the accompanying caustic is returned to the plant. The reduction in volume by water loss and recovery of caustic also lessens pollution by hydraulic seepage. Consolidation of the deposit can also allow for trafficking of the surface to enable implementation of dust control or rehabilitation measures (Robinsky, 1986; Prasad *et al.*, 1996).

2.4 Rehabilitation – Issues & Constraints

Although the red mud is a man made 'soil' type and, therefore, cannot be directly compared to naturally occurring soil types, its physio-chemical properties, as described below, gives it saline and alkaline properties that make it analogous to sodic/alkaline soils. Red mud, therefore, may present plant growth constraints similar to these soils. In addition it also suffers from some of the problems normally associated with some base-metal mine tailings in Ireland such as lack of nutrients, poor structure and exposure.

The technique of covering the waste materials with an inert material such as topsoil and managing the vegetation thereon is a costly approach and will have an impact on the borrow area from where the material is sourced. At least 30cm of soil is normally required and machinery costs can be high. The economic viability of this approach makes it applicable only in exceptional circumstances (Jeffrey *et al.*, 1974).

2.4.1 General Issues and Constraints

While chemical and physical techniques exist for short-term dust control and stabilization against erosion, the long term objective of waste rehabilitation can only be realistically achieved by the use of vegetation as a basis for landscaping, stabilization and pollution control (Bradshaw and Johnson, 1990).

The reclamation approach adopted in Ireland is based on ameliorating the substrate by improving the physical and chemical nature of the residues and selecting the plant species most suited to meet the rigours of the conditions (Jeffrey *et al.*, 1974; Williamson *et al.*, 1982).

Poor physical and chemical properties of the residues, especially the predominance of the fine fraction, are the major constraints limiting red mud reclamation efforts (Wong and Ho, 1994). Problems presented in trying to achieve direct vegetation establishment include pH values of up to 12 and toxic levels of sodium resulting from the presence of caustic remaining after use during the ore processing. Without drainage and reduction in pH, soluble levels of Al and Fe can be high and therefore pose a bio-availability risk. Lack of organic matter as well as low levels of nitrogen and other plant nutrients are also limiting (Meecham and Bell, 1977b; Fuller *et al.*, 1982).

The coarse fraction of the residues presents fewer difficulties in establishing vegetation because of the higher hydraulic conductivity, which increases leaching and thereby reduces the salinity and alkalinity (Meecham and Bell, 1977a).

Rainfall leaching and exposure to CO_2 in the atmosphere could in time reduce the pH and sodium content to levels that would normally support colonisation by tolerant species. However, due to the inherent low permeability, leaching rates would be very low, and during this period the mud would be susceptible to wind and water erosion and therefore would need rapid stabilisation (Williamson *et al.*, 1982; Ho *et al.*, 1985; Thakur & Das, 1994).

2.4.2 Chemical Constraints

2.4.2.1 Substrate pH

The pH of a soil is important as it influences many other soil chemical properties. Maximum plant growth is normally achieved within a pH range of 6.6 to 7.3, but values from slightly alkaline to slightly acid are common in natural environments (Munshower, 1994). Due to entrained residual caustic, high pH levels are an inherent characteristic of red mud. Fuller *et al.* (1982) cited a pH range of 9.2 to 12.1 for the Alcoa red mud stack at Mobile, Alabama. Others authors have reported a pH of 11 at the Gladstone refinery, Queensland (Meecham and Bell, 1977) and 10.5 for both Alcoa's Kwinana plant Australia and the Vaudreuil plant operated by Alcan in Quebec (Wong and Ho, 1993; Fortin and Karam, 1998).

High pH may be toxic in itself (Thorup 1969) and direct detrimental effects due to hydroxyl ion toxicity can occur at pH values greater than about 10.5 (Black, 1968). High pH associated with sodium carbonate in alkaline soils may interfere with anion uptake (Moore, 1974) by preventing the establishment of a pH gradient across the root membrane (Hanson, 1978) through its effect on reducing the solubility of essential nutrients such as calcium, magnesium, iron, manganese, zinc and copper (Truog, 1945).

Phosphorous nutrition of plants can be restricted at high pH as $H_2PO_4^-$, the dominant phosphate ion, is unavailable (Russell, 1972) and the phosphate binding capacity of the soil is high (Bradshaw, 1983). At high pH ammonium nitrogen is converted to ammonia which is toxic and volatile (Tisdale and Nelson, 1975). Other ions such as borate and aluminate become very soluble at high pH and reach toxic concentrations (Waisel, 1972).

2.4.2.2 *Sodium and Salt Affected Soils*

Plant growth in salt-affected soils can be limited by three processes: (a) the restriction of water uptake because of a lowered soil water potential; (b) direct ion toxicity (mainly Na^+ and Cl^-); and (c) competitive inhibition of nutrient uptake (Caines and Sherman, 1999). During salt stress in plant cells there is a decrease in potassium (K^+) uptake and an increase in Na^+ influx. As Na^+ is toxic to some metabolic reactions and K^+ is a major solute contributing to osmotic pressure and ionic strength, salt stressed plants must regulate cation transporters to maintain ion homeostasis (Serrano, 2001). One of the main effects of sodium ion toxicity appears to involve changes in the tonoplast permeability as calcium is replaced by sodium (Ricks, 1987) although differences in species sensitivity make it difficult to provide guidelines for the amounts of each ion that cause plant damage. Supply of Ca^{2+} can ameliorate the negative effects of NaCl through reducing Na^+ uptake and increasing uptake of K^+ and Ca^{2+} (Rengel, 1992). Reid and Smith (2000) reported inhibited growth of wheat by 150mM NaCl but growth increased as calcium concentration increased from 0.51mM to 2.34mM.

The capacity of a soil to adsorb and exchange positive ions (cations) is called Cation Exchange Capacity (CEC). Adsorbed cations are generally available to plant and micro-organisms by exchange with H^+ ions. Some cations e.g. calcium and manganese in exchangeable forms are good sources for promoting good soil structure and good soil tilth.

Soil sodicity is characterised by the presence of excessive amounts of sodium (greater than 15%) on the exchange complex and is detrimental to both soil and plants (Gupta and Sharma, 1990). Such levels cause the soil to disperse with the consequent destruction of soil structure and pore spaces. A dispersed soil is sticky and plastic when wet. When dry it is massive and hard and hence is impermeable to water and air.

High concentrations of sodium and HCO_3^- can be toxic to plants or can competitively inhibit the uptake of calcium and various micro-nutrients by repressing their solubility (Bernstein and Hayward 1958; Rhoades and Miyamoto, 1990).

Since sodium is not an essential element for most plants there has been little concern about assessing its plant availability by soil tests (Knudsen *et al.*, 1982). Elevated concentrations of sodium are expressed by the Sodium Adsorption Ratio (SAR) which reflects the relative balance between Na^+ and Ca^{++} plus Mg^{++} in the solution phase

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

cations expressed in milliequivalents per litre

or the Exchangeable Sodium Percentage (ESP) which reflects the saturation of the exchange complex with Na relative to other cations present. The United States Salinity Laboratory (Richards, 1954) derived the following relationship between SAR and ESP

$$ESP = \frac{[-1.26 + (1.475\,SAR)]}{[0.9874 + (0.0147\,SAR)]}$$

Ratner (1935) and Thorne (1945) cited an ESP of 40-50% as the level above which nutritional disturbances in plants occur from excess sodium although foliar injury and growth reductions have been reported at levels of 15% and lower (Martin and Bingham, 1954; Chang and Dregne, 1955; Pearson and Bernstein, 1958). Bernstein (1974) introduced a critical ESP value of 10% for fine and 20% for coarse textured soils. Various authors have recorded high ESPs for red mud such as 70.4% (Wong and Ho, 1994) and 81% (Meecham and Bell, 1977). Fuller *et al.* (1982) reported a range of ESP values for the red mud site at Mobile, Alabama, with 52.7% recorded 10m from the perimeter dyke and levels increasing to 90.9% at 45m from the dyke. All levels reported for red mud are above the levels cited critical for plant growth.

Bower and Radleigh (1949) generally found that, increasing the ESP of the substrate resulted in a decreased accumulation of calcium, magnesium and potassium in plants. Laboratory experiments have shown that addition of calcium and magnesium to alkali soils can improve plant growth very markedly with an associated increase in the uptake of these added elements by the plants (Bower and Turld, 1946).

Sodium in the soil may exert important secondary effects on plant growth through adverse structural modifications of the soil. Thus, if the exchange complex contains appreciable amounts of sodium, the soil may become dispersed and puddled, thereby causing poor aeration and low water availability (McGeorge and Brazeale, 1938) especially in fine textured soils.

Zeolites, formed during the Bayer Process have a major influence on the chemical properties of the mud. These zeolites are formed when dissolved reactive silica is reprecipitated as sodium-alumino-silicates, commonly known as Desilication Product (DSP). The amount of DSP formed depends on the nature of the bauxite and the conditions of digestion (Ho *et al.*, 1985; Hudson, 1987).

Sodium in red mud is thought to exist in three different forms:

(i) as soluble Na^+ in the solution discharged with the mud,

(ii) as exchangeable Na^+ in minerals like aluminous goethite, haematite, and muscovite,

(iii) as Na in the DSP.

As much as 75% of the total sodium may exist inside the aluminium-silicate framework of the DSP (Wong and Ho, 1995). The soluble and exchangeable Na^+ in non-zeolitic sites can be easily leached or exchanged with other cations. As the DSP decomposes (hydrolyses) over time, sodium will be slowly released raising the sodium content and the alkalinity of solution (Ho *et al.*, 1985; Wong & Ho, 1995).

2.4.2.3 Aluminium

Although aluminium is one of the most common elements in the earth's crust it is not regarded as an essential element for plant growth. It may, nevertheless, fulfil some fundamental role in the physiology of plants adapted to acid environments with a high concentration of soluble Al (Rout *et al.*, 2001) and low concentrations can sometimes increase plant growth or induce other desirable effects.

Aluminium becomes soluble or exchangeable and also toxic depending on the soil pH and many other factors including the predominant clay minerals, organic matter levels, concentrations of other cations, anions and total salts and the plant species (Barnhiscl and Bertsch, 1982; Foy, 1984; Kamprath and Foy, 1985). At pH above 7.5 aluminium becomes soluble as aluminate ion and can be absorbed by plants at a pH above 7.8 (Jones 1961; Munshower, 1994).

Most reports on Al toxicity concern low pH substrates. High soluble aluminium concentrations can be directly toxic (Clarkson, 1965; Foy *et al.*, 1978). Excess aluminium interferes with cell division in roots, fixes phosphorous to less available forms, decreases root respiration and interferes with uptake of various elements such as potassium, calcium, magnesium and manganese (Alan and Adams 1979; Clarkson 1965) and by precipitating magnesium through the formation of Mg-Al hydroxycarbonates (Hunsaker and Pratt 1970; Marshner, 1983). It is also established that Al interferes with the nitrate nutrition of plants (Calba and Jaillard, 1997).

Soluble levels of aluminium at 20 mg/kg soil have been demonstrated to be toxic for roots of lucerne and red clover and above 0.5 mg/kg soil for the growth of cotton seedlings roots (Alam & Adams, 1979).

Plant species and varieties vary widely in tolerance to excess aluminium in the growth medium, some accumulating it to levels of 37% in ashed samples (Williamson et al., 1982). Hackett (1964) found that *Dechampsia flexuosa* can tolerate high levels of aluminium and Rorison (1960) found similar resistance in

Holcus mollis. Oats (*Avena* sp.) are well adapted to acid soils, low calcium demand and are tolerant of aluminium (Alam and Adams, 1979).

Some plants have the ability to accumulate high concentrations of Al in their foliage without any evidence of injury or toxicity. Threshold toxicity levels may vary from 30 mg/kg in soyabean leaves (Wallace and Rommey, 1977) to 640mg/kg in lower leaves sorghum and up to 1220 mg/kg for the upper leaves. Dietary intakes of herbage with Al levels in excess of 1200 mg/kg have been reported as toxic for both cattle and sheep (Puls, 1988). McGrath *et al*. (2001) in a survey of two Irish farms at Askeaton, Co. Limerick reported an average value of 474 mg/kg Al in herbage.

Rees & Sidrak (1955) when investigating the reclaiming of pulverised coal ash deposits found high levels of aluminium accumulated in plants growing on fly ash at a pH of between 8.5 and 9. Jones (1961) demonstrated that mobile Al is present in fly ash at high pH values, presumably as a soluble aluminate and that it is available to plants growing in the ash.

Jackson (1967) stated that toxic effects of Al may result from excess Al in the growth medium with little or no change in the Al contents in the foliage.

Total aluminium in red mud includes all the aluminium present as oxide in undigested ore and alumina is normally available in different forms of sodium alumino-silicates (Thakur and Das, 1994). Total Al_2O_3 in red mud generally ranges from 11.9% - 24.1% depending on the nature of the ore and the digestion process used. AAL muds have an average Al_2O_3 content of 22% (Arup *et al*., 1993). Aluminium values as high as 13,530 mg/l have been extracted from red mud using a 2:1 citric and oxalic acid and subsequent H_2SO_4 addition to lower the pH to 1.5 (Vachon *et al*., 1994). Soluble levels of 1.04 mg/kg Al have been reported for unamended red mud (Wong and Ho, 1993). Levels as determined in saturated extracts have been reported to range from <5mg/l to 464 mg/l with a progressive increase in levels with distance from the perimeter dyke and aluminium concentrations significantly correlated with pH ($r^2 = 0.97$). (Fuller *et al*., 1982). The potential, therefore, exists for aluminium toxicity in red mud.

2.4.2.4 Iron

Iron is a major constituent of most soils. It may be present in highly insoluble forms causing Fe deficiencies or, in some soils, in forms soluble enough to be toxic to plants (Olson and Ellis, 1982). Total soil levels generally range from 3,000 mg/kg to 5,900 mg/kg (McGrath *et al.*, 2001) with extractable levels (DTPA) being much lower, ranging from 1.5 mg/kg to 160mg/kg with a level of 4.5 mg/kg identified as the minimum concentration adequate for healthy crop growth (Follett and Lindsay, 1970). No reference was found in the literature for soil iron levels using DTPA extraction technique that may be toxic (Munshower, 1994). Red muds will, typically, have a high iron oxide (Fe_2O_3) content, Prasad *et al.* (1996) cite a range of 24.5 – 54.8 % wt. for a variety of red mud samples.

Iron is an essential element for plants. It is an active component of many enzymes, essential for chlorophyll synthesis, and is involved in electron transfer. Normal plant concentrations range from 40 mg/kg in many grasses, to several hundred micrograms per gram in specific shrubs (Munshower, 1994). Plant growth can be retarded where Fe content exceeds 200 mg/kg (Chapman, 1966) and levels above 60 mg/kg are considered high for *Lolium perenne* (Reuter & Robinson, 1986). A typical herbage Fe value of 150 mg/kg has been reported for unpolluted Irish pasture although maximum levels can reach over 400 mg/kg (McGrath *et al.*, 2001).

A number of variables can affect iron solubility and plant availability. Iron has minimum solubility in the pH range of 7.4 and 8.5, which is the pH range of soils in which iron deficiencies are most common (Lindsay, 1979). Well drained soils are associated with the ferric ion (Fe^{3+}) which is insoluble compared to ferrous iron (Fe^{2+}) associated with waterlogged soils (Troeh and Thompson, 1993). Excessive concentrations of Fe, mostly in the ferrous state is common in soils having poor aeration and plants growing in such cases may develop toxicity symptoms (Olson and Ellis, 1982). Fe deficiencies have been reported for sodic soils (Gupta and Abrol, 1990).

Water extractable iron in red mud has been reported at 11.3 mg/kg in fine residue and 10.5 mg/kg in coarse residue whilst levels of 35 mg/kg have been extracted with NH_4CO_3 DTPA from fine residue (Bucher, 1985). Total iron levels of >0.2% have been reported for *Agropyron elongatum* and *Cynodon dactylon* grown in unamended red mud and, as such, would retard plant growth (Wong and Ho, 1994).

2.4.2.5 Calcium

Calcium is the most common element on the exchange site of the vast majority of soils (Thomas, 1982). Exceptions to this are acid soils where hydrogen or aluminium ions may dominate or sodic soils in which sodium ions are very common. Calcium in soils can be classified as non-exchangeable, exchangeable and soil solution Ca^{2+}. Exchangeable calcium is the major reserve of soil Ca available to plant roots and can range from less than 25 mg/kg to more than 5,000 mg/kg (Haby *et al.*, 1990).

Calcium has many roles in plants and is associated primarily with cell wall structure. It is also involved in many cellular physiologic activities (Munshower, 1994; Reid and Smith, 2000).

Typical calcium concentrations for Irish grasses are in the region of 0.6%, but can range from 0.14 % to 1.8% (Rogers and Murphy, 2000) with an animal requirement value reported as 0.29% (McGrath *et al.*, 2001). A complicating factor is the interaction of Ca with other elements under abnormal or stress conditions such as high salinity activities (Munshower, 1994; Reid & Smith, 2000). In these circumstances plant growth may relate more to the protective effect of high Ca concentrations than to the amounts needed for incorporation into physical structures such as cell walls. Calcium ameliorates the toxic effects of elevated concentrations of metals such as aluminium, lead and copper (Munshower, 1994).

Increasing NaCl salinity causes an inhibition of growth of most crop plants, possibly caused by the inability to effectively regulate ionic and osmotic environment (Reid and Smith, 2000) and sodic soil conditions may induce Ca deficiency (Rhoades and Miyamoto, 1990). However, amelioration by increasing Ca in the rhizosphere has been shown to improve root elongation (Kent and Läuchli 1985; Kurth *et al.* 1986) and shoot growth (Cramer *et al.* 1989; Yeo *et al.* 1991; Cramer 1992), and to abolish symptoms of Ca deficiency (Maas and Grieve 1987; Ehret *et al.* 1990).

Calcium levels typical of red mud have been reported as ≤3.2 mg/l (Fuller et al., 1982), 8.3 mg/kg for fine bauxite residue (Bucher, 1985), and 5.43 mg/kg for red mud (Wong and Ho, 1993). Such levels are at the lower end of those normally reported for soils (Table 2.1) and have little impact in lowering ESP levels.

2.4.2.6 Magnesium

Magnesium is a recognised essential plant nutrient. Total Mg values for non-polluted Irish Agricultural Soils have been reported at 1,000 to 15,000 mg/kg (McGrath *et al.*, 2001). Concentrations in grasses range from 0.1 to 0.5%. The main concerns about magnesium levels are deficiencies, not excesses. Levels in plant tissues above 0.2% indicate an absence of deficiency symptoms (Chapman, 1966).

Because magnesium soil deficiencies or toxicities are so rare in soils, analysis for the element in mine/tailings related soils would not normally be justifiable except for the determination of SAR (Munshower, 1994).

2.4.2.7 Manganese

Total levels of manganese in Irish soils range from 20-3,000 mg/kg and easily reducible levels range from 10-600 mg/l (McGrath et al., 2001).

Plant levels are variable, but are reported to range from less than 20 mg/kg to slightly over 100mg/kg in most grasses, forbs and shrubs with 120 mg/kg being typical for Irish grasses (Munshower, 1984; Rogers & Murphy, 2000). A value of 40 mg/kg is given for animal requirement (McGrath *et al.*, 2001) and tissue levels below 20 mg/kg are considered deficient for *Trifolium* sp. and many grasses (Reuter and Robinson, 1986). Wong and Ho (1993) highlighted Mn deficiency as a potential limiting factor for vegetative growth on red mud.

2.4.2.8 *Zinc*

Zinc is an essential nutrient for function, structure, and/or plant regulation of many diverse enzymes (Munshower, 1994). A crop adequacy level of 1.0 mg/kg DTPA-extractable zinc has been reported for Colarado soils (Follett and Lindsay, 1970). Phytotoxic responses are generally in the range of 50 mg/kg - 125 mg/kg DTPA-extractable zinc.

Normal plant tissue levels are in the range of 10 mg/kg – 50 mg/kg dry plant tissue. Phytotoxic levels are normally reported at levels in excess of 300 mg/kg and deficiency at levels below 12 mg/kg (Reuter and Robinson, 1986; Kabata-Pendias and Pendias, 1992).

2.4.2.9 Copper

Copper is an essential plant nutrient and plays a direct role in plant metabolism. DTPA extractable copper in U.S soils ranged from 0.1 mg/kg to 3.7 mg/kg (Follett & Lindsay, 1970).

Average copper levels for Irish grasses is 9.2 mg/kg DM (Rogers and Murphy, 2000) with the Agricultural Research Council in the U.K. (1965) recommending 5 mg/kg to 10 mg/kg copper as a dietary requirement for cattle. Levels greater than 5 mg/kg are considered adequate for *Trifolium* sp. growth (Reuter & Robinson, 1986). Toxic symptoms occur when levels exceed 150 mg/kg and most plants die in the presence of 1000 mg/kg total copper in the substrate (Williamson *et al*., 1982).

2.4.2.10 *Potassium*

Total potassium in a soil can range from 1,000 to 30,000 mg/kg (McGrath *et al*., 2001). A relatively small portion of K in soils is exchangeable (approx. 1%) and this form is considered the primary source of K for plant uptake (Knudsen *et al*., 1986). Potassium is an essential element for plant growth with normal levels in Irish grasses being in the region of 2.8% (Rogers and Murphy, 2000). Potassium levels in soil are normally determined by measuring exchangeable levels with ammonium acetate extraction.

2.4.2.11 Plant Nutrients

Typically, mine wastes and wastes derived from mining activities, such as metal refineries, are deficient in essential plant nutrients and have limited availability of essential macro and micro nutrients for plant growth (Wong and Ho, 1994). Nitrogen levels of 0.02% total nitrogen have been reported for red mud (Wong and Ho, 1991) and phosphorous levels are generally low in mine wastes (Bradshaw and Johnson, 1992). Accumulation of nutrients has been identified as a critical issue in the development of vegetative ecosystems in reclamation (Bradshaw *et al.*, 1975). The use of fertilisers is widespread in land rehabilitation with nitrogen being the most commonly applied nutrient (Munshower, 1994).

Compound fertilisers that supply nitrogen, phosphorous and potassium are available and the percent composition of the three nutrients is normally printed on the outside of the fertiliser bag. A NPK fertiliser 17:17:17 supplies 17% N, 17% P_2O_5 (7.5% P) and 17% K_2O (14%K) by weight (Williamson et al., 1982).

One of the main nutritional disorders associated with sodic soils is the impaired uptake of Ca caused by high Na concentrations in the soil solution. Deficiencies of the micronutrients Zn and Mn have been reported in sodic soils (Gupta and Abrol, 1990). Increased sodicity results with lower plant uptake of Zn, Cu and Mn and increased Na concentrations (Summer and Naidu, 1998). Plant-available Mn is more dependent on pH than any other factor (Adams, 1965) and manganese deficiencies are most likely to occur under high pH conditions (Gambrell and Patrick, 1986).

		Ranges (mg/kg)		
Element	Total	Extractable or Soluble	Low or Deficient	High or Toxic
Na (ESP%)			NA	>15%
Al	7,000	varies with pH	NA	0.5-3
Fe	80,000mg/kg	1.5-160	2	60
Ca	3,000-5,900(mg/kg)	<25- 5,000		
Mg	0.1-5%			
Mn	20-3000(mg/kg)	1-40	20	Unknown
Zn			<10	300
Cu	2-90%	0.1-3.7	0.2	Unknown
K	1,000-30,000 mg/kg	1%		

NA Not applicable – element not required for plant growth

Table 2.1 Typical Element Ranges in Soils
(after Chapman, 1966; Follett and Lindsay, 1970; Munshower, 1984)

Element	Deficient	Normal	High	Toxic
Na (%)*	NA	0.3-1.2	1	>1
Al (mg/kg)*	NA		>100	
Fe (mg/kg)	<45	50-150	>200	
Ca (%)	<0.3	0.4-1.8	>4	
Mg (%)	<0.1	0.1-0.5	>3	
Mn (mg/kg)	<20	20-120	>250	
Zn (mg/kg)	<12	10-50	>300	
Cu (mg/kg)	<10	4-12	>10	>150
K (%)	<1	1.2-2.8	>3	

* Plant vary in their tolerance to high levels of these elements
NA Not applicable – element not required for plant growth

Table 2.2 Typical Mineral Levels in Pasture Grass
(after Reuter and Robinson, 1986; Munshower, 1984; Murphy and Rogers, 2000)

2.4.3 Physical Constraints

2.4.3.1 Texture

The term texture describes the proportion by weight of the soil fractions (*sand, silt* and *clay)*. In the classification of these fractions sand has the greatest diameter at 0.05-2mm, silt 0.002-0.05 mm and clay <0.02 mm. Texture has a very important influence on the way a soil can be managed as it influences most of the physical and chemical properties. An excess of particles of one size adversely affects the properties as a growth medium as texture has a direct effect on soil aeration, water infiltration, cation exchange capacity (CEC) and erodibility (Williamson *et al.*, 1982; Munshower, 1993; Troeh and Thompson, 1993).

Sandy material is unstructured and has large pores between particles which allows for good aeration and infiltration. However, water retention is poor and the material tends to dry out easily. Clay material has very small particles with little pore space and poor aeration. It tends to be dense with a high proportion of moisture bound to the particles and unavailable for plant growth (Williamson *et al.*, 1982). Meecham and Bell (1977) attributed poor germination of Rhodes grass in bauxite residue trials to physical limitations of mechanical impedance and low water holding capacity.

Soil texture also has a profound influence on erodibility by wind. Fine-textured soils have too much clay fraction and produce clods, which under the action of wetting and drying and freezing and thawing readily disintegrate to a finely, granulated, erodible condition. Coarse-textured soils lack sufficient amounts of silt and clay to bind individual sand particles together. Such soils form a single grain structure that are susceptible to erosion by wind, or they may form weakly cemented clods that are easily broken down and eroded by the wind (Chepil, 1953).

2.4.3.2 Organic Matter

The organic content of a normal soil is usually in the range of 2-5% but non-rehabilitated mine wastes usually have none. Organic matter, being loose and fibrous, has a beneficial effect on soil in that it binds materials, increases porosity, infiltration, CEC and water holding capacity (Williamson *et al.*, 1982). Its absence from mine wastes can therefore have major deleterious effects on plant growth.

2.5 Chemical Amendment of Sodic/Alkaline substrate

The basic physical and chemical principles for reclaiming alkaline-sodic soils are long established . The underlying principles of ameliorating alkaline soils are:

- creation of drainage if high water table exists
- replacement of sodium absorbed on the soil exchange complex by calcium or other divalent cations
- removal of excess salts by leaching
- rearrangement and aggregation of soil particles so as to improve soil structure

(Bower, 1951).

Calcium chloride ($CaCl_2$), Magnesium Chloride ($MgCl_2$) and phosphogypsum ($CaSO_4.2H_2O$) have all been used for reclamation of alkaline and sodic soils. Magnesium chloride and phosphogypsum are industrial wastes and are not widely used. Calcium chloride is more soluble than gypsum but more expensive (Shainberg *et al.*, 1982; Munshower, 1994). Gypsum ($CaSO_4.2H_2O$) is most commonly used for reclaiming saline/alkaline soils (Overstreet *et al.*, 1951; Loveday and Scotter, 1966) to bring about changes in physical characteristics which affect tillage operations such as infiltration (Shainberg *et al.*, 1982), reduction in exchangeable Na (Loveday and Scotter, 1966), improved seedbed conditions (Webster and Nyborg, 1986) and improving seedling emergence, growth and yield (Shainberg *et al.*, 1982; McKenzie *et al.*, 1993).

Gypsum amendment improves the soil structure through exchange of calcium for sodium from the soil exchange sites resulting in the creation of the soil structure and high permeability of the soil (Oster and Frenkel, 1981; Gupta and Singh 1988; Gupta et al., 1985; Chun *et al.*, 2001). Increased electrolyte concentration following gypsum amendment inhibits clay dispersion, which helps to maintain pore space and markedly increases hydraulic conductivity (Scotter and Loveday, 1966; Munear and Oades 1989). Davidson and Quirk (1961) obtained increased infiltration with gypsum in irrigation water and Sedgeley (1962) showed that gypsum increased pore-space in the seedbed.

Exchange reaction between calcium from gypsum and sodium in alkaline soil has a permanent effect in reducing the ESP (Gupta and Singh, 1988). This, in turn, contributes to a further pH reduction because more OH^- is absorbed by a soil containing calcium at the exchange sites.

The following equations illustrate how gypsum reacts with sodic substrates. Most of the Na^+ ions present on the cation exchange site should be replaced by Ca^{2+} so that dispersion will not occur.

$$2NaX + CaSO_4 \Longleftrightarrow CaX_2 + 2Na^+ + SO_4^{2-}$$ (after Gupta et al., 1985)

where X is the soil exchange complex

$$Na_2CO_3 + CaSO_4 \longrightarrow Na_2SO_4 + CaCO_3$$ (after Troeh & Thompson, 1993)

The sodium sulphate formed is a soluble neutral salt and can be leached from the soil. Enough Ca^{2+} should be present in solution to cause the above reaction to replace nearly all of the Na^+ on the micelles. Also, enough gypsum must be present to remove carbonate ion from solution. Na_2CO_3 in solution produces a high pH (Gupta *et al.*, 1985; Troeh andThompson, 1993).

2.6 Use of Organic Matter as Amendments

The physical characteristics of residues from ore processing have been improved by the addition of organic matter such as sewage sludge and agri-wastes. Organic matter binds soil particles together into aggregates thus increasing water and nutrient holding capacity as well as altering soil structure, thereby, improving surface stability, aeration and water penetration (Williamson *et al.*, 1982; Coker, 1983; Wong and Ho, 1991). Addition of organic matter to sodic soils increases permeability through the creation of pores and microbial or faunal activity that is stimulated by these additions may reduce soil pH and ESP (Robbins, 1986). High organic matter content makes soils less susceptible to the unfavourable influence of exchangeable Na (Aylmore and Sills, 1982). Campbell and Richards (1950) reported that peat and muck soils containing appreciable quantities of exchangeable sodium had good physical properties.

Organic matter also contains small quantities of nutrients as well as providing an energy source for decomposer organisms to break down complex organic molecules into simpler elemental forms. Nutrients are released into the soil solution during the process (Munshower, 1994). Organic matter may also act as a source of micro-organisms thus improving the root zone and increasing germination as well as seedling emergence (Williamson *et al.*, 1982; Munshower, 1994).

The addition of a variety of organic ameliorants is practised in the reclamation of alkaline and sodic soils (Puttaswamygowda, 1973; More, 1994). The addition of organic matter and the microbial and faunal activity that is stimulated by these additions may reduce soil pH and ESP by a number of mechanisms. Acidification mechanisms such as the dissociation of carbonic acid (H_2CO_3) and organic acids may help to reduce pH. Organic matter's cation exchange capacity (CEC) and the selectivity of exchange sites for Ca over Na may decrease the degree of sodicity. (Summer and Naidu, 1998).

2.7 Wastes as Ameliorants

2.7.1 Sewage Sludge

This material is removed from waste-water at sewage treatment plants. Although sewage sludge begins as a material made up primarily of water, its solids content can be increased by any of several successive steps. Waste-water contains <3% dry solids, liquid sludge generally has <10% dry solids and dewatered sewage sludge has a dry solids content of 20-40%. Percent dry solids can be further increased by means of composting (>70%) and ≥90% by drying to granulate form (Mayr, 1998).

Sewage Sludge has frequently been used in reclamation schemes (Wong and Lai, 1982). It tends to have a variable nutrient status but is generally high in nitrogen (2.5%) and low in potassium (1.0% as K_2O_5). The addition of sewage sludge to a soil increases water holding capacity and CEC, while reducing bulk density and surface temperature. It also ameliorates pH extremes (Munshower, 1994). The organic content of sewage sludge binds soil particles together into aggregates which have a significant effect on soil structure by increasing porosity and pore size distribution (Wong and Ho, 1991). Water holding capacity also increases because of the decrease in bulk density and the increase in porosity (Epstein *et al.*, 1976).

Sewage sludge can contain elements that, when occurring in excessive amounts or higher than that normally found in soils, can be of significance. While some of these are plant nutrients at low concentrations they can present a phyto-toxic hazard at high concentrations. Continued application of sewage sludge to a site may produce elevated levels of such elements, including zinc and copper (Coker, 1988; Munshower, 1994). The application of sewage sludge to agricultural soils is governed by the Statutory Instrument No. 148 of 1998, "Use of Sewage Sludge in Agriculture", this enacts the EU Council Directive 86/278 on the protection of the environment when sewage sludge is used in agriculture. While not strictly relevant in all circumstances it is advisable to adhere to the legislation. Routine sampling of both the sample sludge and receiving substrate should ensure no metal or nutrient overload.

Wastewater treatment plant serving population equivalents >1000 produce sludge estimated at 37,577 tonnes dry solids (TDS) per annum (EPA, 2000). Its low solids content (9-13%) makes the material difficult to handle and incorporate in the substrate. Unstabilised sludge generally has a high pathogen content and also presents an odour problem (Coker, 1988).

2.7.1.1 Thermally Dried Sewage Sludge (TDSS)

Thermally dried sludge is derived from secondary sewage sludge via a thermal drying process at temperatures in excess of 400°C. The end product is a 95% dry matter 2mm to 4mm granule with a typical nitrogen content of 3% and a phosphorous content of 4%.

Currently the only thermally dried sewage sludge produced in Ireland is at Ringsend, Co. Dublin by Swiss Combi Technology and is marketed as Biofert™. This plant has a design output of 90 t d/s per day but is currently only producing 40-45 t d/s per day. Further thermal drying sludge units are planned for Limerick, to go on stream by 2003, and for Cork in 2005 both to produce in the region of 18 t d/s per day.

The dry solid content of TDSS is significantly higher than any conventionally produced sludge and therefore, per tonne inputs of organic matter, nitrogen and phosphorous are much greater (Anon, 1998). While it is recognised that TDSS contains the metal elements associated with sewage sludge, regulatory monitoring should ensure that the level of metal loading is within permissible limits.

Thermally dried sewage sludge has been used at former opencast coal mining sites in East Methyr, Mid Glamorgan, Wales. This trial work consisted of the establishment of tree and shrub species (Japanese larch, silver birch, *Rosa* spp., *Cotoneaster* spp.) on spoil heaps (Anon, 1998). Whilst there is no literature supporting the use of TDSS in establishing grass ecosystems on industrial spoil and wastes, it has been used as a nutritional additive to established grasses.

2.7.2 Dairy Industry Biosolid (DIB)

The Waterford Food Plant at Virginia, County Cavan produces 12 t per week. As with all organic wastes, nutrient content will vary. As such, sludges are mostly specific to one plant and have limited sewage content. They offer reduced pathogens and PTEs and consequently may be more attractive than sewage sludge.

