Characterisation of Mining and Industrial By-Products with Potential for Use as Environmental Amendments

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EXECUTIVE SUMMARY

Contaminant removal from natural and waste waters, and amelioration of acidity in both water and soils are core environmental management priorities for a sustainable Western Australia. The goal of the project "Wastewater purification and re-use: Mineral-based sorbents for contaminant removal" (PWF 009-05) is to source and characterize a suite of abundant industrial by-products, principally from Western Australia, with the specific aim of identifying by-product materials "fit for purpose" for specific environmental applications. This report describes the characterisation of by-products to be examined in further studies.

- Effective removal of nutrients and trace metals from industrial, agricultural and domestic wastewater is pivotal to water re-use. Utilisation of abundant, low-cost industrial by-product materials potentially offers a cost-effective wastewater treatment option. We examined the potential re-use of largely unexploited mineral processing materials in Western Australia as "designer" contaminant adsorbents. This work is underlain by a "wealth from waste" strategy aligning the productive re-use of solid by-product materials to treat wastewater previously discarded or treated by less efficient or more costly means.
- One of Western Australia's most pressing environmental concerns involves the highly acidic, hypersaline drainage waters from the WA Wheatbelt. Feasible management options for treatment of WA Wheatbelt drainage waters may include the use of industrial by-products as surface water amendments, within-drain filtration/treatment systems, and/or permeable reactive barriers. The main advantages to using industrial by-products as environmental amendments are economic viability (low cost) and waste reduction.
- A number of industrial by-products are readily available in WA and possess characteristics indicative of potential benefit as soil or surface water amendments, including the heavy minerals processing residue neutralised unused acid (NUA), red mud, red sand, flue gas desulphurisation gypsum, cement kiln dust, steelmaking by-products, fly ash, calcined magnesia and water treatment residue.
- Natural mineral amendments such as mine overburden, carbonates or carbonate derivatives (*e.g.* limestone, lime, dolomite), phyllosilicate (clay) minerals, zeolite minerals and/or hydrotalcite minerals could also be used in conjunction with low-cost industrial by-products to ameliorate acidity and attenuate potentially toxic metals and excess nutrients in effluent waters.
- This report details the physical, mineralogical, chemical, radiological and toxicological properties of some mineral-based by-products, principally from WA, and provides information necessary to assess the potential suitability of each material for use in further trials (Table 1). The materials examined include a heavy minerals processing residue (neutralised unused acid, NUA), a by-product of iron-ore processing (steelmaking by-product), by-products generated during Bayer process alumina production and their derivatives (red mud, red sand, and reduced red sand), lime- and $CaCO_3$-based residues from metropolitan groundwater treatment plants, and a by-product of coal-based energy production (fly ash). Other materials of interest that are available on a large scale and had potentially useful properties either by themselves or if blended with by-products including laterite, calcined magnesia, and a carbonized wood product (granular activated carbon) were also included in this study.
- Based on their Ca, Fe and/or Al content, red mud, red sand, reduced red sand, steelmaking by-product, NUA, fly ash and lime- or $CaCO_3$-based groundwater treatment plant residues may have a high anion uptake capacity and thus a substantial capacity for the uptake of P or dissolved organic carbon (DOC). These materials may be suited to the removal of excess P from surface waters, such as Ellen Brook, or wastewater streams.
- By-products comprised of substantial quantities of poorly crystalline Fe/Al/Mn (oxy)hydroxide minerals (e.g., ferrihydrite) may be useful for sorption of metals. Of the by-

products or other materials examined herein, red mud, red sand, reduced red sand, NUA and laterite may be suitable for metal sorption.

- Radiological analyses and calculated absorbed dose rates (D) indicate that some of the materials examined exhibited radioactivities greater than the UNSCEAR guideline D of 11-54 nGy h^{-1}. However, all by-product D values were less than or comparable to those reported for phosphogypsum fertiliser, and the highest calculated absorbed dose rates for by-products were comparable to those determined for WA's Darling Scarp soils. Results indicate that these materials may require dilution to improve suitability for environmental application, dependent on radionuclide speciation and mobility.
- By-products such as calcined magnesia, red mud, steelmaking by-product, and fly ash have high acid neutralisation capacity and may be suited for remediation of acidic drainage waters of the WA Wheatbelt. Further detailed study is, however, required to quantify the efficacy of acid neutralisation of and removal of potentially toxic elements from drainage waters, to fully characterise the geochemical interactions between potential receiving waters and each by-product or other materials, and to analyse resultant waters/leachate for potential toxicity prior to field trials or full-scale environmental applications.

Table 1. General assessment of characteristics of materials examined that are pertinent to reuse as soil amendments or in water treatment schemes. A = within acceptable range; L = low; H = high. ND = not determined. Values in red fall outside acceptable ranges.

Material	Chemistry			Radioactivity[4]	Environmental Toxicity			Potential Barriers to Application
	pH[1]	EC[2]	Potentially toxic elements[3]		Algal growth	Cladoceran mobility	Microtox®	
Bassendean Sand	L	A	Cr	A	ND	ND	ND	N/A
NUA	A	A	Co, Ni, Se, V	A-H	L	L	L	moderate to high radioactivity, may require dilution
Steelmaking by-product	A	A	Ba, Cr, Tl, V	A-H	L[†]	L[†]	L[†]	moderate to high radioactivity, high leachate pH
Red sand	A	A	Cr, Cu, V	A-H	L[†]	L[†]	L[†]	moderate to high radioactivity, high leachate pH
Reduced red sand	A	A	Cd, Cr, Cu, Ni, Sn, V	A-H	ND	ND	ND	moderate to high radioactivity, may require dilution, processing required
Laterite	A	A	As, Cr, Ni, Tl, V	A-H	ND	ND	ND	moderate to high radioactivity, may require crushing
Fly ash	A	A	Ba, Cd, Co, Cr, Cu, Ni, Pb, Se, Zn, Tl, V	A-H	ND	ND	ND	low density, moderate to high radioactivity, may require dilution, high metal/metalloids
GWTP $CaCO_3$	H	A	Ba, Tl	A	ND	ND	ND	high solid pH
Red mud	H	H	Ag, As, Cd, Cr, Sb, Se, Tl, V	A-H	H	H	L[†]	high solid/leachate pH, moderate to high radioactivity, high EC, moderate - high metal/metalloids
Calcined magnesia	H	A	Ni, Tl	A	L[†]	L[†]	L[†]	high solid/leachate pH
GWTP lime	H	H	Tl	A	ND	ND	ND	may require dewatering, low bulk density, high pH, high EC
GAC	H	A	ND	A	ND	ND	ND	very low density, high pH

[1] A = pH 5.0 - 8.5, acceptable range for plant growth and soil microbial activity (McBride, 1994). Low (L) = <5.0; high (H) = >8.5.

[2] EC > 4 mS cm^{-1} = high (H)/saline (McBride, 1994). Acceptable (A) = <4 mS cm^{-1}.

[3] Elevated concentrations based on existing guidelines for biosolids (DEHP, 2002), soils (Crommentuijn et al., 1997) and sediments (ANZECC/ARMCANZ, 2000).

[4] Acceptable radioactivity (A) = <54 nGy h^{-1} (UNSCEAR guideline radioactivity = 11-54 nGy h^{-1}; UNSCEAR, 1998); Moderate to High (H) = >54 nGy h^{-1} – may require dilution/also dependent on radionuclide speciation and mobility.

[†] Toxicity of leachate adjusted to pH ~8; toxicity of leachate at natural pH may be higher.

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1. INTRODUCTION

Contaminant removal from natural and waste waters and amelioration of acidity in both water and soils are core environmental management priorities for a sustainable Western Australia. The goal of the project "Wastewater purification and re-use: Mineral-based sorbents for contaminant removal" (PWF 009-05) is to source and characterize a suite of abundant industrial by-products and complimentary materials, principally from Western Australia, with the specific aim of identifying by-product materials "fit for purpose" for specific environmental applications.