Lehrsch and Robbins (1994) used cheese whey for amending sodic soil aggregate stability.

2.7.3 Spent Mushroom Compost (SMC)

Mushrooms are produced in compost prepared from straw, animal manure and gypsum at a rate of 70kg per tonne of dry straw. When the compost can no longer produce economic levels of mushroom it is termed 'Spent Mushroom Compost' and is produced at a rate of 260,000 t per annum for the entire Irish industry (Lenehan *et al.*, 1993). Mushroom producers are concentrated into distinct geographic locations such as counties Monaghan, Cavan and Wexford.

SMC is an attractive ameliorant as it has a high organic matter content and is fairly high in macro-nutrients N, P, and K. Calcium levels are, however, variable. It also has a low content of heavy metals (Maher, 1988). Like many other organic sources of nutrients it can be considered an unbalanced fertiliser as macro-nutrients are not in the required proportion for optimal plant nutrition (Munshower, 1994).

Disposal options are limited with just over 55% going to landspreading and the remainder by dumping, land burial, landfills and quarries where the compost is often co-disposed with the bags. Over 8% of SMC disposal is unaccounted for (Lenehan *et al.*, 1993).

2.7.4 Agricultural Manure

Currently 37 M tonnes cattle slurry, 1.8 M tonnes poultry litter and 2.6 M tonnes pig manure is produced annually in Ireland (EPA, 1998). While much of this is applied to agricultural land it is not a feasible option in every case.

Manure is useful in reclamation as it provides a valuable source of organic matter. It provides a slow release source of both major and minor nutrients and is a physical ameliorant. Nutrient content of manure is variable and will depend *inter alia* on the quality of the animal fodder and the animal species. The material can be used fresh or matured (Williamson *et al.*, 1982; Munshower, 1994).

2.8 Red Mud Reclamation

Over the past 20 years many different physical, chemical and biological approaches have been proposed to neutralise and rehabilitate red mud.

Meecham and Bell (1977) achieved pH and alkalinity reduction by the application of H_2SO_4. They also found that $FeSO_4.7H_2O$, FeS_2 and S are effective agents in reducing alkalinity and excessive ESP, while Barrow (1982) demonstrated that the caustic residue can be converted to a material capable of supporting plant growth. However, this requires the addition of gypsum and leaching to remove the resulting sodium sulfate and a supply of nutrients.

Meecham and Bell (1977) at Gladstone, Australia, also successfully used iron sulphate ($FeSO_4.7H_2O$) amendment to lower excessive sodicity in coarse fraction bauxite residue red/process sand. Ho *et al.* (1985) using copperas (iron sulphate) at a rate of 5 to 7 % w/w effectively reduced the alkalinity of red mud. However, their work only addressed the chemical improvement of the residue at pot trial stage and did not deal with vegetation issues.

Meecham and Bell (1977) reduced the constraints of excessive salinity, alkalinity and sodicity of red sand by acidifying with HCl. Poor germination of *Chloris gayanna* (Rhodes grass) in some mixes was attributed to mechanical impedance as well as low water holding capacity of the mud. They concluded that water availability and poor aeration appear to be limiting factors for growth.

Most published work on the reclamation of red mud residue cites the use of gypsum. Marschner (1983) carried out greenhouse pot trials on red mud with a gypsum addition rate of 20 t/ha reducing pH from 11.2 to 9.9 and similar work was carried out by Bucher (1985). Workers Wong and Ho (1991, 1993 and 1994) carried out pot trials with gypsum at rates of 0, 2, 5 and 8% (w/w) to reduce pH and sodicity of red mud to improve conditions for seedling growth. It was reported that optimum plant growth was achieved when red mud was amended with >5% gypsum prior to organic matter addition and seeding.

Growth was also limited by low nitrogen and phosphorous levels. Wong and Ho (1993) noted that the coarse residue fraction presents fewer difficulties in revegetation because of its higher hydraulic conductivity, which effectively reduces its salinity and alkalinity with increased leaching. Earlier studies by the authors (Wong and Ho, 1991) found that the addition of sewage sludge and gypsum significantly improved soil structure and the hydraulic conductivity of red mud in pot trials.

In attempting to establish vegetation on red mud a number of species have been used. Grasses tolerant of alkaline and sodic soils have been used by several workers; *Distichlis spicata* (Fuller *et al.*, 1982; Marschner 1983; Bucher, 1985); *Sporobolus airoides* (Nelson, 1981; Fuller *et al.*, 1982); *Agropyron smithii* (Nelson, 1981; Fuller *et al.*, 1982; Bucher, 1985); *A. elongatum* (Nelson, 1981; Fuller *et al.*, 1982; Marschner, 1983; Bucher, 1985; Wong and Ho, 1991 and 1993); *Cynodon dactylon* (Wong & Ho, 1993); *Chloris gayana* (Meecham and Bell, 1977); and *Puccinellia distans* (Fortin and Karam, 1998).

Meecham and Bell (1977) found acceptable growth for *Chloris gayanna* in greenhouse trials in coarse textured red mud when the pH was reduced to between 7 and 8 by acidification with HCl. They also reported that Alcoa trials found *Cynodon dactylon* (Bermuda grass) amended with paper pulp waste responded well only when also amended with gypsum. Wong and Ho (1993) found that in non-amended red mud *Agropyron* and *Cynodon* seedlings died within the first week of growth. Seedling emergence and biomass were improved with gypsum additions of >5%. Poor plant performance was correlated with soil pH, Al and ESP, and that sodium concentrations were lower in treatments receiving higher gypsum additions. Low Mn concentrations were recorded for all treatments and Mn deficiency is cited as a possible restraint in obtaining satisfactory long-term growth.

Fortin and Karam (1998) using peat-moss/shrimp wastes as an ameliorant in greenhouse trials demonstrated that organic addition decreased exchangeable sodium of the red mud whilst increasing organic carbon and exchangeable calcium. Dry weight biomass for *Puccinellia distans* was improved with an increase in compost rate addition.

Workers Wong and Ho (1991) concluded that more than one growing season would be needed to evaluate the long term effect of gypsum and sewage sludge in improving the properties of red mud.

It is also noted that Fuller (1982), in determining the chemical properties of a red mud impoundment with distance from the perimeter dike, reported wide ranges for the parameters restrictive to plant growth. Levels recorded for pH ranged from 9.2 – 11.5, Al in saturation extracts ranged from 4.4 mg/l to 414 mg/l, Na from 399 mg/l to 4,553 mg/l and ESP from 52.7 to 90.9 with all parameters peaking beyond a distance of 30m. It can therefore be said that rehabilitation procedures developed for one area of a mud disposal area may not always translate to another.

2.9 Plant Species Selection

The success of a reclamation programme is extremely dependant upon species selection. Performance at germination is important as poor crop production results from plants failing to obtain a good stand (Richards, 1954; Williamson *et al.*, 1982).

Several criteria are considered in selecting the most apposite species for a seed mixture. These include:-

- its tolerance to adverse chemical conditions (e.g. pH extremes, high metal content)
- natural colonisers (such species often possess adaptations to particular facets of environmental stress)
- the ability of the species to withstand the adverse environmental conditions, such as drought, and to stabilise the substrate through well developed root systems

- eventual land use
- the commercial availability of the seeds

(Jeffrey *et al.*, 1974; Williamson *et al.*, 1982)

In addition, selected species should contribute to the attainment of the land-use goal for the site. These would typically include soil stabilisation, erosion control, and soil development (Munshower, 1994).

In the screening of species for reclamation trials, growth tests are used to establish the tolerance of a plant by measuring the rate of seedling germination and plant survival in the substrate (Walley *et al.*, 1971). Measurements of biomass and shoot height are also used to determine the suitability of a species (Johnson and Proctor, 1981).

It is also desirable to establish the metal tolerance of species being used in vegetation trials. In addition to measuring plant growth and yield, metal uptake and accumulation in the plants should also be determined (Baker and Walker, 1989).

Available published work on red mud vegetation trials cites the use of species commonly found on saline/sodic soils, such as those listed in Section 2.8, due to the many similarities of the substrates (high pH, high Na). Such species are not indigenous to Ireland and are therefore not regarded as potential candidates for the trial work at AAL. In addition, legislation such as the U.S. Surface Mining Control and Reclamation Act (PL 95-87, August 1977) requires that the plant community on reclaimed land should mimic the life forms, if not the species, found in the pre-disturbance inventory (Munshower, 1994).

Considerable research has been carried out in temperate climates in vegetating mine tailings with grassland species. Table 2.3 shows grass and leguminous species commonly used in reclamation work within European temperate climatic zones.

Scientific Name	Common Name
GRASSES	
Agrostis gigantea	Black Bent
Agrostis stolonifera	Creeping/bentgrass
Agrostis tenuis	Bentgrass (browntop)
Alope curus pratensis	Meadow foxtail
Dactylis glomerata	Cocksfoot
Deschampsia caespitosa	Tufted hairgrass
Deschampsia flexuosa	Wavy hairgrass
Festuca arundinacea	Tall fescue
Festuca ovina	Sheep's fescue
Festuca rubra	Red fescue
Festuca pratensis	Meadow fescue
Lolium perenne	Perennial ryegrass
Phleum pratense	Timothy
Poa compressa	Canada bluegrass
Poa pratensis	Rough stalked meadow grass
LEGUMES	
Coronilla varia	Crown vetch
Lathyrus sylestris	Mat peavine
Lotus coriniculatus	Birdsfoot trefoil
Lupinus arboreus	Tree lupin
Medicago sativa	Lucerne
Melilotus alba	Sweet clover
Trifolium hydridum	Alsike clover
Trifolium pratense	Red clover
Trifolium repens	White clover
Ulex europaeus	Gorse

Table 2.3: Grasses and Legumes commonly used for Mine Waste Rehabilitation in Temperate Climates (after Williamson *et al.*, 1982).

Agricultural forage species such as *Lolium perenne* (ryegrass), *Dactylis glomerata* (cocksfoot) and *Phleum pratense* (timothy) are widely used in vegetating mine wastes Such species can grow over a broad range of pH if adequate nutrients are available. (Williamson *et al.*, 1982).

Where a non-intensive option is being sought the use of amenity grass such as the fine fescues or bents are favoured. Maintenance such as mowing, grazing or fertilisation is reduced. Fescues and bents are slower growing species and will not provide rapid ground cover. It is, therefore, beneficial to include a small percentage of a rapid growing grass such as *Lolium* sp. or *Avena* sp. in the seed mixture to act as a nurse crop for the slower growing species. With time the nurse crop may be replaced by species more suited to low nutrient conditions of the substrate (Williamson *et al.*, 1982).

Long-term growth of vegetation depends on an adequate supply of nitrogen. The use of legumes such as white clover (*Trifolium repens*), birdsfoot trefoil (*Lotus corniculatus*) and related species are important in a seed mixture for initial build-up and long-term maintenance of nitrogen levels. The presence of legumes in N-deficient soils results in greatly increased dry matter production for their own growth and also in increased growth by associated plants (Jeffrey *et al.*, 1974; Bradshaw and Johnson, 1990).

Tolerant cultivars can also be used as potential candidates. *Festuca rubra* cv. Merlin is a useful species for Pb/Zn wastes (Williamson *et al.*, 1982) while *Agrostis stolonifera* cv. Seaside has shown to be successful for the saline environment of the lead/zinc tailings pond at Silvermines, Tipperary (Tierney, 1998). However, many of these cultivars can be superseded by newer cultivars and it is, consequently, difficult to obtain sufficient seed for reclamation schemes.

British grasses most tolerant to salt are the slender creeping red fescues of coastal or sea marsh origin e.g. *Festuca rubra* ssp. *litoralis* "Dawson" and "Oasis" cultivars and *Agrostis stolonifera*. Least tolerant are *Agrostis canina* and *Poa annua* (annual meadow grass) (Williamson *et al*., 1982).

Species used in the vegetation at Irish mine sites include *Agrostis stolonifera* Seaside, *Agrostis tenuis* Parys and *Holcus lanatus* (Tierney, 1998). Below are the species selected from trials conducted at the tailings pond of Outokumpu, Tara Mines Zinc/Lead mine which are most suited to the particular conditions presented (Brady, 1993).

Festuca rubra cv. Merlin;
Poa compressa cv. Reubens;
Agrostis capillaris cv. Goginan;
Agrostis stolonifera cv. Emerald;
Festuca rubra cv. Dawson;
Trifolium repens cv. S 184
Festuca rubra cv. Dawson

2.10 Metal Availability

Availability of metal elements in residues from ore materials or industrial activities can inhibit plant establishment and growth on the wastes (Whitely and Williams, 1993; Pitchel and Salt, 1998). Metals on industrial residues can occur in complex forms and will vary widely in their availability to plants (Kabata-Pendias and Pendias, 1992; Freedman and Hutchinson, 1981; Thornton, 1981). For successful vegetation growth and survival it is important to know the degree of plant tolerance and while plant uptake of metals and dry matter production can serve as a measure of a plant's suitability for a particular site there is little information available on the suitability of soil extractions for prediction of metal availability on contaminated soils (Pitchel and Salt, 1998).

As the single knowledge of the total amount of a metal in a residue does not predict its behaviour, a quantitative determination of the physio-chemical forms of this metal by a speciation scheme becomes necessary for the real assessment of its mobility and plant availability (Gommy *et al*., 1998). Thus an appreciation of the effect of metals in the substrate on crops can only be attained from a knowledge of metal speciation and the response of the plants to each species (Sterritt and Lester, 1980).

Elements can be present in a soil in a variety of physio-chemical forms ranging from free and complexed ions in the soil solution, as non-specifically and specifically adsorbed cations, as occluded and precipitated and in the lattice structure of minerals (Lake et al 1984; Martens & Lindsay, 1990; Basta & Gradwohl, 2000). Increasing evidence demonstrating that exchangeable metals better correlate with plant uptake has lead extraction methodology to evolve towards the use of less and less aggressive solutions (Gupta, 1993).

Extraction procedures can be divided into two groups of tests. The single reagent extraction test, that is one extraction solution and one soil sample; and, sequential extraction procedures where several extraction solutions are used sequentially on the same sample, although this type of extraction is still in development for soils (Rauret, 1998).

Single extraction procedures are designed to dissolve a phase whose element content is correlated with the availability of the element to the plants. Extractants used include a large spectra of extractants ranging from very strong acids, such as aqua regia, nitric acid or hydrochloric, to neutral unbuffered salt solutions, mainly $CaCl_2$ or $NaNO_3$. Other extractants such as buffered salt solutions or complexing agents are frequently applied, because of their ability to form very stable water soluble complexes with a range of cations.

Insoluble forms of trace elements do not influence plant uptake or animal tissue levels. Extractable, available or soluble forms are of greater importance for determining plant availabiltiy. Water soluble elemental concentrations are often used in studies of toxic concentrations of metals (Munshower, 1994). However, extractions with water may give an unbalanced picture of ionic relationships since the plants are able to absorb nutrients from the micellar solutions associated with clays as well as from the true solution (Clarkson, 1970).

In determining the exchangeable fraction several salt solutions have been used. The cations magnesium, calcium, barium, ammonium, potassium or sodium are normally employed with the anions acetate, chloride and nitrate (Gommy *et al.*, 1998). Calcium chloride ($CaCl_2$) has been widely employed (McLaren and Crawford, 1973; Alloway et al, 1979), as has KNO_3 (Silviera and Summers, 1977; Petruzzelli *et al.*, 1981; Sposito *et al.*, 1982).

Little or no measurable Fe is extracted with 1N NH_4OAc in alkaline soils (Olson and Ellis, 1986). Synthetic chelating agents are widely used to determine readily available forms of trace metals. The amount of chelated metals that accumulates in solution during extraction is a function of both the activity of metal ions in the soil and the ability of the soil to replenish those ions. Both factors are important in determining the availability of elements to plants (Norvell and Lindsay, 1972).

The use of a variety of chelating agents has been reported in the literature. Ethylene-diamine-tetraacetic acid (EDTA) (Norvell and Lindsay, 1969; Trierweiler and Lindsay, 1969; Pichtel and Salt, 1998), Mehlich (Vocaseck and Friedericks, 1994; Pichtel and Salt, 1998) and Diethylene-triamine-pentaacetic acid (DTPA) (Norvell and Lindsay, 1972; Lindsay and Norvell, 1978; Petruzzelli *et al.*, 1981; Hooda and Alloway, 1993; Pichtel and Salt, 1998). DTPA is the most useful chelate to use as an extractant for simultaneous measurements of available Zn, Fe, Mn, and Cu (Lindsay & Norvell, 1978).

Good correlations between nutrient concentrations in plants and substrate extracts with DTPA for zinc, copper, iron and manganese have been made (Lindsay and Norvell, 1978; Le Claire *et al.*, 1984; Xian 1989). Tiller *et al.* (1979) reported a positive correlation coefficient of 0.79 between DTPA-Zn and Zn concentration in rice plants. Authors Martens and Lindsay (1990) report the use of DTPA as a universal soil extractant for the determination of micro-nutrients.

Efforts have been made to determine the potential toxic fraction or species in different soils. Exchangeable aluminium, obtained by extraction with 1M KCl, was not correlated to the aluminium content of spruce seedlings (Van Pragg and Weissen, 1985), the aluminium content of roots, rhizomes and shoots of wood anemone (Tyler, 1976) or the aluminium toxicity to cotton (Adams and Lund, 1966; Adams and Hatchcock, 1984). Clarkson (1963) showed that exchangeable Al determined with 0.5M NH_4NO_3 was closely correlated with the amount of Al found in the roots of plants.

3.0 OBJECTIVES

The overall objective of the project is to establish vegetation on red mud, an alkaline sodium rich waste substrate, in a temperate climate at Aughinish Alumina, Co. Limerick. While previous red mud reclamation trials have been conducted they have utilised sodic/alkaline tolerant herbage species under non-temperate climatic conditions e.g. in Western Australia and Jamaica.

The aim of this research is to determine if species typical of Irish grassland are capable of growing in a sodic/ alkaline substrate and if amelioration is necessary. The effects of process sand, gypsum and organic matter amendments on the chemical properties of red mud and plant growth will also be investigated and critical levels of inhibitive parameters for plant growth in red mud will be determined.

A series of greenhouse screening experiments will be employed to determine the most apposite grass species and organic amendments to promote plant growth in red mud.

Field plot trials will also be implemented on the red mud stack at Aughinish Alumina, the aim of which is to investigate how species selected from the greenhouse screening, perform in amended red mud under the climatic conditions prevailing on the mudstack. Plant growth and the availability and uptake of nutritional and potentially toxic elements over a two-year growing period will also be investigated.

4.0 MATERIALS AND METHODS

The project was composed of three specific but related tasks; small pot screening stage, large pot trials and field trials.

4.1 Small Pot Trials

Small pot trials were composed of two separate stages. The initial screening of twenty species is referred to as Small Pot Trials (A). Due to high failure rates of species at this stage (Section 5.1.1) a second trial series was undertaken and this is referred to as Small Pot Trials (B).

All small pot trials were conducted indoors using artificial light and at room temperature. Gypsum was used as an amendment in the trials as other red mud workers had reported it to have a positive effect in lowering levels of critical parameters that inhibit plant growth (Section 2.8). Process sand, itself a by-product from the Bayer Process, was used to improve soil texture conditions due to its greater particle size. Wong and Ho (1993) noted that the coarse residue fraction presents fewer difficulties in revegetation because of its higher hydraulic conductivity, which effectively reduces its salinity and alkalinity with increased leaching.

All grass seeds used for the three trial stages were purchased from either, Dardis and Dunnes Agricultural store, Ashbourne, Co. Meath or Emorsgate Seeds, Norfolk, UK.

4.1.1 Small Pot Trials (A)

Initial screening commenced in April 1998. Red mud samples from AAL were thoroughly mixed with process sand and gypsum using a pug mill[1]. The trials were designed to investigate the effect of gypsum addition on seedling emergence in a red mud/process sand mixture and to determine the species most suited to red mud conditions. Treatments of red mud/ process sand (RMS) and red mud/ process sand with 3% gypsum (RMSG) were created and transferred to flower pots of 17 cm

[1] A pug mill is used in the ceramic industry to blend various clay mixes using rotating blades to chop the clay and then extrude it. It was thought that this method would simulate ploughing action.

diameter. Pots were filled to 18cm depth and the mud in each pot leached prior to seeding by gradually adding 300ml water to remove excess sodium through leaching.

Grasses as listed in Table 4.1 were then seeded in both treatments and the pots arranged in a randomised block fashion. Trials were then monitored on a weekly basis for germination and growth over an eight week period, during which the pots were watered daily.

Scientific Name	Common Name
Agrostis stolonifera Carmen	Creeping/bent grass Carmen
Agrostis stolonifera Providence	Creeping/bent grass Providence
Agrostis tenuis Bardot	Bentgrass (browntop)
Avena sativa	Oats
Carex flacca	Glaucous Sedge
Cynosurus cristatus	Crested Dogstail
Festuca litoralis Merlin	Coast Fescue
Festuca longifolia Dawson	Long Fescue
Festuca rubra	Red Fescue
Holcus lanatus	Yorkshire Fog
Juncus effuses	Soft Rush
Koeleria macrantha	Junegrass
Lolium perenne Wendy	Perennial Ryegrass
Phleum pratense	Timothy
Poa pratensis	Kentucky Bluegrass
Puccinelia distans	Reflexed Saltmarsh Grass
Trifolium pratense Rotra	Red Clover
Trifolium repens Huia	White Clover
Schoenoplectus lacustris	Club rush
Melaleuca leucadendron	White Tea Tree

Table 4.1. Species used for Small Pot Trial (A) Screening

4.1.2 Small Pot Trials (B)

Due to the limited success of the initial trials (Section 5.1.1) a second trial was conducted in June 1998. This work was carried out on different mud treatments using a mixing process similar to that used by Wong and Ho (1993). Mud samples were air-dried and ground to pass through a 2mm aperture sieve. Dried gypsum and/or process sand was then added at the same rates for Section 4.1.1 and thoroughly mixed with the red mud in bags by shaking. Organic matter at 5% w/w was also added to selected samples to determine its effect on plant growth. Mud treatments were:-

1. Red Mud (RM)
2. RM and Organic (RMO)
3. RM and Process Sand (RMS)
4. RM and Process Sand and Organic (RMSO)
5. RMS and Gypsum (RMSG)
6. RMS and Gypsum and Organic (RMSGO)
7. Control (Organic)

A.sativa (Oats) and *H.lanatus* (Yorkshire Fog) were selected for these trials as they had shown best germination success on initial red mud treatments (Section 5.1.1). Replicates (x3) of each of the above treatments were prepared in pots of 20cm diameter. Pots were leached, prior to sowing, with 1,200 ml water, equivalent to 100mm rainfall.

Pots were then seeded at the rate of 15 seeds/pot *A.sativa* and 100seeds/pot *H.lanatus*. Pots were arranged in a random block design and percentage germination as well as average shoot height was recorded on a weekly basis for eight weeks.

4.2 Large Pot Trials

In order for mud treatments to best simulate field conditions mud for these trials was prepared at AAL in early spring 1999. The mud had been deposited on this area of the site approximately two years previously and had been ploughed as a measure to control dusting within the preceding 12 months. An area of 23m^2 was rotovated to a depth of approximately 18 cm and process sand added at 25% w/w. Where gypsum was used it was added at 2% w/w. The amendments were raked in and rotovated a further two times. The site was allowed to weather until late April 1999 during which time it received 75mm rainfall (AAL Weather Data, 1999). At this time mud was put in sealed containers and transported to the Institute of Technology, Sligo (ITS).

Trials were then conducted in the greenhouse at ITS. Red mud treatments were transferred to pots 0.3m by 0.4m and filled to a depth of 0.2m (Table 4.2). Pots were then placed on trestles at 1m height to facilitate monitoring and watering. Organic amendments were added as shown in Table 4.3 and grasses sown in April 1999at rates shown in Table 4.4. Pots were arranged in a randomised design in the greenhouse (Plate 4.1). All treatments received 18:6:12 N:P:K fertiliser at rate equivalent to 250 kg/ha. Pots were intermittently watered at rates equivalent to Aughinish rainfall levels and leachate from pots was collected in a communal drainage trough and disposed of.

The standard agricultural seeding rate applied to normal soils is 20-28kg/ha. Seed application to extreme substrates such as red mud would require a higher rate to compensate for losses. Wide ranges exist in rates of application of seed with 200kg/ha being at the upper end of the scale (Williamson *et al.*, 1982). Seeding rates of 100 kg/ha and 200 kg/ha were chosen for the ITS reclamation trials. This moderately high rate was chosen due to the high failure rate in the small pot trials and, depending on seed size, one of the two rates was chosen. This was done to achieve, as near as possible, similar amounts of seed/m^2.

Organic application rates were determined by assessing moisture and organic content of the wastes and applying a dry weight organic content of 2% to all of them.

The greenhouse was constructed on a hard-standing surface measuring approximately 30m x 30m and had venting at each end to ensure air circulation and avoid high humidity.

During a sixteen week growing period (April-July), average shoot height was recorded on a weekly basis (Section 4.4.1.1.). The trials were allowed to proceed under the prevailing natural light conditions and recorded temperatures generally ranged from 16°C to 28°C. After the 16 weeks growth period pots were harvested at 2cm height and samples oven dried to consistent dry weight for Biomass Yields determination (Section 4.4.1.2.). Grass samples were also digested and assayed for elemental composition (Section 4.4.3.1.)

Plate 4.1. Arrangement of Large Pot Trials in Randomised Block Design

Table 4.2 Project Design for Large Pot Trial Treatments

Mud Treatment (x2)	Mud / Process Sand Mud / Process Sand / Gypsum
Species (x5)	*Fescue longifolia* *Lolium perenne* *Agrostis stolonifera* *Holcus lanatus* *Trifolium pratense*
Organics (x5)	None Dairy Industry Biosolid (DIB) Spent Mushroom Compost (SMC) Thermally Dried Sewage Sludge (TDSS) Agricultural Manure (Agri)

Table 4.3 Organic Application Rates

	equivalent to t/ha
Spent Mushroom Compost	75
Thermally Dried Sewage Sludge	35
Dairy Industry Biosolid	100
Agricultural Manure	90

Table 4.4 Grass Seeding Rate for Large Pot Trials

Species	Common Name	equivalent to kg/ha
Trifolium pratense Rotra	Rotra Red Clover	200
Holcus lanatus	Yorkshire Fog	100
Fescue longifolia Dawson	Creeping Fescue	200
Lolium perenne Master	Perennial Ryegrass	200
Agrostis stolonifera Carmen	Carmen Creeping Bent Grass	100

4.3 Field Plot Trials

Aughinish Island is located on the southern shore of the Shannon Estuary (Schematic 1.2) some 30km west of Limerick at National Grid Reference 128 154. Mean annual rainfall is 919 mm per year, with November, December and January being the wettest months. Field Plot Trials were conducted on the south west side of the mud stack.

Trials were conducted on a terraced part of the mudstack (Schematic 1.2). The area was chosen due to its accessibility by road and the guarantee of the area being undisturbed by future deposits of mud or construction works for a period of two years or more.

Trial site preparation commenced in early summer 1999 with sampling of terraced mud on the south west of the existing mud stack for pH, ESP and soluble elements (Section 4.4.2). Trial implementation work began in July when it was discovered that the mud surface was not capable of supporting rotovation and harrowing traffic. Plate 4.2 illustrates the mud conditions encountered when it was attempted to work the surface. In order to mitigate this, an interceptor channel was dug to aid drainage (Plate 4.3). This was followed by rotovation two weeks later. A second rotovation was conducted after another two weeks when process sand and gypsum were added

(Plate 4.4). Representative samples were taken and pH, ESP and soluble elements determined (Section 4.4.2). The site was then power harrowed after another 2 weeks to further improve substrate tilth (Plate 4.5).

These trials, based on preliminary results from the large pot trials, had in addition, a second process sand application rate of 10% w/w. This was done to compare results to those achieved for process sand applications of 25%. The benefit of a lower application rate would be reduced stockpiling of process sand for eventual, long-term rehabilitation.

Plate 4.2. Condition of mud when 'skin' on the surface was broken

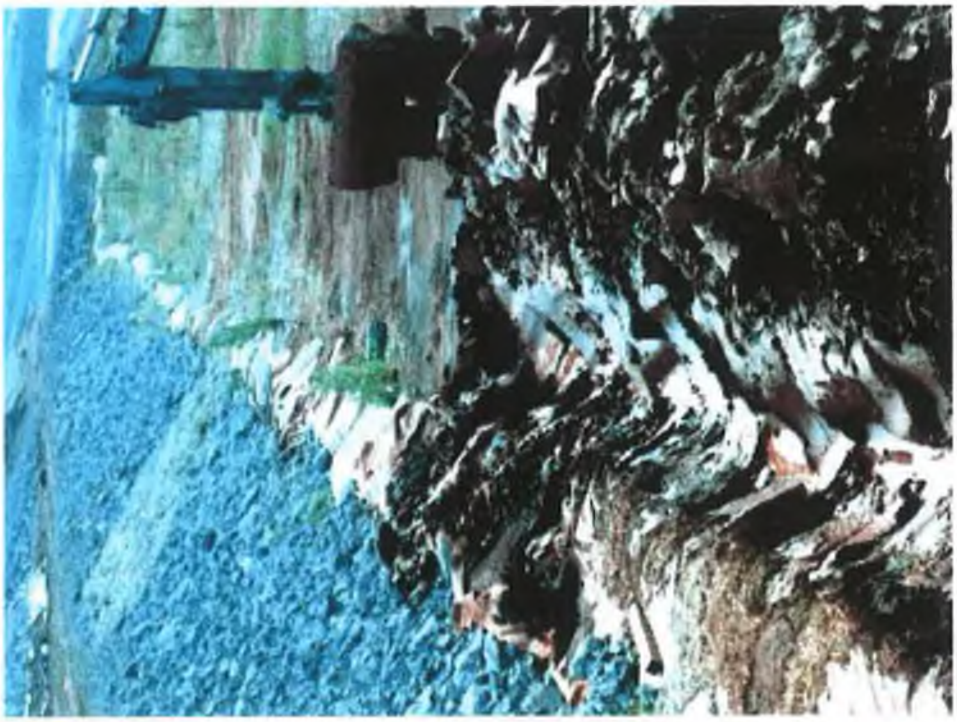
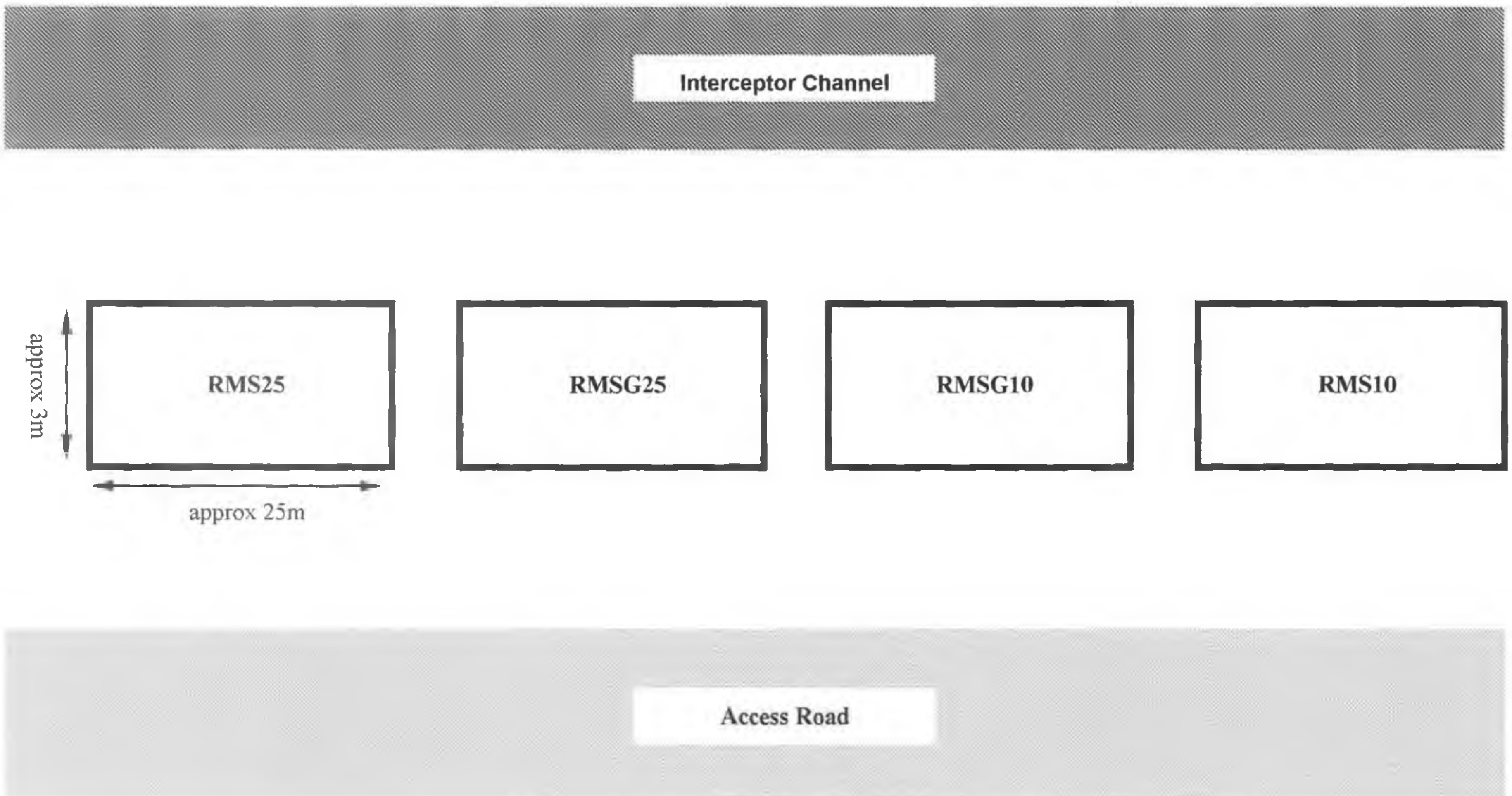


Plate 4.3. Excavation of Dyke to Aid Drainage of Field Plots Site

Four 'Blocks' of red mud treatments were developed as illustrated in Schematic 4.1.

1. Red Mud/ 10% Process Sand (RMS10)
2. Red Mud/ 10% Process Sand + Gypsum (RMSG10)
3. Red Mud/ 25% Process Sand + Gypsum (RMSG25)
4. Red Mud/ 25% Process Sand (RMS25)

Each 'block' was then divided into sub-plots of 1m^2 and organic wastes added at rates shown in Table 4.3. Wastes were added manually and worked into the red mud treatments to a depth of 0.2m. Wooden boards were employed to avoid loss of organic. One week after organic addition grasses were seeded at rates shown in Table 4.4. Each grass species was sown in all the organic treatments in replicates of three. All treatments received 18:6:12 N:P:K fertiliser at a rate equivalent to 250 kg/ha.