In essence, this project examines the potential re-use of largely unexploited mineral processing materials in Western Australia as "designer" contaminant adsorbents. This work is underlain by a "wealth from waste" strategy aligning the productive re-use of low-cost, solid by-products materials to address environmental contamination issues previously treated by less efficient or more costly means.

1.1. By-Products as Soil Amendments

The soils of the Swan Coastal Plain are predominantly porous grey sands. The inherently low fertility, poor water-holding capacities, frequent hydrophobicity, low acid buffering capacities and low nutrient sorption capacities of these sands limits their suitability for plant growth. Regular additions of nutrients, organic matter and other materials are usually required to attain satisfactory plant growth rates. Thus, fertilization of plants grown on Swan Coastal Plain sands frequently results in nutrient loss.

The addition of organic materials such as compost and animal manures improves the utility of Swan Coastal Plain sands as substrate for plant growth, primarily by supplying nutrients in a slow release form, decreasing hydrophobicity and increasing water holding capacity. However, use of these materials does not overcome problems associated with nutrient leaching (particularly P and N). A practical means of addressing these issues is to incorporate suitable fine textured inorganic materials, such as natural clays, loams and some mineral by-products, into Swan Coastal Plain sands.

Desirable attributes of inorganic soil amendments for improving sandy soils include:

- weakly acidic, neutral or slightly alkaline reaction with an acid buffering capacity;
- low salinity/sodicity;
- high P sorption capacity;
- high water-holding capacity, while maintaining moderate drainage;
- high cation exchange capacity (CEC);
- moderate nutrient content;
- moderate amounts of essential trace elements such as Cu, Fe, Mn, B, Mo, and Zn;
- absence or very low concentrations of potentially toxic metals (e.g. Cd, Pb, Hg, As, Se, etc.).

Historically, industrial by-products have been viewed as unsuitable for amendment to agricultural soils due to the possibility of soil contamination by hazardous by-product constituents or to a lack of independent evidence indicating beneficial effect. Some industrial by-products possess characteristics such as high nutrient content or alkalinity that suggest potential value as soil amendments. In the United States, land application of industrial by-products is regulated by the Resource Conservation and Recovery Act of 1976 (RCRA, 40 CRF 257-268) which specifies regulatory limits for disposal of industrial by-products based on flammability, corrosivity and toxicity. Toxicity is generally assessed using the United States Environmental Protection Agency's (USEPA) toxicity characteristic leaching procedure (TCLP) (USEPA, 1986). Some materials initially exempt from regulation under

RCRA include coal fly ash, some types of mining waste and processing dust, although individual states may choose to regulate additional wastes not identified as hazardous by RCRA. As a result, there is considerable interest in characterizing and assessing the potential benefits of land application of industrial by-products to eliminate the necessity of costly disposal in secure facilities.

In contrast, Western Australia does not have set guidelines for the regulation of land application of industrial by-products. The EPA Western Australian Guidelines for Direct Land Application of Biosolids and Biosolids Products (February 2002), which provide guidance on acceptable practices for the beneficial re-use of biosolids, can provide some insight as to minimum criteria, procedures and approval processes that may be applicable to the land application of industrial by-products (Table 2). Biosolids are classified based upon both levels of chemical contaminants and pathogen grade, or level of treatment required to reduce pathogens, vector attraction and odour. Pathogen grade is highly unlikely to be an issue in the beneficial re-use of industrial by-products; however, regulatory classification related to chemical contaminants will be pertinent. Contaminants in biosolids are graded from C1 to C3 based on Contaminant Acceptance Concentration Threshold values. Untested materials or concentrations higher than C2 are classified as C3. The contaminant grade of a product determines its suitability for re-use, and may be improved as necessary by mixing with other suitable materials.

Current Australian guidelines for land application of biosolids provide a single numerical limit for each contaminant in soil and rely heavily on overseas data, which may not be particularly applicable to the range of soil types and climatic variables endemic to Australia. These guidelines are currently under review by the National Biosolids Research Program (NBRP), a national research program designed to develop soil-specific guidelines for biosolids and provide a basis for their sustainable use throughout Australia. The outcome of this process could also provide a framework for the development of regulatory guidelines for the use of industrial by-products as soil and surface water amendments.

Industrial by-products identified as non-hazardous according to government regulations are not necessarily beneficial to the environment or even safe as environmental amendments. One of the main concerns associated with the re-use of industrial by-products is the possibility of environmental contamination via the unintentional release of potentially toxic elements or radionuclides. Considerable research is required to identify potential hazards associated with land application, including surface and groundwater contamination, plant uptake and transport through the food chain. The effects of land application of industrial by-products are dependent upon the properties of both the by-product and the soil to which it is being applied, application rates, management and ambient environmental conditions (*e.g.*, annual precipitation rates).

The total metal content of a material or site is an important measure used to assess risk from contamination; however, total content does not provide information on the bioavailability, mobility or fate of a metal contaminant. Metal contaminants can undergo redox transformations and become more or less labile based on the elemental species formed and the nature of interactions between each species and the solid phase. For example, trivalent Cr (Cr^{3+}), which generally exists in aqueous solution as either $[Cr(H_2O)_6]^{3+}$ or $[Cr(H_2O)_5OH]^{2+}$, is far less toxic than hexavelent Cr (Cr^{6+}), or CrO_4^{2-}. This is due to the ability of the chromate oxyanion to cross cellular membranes using phosphate/sulphate transporters, whereas Cr^{3+} is unable to cross cell membranes (Duffus, 2005).

Table 2. Contaminant acceptance concentration threshold values for inorganic contaminants and maximum allowable soil contaminant concentrations following biosolids application (DEHP, 2002). Recommended interim sediment quality guidelines (ISQG; ANZECC/ARMCANZ, 2000) and maximum permissible concentrations in soil (MPC; Crommentuijn et al., 1997) for selected metals.

Element	**Grade C1 (mg kg^{-1})[†]**	**Grade C2 (mg kg^{-1})[†]**	**Max. soil conc. (mg kg^{-1})[†,‡]**	**ISQG-Low (mg kg^{-1})[†,§]**	**ISQG-High (mg kg^{-1})[†,§]**	**MPC (mg kg^{-1})[†,¥,]**
Ag				1	3.7	
As	20	60	20	20	70	34
Ba						165
Cd	3	20	1	1.5	10	1.6
Co						33
Cr	100	500	100	80	370	100
Cu	100	2500	100	65	270	40
Hg	1	15	1	0.15	1	2.2
Ni	60	270	60	21	52	38
Pb	150	420	150	50	220	140
Sb				2	25	3.5
Se	3	50	5			0.81
Sn						53
Tl						1.3
V						43
Zn	200	2500	200	200	410	160

[†] Values in expressed in mg kg^{-1} dry weight.

[‡] Mean concentration values following biosolids application.

[§] Recommended interim sediment quality guideline (ISQG) for selected metals as outlined in ANZECC/ARMCANZ Guidelines for Fresh and Marine Water Quality, 2000.

[¥] Maximum permissible concentrations in soil as outlined in Crommentuijn et al., 1997.

In addition, the chemical speciation of elements significantly influences their toxicity, bioavailability, lability, biogeochemical behaviour and potential risk. From a risk assessment perspective it would follow that two soils each contaminated with the same concentration of Pb would be equally hazardous to soil biota. However, if one soil contained Pb primarily as galena ($PbS_{(s)}$; $K_{sp} = 10^{-28.1}$) and the other contained Pb mainly in the form of cerussite ($PbCO_{3(s)}$; $K_{sp} = 10^{-13.13}$) the soil with galena Pb would pose significantly less threat due to the *ca.* 15 orders of magnitude lower solubility as compared to cerussite Pb. In the previous example, the chemical speciation of Pb greatly affects its mobility and potential bioavailability. Thus, both the elemental and chemical speciation of a contaminant are relevant to its potential toxicity and are essential to determining the fate and behaviour of elements in the environment. Examination of by-product mineralogy and leaching behaviour will provide insight as to the speciation of potentially toxic elements contained therein and the potential for future release of elements resulting from physicochemical weathering processes or perturbations to chemical equilibria.