Schematic 4.1. Design of Field Plot Trials

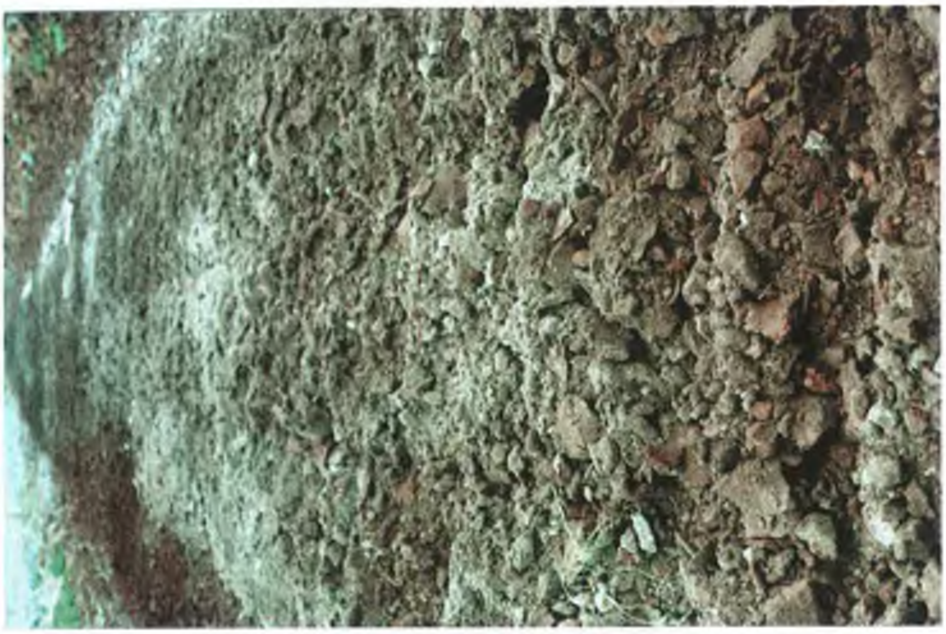


Plate 4.4 Gypsum on mud surface prior to rotovation

Plate 4.5. Amendments being Rotovated into Mud Surface

Plate 4.6. **Mud Surface Following Addition of Process Sand and Gypsum**

Plate 4.7. **Field Trials Site Area Prior to Organic Amendment (excavated drain can be seen on left)**

Following the first year's growth all plots were harvested at 2cm above ground level and bagged. In the laboratory samples were thoroughly washed with de-ionised water before being air-dried for determination of dry weight biomass yields (4.4.1.2). Based on these findings, three species (*Lolium perenne*, *Holcus lanatus* and *Trifolium pratense*) were selected from one organic treatment for analysis of foliar elemental content (Section 4.4.3.2). The substrate conditions associated with these was also investigated (Section 4.4.2).

Immediately after harvesting, representative soil samples were taken from the root zone. Samples were kept in sealed plastic bags until brought to laboratory where they were air dried to consistent weight. All samples were ground to pass through a 2mm aperture sieve before undergoing chemical analysis (Section 4.4.2).

Following a second application of fertiliser, growth was allowed to continue in the treatments for a second year's growth after which the species were again harvested for biomass determination and elemental content. This was done to compare plant performance for the two years.

4.4 Analysis

4.4.1 Biological Parameters

4.4.1.1 Germination Percentage and Shoot Height Measurement

Seeds displaying germination were counted on a weekly basis over an eight week period and expressed as a percentage of total number sown.

On a weekly basis shoot lengths were measured by ruler at six separate areas of the pot and the average figure recorded.

4.4.1.2 Dry Weight Biomass

In the comparison of biomass for different species the fresh or wet weight is often meaningless as water content may vary considerably (Brower et al., 1989). Dry weight biomass determination offers a more useful means for comparing plant yield. Grass samples were harvested and dry weight obtained by oven-drying the samples at 100°C until there was no longer a loss in weight.

4.4.2 Chemical Parameters

4.4.2.1 Soil pH

Soil pH levels were recorded on samples at soil-to-water ratio of 1:2 w/w using a method similar to Peech (1965). Approximately 5g of sieved, air-dried soil was placed in a beaker and 10 ml of distilled water added. The contents were stirred vigorously for 15 seconds and let stand for 30 minutes. Using a calibrated pH meter (Orion Model 210A), the electrodes were placed in the slurry, swirled carefully, and the pH read.

4.4.2.2 Water Soluble Elements

Weighed amounts of air-dried <2mm soil sample (approx. 10g) were placed in a conical flask with 50ml distilled water and placed on a mechanical shaker for 1hr. The suspension was then pre-filtered through a Whatman No. 42 filter before being filtered through a 0.45µm filter. Solutions were then added to 100ml volumetric flasks and brought up to volume with distilled water.

Water soluble Na and K were determined using a Corning 400 flame photometer. Calibration curves were prepared using the appropriate standards (0-15 mg/l Na and 0-20mg/l K) and concentrations determined by extrapolation of absorbances recorded.

Water soluble Al was determined using a Perkin Elmer Emission Spectrometer Plasma 400. Four calibrations were prepared from a working standard of 100ppm. Standards prepared were 1ppm Al at 309.271 nm, 10ppm Al at 394.401 nm, 1ppm Al at 394.401 nm and 1ppm Al at 396.152. Results were then stored on the method database and samples recorded as ppm.

Ca, Mg, Fe and Zn were determined with a Perkin Elmer 2380 Atomic Absorption Spectrophotometer using an air/acetylene flame at the following respective wavelengths, 422.7nm, 285.2nm, 248.3nm, and 213.9nm. Calibration curves were prepared with the appropriate standards (0-7 mg/l Ca, 0-2 mg/l Mg, 0-10 mg/l Fe and 0-4 mg/l Zn) and results extrapolated from the standard curves.

4.4.2.3 Determination of Exchangeable Sodium Percentage

The Sodium Adsorption Ratio (SAR) was calculated using the following method employed by The United States Salinity Laboratory (Richards, 1954) where the concentrations of the ions are expressed as milliequivalents per litre.

$$SAR = \frac{Na^{+}}{\sqrt{\frac{Ca^{++} + Mg^{++}}{2}}}$$

The Exchangeabe Sodium Percentage (ESP) was then calculated by using the equation adopted by The United States Salinity Laboratory (Richards, 1954) derived the following relationship between SAR and ESP

$$ESP = \frac{[-1.26 + (1.475\,SAR)]}{[0.9874 + (0.0147\,SAR)]}$$

4.4.2.4 DTPA extractable elements

The Chelating Reagent Diethylene-triamine-pentaacetic acid (DTPA) was used for determining amounts of extractable zinc, iron, manganese and copper using the method reported by Lindsay and Norvell (1978).

An extracting solution of 0.005M DTPA, 0.01 M$CaCl_2$, and 0.1M TEA was prepared by dissolving 149.2g of TEA [$(HOCH_2CH_2)_3N$], 19.67g DTPA, and 147g $CaCl_2.2H_2O$ in approximately 1000ml of heated distilled water. When fully dissolved the solution was diluted to nine litres in a calibrated, ten litre container. The pH was then adjusted to 7.30 ± 0.05 with dilute HCl before being made up to ten litres.

A known amount of air dried soil of <2mm (approx. 15g) was weighed into a 50ml Erlenmeyer flask and 30ml of DTPA extracting solution was added. The samples were shaken on a gyrotory shaker at a speed of 180 rpm for 2 hours. After shaking, the suspensions were pre-filtered through Whatman No. 2 filter paper before being filtered through a 0.45µm filter into 50ml beakers. The filtrates were analysed for Cu, Fe, Mn, and Zn by flame Atomic Absorption Spectrophotometer Perlin Elmer 2380 using the following respective wavelengths, 324.8nm, 248.3nm, 279.5nm, and 213.9nm. Standard curves were prepared using the appropriate standards (0-4 mg/l

Cu, 0-10 mg/l Fe, 0-2 mg/l Mn and 0-4 mg/l Zn). Results are expressed as mg/kg in soil.

4.4.2.5 Exchangeable Cations (Na, Ca, Mg & K)

Exchangeable cations were determined using the Ammonium Acetate extraction method (Thomas, 1982). A known amount (approximately 10g) of <2mm air-dried soil was placed in a 125ml Erlenmeyer flask and 40ml of 1N NH_4OAc (Ammonium Acetate) added to it. The flask and contents were swirled and let stand. After one hour the contents were pre-filtered through a Buchner funnel fitted with No. 40 Whatman filter paper before being filtered through a 0.45μm filter. The extracts were then transferred into 100ml volumetric flasks and made up to volume by rinsing the suction flask with 1N NH_4Oac. Concentrations of Na and K were determined using a Corning 400 flame photometer. Calibration curves were prepared using the appropriate standards (0-15 mg/l Na and 0-20mg/l K) and concentrations determined by extrapolation of absorbances recorded.

Ca and Mg were then determined with a Perkin Elmer 2380 Atomic Absorption Spectrophotometer using an air/acetylene flame. Ca was determined at wavelength 422.7nm and a calibration curve prepared using standards in the range 0-7 mg/l Ca. Mg was determined at wavelength 285.2nm using standards in the range 0-2 mg/l Mg.

4.4.3 Plant Analysis

4.4.3.1 Large Pot Trials

Plant digestion was conducted using an O.I. Analytical Microwave Digestion System™.

Herbage samples were prepared by first soaking in distilled water to alleviate dust contamination before rinsing and placing in a spin dryer. Samples were then finely chopped and ground, before 0.5g of dry sample was placed in a PFA Teflon® vessel. Five mls of concentrated HNO_3 was then added and a safety disk placed on the vessel. The pressure control vessel was connected to the pressure transducer of the control unit.

This procedure was repeated until the digestion turntable was full and the vessels evenly spaced. A preparation blank was also prepared containing the same amount of reagent (5ml of HNO_3) and 0.5ml of water.

A default program for herbage digestion was selected from the method panel and the procedure allowed to proceed.

After allowing sufficient time for vessels to cool, samples were pre-filtered through glass fibre filter paper and the contents of the vessel rinsed with ultra-pure water. Contents were then filtered through a 0.45μm filter before being transferred to 50ml volumetric flasks and made up to volume.

Ca, Mg, Mn and Fe content were determined using a Perkin Elmer 2380 Atomic Absorption Spectrophotometer and Na content by a Corning 400 Flame Photometer as per Section 4.4.2.2. Al concentrations were determined by Atomic Absorption using a nitrous oxide/acetylene flame.

4.4.3.2 Field Trials

Grasses were soaked and thoroughly rinsed with distilled water prior to oven drying at 80°C. Samples were then chopped to manageable portions before being passed through a Tecator 1093 Cyclotec sample mill with a grid fineness of 1.0mm. Grinding of plant samples is desirable as it provides a material of uniform composition (Jones and Case, 1990).

1.0g of sample was then placed in a digestion tube and 15mls of aqua regia added and the contents placed on an open hot block for 3 hours. Samples were then filtered and made up to volume. Plant reference material (GEW 07604) was also prepared using this method (Section 4.5). Samples were analysed for Al, Fe, Cu, Zn, Mn, Na, Ca, Mg and K content by ADAS Laboratories, Wolverhampton, U.K.

4.4.4 Analysis of Amendments

4.4.4.1 Gypsum

Approximately 10g of dried powdered gypsum was placed in a conical flask with 50ml distilled water and shaken for 1hr. The suspension was then pre-filtered through a Whatman no. 42 filter before being filtered through a 0.45μm filter. Solutions were then added to 100ml volumetric flasks and brought up to volume with distilled water before undergoing analysis as per Section 4.4.2.2.

4.4.4.2 Sewage Sludge

A known amount of oven-dried, finely ground sludge sample (approx. 0.3g) was weighed and placed in glass digestion tube to which 7ml of concentrated HNO_3 was added. The digestion tube was then placed on a heating block and the reaction allowed to proceed for 3hrs. Contents were then allowed to cool before being filtered through glass fibre filter paper. Containers were rinsed with ultra-pure water and the contents transferred to 50ml volumetric flasks and made up to volume. Sample concentrations were then determined by atomic absorption or flame photometer as per Section 4.4.2.2.

4.4.4.3 Organic Matter

The organic matter content of the amendments was determined using the method reported by Nelson and Sommers (1982) which involves the destruction of organic matter at high temperatures (1982). Approximately 10g (recorded to 4 decimal places) of < 2mm air dried sample was placed in a pre-weighed conditioned porcelain crucible (conditioned at 900°C for 15 minutes and then cooled in a dessicator). The sample was then ignited in a muffle furnace at 900°C for 15 minutes after which the crucible was placed in a dessicator to cool and then reweighed. From the loss in weight the percentage organic matter can be calculated using the following formula:

$$\% \text{ Organic Matter} = \frac{A - B}{W} x \frac{100}{1}$$

A = Weight of crucible and soil before ignition (grams)

B = Weight of crucible and soil after ignition (grams)

W = Weight of soil

4.4.4.4 Organic Carbon

The organic carbon content of gypsum and the wastes used in the study was determined using the rapid dichromate oxidation technique (Nelson and Sommers, 1982). A known amount of oven dried sample, not exceeding 0.3g, was transferred to a 500ml wide-mouth Erlenmeyer flask and 10ml of 1N K_2CrO_7 added. The flask was swirled gently to disperse the soil in solution and 20ml of concentrated H_2SO_4 was added. The contents were swirled immediately, gently at first and then more vigorously for 1 min. The flask was then allowed to stand on a sheet of aluminium foil for 30min after which 200ml of distilled water was added to which 10 mls of concentrated phosphoric acid was added in order to sharpen the end-point. One ml of diphenylamine indicator (0.5g of diphenylamine in a mixture of 100 mls of concentrated sulphuric acid and 20 mls distilled water) was added and the contents of the flask were titrated with 0.2N ferrous ammonium sulphate until a colour change from black to blue/purple occurred.

The amount of organic carbon expressed as a percentage of soil is expressed as follows;

$$\% \text{ Organic Carbon} = \frac{(V1 - V2/5)x0.003x100}{W}$$

V1= Volume of 1N potassium dichromate.

V2= Volume of 0.2N ferrous ammonium sulphate.

W= weight of air dried soil.

4.4.4.5 Total Nitrogen

Total nitrogen content of the red mud, gypsum and sewage sludge was determined by a Kjeldahl method similar to that of Bremner and Mulvaney (1982). A known amount of <2mm air-dried sample (0.3 to 3g) was transferred to a clean "Buchi" Kjeldahl digestion flask and 2 Kjeltabs catalyst tablets added. Twenty five mls of redistilled water and 30ml of concentrated sulphuric acid were added and the contents placed in a heating block at low heat. After frothing had ceased, the heat was increased until the digest cleared, boiling continued for a further 2-6 hours. After completion of digestion, the flasks were allowed to cool and 50ml of redistilled water was added (slowly, and with shaking) in order to dissolve any cake of salts. The cold solution was then transferred to a 250ml volumetric flask and made up to volume with redistilled water.

For the distillation of the samples a "Buchi" Kjeldahl Distillation Unit was used. Ten mls of 2% boric acid, containing bromocresol green and methyl red indicator was added to a 50ml Erlenmeyer flask and placed on the drip tray of the distillation unit, ensuring that the tip of the distillation outlet tube was below the surface of the boric acid. Twenty-five mls of the digested sample from the 250ml Erlenmeyer flask, was placed in a clean digestion flask and connected to the distillation unit. Fifteen mls of 32% sodium hydroxide was added to the contents of digestion flask and the distillation reaction allowed to proceed for 5 minutes. After completion of the reaction, the contents of the Erlenmeyer flask were titrated with 0.02N hydrochloric acid until a colour change from green to wine red was observed. A blank sample containing redistilled water instead of soil was used in the same manner as the sample.

The percentage total nitrogen was calculated using the following formula;

$$\% \text{ Nitrogen} = \text{mls HCl}\, x \frac{0.28}{1000} x \frac{250}{25} x \frac{100}{W}$$

W= weight of sample.

Results for the Section 4.4.4 are shown in Appendix 3.

4.5 Quality Control

All analyses were conducted using good laboratory practice. In addition, all analytical sequences incorporated blanks (that is all reagents minus sample), splits (subdivision of gross and analytical samples), spikes (introduction of known amounts of analyte to analytical samples at the earliest practicable stage in the analytical sequence) and standard reference material whose matrices were selected to best replicate the actual samples (Appendix 3). In all cases, standard solutions were made up in a manner such that the standard matrix resembled the matrix of the analytical sample. Calibrations were conducted under the instrumental conditions employed in sample analysis. Linearity of response was considered acceptable via the use of R^2 coefficients, a coefficient value of greater than 0.995 being acceptable.

4.6 Statistical Analysis

4.6.1 Paired T-test

The t-test is commonly used to evaluate if the differences in means between two groups is greater than what can be attributed to random sampling variation. T-tests can be used when variables are normally distributed. Where only two treatments were being compared for differences in the study the Paired T-test was used. The paired T-test examines the changes that occur before and after a single experimental intervention to determine whether or not the treatment had a significant effect. Differences were regarded as significant if $P<0.05$.

4.6.2 Analysis of Variance (ANOVA)

For comparison of more than two groups, data can be analysed using Analysis of Variance (ANOVA). For comparison of treatments in the field trials of this study ANOVA was carried out to test for significant differences using Sigma Stat 2.0. for Windows. One way ANOVA was followed by Turkey's comparison of means test to compare treatments. Differences were regarded as significant if $P<0.05$.

4.6.3 Correlation

Correlation is a measure of the relation between two or more variables. In the study, Pearson Rank Correlation was used to determine the strength of association between plant content and extractable fractions of the parameters. The correlation coefficient r represents the linear relationship between two variables. If the correlation coefficient is squared, then the resultant value (r^2) will represent the proportion of common variation in the two variables (i.e., the 'strength' of the relationship). The correlation coefficient r varies between –1 and +1. A correlation of –1 indicates there is a perfect negative relationship between two variables. A correlation of +1 indicates there is a perfect positive relationship between two variables. A correlation of 0 indicates no relationship between the variables.

5.0 RESULTS AND DISCUSSION

5.1 Small Pot Screening - Seedling Emergence and Growth

5.1.1 Small Pot Trials (A)

Screening of suitable species from the initial twenty (Section 4.1) had limited success due to high failure rates for seed germination in all treatments. This was caused, primarily, by the mud treatments displaying hard setting characteristics following the mixing of amendments. Meecham and Bell (1977) attributed poor germination of *Chloris gayanna* (Rhodes grass) in bauxite residue trials to physical limitations of mechanical impedance and low water holding capacity. Treatments in this study frequently dried out between watering, the resulting drying and cracking of the substrates creating preferential pathways through which there was a loss of seed due to the increased water percolation. Marschner (1983) also reported cracking of the mud substrate and poor germination.

Nelson (1981) achieved no germination for *Agropyron elongatum* (Tall Wheatgrass) seeds in red mud substrate and attributed this to inhibition by excess salts in the mud, which prevents water uptake due to low osmotic potential of the medium and by toxic effects of the ions. Wong and Ho (1993) found high negative correlations for poor seedling emergence of *A. elongatum* and *Cynodon dactylon* (Bermuda grass) seeds in red mud with substrate pH, soluble aluminium and ESP. The findings of both Nelson and Wong and Ho would indicate that the main factors for the poor germination percentages of the remaining seeds in this study were high alkalinity and excess salts.

Of the twenty species used in the Aughinish study, nine failed to germinate in the inhospitable conditions exhibited by the red mud treatments. These species were:-

Juncus effusus
Trifolium repens Huia
Carex flacca
Cynosurus cristatus
Koeleria macrantha
Schoenoplectus lacustris

Poa pratensis

Melaleuca leucadendron

Phleum pratense

Amongst the other eleven there was a marked difference in the germination rates between the different red mud treatments with most germination occurring on red mud amended with gypsum. Eight weeks after sowing and scarifying of the substrate, *Avena sativa* had a germination rate of 64% in the gypsum amendment compared to 13% in non-gypsum treatments (Table 5.1). This reflects the more favourable chemical conditions in gypsum amended mud, *inter alia* a reduction in ESP and pH levels. The only other species to germinate on red mud without gypsum amendment was *Agrostis stolonifera* Providence. This was, however, at a low percentage of 11%. The low germination percentages recorded for the gypsum amended treatments in Table 4.1 can be explained by the seed loss through fissures created in the cracked mud substrate. As a result of the inhibitory physical characteristics exhibited by the mud treatments the method of substrate preparation was modified (Section 4.1.2).

Table 5.1 Percentage Germination for Treatments after 8 weeks

Species	Treatments	
	RMS	RMSG
Avena sativa	13	64
Agrostis stolonifera Carmen	0	27
Agrostis stolonifera Providence	11	45
Agrostis tenuis Bardot	0	41
Festuca litoralis Merlin	0	38
Festuca longifolia Dawson	0	36
Festuca rubra	0	24
Holcus lanatus	0	44
Trifolium pratense Rotra	0	50
Lolium perenne Wendy	0	42
Puccinellia distans	0	32

RMS=Red Mud + Process Sand

RMSG=Red Mud + PS + 3% Gypsum

Species chosen for Large Pot Trials were influenced by the above results.

5.1.2 Small Pot Trials (B)

The results discussed below are from the second series of screening trials which further investigated the use of gypsum, process sand and organic matter on the growth of *Avena sativa* and *Holcus lanatus*. Plates 5.1 and 5.2 illustrate growth of the two species after a four week period.

Germination percentage results for the two species are shown in Table 5.2. *Avena sativa* sown in unamended red mud and mud amended with process sand alone had lower germination rates of 60% and 66% respectively, compared to 80% recorded for seeds sown in mud amended with gypsum. After 3 weeks, shoots in mud treatments and mud amended with sand began to show signs of chlorosis and death occurred after 5 weeks. These mud treatments also produced shorter shoots (14-18cm) than mud amended with gypsum (27cm).

Addition of organic matter alone did not significantly enhance germination for *Avena sativa* (Table 5.2). Growth rates were improved with the addition of organic amendment (Table 5.3). Organic addition increased shoot height in the red mud treatment from 13cm to 25cm and in mud amended with sand from 10cm to 26cm. Shoot height was increase from 26cm to 30cm in the gypsum-amended mud.

Holcus lanatus had a significantly higher germination rate on mud amended with gypsum (70%) than on treatments of red mud (45%) and red mud with process sand (50%). As with *Avena sativa*, organic addition did not greatly improve germination percentages but did enhance plant growth. In the red mud treatment shoot height increased from 5cm to 11cm with organic addition, and for the process sand amended mud, from 5cm to 10cm. Shoot height increased from 12cm for red mud amended with gypsum to 18cm for red mud amended with gypsum and organic.

After four weeks, *Holcus lanatus* shoots in red mud treatments and mud amended with process sand reached an average height of 5cm but then began to die off, reflecting the unfavourable conditions for plant growth. Shoots in mud amended with gypsum and in treatments receiving organic matter grew to 11-14cm. After six weeks shoots in the treatments receiving organic matter but no gypsum began to die off.

Similar results were recorded for the *Avena sativa* treatments where no shoot growth or survival persisted after a 4-5 weeks period in the treatments that had not received gypsum amendment. Optimum plant performance was recorded in red mud that had received both gypsum and organic addition.

These trials demonstrate the beneficial effect of gypsum in alleviating the chemical constraints that inhibit plant germination and growth in red mud. Similar improvement of plant growth conditions was reported by Wong and Ho (1991). Organic matter addition does improve plant growth in red mud but alone is not a sufficient amendment to promote and sustain growth. In order to achieve successful growth on red mud it is necessary to lower the inherent inhibitive parameters to levels capable of supporting plant growth. This is further addressed in Section 5.2.1.

Table 5.2 Percentage Germination after 3 weeks

Treatment	*A.sativa*	*H.lanatus*
RM	60%a	45%a
RMO	59%a	43%a
RMS	66%a	50%a
RMSO	64%a	48%a
RMSG	80%b	70%b
RMSGO	77%b	72%b

RM=Red Mud; RMS=Red Mud + Process Sand

RMSG=Red Mud + PS + 3% Gypsum, O=Organic Amendment

Means within a treatment followed by the same letters are not significantly different at P=<0.05

Table 5.3 Shoot Height for *Avena sativa* and *Holcus lanatus* after 3 weeks growth

Treatment	Shoot Height (cm)	
	Avena sativa	*Holcus lanatus*
RM	13a	5a
RMO	25b	11b
RMS	10a	5a
RMSO	26b	10b
RMSG	26b	12b
RMSGO	30b	18b

RM=Red Mud; RMS=Red Mud + Process Sand

RMSG=Red Mud + PS + 3% Gypsum, O=Organic Amedment

Means within a treatment followed by the same letters are not significantly different at P=<0.05

Plate 5.1. ***Avena sativa*** **sown in unamnended red mud (left) and red mud amended with gypsum and organic (right) after 5 weeks**

Plate 5.2. ***Holcus lanatus*** **sown in red mud with gypsum (left) and red mud with gypsum and organic (right) after 4 weeks.**

5.2 Large Pot Trials

5.2.1 Chemical Properties of Red Mud

5.2.1.1 pH

High pH values would be expected in the mud and sand samples due to residual, entrained caustic from the Bayer process and are reported by other workers (Meecham and Bell, 1977; Fuller *et al.* 1982; Wong and Ho, 1993; Fortin and Karam, 1998). The pH of red mud from the terraced area (pH 9.6 - 9.9), the open dome (9.8 - 10.5) and process sand (9.7 - 10.5) are several units above levels of the normal plant growth range of 6.6 to 7.3 (Munshower, 1994). Workers Amon and Johnson (1942) reported reductions in yield in hydroponic cultures at pH above 8. Substrate pH levels of over 10 (Table 5.4) in non gypsum treatments are important, as detrimental effects due to hydroxyl ion toxicity can occur at pH values greater than about 10.5 (Black, 1968). Therefore it is highly unlikely that red mud is capable of supporting plant growth without alleviating the inherent alkalinity.

Table 5.4 shows the pH values for red mud treatments. Gypsum addition was effective in significantly lowering the pH, with gypsum amendment reducing the initial pH in a red mud/process sand mix from 10.1 to 8.6. Gypsum in solution acts as an acid former (Williams, 1954) and in addition, the added Ca exchanges Na from soil exchange sites. This leads to a pH reduction because OH^- is bound tighter to soil than in a Na saturated soil (Blackmore, 1980). Workers Wong and Ho (1994) reported similar results, achieving a reduction from 10.5 in red mud to values of between 8.6 and 9.9 with gypsum amendment.

By contrast, process sand addition alone increased pH in the treatments but none of these were significant. Values in Table 5.4 show that addition of process sand increased the pH of red mud from 9.8 to 10.1. This was most likely due to the process sand being of an age where insufficient on-site leaching had taken place and, consequently, still exhibited high pH. However, this value should decrease further with improved permeability and, therefore, the rate of leaching.

Table 5.4. Average pH of Treatments in Large Pot Trials

Treatments	RM	PS	RMS	RMSG
pH	9.8 (0.12)	10.3 (0.14)	10.1 (0.2)	8.6 (0.3)

RM= Red Mud; PS= Process Sand
RMSG= Red Mud with Process Sand + Gypsum; RMS= Red Mud with Process Sand
Values in parentheses are standard deviation of mean of 8 samples

5.2.1.2 Aluminium

The relationship between pH and aluminium is illustrated in Fig.5.1. Aluminium in red mud is present as the aluminate ion $Al(OH_4)^-$ (Fuller, 1986). Its solubility increases above pH 9.2 (McLean 1976). Reduced pH levels from gypsum amendment resulted in lower levels of soluble aluminium. Mud with higher pH had higher aluminium levels. The figures show higher soluble aluminium levels at pH above 9.5 (>10mg/kg) with lower levels being recorded at pH levels between 8 and 9 (<4mg/kg). A Pearson correlation test showed a strong positive correlation between pH and soluble Al in the amended treatments (r=0.94).

Table 5.5 shows levels of soluble Al recorded in the red mud treatments. Average levels for gypsum-amended mud were 1.85 mg/kg. This value is significantly lower than the 16.57mg/kg soluble aluminium recorded in red mud that had not received gypsum amendment. Process sand amended treatments also exhibited lower soluble aluminium levels than the 43 mg/kg recorded in un-amended mud. Although the RMS treatments exhibited higher soluble aluminium levels compared to RMSG the results show that process sand addition to the red mud has increased permeability and therefore the leaching of the substrate.

Reducing aluminium availability is desirable as it is potentially toxic to plants. This is further addressed in Section 5.3.1 .

Table 5.5 Soluble Aluminium levels in red mud treatments

Treatment	RM (mg/kg)	PS (mg/kg)	RMS (mg/kg)	RMSG (mg/kg)
Soluble Al	43.31 (16.0)	22.09 (2.0)	16.57 (3.5)	1.85 (0.7)

RM= Red Mud; PS= Process Sand

RMSG= Red Mud with Process Sand + Gypsum; RMS= Red Mud with Process Sand

Values in parentheses are standard deviation of mean of samples

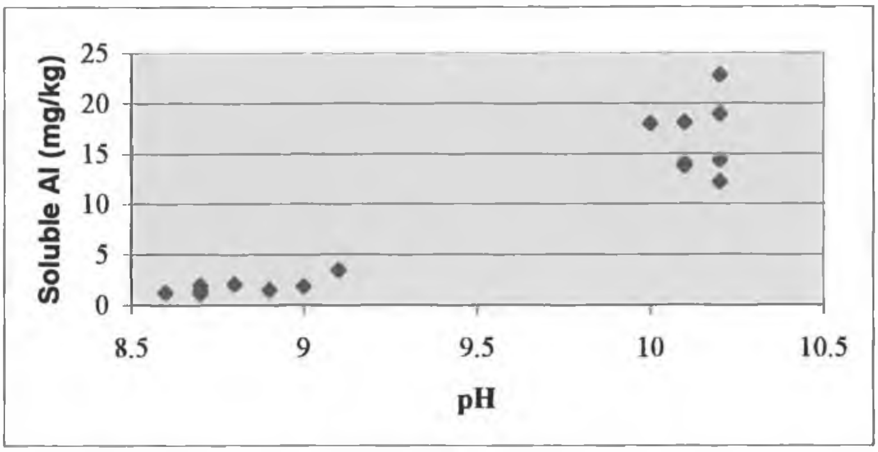


Figure 5.1. Relationship of pH and Soluble Al concentrations in red mud treatments

5.2.1.3 Sodium, Calcium, Magnesium and Potassium

5.2.1.3.1 Exchangeable Cations

The mean values for exchangeable Mg, Na and Ca for the two treatments are listed below (Table 5.6). No significant differences (P=>0.05) between sodium in the two treatments were recorded but there were differences for Ca and Mg. High levels of exchangeable Na are worrying as this form of sodium can be released over time with the decomposition of Desilication Products (DSPs) in the mud thereby raising the sodium content and the alkalinity of the soil solution (Ho *et al.*, 1985; Wong and Ho, 1995).

Table 5.6 Mean values for exchangeable cations

Treatment	Mg (mg/kg)	Na (mg/kg)	Ca (mg/kg)
RMSG	8.4	4200	2005
	(1.87)	(365)	(158)
RMS	4.1	3500	277
	(0.8)	(279)	(38)

RMS=Red Mud + Process Sand ; RMSG=Red Mud + PS + 3% Gypsum
Values in parentheses are standard deviation of mean of 8 samples

Gypsum's high calcium content (>6000mg/kg; Appendix 2) markedly increased the levels of exchangeable calcium from 277 mg/kg in non-amended mud to >2000 mg/kg in treatments receiving gypsum. Magnesium content was also increased from 4.1 mg/kg in treatments without gypsum to 8.4 mg/kg in treatments with gypsum. An increase in levels of Ca and Mg together with an expected decrease of Na levels from increased leaching, results in a lower ESP of the substrate. This is discussed further in Section 5.2.1.3.2. Higher levels of exchangeable calcium and magnesium in the soil would have a positive effect in that they will become available over time and their occurrence should negate the detrimental impact of excessive sodium.

5.2.1.3.2 Soluble Cations

Levels for soluble cations are tabulated below (Table 5.7). Gypsum amendment significantly increased (P=0.005) levels of soluble calcium in the plots with an average value of 564mg/kg soluble calcium in treatment RMSG 564 compared to 7.7 mg/kg in treatment RMS. Soluble Mg levels were also significantly increased (P=0.002) from 1.2 mg/kg in RMS to 2.9 mg/kg in treatment RMSG. Gypsum addition also increased potassium levels from 53.6 mg/kg in RMS to 97.3 mg/kg in RMSG. This latter increase could be due to the 200 mg/kg potassium content in the gypsum (Appendix 2).

The higher sodium value of 2954 mg/kg in gypsum amended mud compared to 1728 mg/kg in RMS may be explained by the supply of Ca to replace Na from exchange sites. As a result, the Na concentration in the soil solution increases, but with time this sodium should be leached from the soil. ESP values for the RMS treatment are high at 67% and are well above critical levels of 10-20% for plant growth (Bernstein, 1974) and the 50% cited by Thorne (1945) above which nutritional disturbances in plants occur from excess sodium. Gypsum addition effectively lowered ESP levels to 31%, and, although levels are still high, addition of organic matter would result in a further reduction of ESP (Summer and Naidu, 1998). A positive correlation of r=0.92 was found between pH values and ESP levels for the red mud treatments used (Figure 5.2). ESP values were also strongly correlated with soluble Al levels r=0.87 (Figure 5.3).

These findings indicate that a longer period of leaching is required for red mud to reach pH and ESP levels more amenable to plant growth. As yet, however leaching time and volume are unknown. Suggested guideline values for plant establishment would be ESP values of <30 and pH values of <9. If such levels would permit long-term growth is also unknown. The addition of gypsum and the resulting decrease in pH would also mean a decrease in both ESP levels and soluble aluminium.