The biological availability of an element in soil is the principal factor determining its potential ecotoxicological risk. In soil environments, an understanding of solution and solid-state speciation is required to determine the fate and behaviour of potentially toxic elements, particularly metals (Nolan et al., 2004). Metal speciation in soils and sediments is influenced by a number of physicochemical properties, including soil or sediment pH, clay and organic matter content, Fe and Mn oxide composition and content, as well as long-term fixation or aging effects and alteration to environmental conditions, such as waterlogging, solid-phase weathering, organic matter degradation, or soil acidification. These solid phase properties and processes largely determine metal speciation and, hence, bioavailability in soils or sediments.

In soils, aging of metals has been demonstrated to be a major factor in determining their availability (Fendorf et al., 2004; Ma et al., 2006; Oorts et al., 2007; Wendling et al., 2009a, 2009b). Several processes contribute to metal aging in soils, including incorporation into mineral structures, diffusion into pore spaces within minerals, nucleation/precipitation, mineral surface oxidation, and entrainment via the formation of chemical complexes with soil solids (Fendorf et al., 2004; Manceau et al., 1997). As a result, risk assessments based on single-time-point assessments of toxicity may overestimate the biologically available fraction in soils and, thus, the potential for toxic effects because of the removal of metals into non-available pools with time. Conversely, the biologically available fraction of a metal or other element associated with the solid phase may increase with time due to physiochemical weathering of the solid phase. In addition, changes in environmental conditions, such as alterations to soil pH or oxidative-reductive (redox) status, may remobilize non-exchangeable or ‘‘fixed’’ pools of an element, thereby increasing its availability and, hence, toxicity in soil environments. Thus, it is clear that to assess the potential ecotoxicological risk associated with the use of any material as an environmental amendment, long-term investigation is required under varying environmental conditions in order to accurately predict the fate and behaviour of potentially toxic elements within the system.

1.2. By-Products as Water Treatment Media

As with land application of industrial by-products, Western Australia does not have set guidelines for the regulation of water treatment using mining and industrial by-products, and the productive re-use of these by-products is currently considered on a case-to-case basis rather than regulated according to established standards. South-West Western Australia currently faces a significant challenge with regard to water resources. This area, while experiencing Australia’s highest rates of climate change, rapid population growth and associated development, has also seen a substantial decrease in winter rainfall since 1975 (Swan River Trust, 2007). This reduction in rainfall has lead to an increase in competition for water resources between the growing urban population and requirements for environmental flow. The safeguarding of existing water resources and investigation of alternatives to potable water supplies are critical to ensure long-term sustainability of water resources in South-West WA. Mining and industrial by-products may be particularly well-suited for the attenuation of nutrients, metals and acidity in agricultural, urban and industrial wastewater, facilitating its re-use. In addition, the use of non-potable water on a fit-for purpose basis, such as managed aquifer recharge or enhancement of environmental flows, may reduce pressure on water resources.

The composition of wastewater is dependent upon its source. For example, agricultural wastewaters may be expected to contain elevated concentrations of nutrients such as N and P, whereas urban wastewater may contain chlorides, metals and hydrocarbons as well as nutrients. Industrial effluents in particular may be comprised of complex mixtures of contaminants (Table 3). Processes as diverse as the manufacture of catalysts, electrical equipment, antibacterial agents, fertilisers, insecticides and fungicides, pyrotechnics, metal alloys, piping, pigments and stabilisers, gasoline additives, cable covering, and ammunition and batteries, and industries such as painting and coating, extractive metallurgy, photography, mining and smelting, metal electroplating, plumbing, heating, roofing and building construction, and water purification all produce waste streams enriched in the potentially toxic elements Cd, Cu, and Pb (Apak et al., 1998). In addition, pharmaceuticals and their metabolites are common constituents of urban wastewaters.

Mining and industrial by-products, particularly those products with large acid neutralisation capacity, may be useful for the amelioration of acid mine drainage (AMD) and the neutralisation of acid sulphate soils (ASS). Acid mine drainage occurs when sulphide-bearing minerals in rock are oxidised, transforming the sulphur in metal sulphides to sulphuric acid (H_2SO_4). The acid can dissolve metals contained in waste rock and tailings such as Pb, Zn, Cu, As, Se, Hg, and Cd, and release them into ground and surface water. Acid generation results from exposure to air and water; thus, the more surface area of rock exposed, the greater the amount of acid. During the mining process, hundreds or sometimes thousands of tons of rock are unearthed and crushed each day. Acid mine drainage and metal pollution can contaminate ground and surface waters, and negatively impact aquatic life and habitats. Ore bodies commonly mined that pose AMD risk via the exposure of sulphide minerals to oxidation include metallic ore deposits (*e.g.*, Au, Ag, Cu, Fe, Pb, Ni, U and Zn or multi-metal combinations), phosphate ores, coal seams, oil shales and mineral sands (Lottermoser, 2007).

A regionally-significant potential application for industrial by-products as sorbent materials is the treatment of agricultural drainage waters from the Western Australian Wheatbelt. Extensive areas of the Western Australian (WA) Wheatbelt region within the Avon River Basin suffer from loss of productivity due to dryland salinity. By 2050, estimated lost agricultural production is expected to value AU$300-400 million, in addition to an estimated loss of AU$3-4 billion in capital value of farmland (Clarke et al., 2002).

Table 3. Major contaminants in effluents from food, chemical and materials industries (McKay, 1996).

Food Industry	*Origin of contaminants*	*Components and characteristics of contaminants*
Canning	Fruit and vegetable preparation	Colloidal, dissolved organic matter, suspended solids
Dairy	Whole milk dilutions, buttermilk	Dissolved organic matter (protein, fat, lactose)
Meat, poultry	Slaughtering, rendering of bones and fats, plucking	Dissolved organics, blood proteins, fats, feathers
Sugar beet	Handling juices, condensates	Dissolved sugar and protein
Yeast	Yeast filtration	Solid organics
Pickles	Lime water, seeds, syrup	Suspended solids, dissolved organics, variable pH
Coffee	Pulping and fermenting beans	Suspended solids
Fish	Processed fish, wash water	Organic solids, odour
Rice	Soaking, cooking, washing	Suspended and dissolved carbohydrates
Soft drinks	Cleanage, spillage, washing	Suspended and dissolved carbohydrates
Chemicals Industry	*Origin of contaminants*	*Components and characteristics of contaminants*
Acids	Wash waters, spillage	Low pH
Detergents	Purifying surfactants	Surfactants
Starch	Evaporation, washing	Starch
Explosives	Purifying and washing TNT, cartridges	TNT, organic acids, alcohol, acid, oil, soaps
Insecticides	Washing, purification	Organics, benzene, acids, highly toxic
Phosphate	Washing, condenser wastes	Suspended solids, phosphorous, silica, fluoride, clays, oil, low pH
Materials Industry	*Origin of contaminants*	*Components and characteristics of contaminants*
Pulp & paper	Refining, washing, screening for pulp	High solids, extremes of pH
Photographic products	Spent developer and fixer	Organic and inorganic reducing agents, alkaline
Steel	Coking, washing blast furnace, flue gases	Acid, cyanogen, phenol, coke, oil
Metal plating	Cleaning and plating	Metals, acid
Iron foundry	Various discharges	Sand, clay, coal
Oil	Drilling and refining	Sodium chloride, sulphur, phenol, oil
Rubber	Washing, extracting impurities	Suspended solids, chloride, odour, variable pH
Glass	Polishing, cleaning	Suspended solids

Deep (2-3 m) open drains, the engineering option of choice in many areas of the WA Wheatbelt, are increasingly being used to protect low-lying areas from salinisation and to rehabilitate marginally saline lands (Ali et al., 2004a; Dogramaci and Degens, 2003). There are currently more than 10,000 km of deep drains in parts of the WA Wheatbelt but few regional linkages (Ali et al., 2004a); thus, there is increasing interest amongst landowners in the WA Wheatbelt to increase the scale of existing drainage systems and to link smaller farm scale systems into larger regional drainage schemes. This will result in hundreds of kilometres of deep open drains covering thousands of square kilometres of drainage area.

Initial investigation of major drainage schemes near Narembeen in the WA Wheatbelt found that the deep drains can discharge waters with pH 2-3 and a salinity of 30,000 to 50,000 mg L^{-1}, at rates of 5-10 ML per day (Ali et al., 2004b). Limited work indicates that these drainage waters can contain elevated concentrations of Al, Mn, Co, Ni and Pb (Ali et al., 2004b; Tapley et al., 2004). In addition, the shallow acidic groundwaters likely to be intercepted by the drains can contain significant concentrations of Al, Cu, Fe, Mn, Pb and Si (Lee and Gilkes, 2005; Mann, 1983). The large scope of the Wheatbelt drainage scheme in combination with the poor quality of Wheatbelt drainage water makes this one of the most significant environmental issues in the State.

There are a number of issues inherent in the determination of appropriate remediation strategies for the acidic, saline waters of the WA Wheatbelt. Challenges include: (i) identifying remedial techniques or technologies suitable for the remediation of the acidic groundwater, including technologies that are environmentally robust in terms of the safe and efficient immobilization (and if appropriate, disposal) of the contaminants after neutralization; and (ii) the long-term management of the site(s) as required to meet regulatory requirements. In addition, technologies must be easily applied, gain statutory approval and wide community acceptance and integrate easily into the WA Wheatbelt environment, and be cost effective on both a local and regional scale.

Feasible management options for treatment of WA Wheatbelt drainage waters may include the use of industrial by-products as surface water amendments, within-drain filtration/treatment systems, and/or permeable reactive barriers. The main advantages to using industrial by-products as environmental amendments are economic viability (low cost) and waste reduction. Extensive study under controlled conditions is required to quantify the efficacy of acid neutralisation of and removal of potentially toxic elements from drainage waters, to fully characterise the geochemical interactions between WA Wheatbelt drainage waters and each by-product, and to analyse resultant waters/leachate for potential ecological toxicity.

1.3. Project Objectives

The industrial by-products and complimentrary materials will undergo geochemical, isotope and mineralogical analyses in addition to characterisation of contaminant uptake and acid neutralization capacity. The contaminants under consideration will include a suite of trace metals and nutrients commonly found in wastewaters (*e.g.* sewage or industrial effluents, agricultural drainage waters). As promising by-product materials are identified or synthesized they will be evaluated in laboratory columns to assess their performance under pseudo-field conditions. Critical by-product material performance indicators will include contaminant uptake capacity, transformations, stabilization, and changes in column porosity and permeability over time. Column solute chemistry as a measure of ultimate material performance will also be closely monitored. Modelling of column processes and wastewater influent/effluent chemistry will also be undertaken using geochemical modelling.

The major outcome of the project will be the first comprehensive characterization of a suite of principally Western Australia-sourced by-product materials (*e.g.* steelmaking by-products, heavy mineral processing residue and mine overburden) that have potential for use in water purification and re-use for a suite of applications as diverse as managed aquifer recharge, and the treatment of urban, industrial, and agricultural wastewaters. In addition, some solid by-product materials may be trialled as soil amendments to ameliorate acidity or enhance nutrient binding capacity. Identification of by-product materials suitable for use as environmental amendments serves the dual purpose of reducing by-product stockpiles with the productive re-use of previously unused or underutilised materials as low-cost contaminant sorbents. The scope and potential benefits of this project are not only limited to Western Australia, but are also applicable elsewhere in Australia and internationally where similar by-product materials are generated and wastewater and land management problems exist. Key technical objectives include:

- Following liaison with mining and mineral processing industries, source and characterise (geochemistry/isotope geochemistry, mineralogy, contaminant uptake capacity) a range of mining and industrial by-product or derivative materials.
- Critically assess the most promising materials or derivatives in column trials to assess performance under controlled pseudo-field conditions, including toxicological assessment of the column leachate.
- Create a classification scheme for by-product materials or derivatives as “fit for application” for specific remedial uses. Specific remediation applications most relevant to Western Australia are: purification of domestic, industrial or agricultural wastewaters and neutralization of acidity in natural and contaminated acid sulphate soils and acidic surface/groundwaters.
- Conduct field trials with the most promising by-product materials or derivatives to assess the sorbent material performance at an appropriate scale.
- Generate interim and final technical recommendations on potential applications and appropriateness thereof of by-product materials or derivatives.

This report concentrates on characterising the geochemical, isotope, mineralogical, toxicological and basic physico-chemical properties of industrial by-products and complimentrary materials with a view to assessing the potential of the materials for environmental applications and further testing including aspects such as contaminant uptake and acid neutralisation capacity.

2. EXPERIMENTAL DESIGN

2.1. Selection and Procurement of By-Products

Detailed discussions were undertaken with major mining and mineral processing companies, principally in Western Australia, including Iluka Resources Ltd., Rio Tinto HIsmelt, BHP Billiton and others to procure representative samples of large volume by-products for characterisation. Materials were also sourced from the Water Corporation of Western Australia. In addition, an advertisement seeking by-products was placed in the March/April 2008 edition of the *Journal of the Australasian Institute of Mining and Metallurgy* (page 30).

Bassendean Sand was included as a reference material, and laterite because although not a by-product per se it is a common constituent of mine overburden (Table 4). Both calcined magnesia and pre-commercial grade granular activated carbon were included because these materials are generated commercially in large volumes in and around Western Australia.

Table 4. By-products, Bassendean Sand reference material, laterite and commercially-available mineral-based materials examined for potential re-use as environmental amendments.

By-product	Brief description
Bassendean Sand	Underlies much of Perth metropolitan area; selected as reference solid phase.
Neutralised unused acid (NUA)	By-product of heavy mineral processing industry, sourced from WA.
Steelmaking by-product (SS)	Non-metallic by-product of iron-ore processing, sourced from WA.
Red mud (RM)	Fine-textured by-product of Bayer process alumina production, sourced from WA.
Red sand (RS)	Coarse-textured by-product of Bayer process alumina production, sourced from WA.
Reduced red sand (RRS)	Red sand by-product produced by calcination with charcoal, sourced from WA.
Laterite	Common regolith material in WA Darling Ranges and Yilgarn, present as overburden on some mine sites.
Calcined magnesia (CM)	Produced via calcination of MgO; produced in large quantities by Australian magnesia industry.
GWTP lime residue	Lime-based metropolitan groundwater treatment plant residue sourced from WA.
GWTP $CaCO_3$ residue	Calcium carbonate-based metropolitan groundwater treatment plant residue from WA, with high Fe content.
Granular activated carbon (GAC)	Pre-commercial grade carbonised mallee eucalyptus sourced from WA.
Fly ash (FA)	By-product of coal combustion during energy production, sourced from WA.