Table 5.7. Water soluble cations and ESP levels for red mud treatments

Treatment	Ca (mg/kg)	Na (mg/kg)	Mg (mg/kg)	K (mg/kg)	ESP
RMSG	564a	2954a	2.9a	97.33a	31a
	(377)	(822)	(0.5)	(4.9)	(8)
RMS	7.7b	1728b	1.2b	53.61b	67b
	(3.9)	(250)	(0.6)	(10.6)	(6)

RMSG= Red Mud with Process Sand + Gypsum; RMS= Red Mud with Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

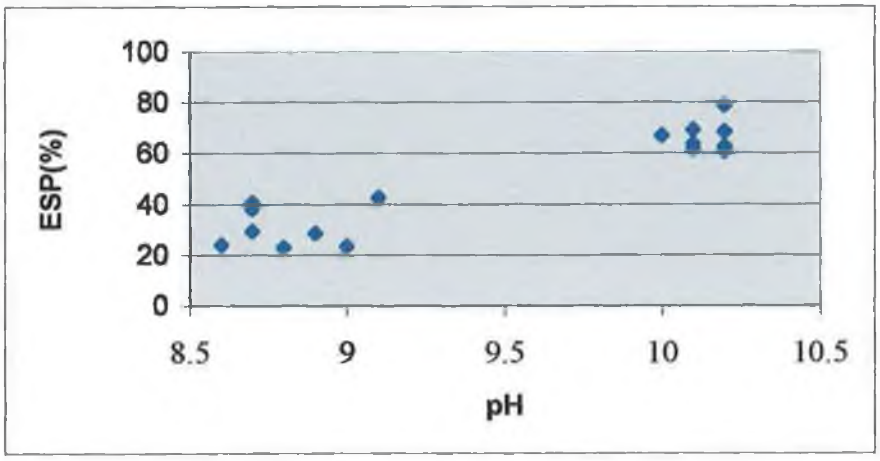


Figure 5.2. Relationship of pH and ESP in red mud treatments

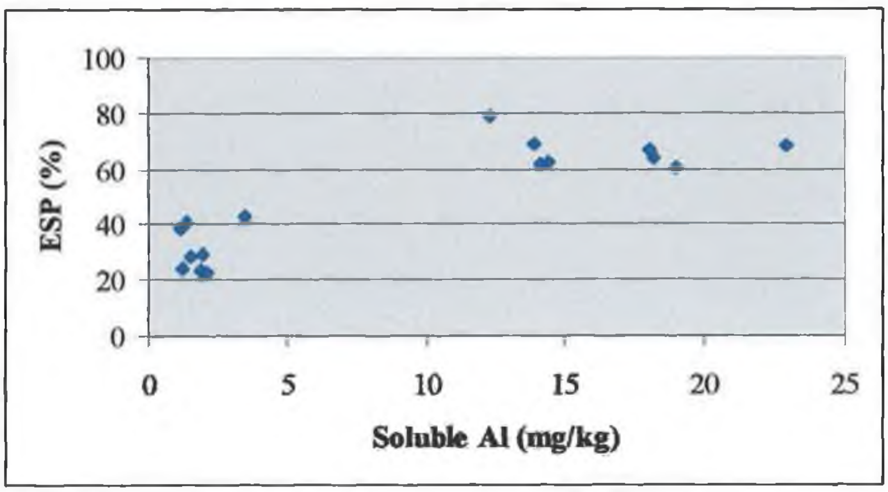


Figure 5.3. Relationship of soluble Al and ESP in red mud treatments

5.2.1.4 Soluble Iron

Gypsum amended treatments had lower iron levels averaging 2 mg/kg compared to treatments without gypsum at 14 mg/kg (Table 5.8). The difference in iron levels can be attributed to the association of the ferric ion (Fe^{3+}) in well drained soils. Addition of gypsum to red mud improves the structure and, thereby, the drainage and aeration of the soil medium. This permits the existence of ferric iron which is insoluble compared to ferrous iron (Fe^{2+}) associated with waterlogged soils (Troeh and Thompson, 1993). A decrease in soluble iron is desirable as Fe concentrations in excess of 0.2% in plants can retard plant growth (Wong and Ho, 1993).

5.2.1.5 Soluble Manganese

Table 5.8 illustrates soluble manganese levels recorded for the red mud treatments. All treatments had very low levels of soluble Mn (<1 mg/kg) with no significant difference between them. Such levels are lower than the critical Mn concentration of 1.8mg/kg cited for plant growth (Soltanpur and Schwab, 1977). Manganese-nutrition in plants is generally reduced on alkaline soils due to precipitation of $Mn(IV)O_2$ (Truog, 1945; Gauch, 1972). As a result of this, Mn uptake and plant concentration would be limited. Wong and Ho (1993) report that Mn deficiency may be limiting in achieving continuous vegetative growth on red mud.

Table 5.8 Soluble Iron and Manganese levels for Red Mud Treatments

Treatments	Fe (mg/kg)	Mn(mg/kg)
RMS	14 (3.2)	<1
RMSG	2 (0.8)	<1

RMSG= Red Mud with Process Sand + Gypsum; RMS= Red Mud with Process Sand
Values in parentheses are standard deviation of mean of 8 samples

5.2.2 Growth and Biomass

Plant growth for Large Pot Trials is shown in Charts 5.1-5.4 and Dry Weight Biomass in Chart 5.5. Measurements of biomass and shoot height are used to determine the suitability of a species for particular substrates (Johnson and Proctor, 1981).

For *Holcus lanatus* (Chart 5.1), seeds sown in red mud treatments without either gypsum addition or organic germinated but died after 4 weeks. High ESP (67), soluble Al (16.6 mg/kg) and pH (10.1) values were displayed in the unamended mud substrate and high negative correlations for poor seedling emergence with these parameters have been reported (Wong and Ho, 1993). Seedling germination and emergence occurred in treatments with gypsum amendment but no organic. Shoot height reached an average height of 3cm in the sixth week and did not increase over a 3month period. This is attributed to gypsum amendment sufficiently lowering pH and ESP to levels that permit germination and growth. However, lack of organic content and essential nutrients inhibits any further growth. Shoots in treatments with organic addition but without prior gypsum amendment reached maximum heights of 6cm over the 3 month growing period but failed to grow any further. These findings illustrate that organic addition alone may not be a sufficient amendment if pH and ESP levels remain high and are inhibitory. Wong and Ho (1991) cited the benefits of gypsum amendment to lower pH and ESP sufficiently, prior to organic waste addition.

Best plant growth was achieved in treatments receiving both gypsum amendment and organic addition. Red mud amended with gypsum exhibited a pH of 8.6, ESP of 31, and soluble Al of 1.8 mg/kg (Section 5.2.1). The lower ESP value is more amenable to plant growth (Bernstein, 1974). SMC without gypsum amendment also promoted good growth, this can be attributed to the inherent gypsum content of the mushroom compost associated from its manufacture (Section 2.6.2).

Results for *Festuca longifolia* (Chart 5.2) are similar to those for *Holcus lanatus*. Treatments without gypsum amendment failed to grow or sustain growth over the 3 month period. Seed that germinated in treatments without either organic or gypsum addition germinated but suffered high mortality after 4 weeks; high pH and ESP levels exhibited by the mud would cause this mortality in the young shoots (Gupta and Sharma, 1989). Similar trends were also found for *Lolium perenne* and *Agrostis stolonifera* (Charts 5.3 – 5.4). Findings suggest that optimum plant growth for all species is achieved when ESP, pH and Al levels are sufficiently lowered prior to organic amendment and sowing of seeds.

Dry weight biomass results are shown on Chart 5.5. Treatments that had no organic matter or gypsum failed to grow and consequently no biomass was produced. Insufficient samples were obtained from substrates with gypsum amendment and no organic, as growth in treatments did not increase over 5cm.

Trifolium pratense only had biomass results for treatments with organics and gypsum as the non-gypsum treatments failed to grow. This result highlights the hostility of unamended red mud substrate to seedling emergence and growth. Mud amended with thermally dried sewage sludge and gypsum also failed to grow. Highest biomass of 332 g/m^2 was achieved in gypsum amended mud with DIB amendment, values of 250 g/m^2 and 124 g/m^2 were produced with SMC and manure amendment. Thermally dried sludge failed to generate sufficient biomass, this is attributed to its dry nature and inability to form a seedbed.

Optimum biomass for *Lolium perenne*, *Holcus lanatus*, *Fescue longifolia* and *Agrostis stolonifera* was generated in gypsum amended treatments with dairy industry biosolid application. Dry weights produced were 600 g/m^2, 660 g/m^2, 590 g/m^2 and 664 g/m^2 respectively. SMC with gypsum amendment produced second best biomass with 230 g/m^2 for *Lolium perenne*, 323 g/m^2 for *Holcus lanatus*, 250 g/m^2 for *Fescue longifolia* and 265 g/m^2 for *Agrostis stolonifera*. The higher biomass for DIB treatments can be attributed to its high nitrogen content of 4-5% compared to <2% for SMC. Manure addition produced less biomass for *Lolium perenne* with 100 g/m^2. Results similar to those for SMC were obtained for the other grasses. Biomass results for thermally dried sewage sludge amended plots were poor. All species produced less than 90 g/m^2 biomass. Although the thermally dried sludge is nutrient rich it is not a suitable organic amendment for red mud if ESP and pH levels are high. Threshold values of <30 ESP and pH of <10 are recommended prior to its addition.

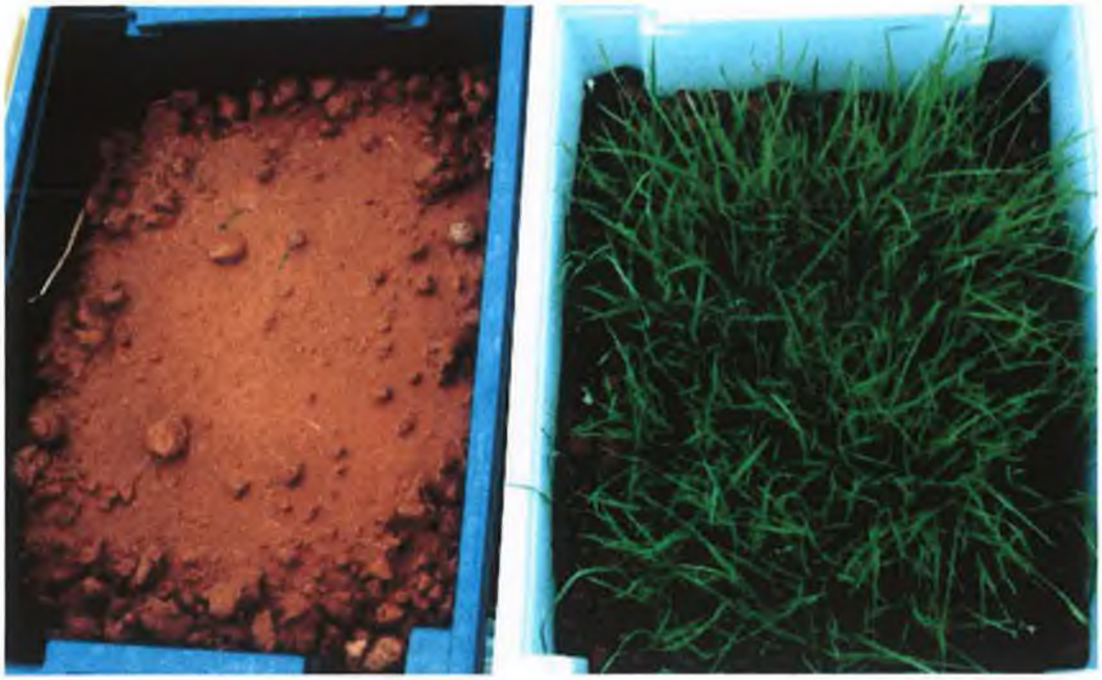


Plate 5.3. ***Holcus lanatus*** **sown in RMS (left) and RMSG & DIB (right) after 3 weeks growth (pot size 0.4m x 0.3m)**

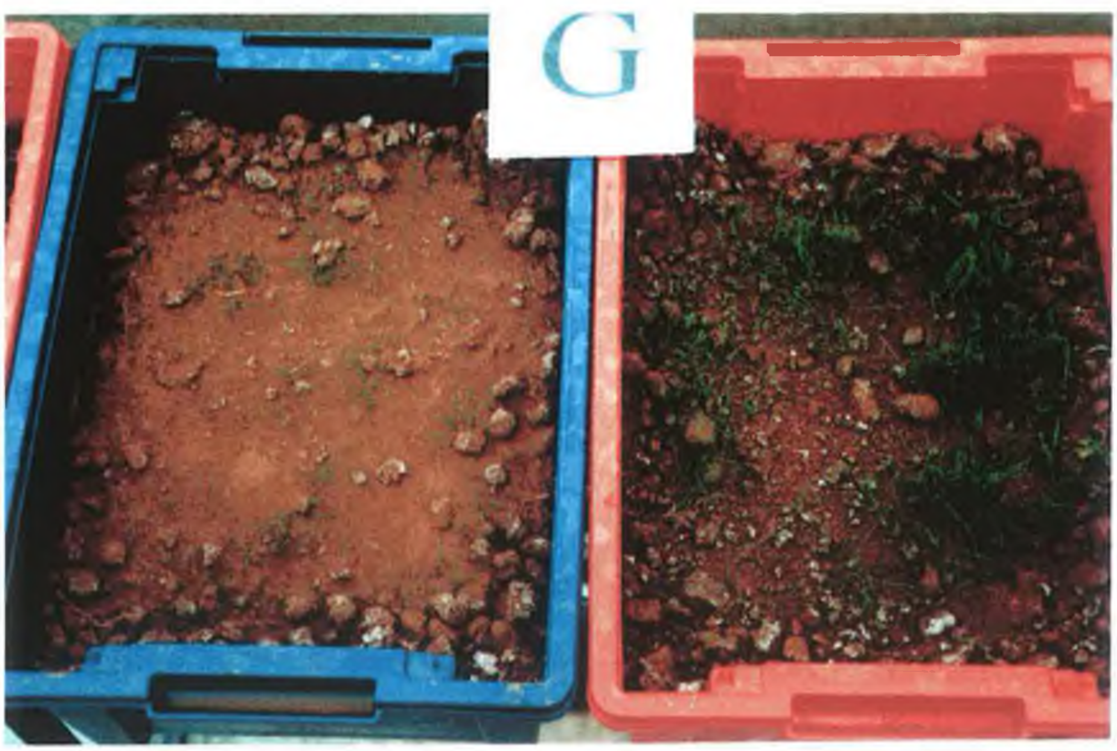
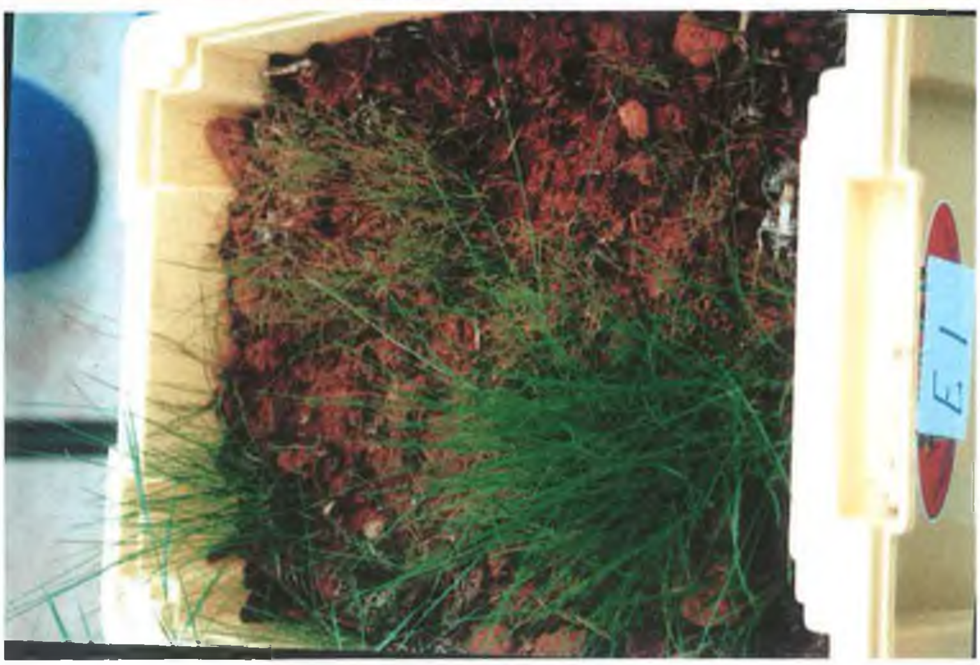


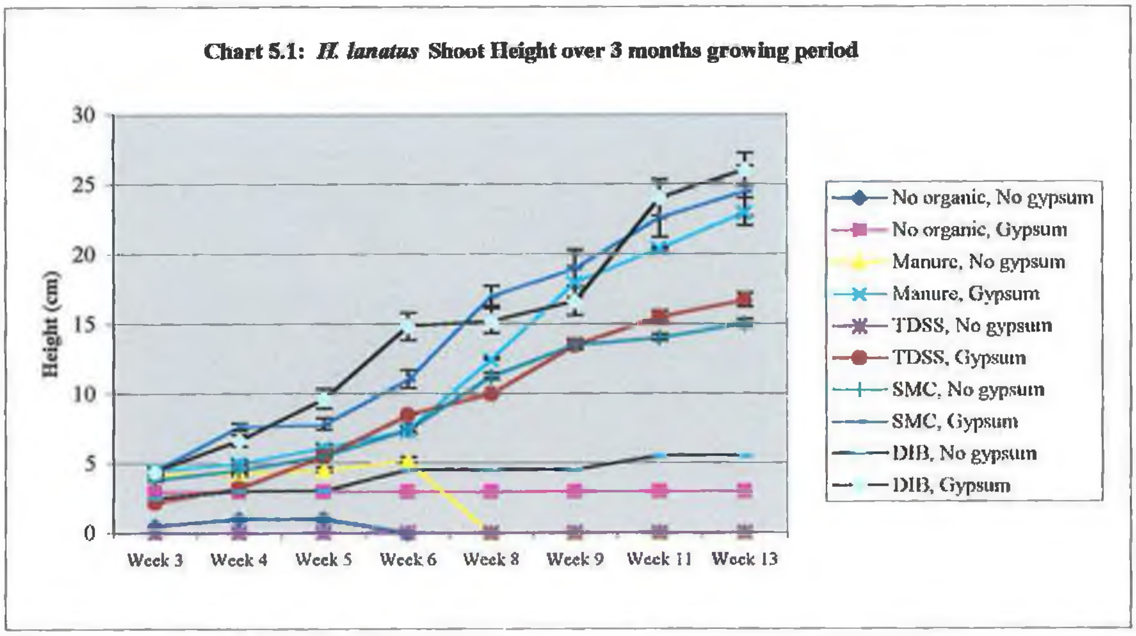
Plate 5.4. ***Fescue longifolia*** **sown in RMSG (left) and RMSG with DIB (right) after 3 weeks growth (pot size 0.4m x 0.3m)**

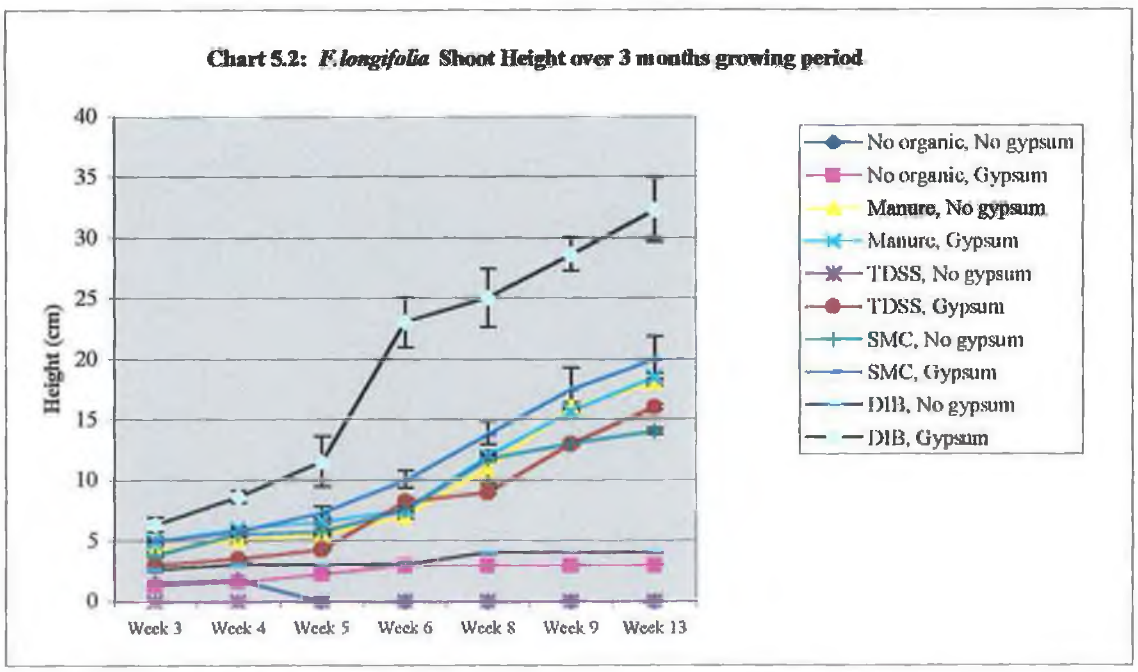
Plate 5.5. ***Fescue longifolia*** **sown in RMSG with DIB after 12 weeks growth (pot size 0.4m x 0.3m, depth 0.2m)**

Plate 5.6. **H*olcus lanatus*** **sown in RMSG with DIB after 13 weeks growth (pot size 0.4m x 0.3m, depth 0.2m)**

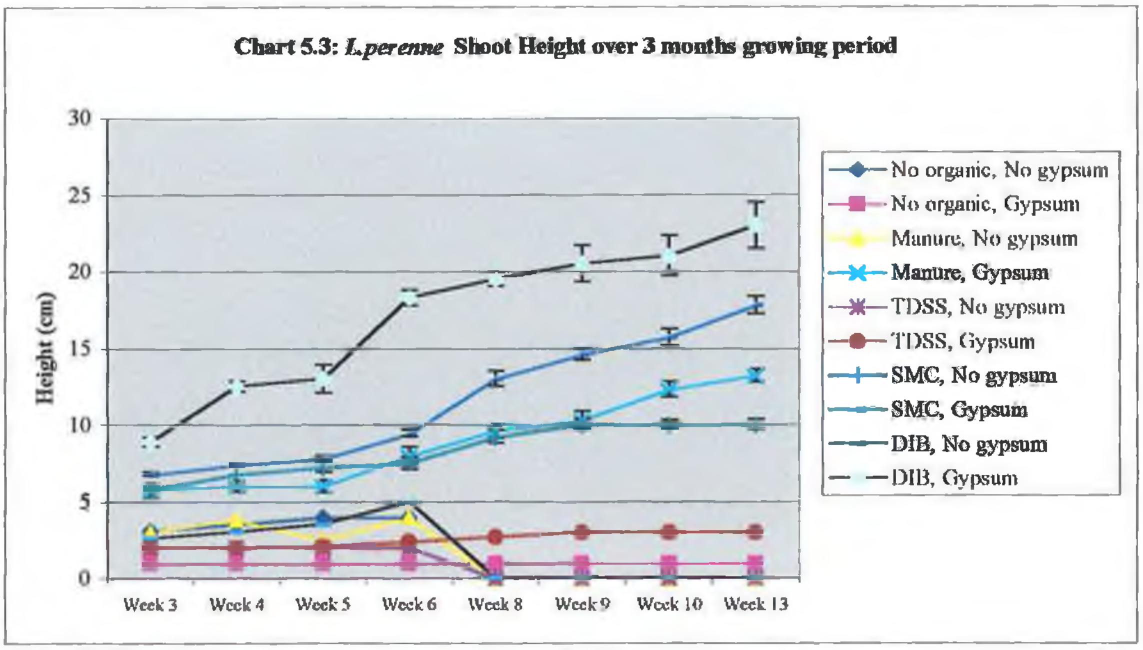


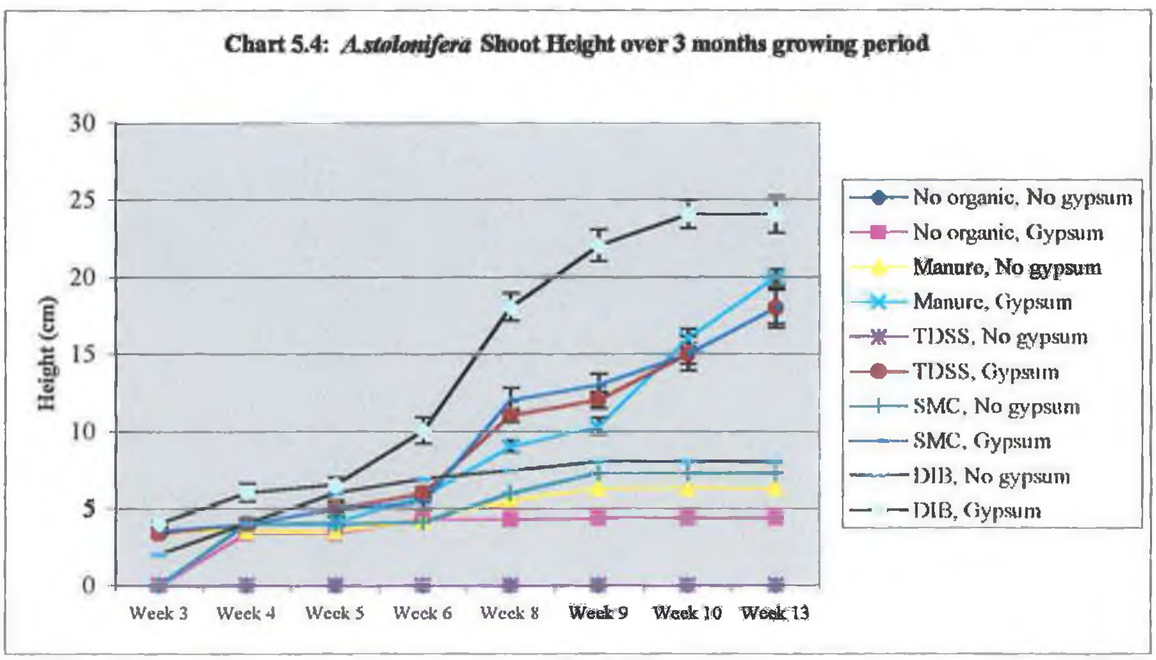
Plates 5.7. & 5.8. ***Lolium perenne*** **sown in RMSG with DIB (top) and RMS with DIB (above) after 13 weeks**



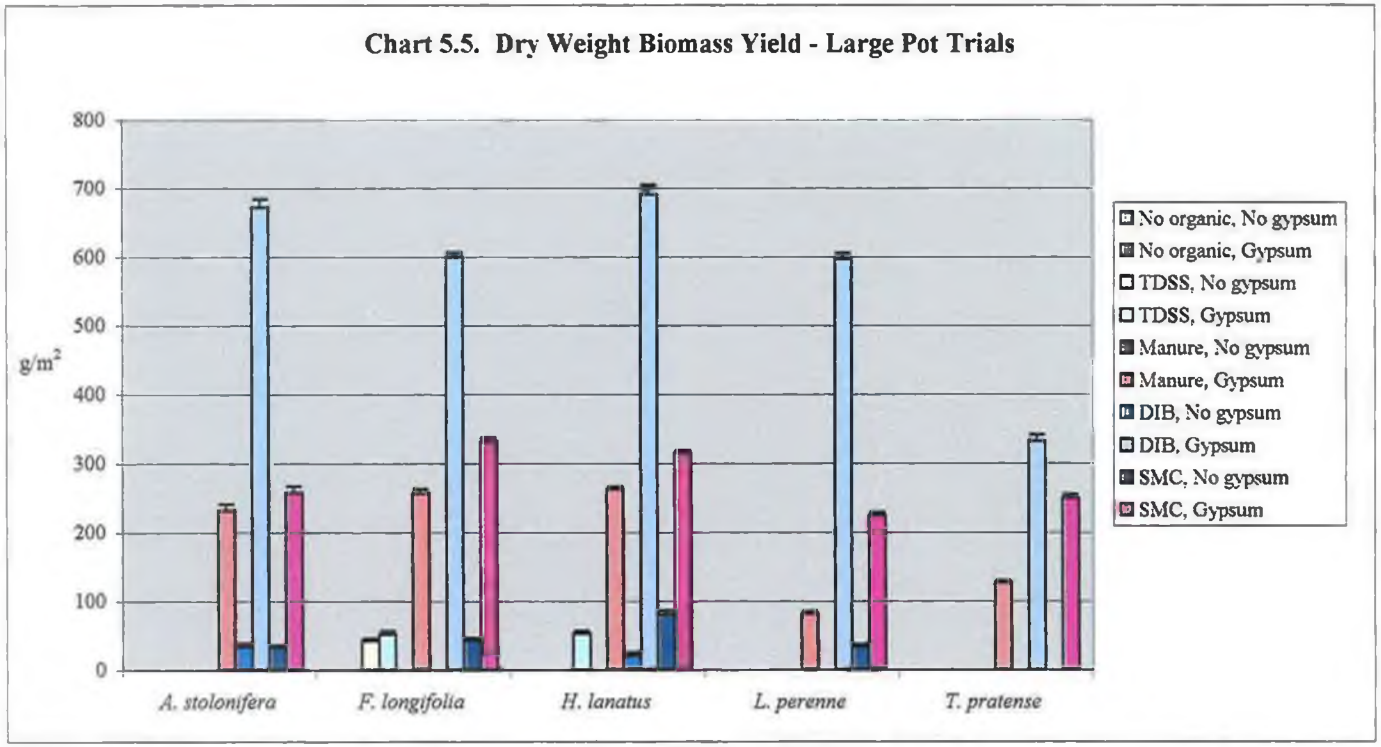


Values shown are mean of 8 replicates. SE bars shown or contained within the size of the symbol.





Values shown are mean of 8 replicates. SE bars shown or contained within the size of the symbol.



Values shown are mean of 8 replicates. SE bars shown or contained within the size of the symbol.

5.2.3 Elemental Composition of Herbage

Grasses were analysed for Ca, Na, Mg, Mn, Fe and Al content. Comparisons between organic treatments with and without gypsum could not be undertaken due to the high failure rate of species in non gypsum treatments. Average results for species shown below were calculated from all organic treatments.

Table 5.9. Elemental contents of foliar aerial portions in Large Pot Trials

	(%)				(mg/kg)	
	Ca	Na	Mg	Al	Mn	Fe
National Average*	0.65	0.29	0.20	209**	119.80	158**
Agrostis/RMS.	0.44	0.91	0.09	37	46.91	127.66
Agrostis/RMSG	0.68	0.90	0.09	35	99.45	100.45
Trifolium/ RMS	Treatments failed to grow					
Trifolium/RMSG	1.53	1.87	0.11	10	35.59	115.48
Holcus/RMS	0.44	1.78	0.08	99	68.01	181.34
Holcus/RMSG	0.57	1.54	0.08	43	84.56	124.57
Fescue/RMS	0.48	0.82	0.07	38	44.42	95.38
Fescue/RMSG	0.68	0.86	0.08	43	98.91	109.95
Lolium/RMS	0.42	2.37	0.06	250	53.89	453.19
Lolium/RMSG	0.79	1.47	0.07	60	82.26	134.42

RMSG= Red Mud with Process Sand + Gypsum; RMS= Red Mud with Process Sand

* Taken from "Levels of Dry Matter, Major Elements and Trace Elements in Irish Grass, Silage and Hay, Rogers, R. and Murphy, W., Teagasc 2000

** Values taken from 'Control Farm' in McGrath *et al.* (2001)

Results obtained for *Trifolium pratense* are only from treatments receiving gypsum. *Trifolium pratense* failed to germinate in any of the organic treatments that had not been previously treated with gypsum. Clover species are known to be sensitive to hostile growing environments. Red mud that had not received gypsum had an ESP value of 67 and pH of 10.1, such levels inhibit the germination of *Trifolium pratense* seeds.

Elemental content values are shown in Table 5.9. Herbage samples from all non-gypsum treatments have calcium levels lower than the national mean of 0.65% (Rogers and Murphy, 2000). Calcium content in *Agrostis stolonifera* increased from 0.44% in RMS treatments to 0.68 % in RMSG treatments. A similar increase was recorded for *Holcus lanatus* with 0.44% in RMS treatments and 0.57% in RMSG treatments. *Fescue longifolia* increased from 0.48% to 0.68% in the gypsum amended treatments and *Lolium perenne* from 0.42% to 0.79%. No *Trifolium pratense* grew in RMS treatments but the 1.53% Ca recorded in RMSG treatments is above the 1.1% deemed adequate for the growth of *Trifolium* sp. (Reuter, 1986).

Ca levels of <1% are generally considered deficient for *Lolium* sp. (Freand and Peech, 1946) and therefore levels detected in the pot trials can be considered deficient. Levels for *Holcus lanatus, Fescue longifolia* and *Agrostis stolonifera* are within the range typical for Irish herbage (Rogers and Murphy, 2000).

Gupta and Abrol (1990) reported impaired uptake and a subsequent low Ca concentration in plants growing in high Na soil. The above results suggest that gypsum addition can impact on calcium availability and uptake at pot-trial stage and the extent to which this occurs is species dependent.

With the exception of *Lolium perenne* there are no significant differences (P>0.05) for Na herbage content from RMS and RMSG treatments (Table 5.9). Levels detected for *Agrostis stolonifera* in the two treatments were 0.9% in RMSG and 0.91% in RMS, both of these are above the 0.8% values cited for *Agrostis tenuis* (Lunt *et al.,* 1961) above which growth restrictions occur. Sodium content in

Trifolium pratense (1.87%) was considerably higher than the range of 0.2-0.32% at which Bernstein and Pearson (1956) reported reduced growth in *Trifolium pratense.*

Sodium herbage content for *Holcus lanatus*, *Fescue longifolia* and *Lolium perenne* are considerably higher than the national average values of 0.28% (Rogers and Murphy, 2000) and the high values detected for sodium in *Lolium perenne* of 1.47% in RMSG and 2.37 in RMS are above the maximum value of 1.25% cited by the same authors. Sodium contents in species grown in red mud can be as high as 2.27% for *Agropyron* and 1.29% for *Cynodon* (Wong and Ho, 1993).

Although ESP values significantly differed between treatments (Table 5.7), levels of exchangeable sodium did not (Table 5.6). It has been reported (Thomas, 1982) that exchangeable sodium is the form most readily taken up by plants. The above results show that high levels of exchangeable sodium in the red mud substrate causes sodium uptake to be excessive.

Magnesium herbage content detected for the species in the pot trials (Table 5.9) show no significant difference ($P>0.05$) between gypsum treatments. *Trifolium pratense* grown in gypsum amended mud had a Mg content of 0.11%, this value is below the adequate range of 0.18-0.22% for *Trifolium* sp. (Reuter, 1986). Mg values detected for the other grass species were below 0.1%. Levels lower than 0.15% are considered deficient for *Lolium perenne* (Reuter, 1986) and 0.2% is typical of Irish grassland (Rogers & Murphy, 2000). The low levels of shoot Mg recorded may be attributed to high Na levels in the substrate and resultant competition for ion uptake (Munshower, 1984). These findings show a deficiency in magnesium availability and uptake in red mud substrates.

Manganese levels recorded for all treatments are shown in Table 5.9. Species grown in gypsum amended red mud had significantly higher ($P<0.05$) Mn herbage content than for species grown in treatments without gypsum. Mn content in *Agrostis stolonifera* was 46.9 mg/kg in RMS treatments compared to 99.4 mg/kg in RMSG treatments. Gypsum amended red mud yielded a manganese herbage content of 84.5 mg/kg for *Holcus lanatus*, 98.9 mg/kg for *Fescue longifolia* and 82.3 mg/kg for

Lolium perenne. Values for the same species in non-gypsum treatments were lower at 68.1 mg/kg, 44,4 mg/kg and 53.9 mg/kg respectively.

All manganese values are lower than the average figure of 119.8 mg/kg reported by authors Rogers and Murphy (2000) and many are close to the 50 mg/kg considered deficient for *Lolium perenne*, *Trifolium* sp. and many grasses (Reuter and Robinson, 1986). The potential for manganese deficiency in species grown in red mud is shown by the above results. Wong and Ho (1993) highlighted Mn deficiency as a potential limiting factor for vegetative growth on red mud

The low herbage levels are due to the low levels of soluble Mn in the substrates (Section 5.2.1.5). Gypsum used in the trials had a Mn content of <1 mg/kg (Appendix 2). Its effect in reducing alkalinity and, thereby the precipitation of $Mn(IV)O_2$ (Gauch, 1972) in the substrate may be why there is greater Mn herbage content in gypsum amended treatments.

Plant uptake of aluminium and iron from red mud is of concern as they may, at high concentrations, inhibit or be toxic to plant growth. Herbage content for the two elements are shown in Table 5.9. *Holcus lanatus* and *Lolium perenne* had significant differences ($P<0.05$) for Al and Fe content between gypsum and non-gypsum treatments. However, with the exception of non-gypsum treatments for *Lolium perenne,* all treatments had aluminium levels lower than the 0.02% (200 mg/kg) concentrations generally found in plants (Hutchinson, 1945) and the 209 mg/kg cited by Teagasc for a control farm (McGrath et al., 2001). This suggests that, although soluble aluminum levels were high in some treatments, aluminium uptake did not present a problem at pot screening stage.

Iron levels above 60 mg/kg are considered high for *Lolium perenne* (Reuter and Robinson, 1986) and plant growth can be retarded where Fe content exceeds 200 mg/kg (Chapman, 1966). With the exception of *Lolium perenne* and *Holcus lanatus* in RMS treatments, species grown in the red mud treatments at pot-screening stage had herbage iron levels below the 150mg/kg typical of unpolluted Irish pasture (McGrath et al., 2001). Although maximum iron levels can reach over 400 mg/kg

(McGrath *et al.*, 2001) the above findings are in keeping with Wong and Ho (1994) who reported excessive levels of iron in grasses grown in unamended red mud.

General Summary

While few significant differences have been recorded in elemental composition of vegetation samples grown in different red mud treatments, results have shown that gypsum ($CaSO_4.H_2O$) amendment significantly enhances growing conditions in the substrate. It is therefore probable that the bioavailability and subsequent uptake of elements is influenced by gypsum and were further examined.

5.3 Field Plots

5.3.1 Parameters during trial construction

Levels for water soluble elements determined in the terraced red mud and process sand at the time of trial implementation are shown below.

Table 5.10: Water Soluble Elements and ESP for Field Trial Area prior to amendment of site

	pH	Na (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	Al (mg/kg)	Fe (mg/kg)	ESP
Mud	9.7 (0.11)	1120 (176)	3.8 (0.4)	1.4 (0.14)	30 (2.4)	52 (4.7)	62 (5.4)
Sand	10.2 (0.13)	3600 (453)	2.6 (0.5)	0.8 (0.02)	22 (3.1)	1.6 (0.4)	86 (7.4)

Values in parentheses are standard deviation of mean of 8 samples

Both unamended red mud and process sand from the stockpile area exhibited high soluble sodium levels (1120-3600 mg/kg). These coupled with the low values for Ca (<4 mg/kg) and Mg (<1.5 mg/kg) resulted in ESP values of >60% (Table 5.10). The soluble Ca levels found are below the 5.4 mg/kg (Wong and Ho, 1993) and 8.3 mg/kg (Bucher, 1985) of other red muds. Wong and Ho (1993) recorded a high value of 1410 mg/kg for soluble sodium in unamended red mud samples.

The high ESP values determined in the terraced red mud are well above the critical levels of 10-20% needed for plant growth (Bernstein, 1974), and above the 50% cited by Thorne (1945) at which nutritional disturbances in plants occur from excess sodium. As such, plant growth could not be sustained in the red mud at this stage and a period of weathering and leaching is needed to reduce levels of sodium to reach ESP values capable of promoting plant growth. The high ESP values are also in keeping with the high values recorded by other red mud workers and are typical of the range of 52.7-90.9 % reported by Fuller *et al.* (1982).

Process sand used as a physical amendment in the trials had extremely high soluble sodium levels. This sand was sourced from the only accessible stockpile and levels would be expected to decrease rapidly with leaching due to the greater permeability exhibited by coarser fractions (Meecham and Bell, 1977).

The average value for soluble Al levels in the unamended mud was 30mg/kg. This high figure is most likely due to pH levels being above 9.2 (Mclean, 1976). The relationship is illustrated in Figure 5.1. Levels of soluble aluminium are decreased when pH levels fall below 7.8 (Jones, 1961; Munshower, 1994), successful leaching of sodium from red mud should lower pH values and, consequently, levels of soluble aluminium.

Table 5.11 Water Soluble Cations and pH levels in Field Plot Trials following substrate amendment and prior to seeding

Treatment	pH	Na (mg/kg)	Ca (mg/kg)	Mg (mg/kg)	ESP
RMS10	9.5	350	148	< 1	8.2
RMSG10	7.9	350	1485	2	2
RMSG25	8.0	377	1990	3	2
RMS25	8.9	261	179	< 1	5.4

RMS10 = Mud & 10% Process Sand
RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum
RMS25 = Mud & 25% Process Sand

Gypsum addition effectively lowered pH in the treatments from 9.7 to 8.0. Treatments without gypsum were also lower but the reduction was not as great (Table 5.11). The pH range recorded in terraced mud (7.9-9.5) is lower than those recorded for the mud treatments used in the pot trials (9.8 – 10.1). This suggests a greater leaching efficiency was achieved in the terraced mud compared to the domed area used for the pot trials. As plant growth was achieved in all field trials this demonstrates that pH and ESP vales were effectively lowered.

Water soluble sodium ranged from 240-370 mg/kg through the four treatments with no statistical difference (P>0.05) between treatments. However, these levels are significantly lower than the mud prior to surface amendment (1200-1600 mg/kg). The difference in the two mud values demonstrates that weathering and sodium release is taking place on the mud stack following the improvement of its physical structure.

Gypsum addition markedly raised soluble Ca content from the initial 3.8 mg/kg to values in excess of 1,900 mg/kg (Table 5.11). Soluble magnesium levels were also increased but not to the same degree as calcium levels. This increase in calcium and magnesium levels together with a decrease in sodium levels resulted in ESP values lower than the value of 10 cited by Bernstein (1974) as critical for fine textured soils. The slight difference between treatments RMSG10 and RMSG25 may be explained by the difficulty in evenly distributing gypsum under field conditions. Workers Wong and Ho (1993) achieved a reduction in ESP from 70 in un-amended mud to around 11 following addition of gypsum and a period of leaching. ESP reductions achieved in non-gypsum treatments can be attributed to increased permeability with the physical amendment of the substrate.

5.3.2 Biomass Production – First Years Growth

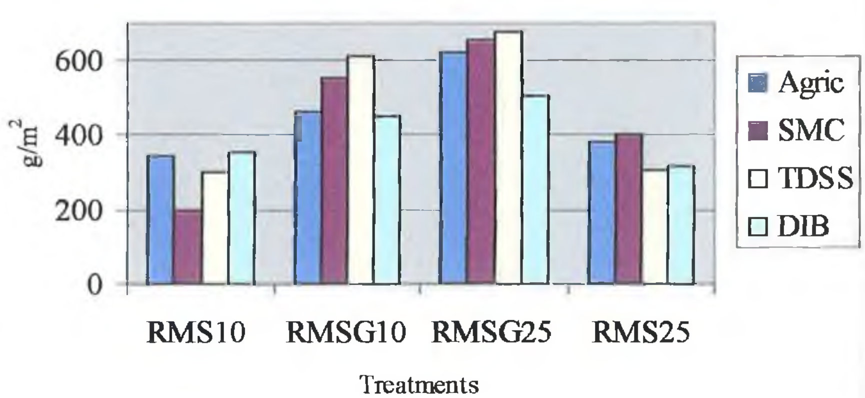
Dry weight biomass results for the first years harvest of field trials are shown in Charts 5.6-5.10. Success of non-gypsum treatment biomasses is in contrast to findings from large pot trials. *T. pratense* amended with SMC improved from 250 g/m^2 in large pot to 600 g/m^2 in field trials. Increases from 332g/m^2 to 475 g/m^2 were recorded for DIB treatments and from 124 g/m^2 to 620 g/m^2 in agricultural dung amended plots. Biomass production also increased for *L.perenne*, *H.lanatus*, *F.longifolia* and *A.stolonifera*. The increase in plant biomass production is attributed to the lower pH and ESP reduction achieved in field trials.

A noticeable difference in biomass production from both trials was the success of thermally dried sewage sludge (TDSS) treatments. This was a successful amendment in both gypsum and non-gypsum treatments. TDSS produced highest biomass for all species in gypsum amended treatments and high biomasses were also recorded for non-gypsum treatments. TDSS is therefore seen as a beneficial organic amendment when ESP and pH values in red mud are sufficiently low.

Significant increases in biomass were not observed for gypsum amended treatments for the species *T.pratense*, *F.longifolia*, and *H.lanatus*, this is due to all treatments having ESP values of <15 and low pH (Table 5.11). TDSS and DIB with gypsum significantly improved biomass for *L.perenne* and *A.stolonifera*, this trend was not repeated with the other organic amendments.

T.pratense was selected for further investigation as it had not previously grown in unamended red mud. Also, long term growth of vegetation depends on an adequate supply of nitrogen, legumes such as clover and related species are important in a seed mixture as they can fix atmospheric nitrogen (Bradshaw & Johnson, 1990). *H.lanatus* and *L.perenne* were also selected as they produced highest TDSS biomass from the remaining species.

Chart 5.6 First Year Biomass - *Trifolium pratense*



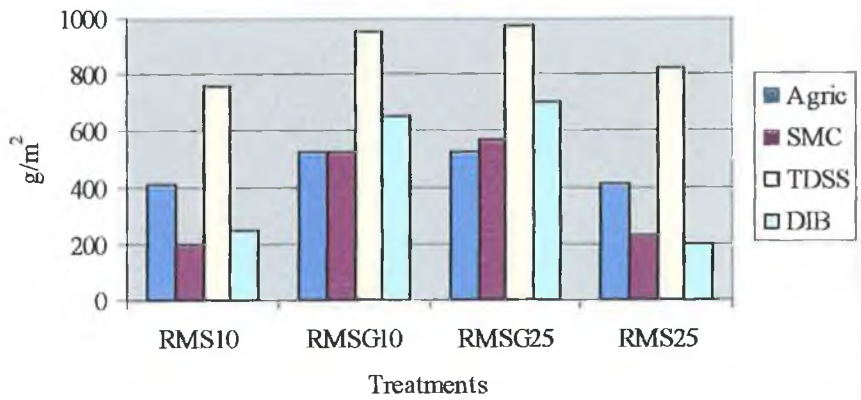


Chart 5.7 First Year Biomass - *Holcus lanatus*

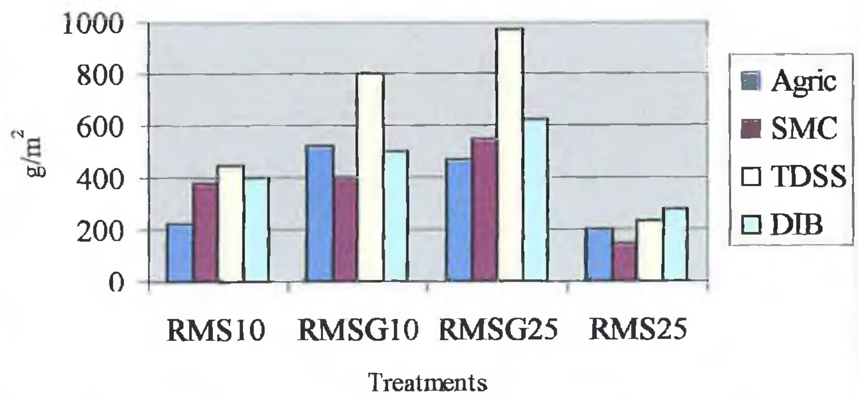


Chart 5.8 First Year Biomass - *Lolium perenne*

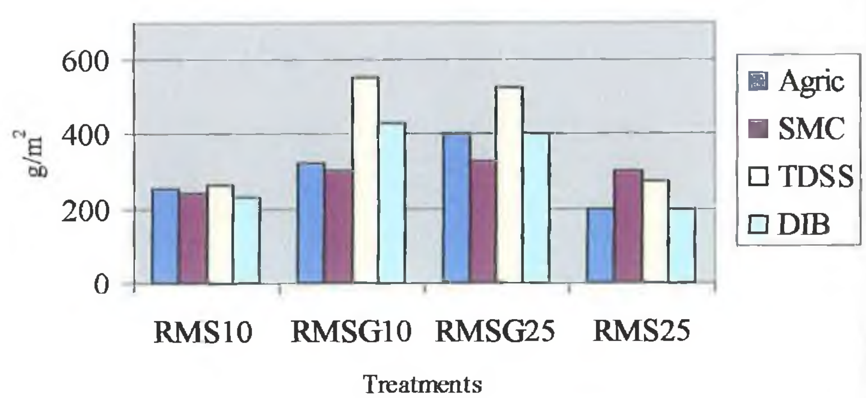
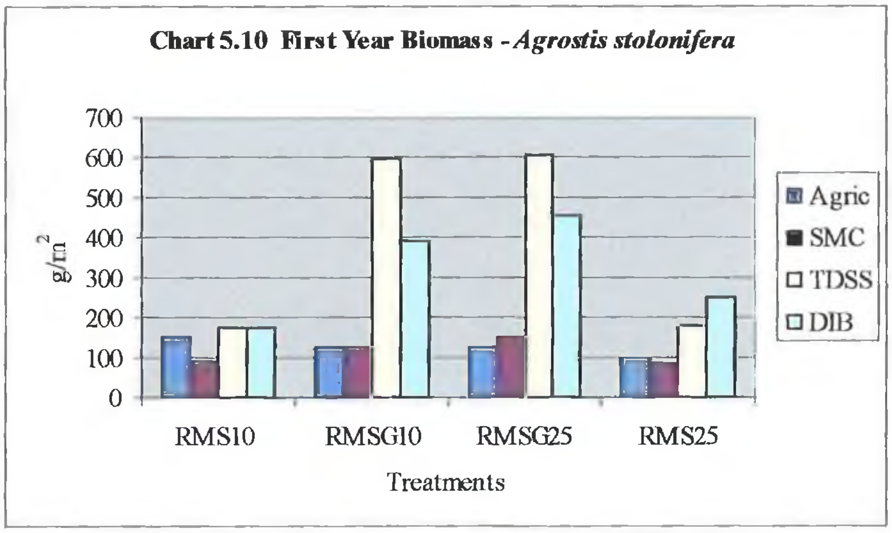


Chart 5.9 First Year Biomass - *Fescue longifolia*



5.3.3 Aluminium

Water soluble aluminium in the field trial plot area prior to any physical and chemical amendment of the substrate had an average value of 30 mg/kg. Process sand used as an additive to improve physical structure, and hence leaching, had a lower value of 22 mg/kg (Table 5.10).

The resultant conditions following amendment with gypsum and process sand increased the permeability of the substrate and reduced pH and ESP levels. Soluble Al concentrations were also markedly decreased in all treatments at time of harvest compared to those recorded at time of trial implementation (0.5mg/kg – 4.7 mg/kg). Section 5.2.1.2 discusses the relationship between pH and aluminium solubility and shows the high correlation (r=0.94) between pH and soluble Al levels.

Due to Al toxicity levels varying widely between plant species and varieties (Williamson *et al.*, 1982) it is difficult to ascertain if the substrate levels recorded in the plots can be regarded as toxic. Tables 5.12-5.14 show that soluble Al levels in the substrates were significantly lower ($P<0.05$) in treatments amended with gypsum than those which received no gypsum. With the exception of Treatment RMSG25 for *Holcus lanatus*, all gypsum amended substrates had soluble Al levels of <1mg/kg. All non-gypsum treatments with the exception of Treatment RMS25 for *Trifolium pratense* had levels in excess of 1.9 mg/kg and ranged as high as 4.72 mg/kg in Treatment RMS25 for *Holcus lanatus*. While gypsum amended plots had

Al levels lower than those for non-gypsum plots, levels reported in the study were above the 0.5 mg/kg cited as toxic for cotton seedlings (Adams, 1979). Conversely, all gypsum-amended substrates were below the 1.9 mg/kg cited as excessive for Alfafa (Schmehl *et al.*, 1950). As such, levels recorded in the non-gypsum plots are in the range that can be described as excessive or toxic to plant growth. However, as plant growth was achieved in all treatments herbage content needs examination to determine if levels in the red mud are excessive or toxic

As can be seen in Table 5.15., gypsum amended treatments produced *Trifolium pratense* with Al content of <50 mg/kg compared to levels of >90 mg/kg in non-gypsum treatment. While the Al shoot content was significantly higher ($P<0.05$) in treatments not receiving gypsum they are not considered excessive. Jones (1961) cites a level of 310 mg/kg as being high for *Trifolium* and 109 mg/kg as high for Barley. No treatments produced *Trifolium pratense* with levels of this magnitude.

Total Al content for *Holcus lanatus* and *Lolium perenne* plants (Tables 5.15 and 5.16) was lower in gypsum amended plots, although this difference was not always significant. Although all species had levels in excess of the 30mg/kg cited as threshold toxic in soyabean leaves (Wallace and Rommey, 1977), they were, with the exception of Treatment RMS25 for *Lolium perenne*, much lower than the average value of 474 mg/kg Al in herbage as reported by McGrath *et al.* (2001) for pasture in the AAL vicinity. In addition, Al herbage content for all species in all treatments was below the 1200 mg/kg reported as toxic for both cattle and sheep intake (Puls, 1988).

Correlations of 0.15, 0.38 and 0.46 were found for relationships between soluble Al levels in the substrate and content in herbage samples for *Lolium perenne*, *Holcus lanatus* and *Trifolium pratense* respectively (Appendix 4). As such, it can be said that the determination of water soluble Al content in red mud does not adequately reflect its potential uptake and toxicity in the species examined.

In summary, it has been demonstrated that the soluble Al content of red mud can be significantly lowered by physical and chemical improvement of red mud followed by a period of leaching. Such substrate levels may be considered as threshold toxic for soils but do not strongly correlate with plant content. It has also been demonstrated that, while plant species grown in gypsum amended red mud have lower Al content, elevated levels of Al in herbage does not occur in the first years growth when pH levels have been effectively lowered.

5.3.4 Iron

Soluble iron in the field trial plot area prior to any physical and chemical amendment of the substrate had an average value of 52 mg/kg (Table 5.10). Values determined at time of harvest had decreased to levels of 2.18 mg/kg –15.5 mg/kg with a lower range of values for the gypsum amended plots.

Tables 5.12 - 5.14 show soluble iron levels in the substrate at time of harvest. It can be seen that levels were significantly lower ($P<0.05$) in treatments receiving gypsum than in treatments without it. The decrease in soluble iron levels can be attributed to an improvement in substrate conditions following the addition of process sand, gypsum and organic matter. The relatively insoluble ferric ion (Fe^{3+}) is associated with well drained soils, compared to ferrous iron (Fe^{2+}) which is associated with waterlogged soils (Troeh and Thompson, 1993).

Bucher (1985) reported an average soluble Fe level of 11.3 mg/kg in red mud and this value is typical of the levels determined in the non-gypsum plots in the AAL study.
For the three species, soluble Fe levels of <4.5 mg/kg were recorded in the gypsum amended plots with average levels ranging from 2.2mg/kg to 4.3 mg/kg compared to the higher range of 9.0 mg/kg to 15.5 mg/kg for non-gypsum treatments. This difference is attributed to the improvement of substrate conditions upon addition of gypsum and is addressed above.

Extractable levels (DTPA) are also used in determining Fe availability in a soil. Treatments that had not received gypsum amendment had levels close to or above the level of 4.5 mg/kg identified as the minimum concentration adequate for healthy crop growth (Follett and Lindsay, 1970), although some gypsum-amended treatments were marginally below this. Data presented in Tables 5.12-5.14 shows extractable levels of Fe as determined in the red mud substrates to be at the lower end (2.2 mg/kg – 15.5 mg/kg) of the range of 1.5 mg/kg to 160mg/kg as reported by Follett and Lindsay (1970).

However, herbage content is of concern as Wong and Ho (1994) reported excessive levels of iron in *Agropyron elongatum* and *Cynodon dactylon* grown in unamended red mud. Normal plant concentrations of iron can have a wide range. Total levels Fe of 68-140 mg/kg are considered the intermediate range and levels less than 70 mg/kg are considered as showing deficiency symptoms for matured *Nicotiana* (tobacco) plants (Chapman, 1965) while levels above 60 mg/kg are considered high for *Lolium perenne* (Reuter and Robinson, 1986). Levels of above 200 mg/kg generally show toxicity symptoms (Chapman, 1965).

Table 5.15 shows iron levels for *Trifolium pratense* grown in the various treatments. Gypsum amended substrates had significantly ($P<0.05$) lower iron content than those without gypsum amendment with levels in the gypsum treatments at $\leq$ 130μg/g compared to values in excess of 260 mg/kg in the non-gypsum plots. Significantly lower values of Fe were also determined for *Lolium perenne* and *Holcus lanatus* grasses grown in gypsum-amended treatments. For *Holcus lanatus* (Tables 5.16), iron levels in the non-gypsum treatments were in excess of 500 mg/kg compared to $\leq$323 mg/kg in the gypsum treatments and *Lolium perenne* (Table 5.17) exhibited iron levels in excess of 1000mg/kg in non gypsum treatments compared to levels of <400mg/kg in foliage harvested from the gypsum amended treatments. Iron content in excess of 1,000mg/kg has been reported in farms investigated in the Askeaton, Co.Limerick area (McGrath *et al.*, 2001). Such levels are considered high for cattle dietary intake but toxic only when in excess of 4000 mg/kg (Puls, 1988).

All Fe levels for *Lolium perenne* were well in excess of the 60mg/kg as considered high for herbage (Reuter and Robinson, 1986) and, all herbage samples from the study had iron contents in excess of the 50 mg/kg Fe recommended for animal requirement (McGrath *et al.*, 2001). With the exception of *Trifolium pratense* gypsum treatments, all samples had levels in excess of the 150 mg/kg iron value typical of Irish pasture and are at the higher end of the range reported by McGrath *et al.* (2001).

Water soluble iron levels were also strongly correlated with iron content in herbage samples. A positive correlation of r=0.72 was found for the relationship between soluble iron in the substrate and total amount in the plant for *Trifolium pratense* and *Holcus lanatus* was also significant at r=0.69 and *Lolium perenne* at r=0.59. These values were much greater than those recorded for correlation with iron content in herbage samples and DTPA extractable levels (Appendix 4).

In summary, based on the above data, determination of water soluble iron is a more valuable method for assessing iron availability to plants. Gypsum amendment significantly lowers both levels of soluble iron in the substrate and total herbage content. Levels recorded for plant content are, however, at levels that may be considered excessive to plant growth and animal dietary intake.

5.3.5 Sodium

Sodium is not routinely tested for in soils, as it not an essential element for most plants (Knudsen *et al.*, 1986). Sodium is however a critical parameter in addressing rehabilitation of red mud. Previous workers on red mud rehabilitation issues have chosen to use ESP values to determine the effects of elevated sodium levels on plant growth and uptake of sodium (Meecham and Bell, 1977; Fuller et al., 1982; Wong and Ho, 1993 and 1994). The amount of ESP in the growth medium and its subsequent effect on plant growth will vary between species (Section 2.3.1.2).

ESP and soluble sodium levels recorded prior to amendment of the field plot trial area are high, with values of ESP 62 and Na 1120 mg/kg (Table 5.10). ESP levels in excess of 50% are typical for red muds (Meecham and Bell, 1977; Fuller *et al.*, 1982; Wong and Ho, 1994) and are above the range where plant growth is restricted and nutritional imbalances occur (Bernstein, 1974). At the time of seeding, ESP levels had dropped significantly to <10 in all treatments, these values are below the 15% value cited as being restrictive to growth for the majority of plants (Chapman, 1966).

Tables 5.12 - 5.14 show sodium levels in the substrate at time of harvest. No statistical differences were found for soluble sodium substrate content between *Holcus lanatus* treatments (Table 5.13), but there were differences for *Lolium perenne* (Table 5.14) with significant differences ($P<0.05$) between all treatments with the exception of RMS10 and RMSG25. In the *Trifolium pratense* (Table 5.12) plots, treatment RMS25 had an average value of 145 mg/kg Na and was significantly lower in soluble sodium levels compared to the three other treatments (209-239 mg/kg). Soluble sodium values determined in all treatments at time of harvesting (140 mg/kg – 240 mg/kg) had also significantly dropped compared to levels determined prior to seeding (>1000 mg/kg).

For all species, gypsum amended treatments had ESP values of less than 1. These values are much lower than values achieved by other workers (Wong and Ho, 1993) and highlight the degree of leaching and weathering that is taking place in field conditions. Treatments that had not received gypsum amendment had ESP values in the range of around 4-9 %. While such values are higher than those in gypsum treatments recorded in this study, they are consistent with values obtained by Wong and Ho (1993). Plant growth should not be adversely affected as it is generally reported that growth restrictions for the majority of plants occurs when ESP values are in excess of 15% (Chapman, 1966).

Amounts of exchangeable sodium as extracted with NH_4OAc were markedly increased compared to water soluble sodium levels. Higher values of exchangeable sodium were obtained for those treatments not receiving gypsum amendment, this can be explained by the exchange sites being occupied by Na (Munshower, 1994) due to insignificant amounts of other cations being present or in supply. The high ESP values for unamended red mud (62%) support this hypothesis.

Sodium contents for herbage samples are shown in Tables 5.15-5.17. Sodium levels were significantly lower ($P<0.05$) for all species amended with 25% process sand. It was found that sand application rate, as opposed to gypsum addition, had a greater impact on sodium content. This is shown for *Holcus lanatus* and *Lolium perenne* in Tables 5.16 and 5.17 where significantly different sodium content was recorded between sand treatments, but not within the treatments where gypsum had been applied.

While gypsum addition did produce significantly lower sodium content for *Trifolium pratense* in the 10% process sand addition rate, concentrations were markedly decreased with 25% process sand addition regardless of gypsum addition. This is attributed to a higher rate of leaching with increased permeability associated with the higher rate application.

All herbage samples, with the exceptions of *Lolium perenne* in RMS25 and RMSG25, had sodium content above the national mean of 0.29% as reported by Murphy and Rogers (2000). As with ESP values, plant species will vary in their tolerance to foliar concentrations of sodium (Chapman, 1966). Bernstein and Pearson (1956) reported reduced growth in *Trifolium pratense* when levels were in the range of 0.2-0.32 %. In this study *Trifolium* results for sodium herbage (Table 5.15) ranged from 0.46% in Treatment RMS25 to 0.93% in Treatment RMS10. Sodium levels determined are therefore excessive in *Trifolium* grown in red mud.

The grassland species *Agrostis tenuis* and *Poa pratensis* suffer growth restrictions at levels greater than 0.8% and 0.3 % respectively (Lunt *et al.*, 1961). Sodium levels for *Holcus lanatus* (Table 5.16) ranged from 0.41% in Treatment RMS25 to 0.79% in Treatment RMSG10. *Lolium perenne* (Table 5.17) sodium concentrations ranged from 0.21% in Treatment RMS25 to 0.42% in 10% process sand addition treatments. Based on the above data, sodium levels in the two grass species are unlikely to restrict plant growth.

Sodium herbage levels recorded in all treatments in the current study are much lower than the maximum sodium contents recorded by Wong and Ho (1993) of 2.27% for *Agropyron* and 1.29% for *Cynodon*. However, these species are known to be tolerant of sodic conditions and *Agropyron* can accumulate sodium levels of up to 4.2 % before growth restrictions occur (Greenway and Rogers, 1963).

Exchangeable sodium was shown to have a stronger relationship with herbage content than water soluble sodium (Appendix 4). An exception to this was for

Holcus lanatus which had a Correlation of r=0.25 for water soluble sodium compared to 0.15 for exchangeable sodium. These findings would suggest that determining exchangeable sodium is a valuable test for assessing bioavailability of sodium.

5.3.6 Calcium

The high ESP values recorded for unamended red mud (62%) highlight the fact that the exchange sites are predominantly filled with sodium. Amendment of the substrate and the subsequent lowering of ESP values to <10% (Table5.11) show an increase in the occurrence of calcium association.

Soluble calcium levels in the red mud treatments are shown in Tables 5.12-5.5.14. Application of gypsum significantly increased ($P<0.05$) levels of soluble calcium in the substrate, with levels in those treatments having a range from 1160-2140 mg/kg Ca compared to 31-57 mg/kg in the treatments without gypsum addition. The values in the non-gypsum treatments are lower than the 148 mg/kg –179 mg/kg range recorded prior to seeding (Table 5.11) and suggest that the limited supply of soluble calcium in those treatments is being leached out or taken up by the plants.

Exchangeable calcium is the major reserve of soil calcium available to plant roots (Haby *et al.*, 1990) as it acts as a supply of calcium over a longer period. Levels of exchangeable calcium cited as low or deficient will vary between plants and soil types. Values of 80 mg/kg and 300 mg/kg are considered to be deficient for tomato and corn plants respectively (Chapman, 1966). Substrate levels recorded in the current study (Tables 5.12-5.14) show all treatments have considerably higher exchangeable Ca than the 660 mg/kg cited as being satisfactory for the growth of corn (Chapman, 1966). The high exchangeable calcium levels in all of the treatments indicate that the thermally dried sludge also acts as a source of calcium as it has a high total content of 2.2% (Appendix 2). The cation exchange capacity (CEC) of the organic matter and the selectivity of exchange sites for Ca over Na may decrease the degree of sodicity in the substrate (Summer and Naidu, 1998).

With the exception of *Holcus lanatus* treatment RMSG10, all gypsum amended plots were significantly ($P<0.05$) higher in exchangeable calcium. This results support the findings of other workers that gypsum exchanges calcium for sodium from the soil exchange sites (Oster and Frenkel, 1981; Gupta and Singh 1988; Chun *et al*., 2001).

In the current study high calcium concentrations in the plant is desirable as it is known to have a protective effect in ameliorating the toxic effects of elevated concentrations of other elements such as aluminium and sodium (Munshower, 1994).

No statistical differences were found between plots amended with gypsum and those that hadn't (Tables 5.15-5.17) for plant calcium content. This indicates that the plants are unable to take up any more calcium from the soil exchange sites.

Levels recorded for *Holcus lanatus* (Table 5.16) range from 0.46% - 0.52% and *Lolium perenne* (Table 5.17) range from 0.56% - 0.63%. These values are within the range typical for Irish herbage (Rogers and Murphy, 2000), although Freand and Peech (1946) cite levels of between 1.04 and 1.75 % as the sufficient range for *Lolium perenne*.

Trifolium pratense (Table 5.15) had higher Ca content compared to *Holcus lanatus* and *Lolium perenne*. The range of calcium levels were $\geq$1.5%, and while there was no statistical differences between the treatments, all had a calcium content higher than the 1.1% deemed adequate for the growth of *Trifolium repens* (Reuter, 1986).

Plants growing in high Na content substrates can have impaired uptake and a subsequent low Ca concentration (Chang and Dregne, 1955; Gupta and Abrol, 1990a) or may display changes in tonoplast permeability as calcium is replaced by sodium (Ricks, 1987). Results from this study contrast with such a finding as none of the plant species can be considered deficient in calcium. As no statistical differences were found for herbage calcium content between treatments it can be deduced that sodium levels in the substrate were not high enough to cause ion toxicity or affect ion regulation in the plant cells.

Correlations performed on substrates levels and herbage content show a stronger relationship for exchangeable calcium compared to water soluble for *Holcus lanatus* and *Trifolium pratense* treatments (Appendix 4). *Lolium perenne* recorded a slightly higher correlation for water soluble calcium (r=0.12) than for the exchangeable fraction (r=0.03). The findings indicate that, due to the high levels of exchangeable calcium in the treatments (>3000 mg/kg), there should be no calcium deficiency for some time. Lower levels of exchangeable calcium in the non-gypsum treatments indicate that calcium deficiency will manifest first in these treatments.

5.3.7 Magnesium

The low soluble magnesium levels of $\leq$ 3 mg/kg recorded prior to seeding (Table 5.11) has been improved as a result of the gypsum and organic amendment as shown in Tables 5.12-5.14. The significantly higher ($P<0.05$) levels of soluble magnesium in the gypsum amended treatments indicate that gypsum is the major source of magnesium in the treatments (Appendix 2). Soluble magnesium content of the gypsum (100 mg/kg) contributed to the lowering of ESP values in the red mud. Because magnesium soil deficiencies or toxicities are so rare in soils, analysis for the element in mine-related soils is normally only carried out when determining the SAR or ESP values of the soil (Munshower, 1994).

Soil levels lower than 15 mg/kg soluble magnesium are considered deficient for the growth of many species (Chapman, 1966). Soluble magnesium levels determined in the red mud substrates show non-gypsum treatments to range from 1.9 - 2.6 mg/kg and from 4.5-6.9 mg/kg in gypsum amended plots. All treatments in the current study can therefore be considered deficient in soluble magnesium. Results obtained in the study are, however, consistent with the increase of Mg-levels from 0.27 to 16.8 mg/kg as achieved by Wong and Ho (1993).

Treatments that had not received gypsum exhibited significantly ($P<0.05$) higher levels of exchangeable magnesium (Tables 5.12-5.14). This can be explained by the exchange complex in the gypsum amended treatments being saturated with Ca^{2+}supplied by the gypsum. The higher Mg-content in the treatments may also be attributed to the ability of the sewage sludge to supply and absorb magnesium.

Highest levels recorded for exchangeable magnesium levels were 45.7 mg/kg in Treatment RMS25 *Holcus lanatus* (Table 5.13). Treatments that had not received gypsum amendment typically had exchangeable magnesium levels of $\geq$30 mg/kg.