A scheme used by CSIRO to characterise and evaluate by-products in outlines in Figure 1. This scheme consists of five phases. In Phase I, if a promising by-product is identified it is sourced from the producer with all relevant information. In addition, extensive testing including mineralogy, major and trace element geochemistry, and radioactivity are used to initially characterise the by-product. In Phase II, column trials up to six months in duration are conducted using one or both of a synthetic acid mine drainage water, or a nutrient- and dissolved organic carbon (DOC)-rich natural water from the Swan Coastal Plain. These two water types are a proxy for potential field applications relevant to Western Australia and elsewhere and as a continuous flow system simulate, albeit on a laboratory scale, an actual field implementation. In Phase III, if based on characterisation results by-products are deemed to possess sufficient promise for one or more potential field applications the by-products are subjected to a range of leachate toxicity testing. The leachate toxicity tests evaluate possible effects of the exposure of sensitive biota to by-products in field applications. Phase IV involves pre-commercial field trials to establish the efficacy, applicability and cost-benefit of selected by-product application. Finally, in Phase V producers of by-products may seek regulatory approvals for specific by-product applications using the data and understanding derived from the previous four characterisation and evaluation Phases.

Unless otherwise stated, analyses were performed on oven-dried materials ground to <63 µm in a WC ring mill. Basic characterisation included measurements of pH and electrical conductivity (EC). For each sample, the EC was determined in a 1:5 aqueous extract using deionised water; by-product pH was determined in 0.01 M $CaCl_2$ (1:5 solid to liquid ratio), as $CaCl_2$ pH measurements are more stable and reproducible than those determined in aqueous solution (Rayment and Higginson, 1992).

Basic physical properties of selected by-products were determined including bulk density (ρ_b), porosity (S_t), saturated hydraulic conductivity (K), and particle size distribution. Average bulk density was determined from the mass of material dry packed into a stainless steel column using manual vibration to optimize packing, where the internal column volume was known. A further check of the average bulk density measurement was obtained by dry packing material into a 100 mL measuring cylinder with manual vibration to optimize packing.

The porosity of selected by-products was determined by:

1. Column bromide (as NaBr) breakthrough measurement.
2. Gravimetric data from the unsaturated and saturated material.

The column Br breakthrough was determined for selected materials by pumping a Br tracer (as NaBr) at 200 mg L^{-1} (Br) through a stainless steel column (1.0 m long, 2.2 cm ID, volume 380 cm^3) packed with the by-product. Column effluent concentrations were monitored to determine the time of breakthrough, defined as the time effluent Br concentrations reached 50% of the maximum stable effluent Br concentration. Based on the Br breakthrough time and column flow rate, a Br breakthrough volume (column pore volume) was subsequently determined. Porosity then follows as the ratio of (i) the column pore volume to (ii) the column total volume.

Saturated hydraulic conductivity (K) of selected materials was determined using the head pressure differential method. By-products were packed into columns (1.0 m long, 2.2 cm ID, volume 380 cm^3) constructed from stainless steel with four sampling ports installed at 10, 25, 50 and 75 cm from the bottom influent end of the column. Two clear tubes were attached to the two column sampling ports farthest apart. The difference in the water level in the tubes was measured along with flow rate. Darcy's Equation (equation 1) was then used to calculate the value of K_{sat}.

$$Q = K \cdot A \cdot (H/L) \qquad (1)$$

Particle size distribution of selected by-products was determined by sieve analysis. A sample of 100 g of well mixed representative material was weighed out and transferred to a set of sieves, assembled and shaken for 10 minutes using a reciprocating sieve shaker (Pascal Engineering, England). The sieve apertures were 1000, 500, 355, 250, 180, 125, 90, 63 µm. Each sieve fraction was weighed and expressed as a percentage of the initial sample weight so as to give a physically determined size distribution.

2.2. Mineralogical Analyses

Quantitative X-ray diffraction (XRD) analysis was used to characterise the mineralogical composition of by-products. For quantitative XRD analysis, 1 g of each sample was ground to <10µm for 10 minutes in a McCrone micronizing mill under ethanol. The resulting slurries were oven dried at 60°C then thoroughly mixed with an agate mortar and pestle before being lightly back pressed into stainless steel sample holders for X-ray diffraction analysis. XRD patterns were recorded with a PANalytical X'Pert Pro Multi-purpose Diffractometer using Fe filtered Co Kα radiation, 1/4° divergence slit, 1/2° anti-scatter slit and fast X'Celerator Si strip detector. The diffraction patterns were recorded in steps of 0.016° 2Θ with a 0.4 second counting time per step, and logged to data files for analysis.

Quantitative analysis was performed on the XRD data using the commercial package TOPAS from Bruker. The results are normalised to 100%, and hence do not include estimates of unidentified or amorphous materials.

2.3. Chemical Analyses

Major elemental composition of by-products was quantified by X-ray fluorescence (XRF) using both borate fusion and pressed powder methods.

2.3.1. Fusion X-Ray Fluorescence (XRF): Major Elements

Approximately 1 g of each oven dried sample (105°C) was accurately weighed with 4 g of 12-22 lithium borate flux. The mixtures were fused at 1050°C in a Pt/Au crucible for 20 minutes then poured into a 32 mm Pt/Au mould heated to a similar temperature. The melt was cooled quickly over a compressed air stream and the resulting glass disks were analysed on a PANalytical AXios Advanced wavelength dispersive XRF system using the CSIRO Mineralogical and Geochemical Services in-house Silicates program. Analyses were undertaken at CSIRO Land and Water Laboratories Adelaide, SA.

2.3.2. Pressed Powder X-Ray Fluorescence (XRF): Trace Elements

Approximately 4g of each oven dried sample (105°C) was accurately weighed with 1g of Licowax binder and mixed well. The mixtures were pressed in a 32mm die at 12 tons pressure and the resulting pellets were analysed on a PANalytical AXios Advanced wavelength dispersive XRF system using the CSIRO Mineralogical and Geochemical Services in-house Powders program. Analyses were undertaken at CSIRO Land and Water Laboratories Adelaide, SA.

2.3.3. Neutron Activation Analysis (NAA)

Selected samples were examined by neutron activation analysis (NAA), in which intact samples were subjected to neutron irradiation. During neutron irradiation, stable isotopes of elements are transformed into radioactive isotopes by neutron capture. Radioisotopes are then analysed and quantified using gamma spectrometry to measure gamma ray decay signatures. The NAA technique measures the total quantity of an element present in a sample without regard to chemical or physical form, and without any sample pre-treatment. Neutron activation analysis facilitates the highly sensitive and accurate simultaneous determination of more than 70 elements, about 30 of which can readily be examined in complex solid matrices such as soil samples (Helmke, 1996). Analyses were undertaken by Actlab, Canada.

2.3.4. U-Th Series, ^{40}K and ^{137}Cs Isotope Analysis

Gamma spectrometry was used for the determination of ^{226}Ra, ^{210}Pb, ^{228}Th, and followed the methods of Murray et al. (1987). Briefly, by-product samples were dried at 50°C, ground in a ring mill and then compressed into sealed perspex container of known geometry. The samples were counted for 1-2 days using intrinsic germanium gamma detectors. The detectors were calibrated using CANMET uranium ore BL-5, and thorium nitrate refined in 1906 (Amersham International). Both ^{40}K and ^{137}Cs were also determined by gamma spectrometry.

Alpha spectrometry was used to measure ^{238}U, ^{234}U, ^{232}U, ^{232}Th, and ^{230}Th in by-products (Martin and Hancock, 2004). This method involves the addition of a tracer isotope (^{232}U and ^{229}Th) to the samples, and the sample dissolved using strong acids, including HNO_3, HCl, HF and $HClO_4$. Radiochemical separation procedures were used to isolate the radionuclides of interest (U and Th). The purified solutions were electroplated and the alpha particle disintegrations counted and analysed by high resolution alpha spectrometry. The chemical yield of the procedure was determined from the known activity of the added tracer isotopes. All isotope analyses were undertaken by CSIRO Land and Water Black Mountain Laboratories, ACT.