Conversely, gypsum treatments had exchangeable magnesium levels of below 30 mg/kg, with most treatments exhibiting values of $\leq$20 mg/kg. Levels of exchangeable magnesium in the range of 25-60 mg/kg can be considered low or deficient for a range of plants (Chapman, 1966). Levels found in the current study can, therefore, be considered to be in the low or deficient range.

Typical figures for magnesium in Irish grasses are 0.2% (Rogers & Murphy, 2000). Levels recorded for *Lolium perenne*(Table 5.17) are $\leq$0.11% with no significant differences between treatments. Levels lower than 0.15% are considered deficient for *Lolium perenne*(Reuter, 1986) and, based on the data presented in Table 5.17, magnesium levels in *Lolium perenne* grown in the red mud are deficient.

Magnesium levels for *Trifolium* are considered adequate when in the range of 0.18-0.22% (Reuter, 1986). Table 5.15 shows Mg levels recorded in *Trifolium* grown in the red mud. No significant differences (P>0.05) were found between treatments and all levels ranged from 0.2% to 0.3%, indicating that the species is more suited to the low levels of plant available magnesium in the red mud substrate.

Magnesium levels for *Holcus lanatus* (Table 5.16) ranged from 0.14% - 0.18%with some significance between treatments. Holcus grown in 25% process sand addition rates was significantly lower than those in the 10% addition rate. This suggests that there may be some leaching of essential nutrients, as well as sodium, in the higher sand application treatments. However, all magnesium levels recorded are marginally lower than the national average and can be considered low. Wong and Ho (1993) found Mg levels in herbage grown on amended red mud to be marginal for plant growth.

As with sodium and calcium, a stronger correlation was found for exchangeable levels in the substrate for *Lolium perene* and *Trifolium pratense* Mg-content than for soluble levels. This relationship was not repeated for *Holcus lanatus* (Appendix 4).

Red mud substrate is deficient in plant available magnesium, and while amendment of the substrate has significantly increased levels, they are still low. As a result, Mg levels in herbage grown in the red mud are in the range considered low or deficient.

5.3.8 Potassium

As an essential element for plant growth, potassium levels in both the substrate and herbage are of concern in this study. Tables 5.12-5.14 show levels of water soluble potassium recorded in the red mud substrates. No significant differences were observed ($P>0.05$) in treatments that had been amended with gypsum, with all treatments displaying results of <8.9 mg/kg. Results are lower than those recorded in amended mud by other workers (Marschner, 1983; Wong and Ho, 1993).

Exchangeable forms of potassium are considered the primary source of K for plant uptake (Knudsen *et al.*, 1986). Levels found in this study (Tables 5.12-5.14) ranged from 20 mg/kg – 44 mg/kg and were inconclusive with regards to the effect of gypsum amendment on potassium levels. Typically, gypsum amended treatments had marginally lower exchangeable potassium compared to the corresponding treatments that had not received gypsum. Again this indicates that the exchange complex in gypsum amended plots is saturated with calcium ions.

Plant K-levels are normally in the region of 2.8% for Irish grasses (Rogers and Murphy, 2000). Potassium levels for *Trifolium* (Table 5.12) range from 1.2% to 1.8% with gypsum or process sand addition having no real effect in plant uptake. All levels are above the critical level of 1.2% cited by Reuter (1986).

As with Trifolium potassium levels, values obtained for *Lolium perenne* (Table 5.14) show gypsum or process sand addition to have no real effect in plant uptake. Average values were below 1%, with Treatment RMS25 exhibiting 0.79%. All treatments are below the 1.7% cited as deficient for *Lolium* (Reuter, 1986).

Levels for *Holcus lanatus* (Table 5.13) were consistent with the trend observed in *Trifolium pratense* and *Lolium perenne*. Levels ranged from 0.8% to 1% and are in the range considered low for a variety of grasses and cereal crops (Chapman, 1966; Reuter, 1986). As with *Lolium*, potassium levels recorded in *Holcus* can therefore be considered deficient. These findings also indicate the ability of *Trifolium* to accumulate sufficient levels of potassium where there is a deficiency in supply.

These findings stand in contrast to Wong and Ho (1993) who achieved significant uptake of potassium in *Agropyron* in treatments amended with gypsum. However, their work was carried out at pot stage, whereas findings in this study are for field trials. Plant K-content can be decreased in substrates of high Na-content (Chang and Dregne, 1955; Gupta and Abrol, 1990a) and this is generally attributed to competition of the two monovalent cations for the same carrier in the root cell membrane.

As with magnesium, plant available potassium is limited in the red mud substrates and plant levels are therefore deficient. In keeping with results for magnesium, *Trifolium* also exhibits an ability to accumulate sufficient amounts of potassium from the low levels in the substrate.

5.3.9 Manganese

Wong and Ho (1993) highlighted Mn deficiency as a potential limiting factor for vegetative growth on red mud. In the current study water-soluble levels of Mn were below the limit of detection of instrumentation used. Manganese extracted with DTPA is shown in Tables 5.12-5.14. Levels ranges from 0.49 mg/kg to 1.06 mg/kg and are therefore below the 1 mg/kg level cited as being low or deficient for plant growth (Munshower, 1993). Manganese-nutrition in plants is generally reduced on alkaline soils due to precipitation of $Mn(IV)O_2$ (Truog, 1945; Gauch, 1972).

Herbage content for manganese in *Trifolium pratense* is shown in Table 5.15. Tissue levels from the gypsum treatments were significantly higher ($P<0.05$) ranging from 17-18 mg/kg compared to levels of 12 mg/kg in non-gypsum treatments.

Significant differences ($P<0.05$) were also found for herbage content in *Holcus lanatus* (Table 5.16) and *Lolium perenne* (Table 5.17) between treatments that had received gypsum amendment and those that had not. Levels are also higher than those recorded for *Trifolium* content, with lowest levels in the two grasses at 21 mg/kg in non-gypsum treatments ranging up to 48 mg/kg in the gypsum treatments.
While the grasses from gypsum amended plots had levels closer to the 50 mg/kg considered deficient for *Lolium perenne*, *Trifolium* sp. and many grasses (Reuter and Robinson, 1986) all species were less than this critical value and also lower than the

Irish mean values (Rogers and Murphy, 2000). Values obtained show manganese deficiency and, therefore, a potential limiting constraint in achieving long-term growth of native species on red mud.

Poor correlations were found for all species between Mn content and DTPA extractable Mn, suggesting that DTPA is not a suitable extracting agent for determining the availability of Mn in red mud.

5.3.10 Copper

Analysis of unamended red mud shows the DTPA extractable copper level to be 1.3 mg/kg. Levels of DTPA extractable copper at time of harvest are shown in Tables 5.12-5.14. The background figure of 1.3 mg/kg increased in all treatments to a range of 2.3 mg/kg to 4.5 mg/kg. Amendment with gypsum or process sand had no significant effect ($P>0.05$) on extractable Cu levels. Total copper content in the sewage sludge of 480 mg/kg (Appendix 2) is the main source of copper in the treatments. Copper levels are, therefore, at the higher end of the 0.1 mg/kg to 3.7 mg/kg range cited by Follett and Lindsay (1970) for soils.

Foliar analysis shows some significant differences between treatments (Tables 5.15 – 5.17). In all cases this is where one treatment exhibited higher levels than the others and this can be possibly attributed to the difficulty of evenly applying the sludge under field conditions. All treatments do, however, exhibit high Cu-content. Lowest levels for *Lolium perenne* (Table 5.17) are 14.8 mg/kg and reach as high as 50.2 mg/kg. Levels greater than 7 mg/kg are considered high for *Lolium perenne* (Reuter, 1986), although no levels considered as toxic are listed.

Trifolium pratense levels are lower (Table 5.15) and range from 16.9 mg/kg to 26.5 mg/kg. Levels of 7mg/kg –16 mg/kg are cited as the intermediate range for some *Trifolium* species (Chapman, 1966), and levels from *Trifolium pratense* grown in red mud are therefore high.

Levels determined in *Holcus lanatus* (Table 5.16) range from 18.6 mg/kg to 26.1 mg/kg. These values are high when compared to research conducted by Rogers and Murphy (2000) who found a range from 1.6 mg/kg -23.7 mg/kg Cu for Irish grasses during a four-year study. Wong and Ho (1992) also reported high levels of Cu in plants grown in red mud amended with sewage sludge.

5.3.11 Zinc

Tables 5.12-5.14 show levels of DTPA extractable zinc levels as determined in the red mud plots at time of plant harvest. Amendment with gypsum or process sand had no significant effect ($P>0.05$) on extractable zinc levels, but levels have increased from an initial 0.46 mg/kg value recorded at time of trial. As with copper, this increase can be attributed to the metal content of the sewage sludge (Appendix 2).

The trend for significant differences between treatments is due to the uneven application of sludge in the field and the heterogeneity of the substrate. There was no deficiency range for extractable Zn reported in the literature but no levels recorded in the red mud treatments were below the crop adequacy level for DTPA-extractable zinc of 1.0mg/kg (Follett and Lindsay, 1970). Phytotoxic responses are generally in the range of 50-125 mg/kg DTPA-extractable zinc (Munshower, 1986) and all levels determined in the study were well below this. Zn levels recorded in this study can, therefore, be considered adequate.

Tissue levels for the three species are shown in Tables 5.15-5.17. Amendment with gypsum or process sand addition rate did not significantly ($P>0.05$) affect zinc content. Some treatments, RMS10 treatments for *Holcus* and *Trifolium*, had significantly higher ($P=<0.05$) Zn content with levels of 27.7 mg/kg and 36.9 mg/kg respectively. Sewage sludge, at the application rate used, increased bioavailable zinc to levels that are more than sufficient for plant growth. Wong and Ho (1991) also found increased levels of zinc in grasses grown on red mud amended with sewage sludge. They did not, however, record a statistically higher zinc content when sewage sludge application rates were raised from 8% to 16%.

Herbage levels recorded were, generally, in the normal plant content range, although levels in excess of 20 mg/kg are considered high for *Lolium perenne* and *Trifolium* species (Reuter, 1986). Levels as high as 84 mg/kg have been recorded for Irish grasses (Murphy and Rogers, 2000) but phytotoxic levels are normally reported only at levels in excess of 300 mg/kg (Munshower, 1986). The highest level recorded in the species from red mud treatments was 37 mg/kg (Table 5.15). Although levels recorded in herbage samples are high, they are not at levels that can be classed as phytotoxic.

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Soluble				
Al (mg/kg)	3.07a (1.17)	0.49bc (0.06)	0.6c (0.14)	1.48d (0.35)
Fe (mg/kg)	11.8a (3.74)	2.18b (1.08)	2.57b (1.59)	9.01a (3.67)
Zn (mg/kg)	0.24a (0.18)	0.43ab (0.19)	0.32a (0.1)	0.17ac (0.04)
Na (mg/kg)	209a (26)	236a (23)	239a (39)	145b (12)
Ca (mg/kg)	52.18a (11.9)	2140.3b (133.9)	2069.4b (437.8)	57.5a (12.7)
Mg (mg/kg)	2.45a (0.7)	6.99b (1.3)	5.5b (1.7)	2.32a (0.4)
K (mg/kg)	8.35a (2.54)	8.93a (1.2)	8.46a (1.86)	5.76b (0.81)
ESP	8. 5 (1.6)	0.5 (0.2)	1.5 (1.7)	5.0 (0.81)
Extractable				
Fe (mg/kg)	6.05a (0.64)	3.93b (0.62)	4.4b (0.7)	4.15b (0.87)
Mn (mg/kg)	0.72aa (0.27)	0.67a (0.08)	0.77a (0.17)	0.6a (0.07)
Cu (mg/kg)	3.00a (0.63)	2.97a (0.48)	2.91a (0.68)	2.32a (0.28)
Zn (mg/kg)	5.77a (2.04)	5.13a (0.72)	5.39ac (1.77)	3.08bc (0.73)
Na (mg/kg)	718a (59)	427b (16)	428b (65)	416b (20)
Ca (mg/kg)	3908a (265)	9554b (1954)	6120c (1560)	3716a (316)
Mg (mg/kg)	33.9a (8.2)	18.36b (1.9)	18.4b (3.9)	27.1a (3.7)
K (mg/kg)	28.05a (5.7)	24.28a (4.3)	27.7a (6.4)	44.0b (4.1)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.12. Chemical properties of substrate in *Trifolium pratense* plots at time of first harvest

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Soluble				
Al (mg/kg)	3.86a (1.52)	0.57b (0.11)	1.16b (0.29)	4.72a (1.2)
Fe (mg/kg)	15.5a (1.7)	2.9b (0.3)	4.3b (2.4)	13.8a (1.3)
Zn (mg/kg)	0.24a (0.1)	0.24a (0.1)	0.22a (0.1)	0.25a (0.1)
Na (mg/kg)	161a (33)	193a (36)	152a (58)	156a (13)
Ca (mg/kg)	31.2a (13.4)	1478.9b (660.5)	1161.08b (608.2)	43.2a (3.7)
Mg (mg/kg)	1.9a (0.5)	5.1b (2.8)	4.5bc (2.0)	2.4ac (0.3)
K (mg/kg)	8.35a (2.6)	8.9a (1.2)	8.4a (1.8)	6.7a (0.4)
ESP	9.3 (2.8)	0.6 (0.4)	0.3 (0.3)	6.2 (1.0)
Extractable				
Fe (mg/kg)	6.2a (2.7)	5.4ab (1.2)	3.6ab (1.8)	9.3ac (2.2)
Mn (mg/kg)	0.77a (0.2)	0.68a (0.1)	0.49a (0.1)	0.59a (0.1)
Cu (mg/kg)	3.12a (0.97)	3.05a (0.68)	2.28b (0.84)	3.79ac (1.08)
Zn (mg/kg)	5.3a (1.6)	5.4a (1.7)	3.3ab (2.0)	7.1ac (0.9)
Na (mg/kg)	408a (19)	389ac (40)	346b (40)	446ad (24)
Ca (mg/kg)	3701a (163)	5614bc (1523)	4687ac (712)	3939a (202)
Mg (mg/kg)	31.4a (9)	18.6b (3.4)	28.6a (9.5)	45.7c (4.8)
K (mg/kg)	28.9a (7.5)	20.1b (3.7)	33.6ad (4.2)	39.1cd (7.1)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.13. Chemical properties of substrate in *Holcus lanatus* plots at time of first harvest

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Soluble				
Al (mg/kg)	3.46a (1.83)	0.64b (0.16)	0.54b (0.2)	2.17a (0.86)
Fe (mg/kg)	13.3a (2.8)	3.0b (0.47)	2.6b (1.52)	13.5a (2.5)
Zn (mg/kg)	0.3a (0.1)	0.29b (0.1)	0.28a (0.1)	0.18c (0.05)
Na (mg/kg)	157a (15)	186b (28)	151a (15)	118c (16)
Ca (mg/kg)	38.2a (6.2)	1508.5b (614)	1360.0b (771)	49.4a (12)
Mg (mg/kg)	2.32a (3)	6.38b (0.5)	5.66bc (0.9)	2.62a (0.4)
K (mg/kg)	8.3a (2.5)	8.9a (1.2)	8.5a (1.9)	5.8a (0.8)
ESP	5.3 (0.7	<1	<1	3.7 (1.1)
Extractable				
Fe (mg/kg)	7.85a (3.4)	8.43a (4.22)	6.08a (1.96)	7.96a (2.69)
Mn (mg/kg)	1.06a (0.1)	0.79ac (0.3)	0.56bc (0.08)	0.62bc (0.2)
Cu (mg/kg)	4.44a (1.75)	4.29a (1.44)	3.53a (1.17)	3.76a (1.08)
Zn (mg/kg)	5.7a (2.2)	7.3a (2.6)	6.1a (2.1)	6.2a (1.5)
Na (mg/kg)	508a (39)	342b (8)	316b (19)	344b (17)
Ca (mg/kg)	3750a (364)	6476b (1488)	6696b (2114)	3786a (180)
Mg (mg/kg)	34.6a (6)	19.6b (5.7)	18.4b (6.7)	31a (2.7)
K (mg/kg)	32.9a (7.8)	23.6b (4.2)	20.2b (4.7)	20.2b (3.2)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.14. Chemical properties of substrate in *Lolium perenne* plots at time of first harvest

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Al (mg/kg)	90a (38)	44b (14)	47b (13)	93a (12)
Fe (mg/kg)	264.6a (84)	112.5b (81)	130.7b (82)	274.4a (142)
Cu (mg/kg)	18.2a (1.8)	19.5a (2.4)	26.5b (4.3)	16.9a (1.4)
Zn (mg/kg)	36.9a (2.0)	33.5acb (2.3)	31.8bc (3.4)	30.7ce (2.0)
Mn (mg/kg)	12.24a (1.49)	17.88b (3.4)	18.3b (1.7)	12.7a (1.9)
Na (%)	0.93a (0.09)	0.62b (0.09)	0.5c (0.03)	0.46c (0.03)
Ca (%)	1.5a (0.1)	1.6a (0.1)	1.5a (0.1)	1.5a (0)
Mg (%)	0.3a (0)	0.2a (0)	0.2a (0)	0.2a (0)
K (%)	1.2a (0.1)	1.6b (0.2)	1.6b (0.2)	1.8b (0.1)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.15. Herbage elemental content for *Trifolium pratense* First years growth

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Al (mg/kg)	181a (36)	108b (42)	158ab (64)	213a (47)
Fe (mg/kg)	518a (142)	255bc (125)	323ac (150)	585ad (114)
Cu (mg/kg)	19.5a (2.7)	26.1a (9.8)	23.9a (9.1)	18.6a (9.8)
Zn (mg/kg)	27.7a (4.7)	24.5ac (4.4)	24.1ac (5.8)	19.8bc (2.2)
Mn (mg/kg)	26.7a (3.4)	47.8b (10.3)	43.4b (13.7)	26.2a (3.1)
Na (%)	0.72a (0.1)	0.79a (0.2)	0.43b (0.1)	0.41b (0.1)
Ca (%)	0.47a (0.03)	0.47a (0.03)	0.52a (0.03)	0.46a (0.03)
Mg (%)	0.18a (0.01)	0.17ac (0.03)	0.14bc (0.03)	0.14b (0.02)
K (%)	0.96a (0.1)	1.00a (0.1)	0.89ac (0.1)	0.8bc (0.04)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.16. Herbage elemental content for *Holcus lanatus* First years growth

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Al (mg/kg)	218a (104)	143a (55)	175a (91)	589b (127)
Fe (mg/kg)	463a (160)	262a (161)	389a (219)	1600b (302)
Cu (mg/kg)	22.4a (6.4)	50.2b (17.9)	20.6a (7.4)	14.8a (1.7)
Zn (mg/kg)	33.4a (4.5)	31.5a (5.2)	30.1a (4.6)	26.5a (3.9)
Mn (mg/kg)	21.6a (1.9)	36.3b (5.6)	41.9c (7.2)	23.8a (1.5)
Na (%)	0.42a (0.07)	0.42a (0.09)	0.24b (0.05)	0.21b (0.04)
Ca (%)	0.56a (0.04)	0.59ab (0.03)	0.59ab (0.03)	0.63a (0.02)
Mg (%)	0.11a (0.01)	0.09b (0.01)	0.08b (0.02)	0.08b (0.01)
K (%)	0.94a (0.1)	0.98ab (0.2)	0.89a (0.1)	0.79ac (0.1)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.17. Herbage elemental content for *Lolium perenne*
First years growth

5.4 Comparison of Results of Trial Tasks

In the comparison of results from the three separate tasks it is important to note that the muds used came from three separate areas of the mud stack. The initial screening of species used mud from a terraced area of the stack. The large pot trials used mud that was prepared in the field using agricultural machinery. This came from an open domed area of the stack. Field trials were constructed on a terraced area on the south west of the mud stack.

5.4.1 Physical Status of Substrate Conditions

Physical conditions exhibited by mud treatments in the small pot trials (Section 5.1.1) included hard setting and poor water retention. It is accepted that the original method employed for mixing the muds poorly replicates what would happen under field conditions. The second method employed for mixing treatments (Section 5.1.2), while improving both physical and chemical parameters of the substrate, does not replicate conditions that would be expected under field conditions. The methodology adopted for the large pot trials and field trials involved amendment and improvement of the substrate under actual field conditions. Plate 4.6 illustrates the quality of tilth achieved under such conditions. This overcomes the problems encountered with the small pot trials where the extruding of the mixed material from the pug mill resulted in a compacted substrate, increasing its bulk density, compacting and decreasing pore space for air and water retention. The improved success of the latter treatments shows the importance of a good physical structure in achieving vegetative growth on red mud.

5.4.2 Chemical Conditions

As mentioned above, muds came from different areas of the stack. As such, the muds would be of different ages and, consequently, would have been subjected to varying periods of weathering.

Soluble cations and pH levels as recorded in unamended mud from both the terraced area and the open dome are shown below (Table 5.18a). Comparison of mud samples from the terraced area and the open dome show a higher pH range in the fresher mud from the open dome. Levels recorded in the terraced area average 9.7, levels from the open dome average10.2. Mud pH values recorded between the two do not vary considerably and all exhibit levels cited by other authors as either being inhibitory to plant growth or having a detrimental effect on plant growth (Meecham and Bell, 1977; Fuller *et al.*, 1982; Wong and Ho, 1994).

	Soluble (mg/kg)				
Location	Na	Ca	Mg	ESP	pH
Field Trials	1120a	3.8a	1.4a	62a	10.2a
Large Pot Trials	1728b	7.7b	1.2a	67a	9.7a

Means within a column followed by the same letters are not significantly different at P=<0.05

Table 5.18a. Soluble Cations from Field Trials and Large Pot Trials of Mudstack prior to Amendment of Mud

Average ESP values in unamended samples from both trials are not significantly different (P>0.05) and both are well above the level where nutritional disturbances occur. High ESP values result from <10 mg/kg calcium levels and magnesium of less than 2 mg/kg coupled with sodium values in excess of 1,000 mg/kg.

Table 5.18b shows a comparison of critical parameters following amendment with gypsum and process sand. Significantly higher (P>0.05) soluble calcium content was found for terraced mud (1737 mg/kg) compared to 564 mg/kg from the open dome area. This higher calcium content coupled with the lower sodium content produces a significantly lower (P>0.05) ESP value. ESP levels of 2 recorded in gypsum treatments in terraced mud are less than the critical value of 10 for fine and 20 for coarse textured soils (Bernstein, 1974). Conversely, values for the amended mud from the dome area are still high at 31%, close to 40-50% threshold level, above which nutritional disturbances in plants occur from excess sodium (Thorne, 1945).

Mud pH values for both treatments have both decreased from their initial high values to levels more common in natural environments (Munshower, 1994). Results demonstrate the degree of weathering achievable on the stack. A greater reduction in ESP values was obtained for the terraced area. This is due to the higher calcium content of the substrate. Lower levels of sodium were also obtained for terraced mud (Table 5.18b). This is due to the high calcium supply causing leaching of the sodium. The close proximity of the site to the rockfill retainer banks may also have aided in the weathering process as this would produce a freer draining area.

Figures 5.2 and 5.3 illustrate the strong relationship of ESP values with pH and soluble Al. It is therefore likely that a reduction in any one of these parameters would result in a reduction of the other two. In can therefore be said that an improvement of physical conditions and a supply of calcium improves the red mud substrate for plant growth.

	Soluble (mg/kg)				
Location	Na	Ca	Mg	ESP	pH
Terraced Mud	363a	1737a	2.5a	2a	8.0a
Open Dome	2954b	564b	2.9a	31b	8.6a

Means within a row followed by the same letters are not significantly different at P=<0.05

Table 5.18b. Soluble Cations from Field Trials and Large Pot Trials following amendment of Mud with Gypsum

5.4.4 Plant Performance

This section addresses plant performance for all trials after the first years growth.
Poor plant performance at small pot stage can be attributed to the predominance of poor physical structure as discussed previously in Section 5.1.1. However, a marked difference in plant performance was achieved between growth in large pot trials and field trials. The much lower sodium and ESP values achieved in the field trials (Table 5.18a) are the principal reason for this marked improvement.

ESP values of <10 were achieved in non-gypsum treatments, such levels are below the critical value of 10 cited by Bernstein (1974) for fine-textured soils. This finding stands in contrast to that of the large pot stage where a high percentage of non-gypsum trials failed. This was most noticeable with *Trifolium pratense* where all non-gypsum treatments failed at large pot stage and can be attributed to ESP values of 67 (Table 5.7) and pH above 10. The success of non-gypsum treatments in the field illustrate that its addition is not always necessary to establish plant growth.

It was also found that the thermally dried sewage sludge was not a sufficient amendment at large pot stage unless accompanied by gypsum (Section 5.2.2). These findings suggest that organic matter in this form, dry pelletised, is only a useful amendment to red mud if ESP and pH levels are reduced to suitable levels. Wong and Ho (1993) reported the need to successfully lower ESP and pH levels prior to organic addition.

As no growth was achieved for *Trifolium pratense* in non-gypsum treatments it is only possible to compare the results obtained from the gypsum amended treatments. Calcium content did not significantly differ ($P<0.05$) between the two trials with an average value of 1.5% for both trials. No significant difference ($P<0.05$) was observed either for iron content with 115mg/kg for pot trials and 121mg/kg for field trials.

Magnesium levels were higher in field conditions, 0.3 % compared to 0.11% recorded for the large pot trials. As substrate magnesium concentrations did not vary considerably in the two trials the lower magnesium uptake may be attributed to the higher substrate sodium content found in the large pot trials.

Sodium levels were significantly higher ($P>0.05$) in *Trifolium pratense* grown in the large pots with an average value of 1.9%, whilst samples from the gypsum amended field plots exhibited levels in the region of 0.6%. This is a reflection of the higher sodium levels exhibited in pot trial work, 2954 mg/kg in pot trials and 1120 mg/kg for field trials. The higher Na^+ substrate content in large pot treatments may also explain the high mortality rate for *Trifolium pratense*.

Manganese levels in both trials were at levels deemed deficient. Levels found in field trials were 18 mg/kg compared to 35 mg/kg for pot trials. The low levels for both treatments reflect the deficiency status of red mud.

Calcium, sodium and magnesium levels for *Lolium perenne* and *Holcus* lanatus repeated the same trend as reported for *Trifolium pratense.* Although levels of manganese and iron differed between trials the same trend was found in the effect of gypsum in increasing Mn and decreasing Fe uptake.

Dry weight biomass production increased for all treatments in field trials. *T. pratense* amended with SMC improved from 250 g/m^2 in large pot to 600 g/m^2 in field trials. Increases from 332g/m^2 to 475 g/m^2 were recorded for DIB treatments and from 124 g/m^2 to 620 g/m^2 in agricultural dung amended plots. TDSS yielded biomasses of 306 g/m^2 and 675 g/m^2 in non-gypsum and gypsum amended plots respectively.

SMC treatments for *L.perenne* increased from 232 g/m^2 to 550g/m^2 in gypsum plots and from 66 g/m^2 to 150 g/m^2 in non-gypsum plots. For *H.lanatus* increases from 323g/m^2 to 570g/m^2 occurred and for *F.longifolia* from 250 g/m^2 to 323 g/m^2.

Increase also occurred for agricultural dung amendments to all species. Increased biomass is indicative of the improved substrate conditions previously discussed.

5.5 Field Trials - Second Years Growth

5.5.1 Herbage Elemental Content

This section addresses elemental content of grasses as determined after a second years growing season. A fertiliser application at same rate as the first year was applied to the field trials during the second years growth. Results are shown in Tables 5.19 to 5.21. Section 5.6 compares herbage elemental content as determined on a yearly basis.

Gypsum addition did not produce a significant difference ($P<0.05$) in Al herbage content for *Trifolium pratense* in Treatments RMS10, RMSG10 and RMSG25 but RMS25 had higher levels than the other treatments. Results determined for Treatments RMS10, RMSG10 and RMSG25 were <120 mg/kg, the higher value of 164 mg/kg in Treatment RMS25. None of these levels are in excess of the 310 mg/kg cited by Jones (1961) as being high for *Trifolium* sp.

Aluminium levels for *Holcus lanatus* and *Lolium perenne* are shown in Tables 5.20 and 5.21. Highest values were obtained in treatments with 25% process sand addition. Lowest values were obtained in RMSG10 from although this difference was not always significant. Aluminium levels of 209 mg/kg for unpolluted Irish pasture have been cited by McGrath *et al.* (2001). Treatments with 25% process sand have aluminium levels in excess of this figure and all treatments are above the 0.2% values generally found in grasses (Hutchinson, 1945). No levels were in excess of the 1200 mg/kg considered toxic for cattle and sheep dietary intake (Puls, 1988).

Sodium levels for the three species are shown in Tables 5.19 to 5.21. No significant difference ($P<0.05$) was found between treatments. The sodium content levels for *Trifolium pratense* were 0.43% for RMS10; 0.33% for RMSG10; 0.37% for RMSG25 and 0.36 % for RMS25. A reduction *in Trifolium pratense* growth occurs when levels are in the range of 0.2-0.32%. As such growth restrictions may occur in non-gypsum treatments. In addition, some pasture grasses have reduced growth above 0.3% (Lunt *et al.*, 1961). Sodium herbage content in herbage for the trials may be considered to be at critical levels after a second years growing season.

Calcium levels for *Trifolium pratense* are shown in Table 5.19. Values were between 1.38% and 1.5% and no statistical differences ($P<0.05$) between the treatments was found. As such, all levels are higher than the 1.1% deemed adequate for the growth of *T.repens* (Reuter, 1986) and are not considered deficient. *Lolium perenne* had higher Ca content in treatments with 25% process sand (Table 5.21), possibly demonstrating an increase in the leaching of available Na^{+}. No statistical differences were found between the treatments for *Holcus lanatus* with levels at 0.3% (Table 5.20). However, calcium contents for *Lolium perenne* and *Holcus* *lanatus* are lower than sufficient levels cited between 1.04% and 1.75 % (Fred and Peech, 1946). Whilst calcium deficiency is not prevalent in *Trifolium pratense* it may be a problem in the two grasses.

No significant difference ($P<0.05$) was recorded between treatments for magnesium levels. No significant differences were recorded between treatments in Mg-content for any species. Levels in *Trifolium pratense* averaged 0.14%; for *Holcus lanatus* 0.06% and for *Lolium perenne* 0.06%. Although levels for *Trifolium pratense* were higher than for the other two species, levels lower than 0.15% are considered deficient for *Lolium perenne* and levels for *Trifolium* are considered adequate when in the range of 0.18-0.22% (Reuter, 1986). Magnesium levels recorded for the second years growth can be considered deficient.

Potassium levels for *Trifolium pratense* in the four treatments did not significantly differ ($P<0.05$) with the lowest value of 1.47% recorded for treatment RMS10. All treatments are above the critical level for adequate plant growth of 1.2% (Reuter, 1986). Levels for *Holcus lanatus* and *Lolium perenne* did not have significant differences and averaged 1% and 0.85% respectively. Such levels are in the range considered low for a variety of grasses and cereal crops (Chapman, 1966l; Reuter, 1986). As with calcium results, potassium deficiency is not present in *Trifolium pratense* but may be a concern for the two grass species.

The addition of gypsum to treatments had a marked effect on manganese content with each species having significantly higher herbage content ($P<0.05$) in gypsum amended plots (Tables 5.19-5.21). Highest values achieved for the grasses were 18.2 mg/kg for *Trifolium pratense*, 14.4 mg/kg for *Holcus lanatus* and 12.9 mg/kg for *Lolium perenne*. Such levels are severely below the threshold 50 mg/kg value considered deficient for *Lolium perenne*, *Trifolium* sp. and many grasses (Reuter and Robinson, 1986). Wong and Ho (1993) cite manganese deficiency as a potential limiting factor in achieving long-term growth in red mud. Levels determined in the second years growth are, therefore, of concern.

Trifolium pratense copper content ranged from 12.8 mg/kg to 18.2 mg/kg (Table 5.19) and does not exceed the 7-16mg/kg range cited as the intermediate range for some *Trifolium* species (Chapman, 1966). No significant difference was found between treatments. Levels recorded for *Lolium perenne* treatments can be considered moderately high as levels greater than 7mg/kg are considered high for *Lolium perenne* (Reuter, 1986), levels in the treatments range from 10.5 mg/kg to 14.5 mg/kg. *Holcus lanatus* results range 12.5 mg/kg to 16.8 mg/kg (Table 5.20). Levels for the three species in all treatments are within the 1.6-23.7 mg/kg Cu range recorded in Irish grasses (Rogers and Murphy, 2000) and are not considered toxic as such symptoms do not normally occur at levels less than 150 mg/kg (Williamson *et al.*, 1982).

Zinc content in *Trifolium pratense* ranged from 25-27 mg/kg (Table 5.19) with no significant differences between treatments ($P<0.05$). *Holcus lanatus* had no significant differences between treatments ($P<0.05$) and plant content ranged from 13-15 mg/kg (Table 5.20). Some variation was recorded for *Lolium perenne* (Table 5.21) but all of the three species had levels below the 20 mg/kg considered high for *Lolium perenne* (Reuter, 1986). Phytotoxic symptoms normally occur in plant when zinc levels exceed 300 mg/kg (Reuter and Robinson, 1986) and, therefore, zinc content for all species are not considered excessive.

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Al (mg/kg)	105.2a (37)	118a (34)	105a (41)	164b (22)
Fe (mg/kg)	279a (58)	285a (101)	253a (82)	507b (70)
Cu (mg/kg)	18.2a (5.5)	17.0a (5.2)	16.7a (3.7)	12.8a (1.9)
Zn (mg/kg)	26.3a (2.8)	27.5a (3.9)	26.1a (3.2)	25.6a (3.8)
Mn (mg/kg)	13.45a (2.4)	16.4b (2.6)	18.2b (2.4)	13.0a (2.7)
Na (%)	0.43a (0.13)	0.33a (0.o4)	0.37a (0.1)	0.36a (0.05)
Ca (%)	1.54a (0.16)	1.50a (0.19)	1.59a (0.22)	1.38a (0.1)
Mg (%)	0.14a (0.02)	0.13a (0.01)	0.13a (0.02)	0.15a (0.01)
K (%)	1.47a (0.18)	1.76a (0.3)	1.60a (0.45)	1.78a (0.12)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.19. Herbage elemental content for *Trifolium pratense* Second years growth

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Al (mg/kg)	230.4a (68)	188.8a (44)	275.7ac (70)	334.8bc (46)
Fe (mg/kg)	611a (194)	364b (65)	684a (208)	811a (114)
Cu (mg/kg)	12.7a (2.6)	12.5a (2.3)	12.9a (2.1)	16.8b (1.7)
Zn (mg/kg)	13.5a (3.2)	15.2a (2.2)	13.1a (1.7)	13.0a (0.7)
Mn (mg/kg)	7.7a (1.7)	14.4bc (4.9)	12.1ac (2.3)	8.4a (0.8)
Na (%)	0.38a (0.03)	0.34ac (0.1)	0.29bc (0.03)	0.32ac (0.02)
Ca (%)	0.31a (0.09)	0.31a (0.04)	0.30a (0.02)	0.30a (0.04)
Mg (%)	0.07a (0.003)	0.07a (0.005)	0.06a (0.005)	0.06a (0.005)
K (%)	1.01a (0.16)	1.01a (0.08)	0.99a (0.14)	1.02a (0.43)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.20 Herbage elemental content for *Holcus lanatus* Second years growth

	Treatment*			
	RMS10	RMSG10	RMSG25	RMS25
Al (mg/kg)	260a (77)	150ac (38)	302ad (76)	492b (85)
Fe (mg/kg)	530a (83)	288a (106)	466a (51)	1567b (247)
Cu (mg/kg)	11.4a (2.4)	10.5ab (1.6)	14.5ac (2.7)	14.5ac (2.6)
Zn (mg/kg)	19.4a (3.3)	15.9bc (0.9)	17.7ac (2.6)	17.1ac (1.1)
Mn (mg/kg)	9.2a (1.05)	12.1b (0.82)	12.9b (2.3)	9.7a (0.6)
Na (%)	0.35a (0.04)	0.32a (0.03)	0.25b (0.03)	0.33a (0.03)
Ca (%)	0.55a (0.07)	0.46ab (0.06)	0.57ac (0.07)	0.60 ac (0.04)
Mg (%)	0.07a (0.003)	0.07a (0.005)	0.06a (0.005)	0.06a (0.005)
K (%)	0.79a (0.07)	0.91bc (0.12)	0.83ac (0.04)	0.75a (0.06)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Means within a row followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.21. Herbage elemental content for *Lolium perenne* Second years growth

5.6 Comparison of First and Second Years Plant Performance

5.6.1 Elemental Composition

Statistical comparison of herbage content from first and second years growth is shown in Tables 5.22 – 5.24. Aluminium levels recorded in *Trifolium pratense* increased in all treatments following a second year's growth. This increase was significant ($P<0.05$) in treatments RMSG10, RMSG25 and RMS25 but not in treatments RMS10. Significant increases also occurred for *Holcus lanatus* in treatments RMSG10 and RMSG25 (Table 5.23) and for *Lolium perenne* in treatment RMSG25 (Table 5.24). These increases indicate that levels of available Al have increased. This may be due to the calcium supply from gypsum diminishing and a resultant rise in pH levels. Section 5.2.1.2 demonstrates a strong correlation between pH and soluble Al levels.

Although Al content increased in each treatments all levels for *Trifolium pratense* and *Holcus lanatus* are still less than the 310 mg/kg cited as being high for *Trifolium* sp. (Jones, 1961). High Al content for *Lolium perenne* in treatment RMS25 of 492mg/kg is higher than 474mg/kg found in unpolluted Irish pasture (McGrath, 2001). Levels are therefore of concern as a strong correlation was found for seedling growth and Al content (Wong and Ho, 1993). The increase in Al uptake in herbages may be a contributing factor in the decline of plant growth in the second year growing season as shown in dry weight biomass results (Charts 5.11-5.13).

Iron levels also increased in the three species for all treatments although this was not always a significant increase (Table 5.22-5.24). Significant differences ($P<0.05$) were recorded for *Trifolium pratense* in both gypsum treatments with contents increasing from 112-130 mg/kg to 253-279 mg/kg. *Holcus lanatus* in treatment RMSG25 significantly increased from 323 mg/kg to 684 mg/kg. These findings indicate that the effect of gypsum has decreased in the second year's growth, possibly due to leaching of the calcium. Excessive levels of >1500 mg/kg were recorded for *Lolium perenne* in each of the 2 years in treatment RMS25, these levels are of concern as dietary levels of 1000-2000 mg/kg are considered high for cattle (Puls, 1988). The increases in herbage iron content may be a factor in the poorer biomass levels recorded in the second years growth (Charts 5.11-5.13).

Herbage levels for copper and zinc decreased for all species in the four treatments after the second years growth (Tables 5.22-5.24). *Trifolium pratense* copper levels ranged from 12.8 mg/kg in treatment RMS25 to 18.2 mg/kg in RMS10, these levels are in keeping with the 7-16 mg/kg intermediate range for some *Trifolium* species (Chapman, 1966). Maximum copper levels for *Lolium perenne* and *Holcus lanatus* were 14.5 mg/kg and 16.8 mg/kg respectively. Treatment RMSG10 for *Holcus lanatus* had decreased from 26.1 mg/kg to 12.5mg/kg and in RMSG25 from 23.9 mg/kg to 12.9 mg/kg and for *Lolium perenne* decreases from 22.4 mg/kg to 11.4 mg/kg and 50.2 mg/kg to 10.5 mg/kg in treatments RMS10 and RMSG10. Decreases were not always significant (P>0.05), illustrating the heterogeneity of the substrate and the complex interaction of the root systems. The decreases in plant content show the breakdown of the organic medium as an element supply source.

Significant decreases in zinc levels were recorded for the three species in all treatments in the second years plant content (Tables 5.22-5.24). *Lolium perenne* had a maximum value of 33.4 mg/kg in the first years growth and decreased to 19.4 mg/kg. *Holcus lanatus* treatment RMS10 decreased from 27.7 mg/kg to 13.5 mg/kg. Levels recorded for the second years plant content are below the 20 mg/kg considered high for many species (Reuter, 1986). *Trifolium pratense* levels have also significantly decreased from the previous year (Table 5.22).

Wong and Ho (1993) reported that Mn-deficiency may be a limiting factor in achieving vegetative growth on red mud. Levels obtained in the current study following one years growth showed all grasses to be deficient in manganese although gypsum addition did significantly improve its uptake. Analysis following the second years growth showed a significant decrease (P<0.05) in manganese for *Holcus lanatus* and *Lolium perenne* in all treatments. The results for *Trifolium pratense* showed no change but all treatments exhibit deficient levels. Decreases from >40 mg/kg to 12 mg/kg were recorded for *Holcus lanatus* (Table 5.23) and from 30 mg/kg to 15.9 mg/kg for *Lolium perenne* gypsum treatments (Table 5.24). As levels were already deficient this further decrease in levels shows that some form of site management is necessary if sustainable growth is to be achieved on the red mud.

Levels of sodium recorded in the second years harvest are significantly lower ($P<0.05$) than for the previous years. This finding does not support the hypothesis put forward by Wong and Ho (1995) that sodium is slowly released from the sodium-alumino-silicates in the mud, because in this study strong correlations were found between exchangeable sodium levels and *Trifolium pratense* and *Lolium perenne* (Section 5.3.3). *Trifolium pratense* Na-content decreased from a maximum 0.93 % to $\leq$0.43% and in *Holcus lanatus* from 0.7% to 0.3% (Table 5.23) and for *Lolium perenne* decreases from 0.42 % to 0.32% (Table 5.24) occurred. However, many of the levels recorded can be considered high and are within the range of 0.3-0.8% where growth restrictions occur (Bernstein and Pearson, 1956; Lunt *et al.*, 1961). Although levels are still high the decrease in sodium content for all species indicates that sodium uptake in not a contributing factor for the decrease in dry weight biomass recorded in the second years growth.

Calcium content for *Trifolium pratense* has not significantly decreased in the second years growth and levels are still above the 1.1% deemed adequate for the growth of *Trifolium* sp. (Reuter, 1986). In contrast, calcium levels have signifcantly decreased for the second years growth in *Holcus lanatus* from maximum values of 0.52% to 0.30% (Table 5.23). *Lolium perenne* levels also decreased but this was not always significant (Table 5.24). The decrease in calcium herbage content indicates a deficiency in available calcium in the substrate.

Magnesium levels for all species in the four treatments are significantly lower ($P<0.05$) in the second years growth. This finding suggests that most of the exchangeable magnesium present in the soil has been leached. Levels recorded for *Trifolium pratense* after the first years growth were above the adequate range of 0.18-0.22% (Reuter, 1986) but all are deficient in the second years growth at levels of <0.15% (Table 5.22). Levels found in *Holcus lanatus* and *Lolium perenne* decreased to levels of <0.1%, with values as low as 0.06% in RMSG25 and RMS25 treatments (Tables 5.22-5.23). These values are much lower than the 0.15% cited for many grasses as being the critical threshold for deficiency symptoms (Reuter, 1986).

Trifolium pratense potassium content in the second years growth ranges from 1.47% in RMS10 to 1.78 % in RMS25, these values have not decreased from the previous years and are above the critical level of 1.2% (Reuter, 1986). While some variations were recorded in potassium content between the two years growth for *Holcus lanatus* and *Lolium perenne* treatments, plant levels deficient in potassium (Tables 5.23-5.24).

A decrease in plant performance is evident from dry weight biomass results as shown in Charts 5.11-5.13. Dry weight biomass results did not significantly decrease for *Trifolium pratense* treatments (Chart 5.11). Although increases in aluminium and iron herbage content occurred for *Trifolium pratense*, levels of manganese and calcium had not significantly decreased ($P<0.05$). The increase in both aluminum and iron did not have a significant impact on *Trifolium pratense* growth during the second year growing season as biomass did not significantly decrease. Major decreases in biomass were recorded for *Holcus lanatus* and *Lolium perenne* (Charts 5.12 and 5.13). Aluminium and iron content increased for the two species, but in addition, calcium, magnesium and manganese content significantly decreased ($P<0.05$). The decline in plant performance can therefore be attributed to the deficiency in these elements and to the increase in aluminium and iron content.

	Treatment*							
	RMS10		RMSG10		RMSG25		RMS25	
	1	2	1	2	1	2	1	2
Al (mg/kg)	90a (38)	105a (37)	44a (14)	118b (34)	47a (13)	105b (41)	93a (12)	164b (22)
Fe (mg/kg)	264a (84)	279a (58)	112a (81)	285b (101)	130a (82)	253b (82)	274a (142)	507b (70)
Cu (mg/kg)	18.2a (1.8)	18.2a (5.5)	19.5a (2.4)	17.0a (5.2)	26.5a (4.3)	16.7b (3.7)	16.9a (1.4)	12.8b (1.9)
Zn (mg/kg)	36.9a (2.0)	26.3a (2.8)	33.5a (2.3)	27.5b (3.9)	31.8a (3.4)	26.1b (3.2)	30.7a (2.0)	25.6b (3.8)
Mn (mg/kg)	12.2a (1.49)	13.45a (2.4)	17.8a (3.4)	16.4a (2.6)	18.3a (1.7)	18.2a (2.4)	12.7a (1.9)	13.0a (2.7)
Na (%)	0.93a (0.09)	0.43b (0.13)	0.62a (0.09)	0.33b (0.o4)	0.5a (0.03)	0.37b (0.1)	0.46a (0.03)	0.36b (0.05)
Ca (%)	1.5a (0.1)	1.5a (0.16)	1.6a (0.1)	1.50a (0.19)	1.5a (0.1)	1.5a (0.22)	1.5a (0)	1.4a (0.1)
Mg (%)	0.3a (0)	0.14b (0.02)	0.2a (0)	0.13b (0.01)	0.2a (0)	0.13b (0.02)	0.2a (0)	0.15b (0.01)
K (%)	1.2a (0.1)	1.47b (0.18)	1.6a (0.2)	1.76a (0.3)	1.6a (0.2)	1.6a (0.45)	1.8a (0.1)	1.78a (0.12)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum

RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand

1= 1st years harvest; 2= 2nd years harvest

Means within a treatment followed by the same letters are not significantly different at P=<0.05

Values in parentheses are standard deviation of mean of 8 samples

Table 5.22. Statistical comparison of herbage elemental content for *Trifolium pratense* – First and Second Years Growth

	Treatment*							
	RMS10		RMSG10		RMSG25		RMS25	
	1	2	1	2	1	2	1	2
Al (mg/kg)	181a (36)	230a (68)	108a (42)	189b (44)	158a (64)	275b (70)	213a (47)	334b (46)
Fe (mg/kg)	518a (142)	611a (194)	255a (125)	364a (65)	323a (150)	684b (208)	585a (114)	811b (114)
Cu (mg/kg)	19.5a (2.7)	12.7b (2.6)	26.1a (9.8)	12.5b (2.2)	23.9a (9.1)	12.9b (2.1)	18.6a (9.8)	16.8a (1.7)
Zn (mg/kg)	27.7a (4.7)	13.5b (3.2)	24.5a (4.4)	15.2b (2.2)	24.1s (5.8)	13.1 b (1.7)	19.8a (2.2)	13.0b (0.7)
Mn (mg/kg)	26.7a (3.4)	7.7b (1.7)	47.8a (10.3)	14.4 b (4.9)	43.4a (13.7)	12.1b (2.3)	26.2a (3.1)	8.4b (0.8)
Na (%)	0.72a (0.1)	0.38b (0.03)	0.79a (0.2)	0.34b (0.1)	0.43a (0.1)	0.29b (0.03)	0.41a (0.1)	0.32a (0.02)
Ca (%)	0.47a (0.03)	0.31b (0.09)	0.47a (0.03)	0.31b (0.04)	0.52a (0.03)	0.30b (0.02)	0.46a (0.03)	0.30b (0.04)
Mg (%)	0.18a (0.01)	0.07b (0.003)	0.17a (0.03)	0.07b (0.005)	0.14a (0.03)	0.06b (0.005)	0.14a (0.02)	0.06b (0.005)
K (%)	0.96a (0.1)	1.47a (0.18)	1.00a (0.1)	1.01a (0.08)	0.89a (0.1)	0.99b (0.14)	0.8a (0.04)	1.02a (0.43)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
1= 1st years harvest; 2= 2nd years harvest
Means within a treatment followed by the same letters are not significantly different at P=<0.05
Values in parentheses are standard deviation of mean of 8 samples

Table 5.23. Statistical comparison of herbage elemental content for *Holcus lanatus* – First and Second Years Growth

	Treatment*							
	RMS10		RMSG10		RMSG25		RMS25	
	1	2	1	2	1	2	1	2
Al (mg/kg)	218a (104)	260a (77)	143a (55)	150a (38)	175a (91)	302b (76)	589a (127)	492a (85)
Fe (mg/kg)	463a (160)	530a (83)	262a (161)	288a (106)	389a (219)	466a (51)	1600a (302)	1567a (247)
Cu (mg/kg)	22.4a (6.4)	11.4b (2.4)	50.2a (17.9)	10.5b (1.6)	20.6a (7.4)	14.5a (2.7)	14.8a (1.7)	14.5a (2.6)
Zn (mg/kg)	33.4a (4.5)	19.4b (3.3)	31.5a (5.2)	15.9b (0.9)	30.1a (4.6)	17.7b (2.6)	26.5a (3.9)	17.1b (1.1)
Mn (mg/kg)	21.6a (1.9)	9.2b (1.05)	36.3a (5.6)	12.1b (0.82)	41.9a (7.2)	12.9b (2.3)	23.8a (1.5)	9.7b (0.6)
Na (%)	0.42a (0.07)	0.35b (0.04)	0.42a (0.09)	0.32b (0.03)	0.24a (0.05)	0.25a (0.03)	0.21a (0.04)	0.33b (0.03)
Ca (%)	0.56a (0.04)	0.55a (0.07)	0.59a (0.03)	0.46b (0.06)	0.59a (0.03)	0.57a (0.07)	0.63a (0.02)	0.60a (0.04)
Mg (%)	0.11a (0.01)	0.07b (0.003)	0.09a (0.01)	0.07b (0.005)	0.08a (0.02)	0.06b (0.005)	0.08a (0.01)	0.06b (0.005)
K (%)	0.94a (0.1)	0.79b (0.07)	0.98a (0.2)	0.91a (0.12)	0.89a (0.1)	0.83a (0.04)	0.79a (0.1)	0.75a (0.06)

* RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum

RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand

1= 1^{st} years harvest; 2= 2^{nd} years harvest

Means within a treatment followed by the same letters are not significantly different at P=<0.05

Values in parentheses are standard deviation of mean of 8 samples

Table 5.24. Statistical comparison of herbage elemental content for *Lolium perenne* – First and Second Years Growth

5.6.2 *Plant Biomass Yield*

Charts 5.11-5.13 illustrate biomass results for the field trials over the two year growing period. It can be seen that for the first years growth gypsum addition did not have a significant impact on plant yield for *Holcus lanatus* with biomass levels of 805 g/m^2 for RMS10; 1032 g/m^2 for RMSG10; 960 g/m^2 for RMSG25 and 973 g/m^2 for RMS25. Gypsum addition increased yields for *Trifolium pratense* in the first year with biomass values increasing from 300 g/m^2 in non-gypsum treatments to 600-700 g/m^2 in gypsum treatments. *Lolium perenne* dry weight biomass was also significantly increased with gypsum addition, from 200-450 g/m^2 in non-gypsum to 820-1200 g/m^2 with gypsum addition. The effect of gypsum on substrate conditions and plant uptake is addressed in Section 5.3.

Trifolium pratense biomass yield did not significantly differ ($P<0.05$) in the second year. Non-gypsum treatments decreased from 300 g/m^2 to 280 g/m^2 and for gypsum treatments from 650 g/m^2 to 450 g/m^2 (Chart 5.11). This may be due to its ability to extract sufficient levels of the essential elements calcium, magnesium and potassium (Section 5.6.1), as, although there was significant increases in aluminium and iron content the biomass did not significantly decrease.

Plates 5.9 and 5.10 illustrate the regression in plant performance for the species in the second years growth. Biomass yield significantly decreased for both *Lolium perenne* and *Holcus lanatus* in the second year. High biomass values recorded for *Holcus lanatus* in the first year significantly decreased from the region of 805 g/m^2 to levels of <110 g/m^2 (Chart 5.12) and for *Lolium perenne* gypsum treatments from >815 g/m^2 to <80 g/m^2, non-gypsum treatments decreased to 50 g/m^2 from the 200-450 g/m^2 in the first year. The decrease in plant biomass may be attributed to the increases in the aluminium and iron herbage content as well as decreases in manganese, calcium and magnesium levels. The decreases for plant Na-content indicate that its high availability is not contributing to the regression in plant growth. Actual cause for the decline in plant performance is highlighted for further study.

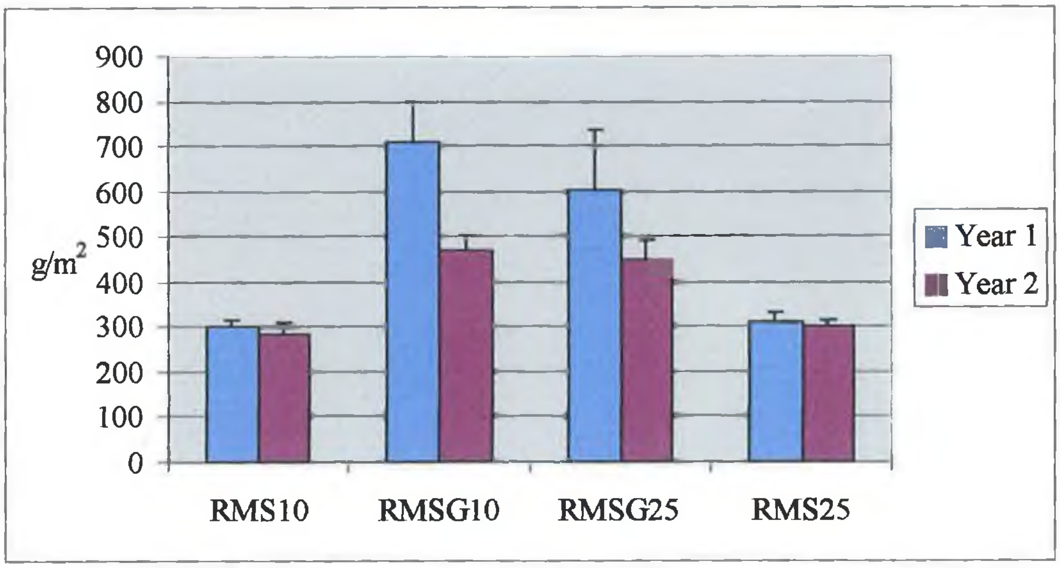


Chart 5.11. **Dry weight biomass for *Trifolium pratense* treatments over a two year growing period in TDSS amended plots**

RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Values shown are mean of 8 replicates. SE bars shown or contained within the size of the symbol.

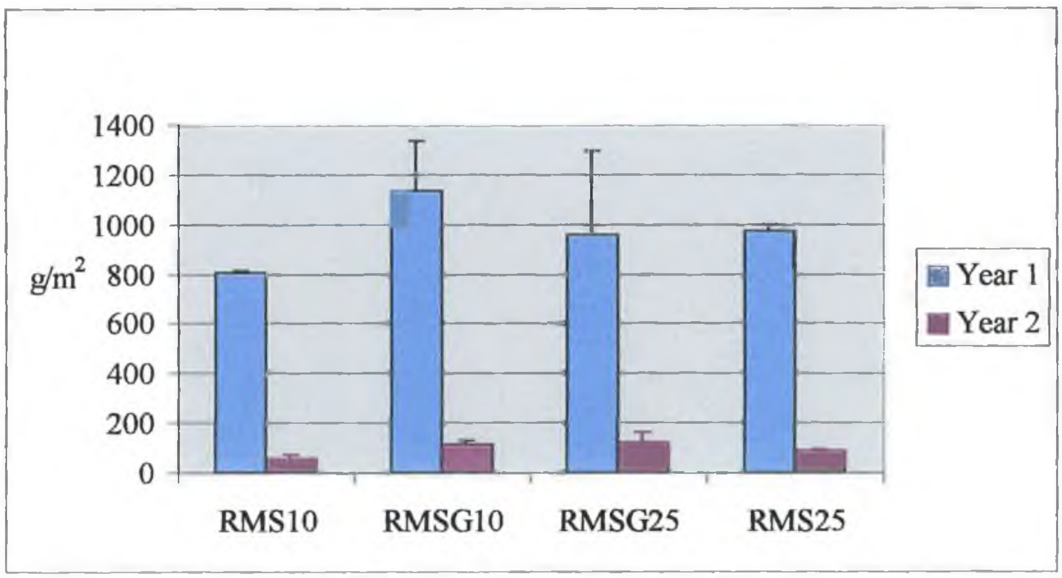


Chart 5.12. **Dry weight biomass for *Holcus lanatus* treatments over a two year growing period in TDSS amended plots**

RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Values shown are mean of 8 replicates. SE bars shown or contained within the size of the symbol.

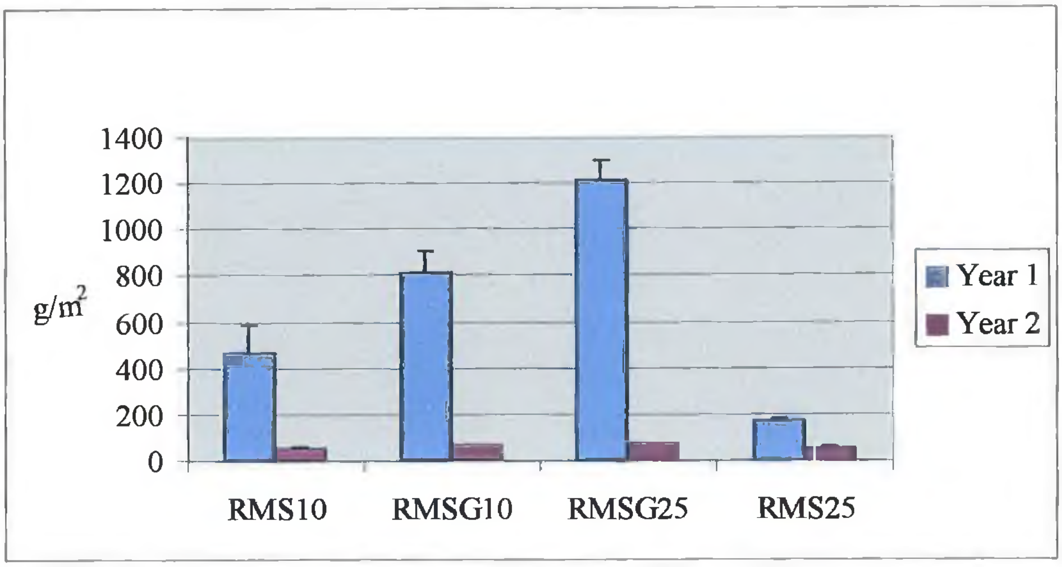


Chart 5.13. Dry weight biomass for *Lolium perenne* treatments over a two year growing period in TDSS amended plots

RMS10 = Mud & 10% Process Sand; RMSG10 = Mud & 10% Process Sand & Gypsum
RMSG25 = Mud & 25% Process Sand & Gypsum; RMS25 = Mud & 25% Process Sand
Values shown are mean of 8 replicates. SE bars shown or contained within the size of the symbol.

Plate 5.9. View of Field Trial Area prior to First Year Harvest

Plate 5.10. View of Field Trial Area prior to Second Year Harvest

6.0 CONCLUSION & RECOMMENDATIONS

6.1 Conclusions

Initial screening of twenty candidate species showed restricted germination and growth due to poor physical structure of the mud. Poor germination of grasses in red mud has previously been attributed to the physical limitations of mechanical impedance and low water holding capacity. Several authors (Fuller *et al.*, 1982; Meecham and Bell, 1977; Wong and Ho, 1993) have also highlighted the inherent high pH and Exchangeable Sodium Percentage (ESP) of the mud as constraints in achieving plant growth.

Unamended mud from this study exhibited an ESP of 67 and pH values in excess of 10, such levels are above critical levels for plant growth (Munshower, 1982). Levels of soluble aluminium at 43 mg/kg and iron at 14 mg/kg were also high. The physical and chemical properties of the red mud were improved following the incorporation of process sand and gypsum and a period of leaching. It was found that pH levels could be reduced to 8.5 from initial levels in of greater than10, and the ESP to levels from in excess of 67 to values lower than the critical threshold of 15%. Where levels were not reduced to these threshold values, plant growth was limited and, in some cases, high mortality ensued.

Substrate pH had a strong relationship with ESP levels and soluble aluminium concentrations. These three factors are the chemical constraints reported to be the main inhibitors in achieving plant growth in red mud (Fuller *et al.*, 1982; Wong and Ho, 1993). Improvement of the mud's physical and chemical characteristics through the addition of process sand and gypsum was shown to significantly lower these limiting factors. Gypsum amendment was also shown to decrease levels of soluble iron in the substrate due to the association of insoluble ferric ion in well drained soils. Manganese content in all treatments was consistently lower than 1.8 mg/kg considered critical for plant growth.

Gypsum amendment was shown to significantly decrease ESP in the substrate through exchange of sodium from exchange sites with calcium and magnesium. A decrease in pH and soluble aluminium levels was also achieved through lowering of ESP and exchangeable sodium content. Soluble iron was decreased through improvement of substrate and drainage. The addition of gypsum is therefore seen as critical in alleviating the inhibitory chemical parameters of the substrate.

The necessity for gypsum amendment for plant growth was demonstrated at pot trial stage as seed emergence was severely inhibited in treatments that had not received gypsum. This was demonstrated by failure of seedlings to germinate, stunted growth and poor biomass production. Poor plant performance was attributed to ESP levels in excess of 65 and pH levels greater than 10. Organic matter addition did not significantly improve germination rates but did have a major effect on plant growth and biomass production. This is due to its inherent nutrient supply and ability to bind soil particles together into aggregates thus increasing water holding and chelating capacity.

Analysis of herbage from the trials showed all species to have sodium content in excess of the national mean and above levels reported to cause a reduction in growth. It was also found that, with the exception of *Trifolium pratense*, all species were low in calcium but uptake was increased in gypsum amended treatments. Impaired uptake and a subsequent low Ca concentration is common in plants growing in a high sodium content (Gupta and Abrol, 1990). Deficiencies were recorded for magnesium herbage content, this is attributed to competition for ion uptake with the high sodium content and low levels of magnesium in the substrate. Manganese deficiency in herbage was also found and it is considered that this is due to low levels of this element in the red mud.

Three species, *Trifolium pratense, Holcus lanatus* and *Lolium perenne,* were sown in field plots of amended red mud/process sand containing thermally dried sewage sludge. Growth was sustained for the duration of a two year study in both gypsum amended plots and those that had not received gypsum amendment. The success of plant species in non-gypsum treatments can be attributed to a lowering of initial levels of ESP in excess of 60% and pH over 10 to levels capable of supporting plant growth. These changes were brought about by the process sand and sewage sludge additions improving the physical characteristics of the substrate and, thereby, increasing permeability. Leaching of excess sodium and a supply of calcium and magnesium reduced the ESP of the mud. While previous workers achieved reduction in ESP values no literature cited reductions of red mud ESP to less than 15.

Elemental analysis of herbage samples following the first years' growth showed samples from gypsum amended plots to have lower aluminium and iron than those from treatments without gypsum. It has been demonstrated that gypsum addition lowers soluble levels of aluminium and iron in red mud. Addition of gypsum also improved uptake of manganese.

Although gypsum was shown to significantly lower the ESP levels in the substrate, plant content of calcium and sodium was not significantly affected by gypsum addition. This is attributed to the low ESP levels exhibited by both treatments. Sodicity is not normally encountered in substrates with an ESP of less than 15. Treatments amended with 25% process sand did, however, have significantly lower sodium levels than recorded for the10% process sand plots. This is attributed to improved leaching with the higher process sand rate application.

While herbage calcium content of after one year's growth was within the normal plant growth range for normal soils, tissue levels for manganese, magnesium and potassium can be considered low and, in some cases, deficient. These deficiencies are attributed to either low levels in the substrate or competition for ion uptake. Levels for copper and zinc were high but not at levels considered toxic, sewage sludge provided the main source for these elements and levels should decrease over time. Sodium and iron herbage levels were, in some treatments, at, or above, values where growth restrictions occur. Lower biomass results may be due to these excesses. After one year aluminium tissue levels after one year were below the critical values for plant growth.

Elemental analysis of herbage taken after the second years' growth showed a significant increase in aluminium tissue content for *Trifolium pratense* and *Holcus lanatus*, increases also occurred for *Lolium perenne*. *Trifolium pratense* iron levels also significantly increased and some increases were recorded for *H.lanatus* and *L.perenne*. Sodium content significantly decreased in the second year indicating that leaching of available sodium from the substrates is continuing. Some levels can still, however, be regarded as high and may restrict growth.

Calcium levels were also decreased in *Holcus lanatus* and *Lolium perenne* samples to levels that are considered deficient. *Trifolium pratense* calcium content was still within the range deemed adequate for plant growth. The decrease in calcium content for the two species indicates a deficiency in the substrate although *T.pratense* does not show deficiency.

Levels for magnesium and manganese were significantly decreased for all treatments after the second years' growth. Decreased levels of both calcium and magnesium herbage content indicates a deficiency in the substrate as sodium content in herbage has also dropped. Manganese deficiency is a potential limiting factor in achieving long-term growth on red mud, as herbage content also significantly decreased in the second year to levels that are extremely deficient. First year manganese content was already deficient and a further decrease indicates minimal manganese supply in the substrate. Manganese deficiency was previously noted by Wong and Ho (1993).

Although sodium content of herbage did not increase, the higher levels for aluminium and iron are attributed to a deterioration of some substrate conditions. Excess sodium was successfully leached from red mud following physical and chemical amendment but iron and aluminium was not. Increased plant uptake is due to higher levels of soluble fractions. It has been demonstrated that aluminium becomes more soluble at pH in excess of 9.4, release of alkalinity from red mud and loss of organic may have caused this change.

Iron levels for all species were above the critical threshold value where toxicity symptoms occur and the maximum value previously reported by McGrath (2001) for unpolluted pasture. High levels in one *L.perenne* treatment are of concern as dietary levels of this magnitude are considered high for cattle. Aluminium levels in excess of 300 mg/kg are considered high for dietary intake, this level was exceeded in *L.perenne* without gypsum amendment and high sand application rate.

Biomass levels recorded for the second years growth were significantly decreased from the previous years for *H.lanatus* and *L.perenne*. Biomass also decreased for *T.pratense* but this change was not significant. Aluminium and iron levels increased in all species to levels that can, in some cases, be considered excessive. This drop in biomass is attributed, in part, to the significant decrease in the essential plant elements manganese, calcium and magnesium for *H.lanatus* and *L.perenne*. Calcium and manganese herbage content did not significantly decrease for *T.pratense* and its biomass decrease was not significant. Deficiencies of calcium and other essential elements are therefore seen as the main parameters afflicting plant growth established on red mud.

This study originated out of necessity for finding a solution to the problem of establishing vegetation on red mud in Ireland. The necessity arose from conditions attached to the Planning Permission's and Integrated Pollution Control Licence issued to Aughinish Alumina Limited. These conditions, *inter alia*, included the necessity for the preparation of a Closure Plan, an important component of which was the establishment of vegetation on the red mud stack and the provision of aftercare sufficient to guarantee its ecological stability in perpetuity. The study will contribute to an understanding as to how this might be achieved.

This study has demonstrated that grassland species such as *Trifolium pratense, Holcus lanatus* and *Lolium perenne* are capable of growing in red mud that has been adequately amended to overcome its physical and chemical limitations. To achieve this, several inhibitory characteristics of red mud, such as high pH and sodium levels, must first be alleviated. The amendments process sand, gypsum and organic matter were used to improve the poor physical and chemical properties of the substrate. Although it has also been shown that gypsum addition may not always be necessary to establish growth this study had demonstrated its beneficial role in the nutrition of plants growth. It was also demonstrated that a period of weathering is needed for critical parameters such as pH, ESP and Al to reach levels capable of supporting growth. While initial results have been promising, the subsequent decrease in plant biomass performance indicates a deficiency in essential elements. Further management with appropriate monitoring is recommended to determine if long-term sustainable growth is achievable.

6.2 Recommendations

From the results of the study, as described, the following recommendations are made for further research;

- Vegetation was established on red mud that had not received gypsum application. Long-term growth on such a treatment should be monitored as the consequences of calcium and magnesium deficiencies would be expected to manifest earlier than in gypsum amended treatments.

- Monitoring of the essential elements calcium, manganese and magnesium levels in herbage and substrate should be undertaken as their deficiencies were highlighted through poor biomass production in the second year. Trials should continue to receive aftercare management via amendment with nutrients, trace elements and organic ameliorants. Decreases in plant performance are, in part, attributed to elemental deficiency in both substrate and plant.

- ESP levels from amended mud samples on the open dome area were significantly higher than from terraced mud. Further trial work should assess leaching rate of ESP and exchangeable sodium from the stack as these parameters are limiting to plant emergence and growth.