The absorbed dose rate in air (D) at 1 m above a semi-infinite plane has been calculated using the equation:

$$D = 0.427 \times {}^{238}U + 0.662 \times {}^{232}Th + 0.043 \times {}^{40}K$$

where D is the absorbed dose rate in air ($nGy\ h^{-1}$), and ${}^{238}U$, ${}^{232}Th$, and ${}^{40}K$ are the activity concentrations in $Bq\ kg^{-1}$ (Toussaint, 2005). This formula was used to determine D for materials examined in this study.

2.4. Ecotoxicological Analyses

Leachates of selected by-product were prepared and subjected to toxicity testing to evaluate potential impact on water quality. All testing was undertaken at CSIRO Land and Water Laboratories, Lucas Heights, NSW

2.4.1. Algal Growth Rate Toxicity Test

Chronic 72-hour algal growth rate toxicity tests were conducted using the freshwater alga *Chlorella* sp.12. The chronic algal growth rate toxicity test measures the decrease (inhibition) in algal growth rate, as indicated by cell division, of the tropical freshwater alga *Chlorella* sp. 12 after exposure to the leachate sample for 72 hours. Initial algal cell density was 2-4 x 10^3 cells mL^{-1}. Toxicity is expressed as the concentration of sample leachate that causes a 50% inhibition in algal growth (IC50). Test results also indicate the lowest observable effect (LOEC) and no observable effect (NOEC) concentrations.

Synthetic softwater for use as the diluent and control water for algal growth rate toxicity tests was prepared according to the USEPA protocol (USEPA, 1994), and was filtered through an acid-washed (10% HNO_3) 0.45 µm filter. Two litres of leachate were prepared for each algal growth rate toxicity test according to the Toxicity Characteristic Leaching Procedure (TCLP – USEPA, 1986), except that synthetic softwater was used as the extraction fluid in place of acetic acid. Fifty grams of powdered by-product material were mixed with 1 L of synthetic softwater in 1 L LDPE Nalgene® bottles and mixed by tumbling end-over-end at 30 ± 2 rpm for 18 hours. Method blanks were also prepared by filling 1 L LDPE Nalgene® bottles with synthetic softwater, which were tumbled end-over-end alongside sample leachates. Both leachates and method blanks were centrifuged for 7 minutes at 2500 rpm. For each sample, the by-product leachate, method blank, and synthetic softwater control were then filtered through acid-washed (10% HNO_3) 0.45 µm membrane filters prior to toxicity testing. Test protocol was based on the OECD Test Guideline 201 (1984). The IC50, LOEC, and NOEC were determined using ToxCalc Version 5.0.23 (Tidepool Software). The LOEC and NOEC are calculated using Bonferroni’s t-test (ToxCalc Version 5.0.23, Tidepool Software).

2.4.2. Cladoceran Immobilisation Toxicity Test

Acute 48-hour cladoceran immobilisation tests were conducted using the cladoceran, *Ceriodaphnia dubia*. The acute cladoceran immobilisation test measures the mobility of the freshwater cladoceran during a 48-hour exposure period. Toxicity is expressed as the concentration of sample leachate that causes a 50% reduction in cladoceran mobility (EC50). Test results also yield LOEC and NOEC values.

Synthetic softwater and by-product leachates were prepared as in the algal growth rate toxicity tests. Following centrifugation, the by-product leachate, method blank and synthetic softwater control samples were then filtered through acid-washed (10% HNO_3) 0.45 µm membrane filters and supplemented with Se and Vitamin B_{12} prior to toxicity testing. Dilute mineral water (DMW) was used as the diluent and control water in all quality assurance (QA) test solutions. The DMW (20% Perrier® diluted in Milli-Q water with added Se and Vitamin B_{12} nutrient supplements) was aerated for at least 24 hours prior to use. The pH, conductivity, dissolved oxygen and temperature was measured in sub-samples of test concentrations at the beginning and end of each test. The protocol for the acute 48-hour cladoceran immobilisation test was based on the USEPA (1994) acute toxicity test protocol. Results were analysed using ToxCalc Version 5.0.23 (Tidepool Software). The LOEC and NOEC are calculated using Bonferroni's t-test (ToxCalc Version 5.0.23, Tidepool Software).

2.4.3. Microtox® Test

Microtox® tests were carried out using the marine bacterium *Vibrio fischeri*. The Microtox® test measures the decrease in light output of *Vibrio fischeri* after exposure to the leachate sample for 5 and 15 minutes. Toxicity is expressed as the concentration of sample leachate that causes a 50% reduction in the light output of the bacteria (EC50 value). Synthetic softwater and by-product leachates were prepared as in the algal growth rate toxicity tests. Following centrifugation, the by-product leachate, method blank and synthetic softwater control samples were then filtered through acid-washed (10% HNO_3) 0.45 µm membrane filters. Because Microtox® uses a marine bacterium, the method blanks and leachates were adjusted to a salinity of 20% with Microtox® Osmotic Adjustment Solution (MOAS) prior to use in toxicity tests.

The 90% Basic Test Protocol with MOAS adjustment was used (Azur Environmental, 1998); therefore, the highest concentration that could be tested was 82% (where 100% is undiluted leachate sample). Seven concentrations of each sample (0.1 to 82%) were tested, each in duplicate, using 2% NaCl as the diluent and control water. Exposure duration was 5 and 15 minutes. The EC50, LOEC, and NOEC values for Microtox® tests were determined using ToxCalc Version 5.0.23 (Tidepool Software). The LOEC and NOEC are calculated using Bonferroni's t-test (ToxCalc Version 5.0.23, Tidepool Software).

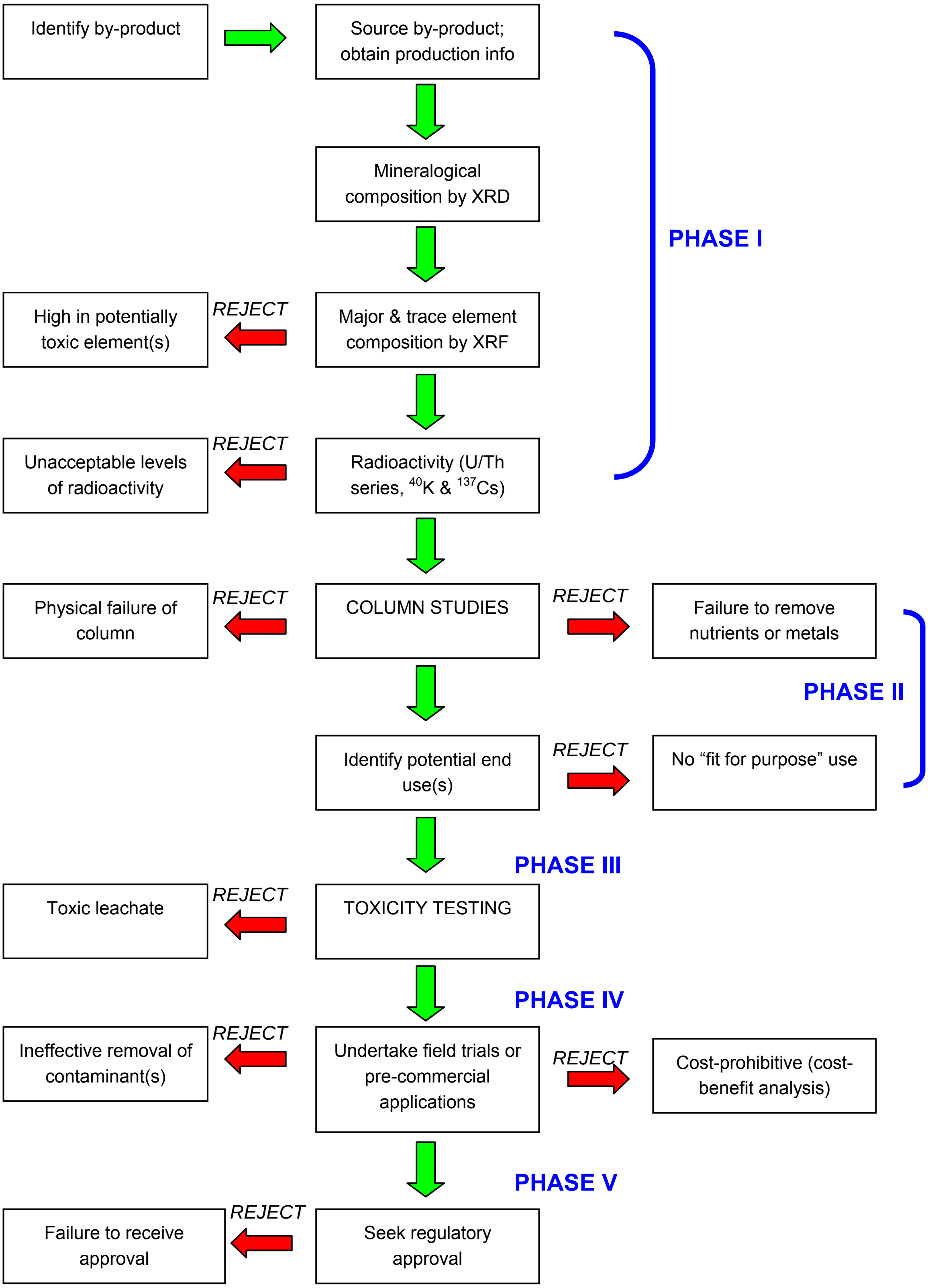

Figure 1. By-product characterisation scheme.

3. RESULTS: REFERENCE AND INDIVIDUAL BY-PRODUCT MATERIALS

3.1. Bassendean Sand Reference Material

A large portion of Western Australia's Swan Coastal Plain is comprised of heavily leached, siliceous dune systems, including Bassendean Sands (Playford et al., 1976). Due to its widespread distribution underlying the Perth metropolitan area, Bassendean Sand was selected as the reference solid phase for control columns, and for fill material to mix with potentially sorptive solid phases in experimental columns. Bassendean Sands are predominantly (99.8%) SiO_2. Apart from a small amount of Al_2O_3 (0.14%) and Fe_2O_3 (0.04%) other major element concentrations in Bassendean Sands are low (Playford et al., 1976).

3.1.1. Bassendean Sand General Characteristics

The Bassendean Sand sourced for use in this research project was typical of the porous grey sands found on the Swan Coastal Plain, exhibiting low EC and moderately acidic pH (Table 5).

Table 5. Electrical conductivity (EC) and pH of Bassendean Sand.

	EC (µS cm^{-1})	pH
Bassendean Sand	25.5	4.8

The bulk density determined for the Bassendean Sand was consistent with sands of the Swan Coastal Plain, within the range from 1.40 to 1.80 g cm^{-1} (Pollock et al., 2002; Rümmler et al., 2005) (Table 6). Playford et al. (1976) measured a mean hydraulic conductivity of 13 m d^{-1} for Swan Coastal Plain Bassendean Sands, equivalent to 0.9 cm min^{-1}.

Table 6. Bassendean Sand porosity, bulk density and saturated hydraulic conductivity.

Parameter	Bassendean Sand
Porosity (calculated)	0.34
Bulk Density by measuring cylinder (g cm^{-3})	1.80
Bulk Density by gravimetric measurement (g cm^{-3})	1.69
Hydraulic conductivity (cm min^{-1})	0.90†

†From Playford et al., 1976.

Particle size analysis of Bassendean Sands indicated that the majority of the sand grains were within the size range 150-425 µm (Abeysinghe, 2003) (Table 7).

Table 7. Particle size distribution of a representative sample of Bassendean Sand from the Swan Coastal Plain (from Abeysinghe, 2003).

Size fraction (µm)	Bassendean Sand (%)
> 850	0.01
600 – 850	0.08
500 - 600	0.33
425 – 500	2.39
300 – 425	37.99
212 – 300	41.64
150 – 212	14.28
106 -150	3.04
75 - 106	0.20
< 75	0.04

3.1.2. Bassendean Sand Mineralogy

As expected, mineralogical analysis of Bassendean Sand using powder X-ray diffraction analysis (XRD) indicated that the main ordered phase was quartz (SiO_2). X-ray diffraction analysis indicated that the sand also contained minor, but detectable, quantities of halite ($NaCl$), calcite ($CaCO_3$), and hematite (α-Fe_2O_3) (Figure 2).

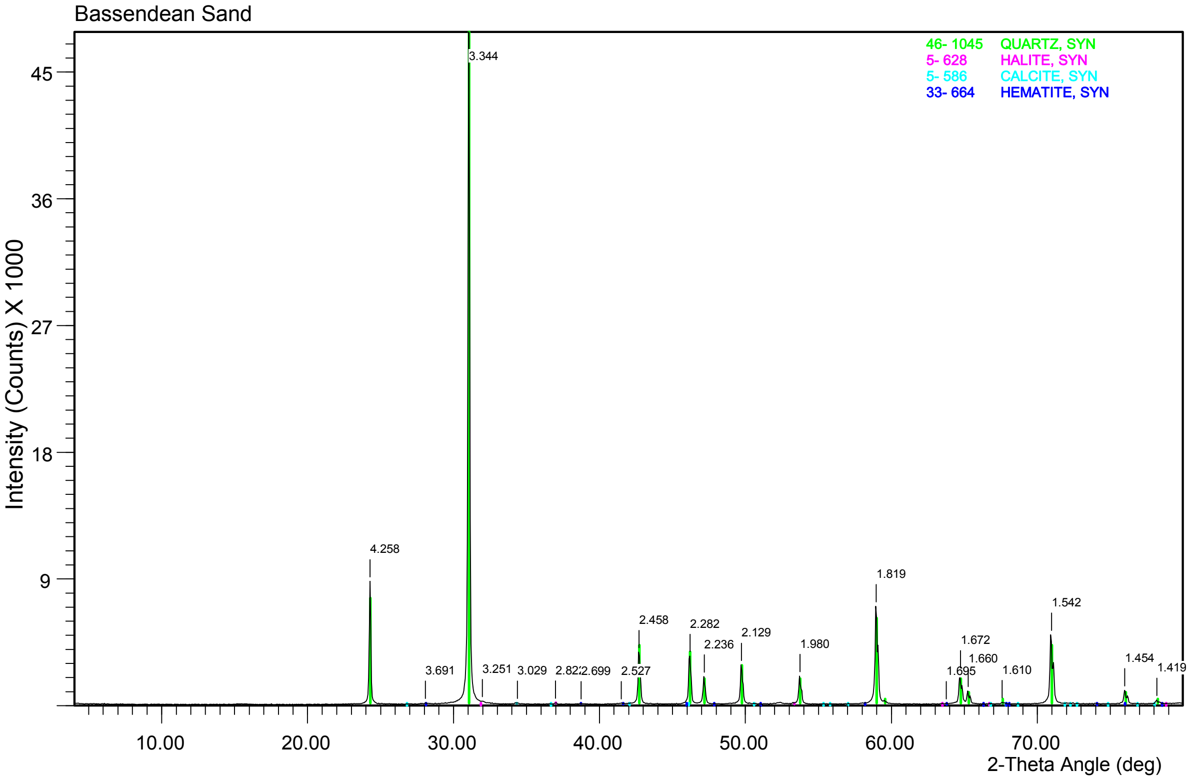

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Figure 2. Powder X-ray diffraction (XRD) spectra of Bassendean Sand.