- Chemometric profiling of ESP and exchangeable levels in the stack should be undertaken to facilitate rehabilitation planning e.g. gypsum application rates.

- Assessment of uptake of potentially toxic elements iron and aluminium should be continued. Trials demonstrate a significant increase in plant content over a two year growing period. If this trend continues high levels may either restrict growth or have implications in the food chain.

REFERENCES

Adams, F. (1965) Manganese, In: *Methods of Soil Analysis*, *Part 2*, Black, Wd. (ed.), American Society of Agronomy and Soil Science Society of America, Madison

Adams, F. and Lund, Z.F. (1966) Effect of chemical activity of soil solution aluminium on cotton root penetration of acid subsoils, *Soil Science*, 101:193-198

Adams, F and Hatchcock, P.J. (1984) Aluminium toxicity and calcium deficiency in acid subsoil horizons of two Coastal Plain soils, *Soil Sci. Soc. Am. J.*, 48:1305-1309

Alam, S.M and Adams, W.A. (1979) Effects of aluminium on nutrient composition and yield of oats, *Journal of Plant Nutrition*, 1(4), 365-375

Alloway, B.J., Gregson, M., Gregson, S.K. and Tanner, R. (1979) p. 545-548, In: *Management and control of heavy metals in the environment*, Int. Conf., London, CEP Consultants Ltd., Edinburgh

Anon (1998) *The use of Biogran on Reclamation Sites – Technical Information Notice*

Arup Environmental (1993) Extension to Bauxite Residue Storage Area at Aughinish Island, Askeaton, Co. Limerick, Environmental Impact Statement, Ove Arup and Partners, Limerick

Aylmore, L. and Sills, I. (1982) Characterisation of soil structure and stability using modulus of rupture-exchangeable sodium percentage relationships, *Aust. J. Soil Res.*, 20:213-224

Baker, A.J.M. and Walker, P.L. (1989) Physiological responses of plants to heavy metals and the quantification of tolerance and toxicity, *Chemical Speciation and Bioavailability*, 1, 7-17

Barnhisel, R. and Bertsch, P.M. (1982) Aluminium, In: *Methods of Soil Analysis, Part 2*, Page, A.L. (ed.), American Society of Agronomy and Soil Science Society of America, Madison

Barrow, N.J. (1982) Possibility of using caustic residue from bauxite for improving the chemical and physical properties of sandy soils, *Aust. J. Agric. Res.*, 33:275-285

Basta, N. and Gradwohl, R. (2000) Estimation of Cd, Pb, and Zn bioavailability in smelter-contaminated soils by a sequential extraction procedure, *Journal of Soil Contamination*, 9:149-164

Bate, K.J. and Coppin, N.J. (1991) Dust impacts from mineral workings, *Mine and Quarry*, 31-35

Bernstein, L. (1974) Crop growth and salinity, In: *Drainage for Agriculture*, Van Schilfgaarde, J. (ed.), Madison, WI

Bernstein, L. and Hayward, H.E. (1958) Physiology of salt tolerance, *Ann. Rev. Pl. Phys.*, 9:25-46

Black, C. (1968) "*Soil - Plant Relationships*", 2nd Edition., John Wiley and Sons, New York, p401

Blackmore, A.V. (1980) Hydroxyl Interaction with an alkaline clay soil during column leaching, *Aust. J. Soil. Res.*, 18, 233-243

Bower, C. and Turld, L. (1946) Calcium and magnesium deficiencies in alkali soils, *Amer. Soc. Agron. Jour.*, 38: 723-727

Bower, C. and Radleigh, C. (1949) Growth and cationic accumulation by four species of plants as influenced by various levels of exchangeable sodium, *Soil Sci. Soc. Amer. Proc.* 13:218-223

Bower, C.A., Swarner, L.R., Marsh, A.W. and Tileston, F.M. (1951) The improvement of an alkali soil by treatment with manure and chemical amendments, Oregon State College, Technical Bulletin 22

Bradshaw, A. (1983) The reconstruction of ecosystems, Journal of Applied Ecology, 20:1-17

Bradshaw, A. and Johnson, M. (1990) Revegetation of metalliferous mine waste: the range of practical techniques used in western Europe

Bradshaw, A.; Dancer, W.S.; Hanmdley, J. and Sheldon, J. (1975) Biology of land revegetation and reclamation of china clay wastes of Cornwall, In: *The ecology of resource degradation and renewal*, ed. Chadwick, M. and Goodman, G.T., Blackwell, Oxford

Brady, E. (1993) Revegetation and Environmental Management of Lead and Zinc Mine Tailings, MPhil Thesis, University of Liverpool

Bremner, J.M. and Mulvaney, C.S. (1982) Nitrogen – Total, In: *Methods of Soil Analysis*, *Part 2*, Page, A.L. (ed.), American Society of Agronomy and Soil Science Society of America, Madison

Brower, J., Zar, J. and von Ende, C. (1989) Field and Laboratory Methods for General Ecology, WCB Publishers

Bucher, M. (1985) The effects of gypsum and sewage sludge on plant growth and nutrition on alkaline, saline, fine textured bauxite residue, M.Sc Thesis, Dept. of Forestry and Environmental Studies, Duke University, Durham

Caines, A.M. and Sherman, C. (1999) Interactive effects of Ca^{2+} and NaCl salinity on the growth of two tomato genotypes differing in Ca^{2+} use efficiency, *Plant Physiol. Biochem.*, 37:569-576

Calba, H. and Jaillard, B. (1997) Effect of aluminium on ion uptake and H^+ release by maize, *The New Phytologist*, 1997, vol. 137, 4:607

Campbell, R. and Richards, L. (1950) Some moisture and salinity relationships in peat soils, *Soil Agron. Jour.*, 43:582-585

Chang, C.W. and Dregne, H.E. (1955) Effect of exchangeable sodium on soil properties and growth and cation content of Alfalfa and Cotton, *Soil Science Society America Proceedings*, 19: 29-35

Chapman, H.E. (1965) *Diagnostic criteria for plants and soils*, California, U.S.A.; University of California

Chepil, W.S. (1953) Factors that influence clod structure and erodibility of soil by wind: I. Soil Texture, *Soil Sci.*, 75:473-483

Chun, S., Nishiyama, M. and Matsumoto, S. (2001) Sodic soils reclaimed with by-product from flue gas desulfurization: corn production and soil quality, *Environmental Pollution*, 114:453-459

Clarkson, D. (1965) Aluminium tolerance in species within the Genus Agrostis, *Journal of Ecology*, 167-178

Coker, E.G. (1988) Biological aspects of the disposal-utilisation of sewage sludge on land., *Adv. Applied Biology*, V 19, 257-322

Council Directive on 15 July 1975 Waste Framework Directive (75/442), *Official Journal of the European Communities* No L 194

Council Directive on 18 March 1991on Waste Framework Directive (91/156), *Official Journal of the European Communities* No L 078

Council Directive on 26 April 1999 on Landfill of Waste (99/31), *Official Journal of the European Communities* No L 182

Cramer, G., Lauchli, A. and Epstein, E. (1989) Na-Ca interactions in barley seedlings: relationship to ion transport and growth, *Plant, Cell and Environment*, 12:551-558

Cramer, G. (1992) Kinetics of maize-leaf elongation. II. Responses of a Na-excluding cultivar and Na-including cultivar to varying Na/Ca salinities, *Journal of Experimental Botany*, 43:857-864

Davidson, J. and Quirk, J.P. (1961) The influence of dissolved gypsum on pasture establishment on irrigated sodic clays, *Aust. Journal Agric. Res.*, 12:100-110

Department of Environment and Local Government (DELG), Ireland (1998) *Local Government, Use of Sewage Sludge in Agriculture*, Statutory Instrument No 148 of 1998, Government Supplies Agency, Dublin

Ehret, D.L., Redman, R.E., Harvey, B.L. and Cipwnyk, A. (1990) Salinity induced calcium deficiencies in wheat and barley, *Plant and Soil*, 138:143-151

EPA (1998) *Integrated Pollution Control Licence – No. 35, Aughinish Alumina Ltd.*, EPA, Wexford, Ireland

EPA (2000) *Irelands Environment – A millennium report*, EPA, Wexford, Ireland

Epstein, E, Taylor, J.M. and Chaney, R.L. (1976) Effects of sewage sludge compost applied to soil on some physical and chemical properties, *J. Environ Qual.* 5:4, 422-426

Follett, R.H. and Lindsay, W.L. (1970) *Profile distribution of zinc, iron, manganese and copper in Colorado soils*, Exp. Sta. Tech. Bull. 110, Colorado State University

Foy, C.D. (1984) Physiological effects of hydrogen, aluminium and manganese toxicities in acid soils, In: *Soil Acidity and Liming*, 2nd ed., Adams, F. American Society of Agronomy, Madison

Foy, C.D., Fleming, A.L., Burns, G.R. & Armiger, W.H. (1967) Characterisation of differential aluminium tolerance among varieties of wheat and barley, *Soil Sci. Soc. Amer. Proc.*, 31:513-521

Foy, C.D., Fleming, A.L. and Armiger, W.H. (1978) The physiology of metal toxicity in plants, *Annu. Rev. Plant Physiol.*, 29:511-566

Fortin, J. and Karam, A. (1998) Effect of a commercial peat moss-shrimp wastes compost on Pucinellia growth in red mud, *International Journal of Surface Mining, Reclamation and Environment*, 12:105-109

Freedman, B. and Hutchinson, T. (1981) Sources of metals and elemental contamination in soils, In: *Effect of heavy metals pollution on plants* ed. Lepp, N., Applied Science Publ., London

Fuller, R., Nelson, E. and Richardson, C. (1982) Reclamation of red mud (bauxite residues) using alkaline-tolerant grasses with organic amendments, *Journal of Environmental Quality,* 11(3):533-539

Gommy, C., Perdrix, E., Galloo, J. and Guillermo (1998) Metal speciation in soil: extraction of exchangeable cations from a calcareous soil with a magnesium nitrate solution, *Intern. J. Environ. Anal. Chem.*, 72:27-45

Gupta, R. and Abrol, I.P. (1990) Reclamation and management of alkali soils, *Indian J. Agric. Sci.*, 60:1-16

Gupta, S.K. and Aten, C. (1993) *Int. Journal Environ. Anal Chem.*, 51:25-46

Gupta, R. and Sharma, S.K. (1990) Response of crops to high exchangeable sodium percentage (1990) *Irrig. Sci.* 11:173-179

Gupta, R. and Singh, R.R. (1988) A comparative evaluation of the reclamation efficiency of surface-concentrated versus internally incorporated calcium chloride and gypsum in an alkali soil, *Soil Science*, 146(4)277-286

Gupta, R., Singh, R.R. and Abrol, I.P. (1985) Dissolution of gypsum in alkali soils, *Soil Science*, 140(5)382-386

Haby, V.A., Russelle, M.P. and Skogley, E.A. (1990) Testing soils for potassium, calcium, and magnesium, In: *Soil Testing and Plant Analysis*, ed. Westerman, R.L., 3rd ed, p. 229-264, Madison, WI, Soil Science Society of America

Hackett, C. (1964) Ecological aspects of the nutrition of *Deschampsia flexuosa* (L.) I. The effect of aluminium, manganese and pH on germination, *J. Ecol.*, 52:159-168

Hanson, J.B. (1978) Application of the chemiosmotic hypothesis to ion transport across the root, *Plant Physiol.*, 62, 402-405

Harben, P.W. and Bates, R.L. (1990) *Industrial Minerals Geology and World Deposits*, Industrial Mineral Division, Metal Bulletin Plc, London

Hartney, T.F. (1983) Global Environmental Review of Tailings Residue Practises for Bauxite and Red Mud in the Aluminium Industry, Post Graduate Diploma Thesis, Dept. of Civil and Environmental Engineering, University College Cork

Hartney, T.F. & Courtney, R.G. (1998) Development of a rehabilitation programme for the red mud stack at Aughinish Alumina Ltd. in Ireland, In: *Proceedings of International Workshop on Rehabilitation of Mined Bauxite Lands and Red Mud Disposal Ponds*, Jamaica Bauxite Institute, Sep.28-Oct2., 1998

Ho, G.E, Newman, P.W.G, Mathew, K and Potter, H. (1985) Neutralisation of Bauxite Processing Residue with Copperas, *Chemeca*, 103-108

Hooda, P.S. and Alloway, B.J. (1993) The plant availability and DTPA extractability of trace metals in sludge-amended soils, *The Science of the Total Environment*, 149:39-51

Hudson, L.K. (1987) Alumina production, *Crit. Rep. Appl. Chem.*, 20:11-46

Hunsaker, V.E. and Pratt, P.F. (1970) The formation of mixed magnesium-aluminium hydroxides in soil materials, *Soil Sci. Soc. Amer. Proc.*, 34, 813-816

Hutchinson, G.E. (1945) Aluminium in soils, plants and animals, *Soil Science*, 60; 29-40

Jackson, W.A. (1967) Physiological effects of soil acidity, In: *Soil Acidity and Liming*. Pearson, R. W. and Adams, F. (eds), Am. Soc. of Agron., Madison, USA

Jeffrey, D.W.; Maybury, M. and Levinge, D. (1974) *Ecological approach to mining waste revegetation*, Minerals and the Environment, The Institute of Mining and Metallurgy, London

Johnson, W.R. and Procter, J. (1981) Growth of serpentine and non-serpentine races of *Festuca rubra* in solutions simulating the chemical conditions in a serpentine soil, *Journal of Ecology*, 69:855-868

Jones, L. (1961) Aluminium uptake and toxicity in plants, *Plant and Soil XIII*, 4, 297-310

Jones, J.B. and Case, V.W. (1990) Sampling, handling and analysing plant tissue samples, In: *Soil Testing and Plant Analysis*. Westerman, E.L. (ed.), Soil Sci Soc. Am.

Kabata-Pendias, A. and Pendias, H. (1992) *Trace elements in Soils and Plants*, 2nd edition, CRC Press, Boca Raton

Kamprath, E.J.and Foy, C.D. (1985) Lime-fertiliser-plant interactions in acid soils, In: *Fertiliser Technology and Use.* Engelstad, O.P. (ed), 3rd ed., Soil Sci. Soc. Am., Madison, Wisconsin

Kent, L.M. and Lauchli, A. (1985) Germination and seedling growth of cotton salinity-calcium interactions, *Plant, Cell and Environment*, 8:155-159

Knudsen, D., Peterson, G.A. and Pratt, P. (1982) Lithium, sodium and potassium, In: *Methods of Soil Analysis*, *Part 2*, 2nd ed., Page, A.L. (ed.), American Society of Agronomy and Soil Science Society of America, Madison

Kurth, E., Cramer, G.R., Lauchli, A. and Epstein, E. (1986) Effects of NaCl and $CaCl_2$ on cell enlargement and cell production in cotton roots, *Plant Physiology*, 82:1102-1106

Lake, D.L., Kirk, P.W. and Lester, J.N. (1984) Fractionation, characterisation, and speciation of heavy metals in sewage sludge and sludge-amended soils: A review, *Journal of Environmental Quality*, 13:175-183

Le Claire, J.P., Chang, A.C., Levesque, C.S. and Sposito, G. (1984) Trace metal chemistry in arid-zone field soils amended with sewage sludge: IV Correlations between zinc uptake and extracted soil fractions, *Soil Sci. Soc. Am. J.*, 48:509-513

Lehrsch, G.A. and Robbins, C.W. (1994) Cottage cheese whey effects on sodic soil aggregate stability, *Arid Soil Res. Rehabil*, 8:19-31

Lenehan, J.S.; Maher, M.J. and Staunton, W. (1993) *Spent mushroom compost-options for use*, Teagasc Publications, Wexford

Li, L.Y. (1998) Properties of Red Mud Tailings Produced under Varying Process Conditions, *Journal of Environmental Engineering*, 124:3, 254-265

Lindsay, W.L. and Norvell, W.A. (1978) Development of a DTPA soil test for zinc, iron, manganese and copper, *Soil Sci. Soc. Am. J.*, 42:421-428

Loveday, J. and Scotter, D.R. (1966) Emergence response of subterranean clover to dissolved gypsum in relation to soil properties and evaporative conditions, *Aust. J. Soil Res.*, 4:55-68

Maas, E.V. and Grieve, C.M (1987) Sodium induced calcium deficiency in salt stressed corn, *Plant Cell and Environment*, 10:559-564

Maher, M.J. (1988) Spent Mushroom Compost as an organic manure and potting compost component, In: Compost processes in waste management, Bidlingmaier, W. and Hermite, P. (eds.), 71-82, CEC, Brussels

Marschner, B (1983) The reclamation of fine textured bauxite residues using alkaline and aluminium tolerant grasses with organic and chemical amedments, M.Sc Thesis, Dept. of Forestry and Environmental Studies, Duke University, Durham

Martens, D.C. and Lindsay, W.L. (1990) Testing soils for copper, iron, manganese and zinc, In: *Soil Testing and Plant Analysis*, Westerman, R.L (ed.), p. 229-264, Madison, WI, Soil Science Society of America

Martin, J.P. and Bingham, F.T. (1954) Effects of various exchangeable cation ratios in soils on growth and chemical composition of avocado seedlings, *Soil Sci.*, 78:349-360

Mayr, H. (1998) *Views on the use of organic recycling derivates in forests*, Deutsche Zusammenfassung, Wien

McGeorge, W.T. and Brazeale, J.F. (1938) *Studies on soil structure: effect of puddle soils on plant growth*, Ariz. Agr. Expt. Sta. Tech. Bulletin

McGrath, D., Carton, O.T., Diamond, S., O'Sullivan, A.M., Murphy, W.E.M., Rogers, P.A.M., Parle, P.J. and Byrne, E. (2001) Soil, Herbage, Feed and Water, In: *Investigations of Animal Health Problems at Askeaton, Co. Limerick*, Environmental Protection Agency, Ireland

McKenzie, D.C., Abbott, T.S., Chan, K.Y., Slavich, P.G. and Hall, D.J. (1993) The nature, distribution and management of sodic soils in New South Wales, *Aust. J. Soil Res.*, 31:839-868

McLaren, R.G. and Crawford, D.V. (1973) Studies on soil copper, The fractionation of copper in soils, *J. Soil Sci.*, 24:172-181

McLean, O. (1976) Chemistry of soil aluminium, *Commun. in Soil Science and Plant Analysis*, 7(7) 619-636

Meecham, J. & Bell, L. (1977a) Revegetation of alumina refinery wastes. 1. Properties and amelioration of the materials, *Australian Journal of Experimental Agriculture and Animal Husbandry*: 17, 679-688

Meecham, J. & Bell, L. (1977b) Revegetation of alumina refinery wastes.2. Glasshouse experiments, *Australian Journal of Experimental Agriculture and Animal Husbandry*, 17, 689-696

Moore, D.P. (1974) Physiological effects of pH on roots, In: *The plant root and its environment,* Carson, E.W (ed.), Univ. Press of Virginia, Charlottesville

More, S.D. (1994) Effect of farmwastes and organic manures on soil properties, nutrient availability and yield of rice-wheat grown on sodic vertisol, *J. Indian Soc. Soil Sci.*, 42:253-256

Munear, M. and Oades, J.M. (1989) The role of Ca-organic interactions in soil aggregate stability, *Aust. J. Soil Res.*, 27:389-399

Munshower, F.F. (1994) Practical Handbook of Disturbed Land Revegetation, Lewis Publishers, CRC Press, Florida

Nelson, E.D.P. (1981) Factors influencing growth of three grasses on alkaline bauxite residue (red mud), M.Sc Thesis, Dept. of Forestry and Environmental Studies, Duke University, Durham

Nelson, D.W. and Summers, L.E. (1982) Total carbon, organic carbon and organic matter, In: *Methods of Soil Analysis*, *Part 2*, Page, A.L., (ed.), American Society of Agronomy and Soil Science Society of America, Madison

Nguyen, Q.D. & Boger, D.V. (1998) Application of rheology to solving tailing disposal problems, *Int. J. Miner*. Process, 54, 217-233

Norvell, W.A. and Lindsay, W.L. (1969) Reactions of EDTA complexes of Fe, Zn, Mn and Cu with soils, *Soil Sci. Soc. Am. Proc*., 33:86-91

Norvell, W.A. and Lindsay, W.L (1972) Reactions of DTPA chelates of iron, zinc, copper, and manganese in soils, *Soil Sci. Soc. Am. Proc*., 36:778-783

Olson, R.V. and Ellis, R. (1982) Iron, In: *Methods of Soil Analysis*, *Part 2*, Page, A.L., (ed.), American Society of Agronomy and Soil Science Society of America, Madison

Oster, J.D. & Frenkel, H. (1980) The chemistry of the reclamation of sodic soils with gypsum and lime, *Soil Soc. Am. J*., 44:41-45

Overstreet, R, Martin, J.C and King, H.M. (1951) Gypsum, Sulfur, and sulfuric acid for reclaiming an alkali soil of the fresno series, *Hilgardia*, 21:5

Patterson, S.H. (1984) Bauxite and nonbauxite aluminium resources and production – an update, In: *Proceedings of the 1984 Bauxite Symposium*, AIME, Los Angeles

Pearson, G.A. and Bernstein, L. (1958) Influence of exchangeable sodium on yield and chemical composition of plants (2) wheat, barley, oats, rice, tall fescue and tall wheat grass, Soil Sci., 86:254

Peech, M. (1965) Hydrogen-ion activity, In: *Methods of Soil Analysis, Part 2*, Black, Wd., American Society of Agronomy and Soil Science Society of America, Madison

Petruzzelli, G., Lubrano, L. and Guidi, G. (1981) The effect of sewage sludges and composts on the extractability of heavy metals from soil, *Environmental Technology Letters*, 2:449-456

Pitchel, J. and Salt, C.A. (1998) Vegetative growth and trace metal accumulation on metalliferous wastes, *J. Environ. Qual.*, 27:618-624

Prasad, P.M., Chandwandi, H.K. and Mahadevan, H. (1996) Disposal practices for Bauxite Tailings at the Alumina Refineries, *Trans. Indian Inst. Met.*, 49:6: 817-839

Prasad, P.M. and Subramanian, S. (1997) Problems and Perspectives of Red Mud Utilisation, *Trans. Indian Inst. Met.*, 50:5: 427-442

Puls, R. (1988) *Mineral Levels in Animal Health – Diagnostic Health*, Clearbrook, B.C., Sherpa International

Puttaswamygowda, B.S. and Pratt, P.F. (1973) Effect of straw, $CaCl_2$ and submergence on a sodic soil, *Soil Sci. Soc. Am. Proc.*, 37:208-212

Ratner, E. (1935) The influence of exchangeable sodium in the soil on its properties as a medium for plant growth. *Soil Sci.* 40:459-471.

Rauret, G. (1998) Extraction procedures for the determination of heavy metals in contaminated soil and sediment, *Talanta*, 46:449-455

Rees, W.J. and Sidrak, G.H. (1955) Plant growth on fly-ash, *Nature*, 176:353-354

Reid, R.J. and Smith, F.A. (2000) The limits of sodium/calcium interactions in plant growth, *Aust. J. Plant Physio.*, 27:709-715

Rengel, Z. (1992) The role of calcium in salt toxicity, *Plant Cell Environ.*, 15:625-632

Reuter, D.J. and Robinson, J.B. (1986) *Plant analysis, an Interpretation Manual*, Inkata Press, Melbourne

Rhoades, J.D. and Miyamoto, S. (1990) Testing soils for salinity and sodicity, In: *Soil Testing and Plant Analysis*. Westerman, R.L (ed.), p. 229-264, Madison, WI, Soil Science Society of America

Richards, L.A. (1954) *Diagnosis and improvement of saline and alkali soils*, United States Salinity Laboratory, California

Ricks, G. (1987) *Salt-affected soils and plant growth – Technical Notes*, Department of Landscape Architecture, School of Environmental Design, King Abdulaziz University, Saudi Arabia

Robbins, C.W. (1986) Sodic calcareous soil reclamation as affected by different amendments and crop, *Agron. J.*, 78:916-920

Robinsky, E.I. (1986) Current Status of the Sloped Thickened Tailing Disposal System, In: *Proceedings of an International Conference*, Kingston, Jamaica, 26-31 October, 1986

Rogers, P.A. and Murphy, W. (2000) *Levels of dry matter, major elements and trace elements in Irish grass, Silage and Hay*, Teagasc Publications, Wexford

Rorison, I.H. (1960) Some experimental aspects of the calciole-calcifuge problem. II. The effects of mineral nutrition on seedling growth in solution culture, *J. Ecol.*, 48:679-688

Rout, G.R., Samantary, S. and Das, P. (2001) Aluminium toxicity in plants: A review, *Agronomie*, 21:3-21

Russell, R. (1972) *Soil conditions and plant growth*, 10th ed. Longman Press

Salopek, B. and Strazisar, J. (1992) The influences of red mud impoundments on the environment, *Light Metals*

Schaffer, J.W. (1983) Bauxitic Raw Materials, In: *Industrial Minerals and Rocks*, Lefond, S.J. (ed.), American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York

Scotter, D. and Loveday, J. (1965) Physical changes in seedbed material resulting from the application of dissolved gypsum, *Aust. J. Soil. Res.*, 4, 698-75

Sedgeley, R.H. (1962) Effects of disruption and flocculation on pore space changes in beds of clay aggregates, *Soil Sci.,* 94:357-365

Serrano, R. and Rodriguez-Navarro, A. (2001) Ion homeostasis during salt stress in plants, *Current opinion in cell biology*, 13:399-404

Shainberg, I., Keren, R. & Frenkel, H. (1982) Response of sodic soils to gypsum and calcium chloride application, *Soil Sci. Soc. am. J.*, Vol. 46, 1982

Silveria, D.J. and Summers, L.E. (1977) Extractability of copper, zinc, cadmium and lead in soils incubated with sewage sludge, *J. Environ. Qual.*, 6:47-51

Soltanpour, P.N. and Schwab, A.P. (1977) A new soil test for simultaneous extraction of macro and micro-nutrients in alkaline soils, *Commun. Soil Sci. Plant Anal.*, 8:195-207

Solymar, K. and Bujdoso, E. (1993) Properties of red mud in the Bayer Process and its properties, *Light Metals*, 2:717-744

Sposito, G., Lund, L. and Chang, A.C. (1982) Trace metal chemistry in arid-zone field soils amended with sewage sludge: I. Fractionation of Ni, Cu, Zn, Cd, and Pb in solid phases, *Soil Sci Soc. Am. J.*, 46:260-264

Smurthwaite, A.J. (1990) Alumina, In: *Geology and Mineral Resources of Western Australia*, Geological Survey of Western Australia, State Printing Division, Perth

Sterrit, R.M. and Lester, J.N. (1980) Significance and behaviour of heavy metals in wastewater treatment processes, *Sci. Total Environ.*

Summer, M.E. and Naidu, R. (eds.) (1998) *Sodic Soils – Distribution, Properties, Management, and Environmental Consequences*, Oxford University Press

Thakur, R.S. & Das, S.N. (1994) Red Mud Analysis and Utilisation,

Thomas, G.W. (1982) Exchangeable Cations. In *Methods of Soil Analysis*, Part 2, Page, A.L. (ed.) American Society of Agronomy and Soil Science Society of America, Madison

Thorne, D. (1945) Growth and nutrition of tomato plants as influenced by exchangeable sodium, calcium and potassium. *Soil Sci. Soc. Amer. Proc.*185-189

Thornton, I. (1981) Geochemical aspects of the distribution and forms of heavy metals in soils, In: *Effect of heavy metal pollution on plants*, Lepp, N.W. (ed.) Applied Science Publ., London

Thorup, J.T. (1969) pH effect on root growth and water uptake by plants. *Agron. J.*, 61:2:225-227

Tierney, P. (1998) An investigation into the ecological status of metalliferous mine tailings sites in counties Galway, Sligo and Tipperary, MSc Thesis, School of Science, Institute of Technology, Sligo

Tiller, K.G., Suwadjii, E. and Beckwith, R.S. (1979) An approach to soil testing with special reference to the zinc requirement of rice paddy, *Commun. Soil Sci. Plant Anal.*, 10:703-715

Trierweiler, J.F. and Lindsay, W.L. (1969) EDTA-ammonium carbonate soil test for zinc, *Soil Sci. Soc. Am. Proc.*, 33:49-540

Troeh, R. T. and Thompson, L. (1993) *Soils and Soil Fertility*, Fifth Edition; Oxford University Press

Truog, E. (1947) Soil reaction influence on availability of plant nutrients. *Soil Sci. Soc. Am. Proc.* 11:305-308

Tyler, G. (1976) Soil factors controlling metal ion absorption in the wood anemone *Anemone nemorosa, Oikos*, 27:71-80

Tisdale, S. and Nelson, W. (1975) *Soil fertility and fertilisers*. Macmillian Publishing Co., Inc., New York.

Van Pragg, H.J. and Weissen, F. (1985) Aluminium effects on spruce and beech seedling. I. Preliminary observations on plant and soil, *Plant and Soil*, 84:331-338

Vocaseck, F.F and Friedericks, J.B. (1994) Soil micronutrient extraction by Mehlich-3 compared to DTPA, *Commun. Soil Sci. Plant Anal.*, 25:1583-1593

Waisel, Y. (1972) *Biology of Halophytes*. Academic Press, New York

Wallace, A. and Rommey, E.M. (1977) Aluminium toxicity in plants grown in solution culture, *Commun. Soil Sci. Plant Anal.*, 8:791-794

Walley, K.A.; Khan, M.S. and Bradshaw, A. (1971) The potential for evolution of heavy metal tolerance in plants, *Heredity*, 32(3):309-319

Webster, G.R. and Nyborg, M. (1986) Effects of tillage and amendments on yields and selected soil properties, *Can. J. Soil Sci.*, 66:455-470

Whitely, G.M. and Williams, S. (1993) Effects of treatment of metalliferous mine spoil with lignite derived humic substances on the growth responses of metal tolerant and non-tolerant cultivars of *Agrostis capillaris*, *Soil Technology*, 61:163-171

Williamson, N.A., Johnson, M.S. and Bradshaw, A.D. (1982) Mine wastes reclamation, Mining Journal Books, London

Wong, J. and Ho, G. (1991) Effects of gypsum and sewage sludge amendment on physical properties of fine bauxite residue, *Soil Science*, 152(5):326-321

Wong, J. and Ho, G. (1993) Use of waste gypsum in the revegetation on red mud deposits: A greenhouse study, *Waste Management and Research*, 11:249-256

Wong, J. and Ho, G. (1994) Effectiveness of acidic industrial wastes for reclaiming fine bauxite refining residue, *Soil Science*, 158:2

Wong, J. and Ho, G. (1995) Cation exchange behaviour of bauxite refining residues from western Australia, *J. Environ. Qual.*, 24:461-466

Wong, M.H. and Lai, K.W. (1982) Application of activated sludge for improving iron-ore tailings, *Reclamation and Revegetation Research*, 1: 83-87

Xian, X. (1989) Effect of chemical forms of cadmium, zinc, and lead in polluted soils on their uptake by cabbage plants, *Plant and Soil*, 113:257-264

Yeo, A.R., Lee, K., Izard, P., Boursier, P. and Flowers, R.J. (1991) Short and long-term effects of salinity on leaf growth in rice (*Oryza sativa*), *Journal of Experimental Botany*, 42:881-889

Zambo, J. (1979) Red mud: its properties, handling, storage, and utilisation, *Travaux*, 15:265-277

Country	Quantity of Red Mud Generation (Mtpy) 1985	1992
Australia	9.5	18
CIS Countries	4.6	5.3
USE	4.5	5.1
Jamaica	2.7	3.7
China	0.8	3.5
Venezuela	-	2.2
India	0.7	2.0
Germany	1.5	1.6
Surinam	1.2	1.5
Brazil	1.0	1.3
Canada	1.1	1.3
Hungary	0.7	1.0
Japan	1.4	1.0
Spain	0.7	1.0
Guinea	0.6	0.9
France	1.1	0.9
Former Yugoslavia	1.3	low
Others	<2	<20
Total (approx)	45	67

Appendix 1: Red Mud Generation in the World (from Prasad *et al.*, 1996)

Appendix 2 – Results of Amendment Analyses

	Gypsum	Sewage Sludge
Total N (%)	0.02	5-6
Organic C (%)	<0.2	
	Soluble	Total
Na	<0.02%	0.13%
Ca	0.63%	2.2%
Fe	<5 mg/kg	7000mg/kg
Mg	0.01%	
K	0.02%	
Al	<10mg/kg	<10mg/kg
Mn	<1 mg/kg	290mg/kg
Cu	1.2 mg/kg	480mg/kg
Zn	<5mg/kg	800mg/kg

Appendix 3: Percentage Recovery for Plant Reference Material (GEW 07604)

Element	Concentration Determined	% Recovery
Total Ca%	1.63	90
Total Fe mg/kg	225	85
Total Na %	0.02	100
Total K%	1.3	94
Total Mg%	0.58	89
Total Zn mg/kg	35	94
Total Mn mg/kg	41	91
Total Cu mg/kg	8.2	88

Appendix 4: Pearson Correlations for Plant Content and Soil Fractions

	water	exchangeable
T.pratense	0.13	0.84
H. lanatus	0.25	0.15
L.perenne	0.47	0.56

Correlation Matrix of plant content and soil fractions for Sodium

	water	exchangeable
T.pratense	0.21	0.51
H. lanatus	0.25	0.51
L.perenne	0.12	0.03

Correlation Matrix of plant content and soil fractions for Calcium

	water	exchangeable
T.pratense	-0.71	0.69
H. lanatus	0.08	0.33
L.perenne	-0.36	0.43

Correlation Matrix of plant content and soil fractions for Magnesium

	water	exchangeable
T.pratense	0.31	0.37
H. lanatus	0.24	0.39
L.perenne	0.36	0.12

Correlation Matrix of plant content and soil fractions for Potassium

	water	exchangeable
T.pratense	-0.31	NA
H. lanatus	-0.39	NA
L.perenne	-0.21	NA

Correlation Matrix of plant content and soil fractions for Manganese

	water	exchangeable
T.pratense	0.73	0.13
H. lanatus	0.69	0.44
L.perenne	0.59	0.09

Correlation Matrix of plant content and soil fractions for Iron

	water	exchangeable
T.pratense		0.26
H. lanatus		-0.04
L.perenne		0.22

Correlation Matrix of plant content and soil fractions for Copper

	water	exchangeable
T.pratense	0.02	0.21
H. lanatus	0.16	0.19
L.perenne	0.08	0.26

Correlation Matrix of plant content and soil fractions for Zinc

	water	exchangeable
T.pratense	0.38	NA
H. lanatus	0.46	NA
L.perenne	0.22	NA

Correlation Matrix of plant content and soil fractions for Aluminium