3.1.3. Bassendean Sand Major and Trace Element Analysis

X-ray fluorescence analysis showed that the Bassendean sand was comprised almost entirely of SiO_2, indicative of the high quartz content (Table 8). Apart from a small amount of Al_2O_3 (0.11%) and Fe_2O_3 (0.39%), other major element concentrations were low.

Table 8. Fusion X-ray fluorescence (XRF) major elemental composition of Bassendean sand (BS).

	SiO_2 (%)	**TiO_2 (%)**	**Al_2O_3 (%)**	**Fe_2O_3 (%)**	**MnO (%)**	**MgO (%)**	**CaO (%)**	**Na_2O (%)**	**K_2O (%)**	**P_2O_5 (%)**	**SO_3 (%)**	**Cl (ppm)**	**Sum (%)**
BS	98.21	0	0.11	0.39	0	0	0.07	0	0	0.07	0.02	0	98.9

Trace elements were generally impoverished in Bassendean Sand (Table 9), with the only trace element enrichments of note being Cr, Zr and the light rare earth elements (La, Ce).

Table 9. Pressed powder X-ray fluorescence (XRF) trace elemental composition of Bassendean Sand (BS). All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
BS	0.3	<0.4	21	1	2	0.5	39	<2.0	287	3
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
BS	3	1	<0.4	0	1	1	30	ND[†]	14	8
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
BS	ND	16	3	2	<0.8	ND	1	ND	2	7
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
BS	ND	ND	7	3	<0.9	9	5	1	3	72

[†] ND = not determined.

3.1.4. Bassendean Sand U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of Bassendean Sand is given in Table 10. For the Bassendean Sand, the calculated absorbed dose rate (D) was 4 nGy h^{-1}. In comparison, Darling Scarp soils have D values between 35 and 378 nGy h^{-1} (average 195 nGy h^{-1}) (Toussaint, 2005). The UNSCEAR quoted range is 11-54 nGy h^{-1} (mean 33 nGy h^{-1}, UNSCEAR, 1998).

Table 10. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of Bassendean Sand (BS).

Radionuclide	BS (Bq kg^{-1})
^{238}U	2.5
^{234}U	2.5
^{230}Th	2.7
^{226}Ra	4.8
^{210}Pb	5.2
^{232}Th	4.3
^{228}Ra	4.5
^{228}Th	4.9
^{40}K	3.2
^{137}Cs	0.4

3.2. Neutralised Unused Acid (NUA)

The by-product neutralised unused acid (NUA) was sourced from Iluka Resources Ltd., a global miner and processor of mineral sands with large operations in Western Australia. The mineral sands are separated physically into ilmenite ($FeTiO_3$), rutile (TiO_2) and zircon (ZrO_2). The low value ilmenite is upgraded to synthetic rutile at two sites in WA in a chemical process that includes a sulphuric acid leach. The used acid from the leach is neutralised with lime to produce a gypsum based solid residue containing Fe and Mn (NUA) via the following reaction:

$$2Fe^{3+} + 3SO_4^{2-} + 3CaO + 3H_2O \rightarrow 2FeOOH + 3CaSO_4 \cdot 2H_2O$$

A substantial quantity of Mn present within the system also precipitates upon neutralisation, but at a lower pH than other minerals involved in the reaction. The synthetic rutile industry generates significant quantities of NUA that is normally disposed of in lined storage systems. Iluka Resources Ltd. is the world's largest producer of zircon, synthetic rutile, natural rutile and chloride ilmentite. Millions of tonnes per annum of NUA and similar residues are currently produced in Australia by Iluka Resources Ltd. and other companies worldwide; approximately 20,000 tpa NUA are presently generated at the Iluka Resources Ltd. North Capel facility in Western Australia alone. Iluka Resources Ltd. has recently established a new mineral sands mine in South Australia, which will also generate NUA. The NUA used in the characterisation investigation was obtained from the Capel operations of Iluka Resources, Ltd. and ground in a WC ring mill prior to characterisation.

3.2.1. NUA General Characteristics

The NUA exhibited a moderately high EC (Table 11), most likely due to the dissolution of some gypsum ($CaSO_4$) in the 1:5 solution (Rhoades, 1996). The measured pH of NUA in 1:5 0.01 M $CaCl_2$ solution was slightly acidic (Table 11).

Table 11. Electrical conductivity (EC) and pH of neutralised unused acid (NUA).

	EC (mS cm^{-1})	pH
NUA	2.54	5.3

The mean bulk density of NUA was approximately 0.87 g cm^{-1} (Table 12). The Br breakthrough curve for NUA is shown in Figure 3. Based on the 50% breakthrough volume, a porosity of 0.59 was determined for NUA. In comparison, the porosity of sandy soils generally ranges from 0.25 to 0.50 (Freeze and Cherry, 1979).

Table 12. Neutralised used acid (NUA) porosity, bulk density and saturated hydraulic conductivity.

Parameter	NUA
Porosity by Br- breakthrough	0.59
Bulk Density by measuring cylinder (g cm^{-3})	0.87
Bulk Density by gravimetric measurement (g cm^{-3})	0.81
Saturated hydraulic conductivity by head pressure differential (cm min^{-1})	0.54

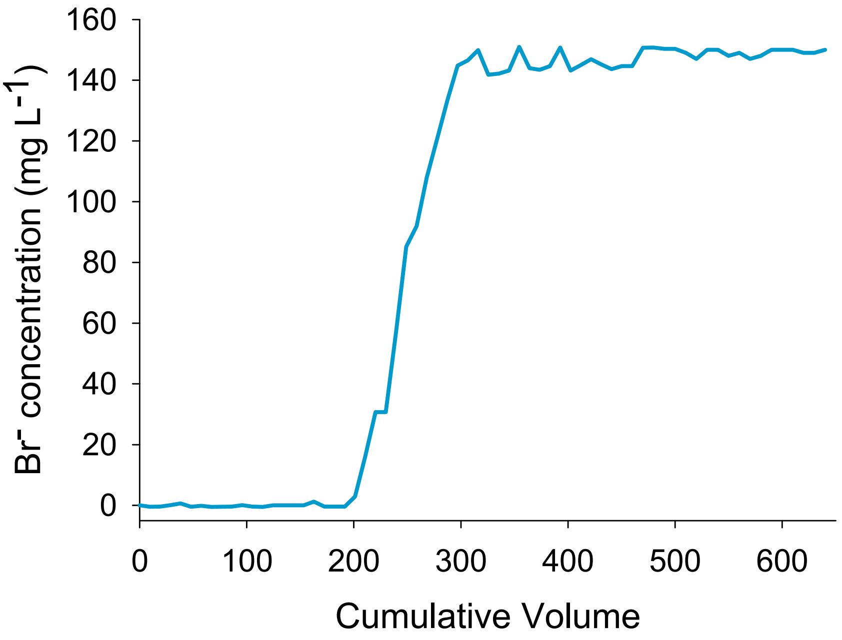

Figure 3. Bromide (as NaBr) breakthrough for a column containing neutralised used acid (NUA).

Sieve analysis (Table 13) showed that the majority of the NUA was <63 µm. The small particle size of the NUA explains its low hydraulic conductivity.

Table 13. Neutralised used acid (NUA) particle size distribution by sieve analysis.

Size fraction (µm)	NUA composition (%)
> 1000	0.00
500 – 1000	1.21
355 -500	8.38
250 – 355	7.77
180 – 250	5.13
125 – 180	5.09
90 – 125	4.96
63 -90	10.17
< 63	57.29

3.2.2. NUA Mineralogy

Powder XRD analysis indicated that the main ordered mineral phase contained in NUA was gypsum ($CaSO_4{\cdot}2H_2O$), with minor quantities of magnetite (Fe_3O_4) and quartz (SiO_2) (Figure 4). If partially hydrated, bassanite ($CaSO_4{\cdot}0.5H_2O$) may also occur while amorphous Fe and Mn oxides/oxyhydroxides may also be present.

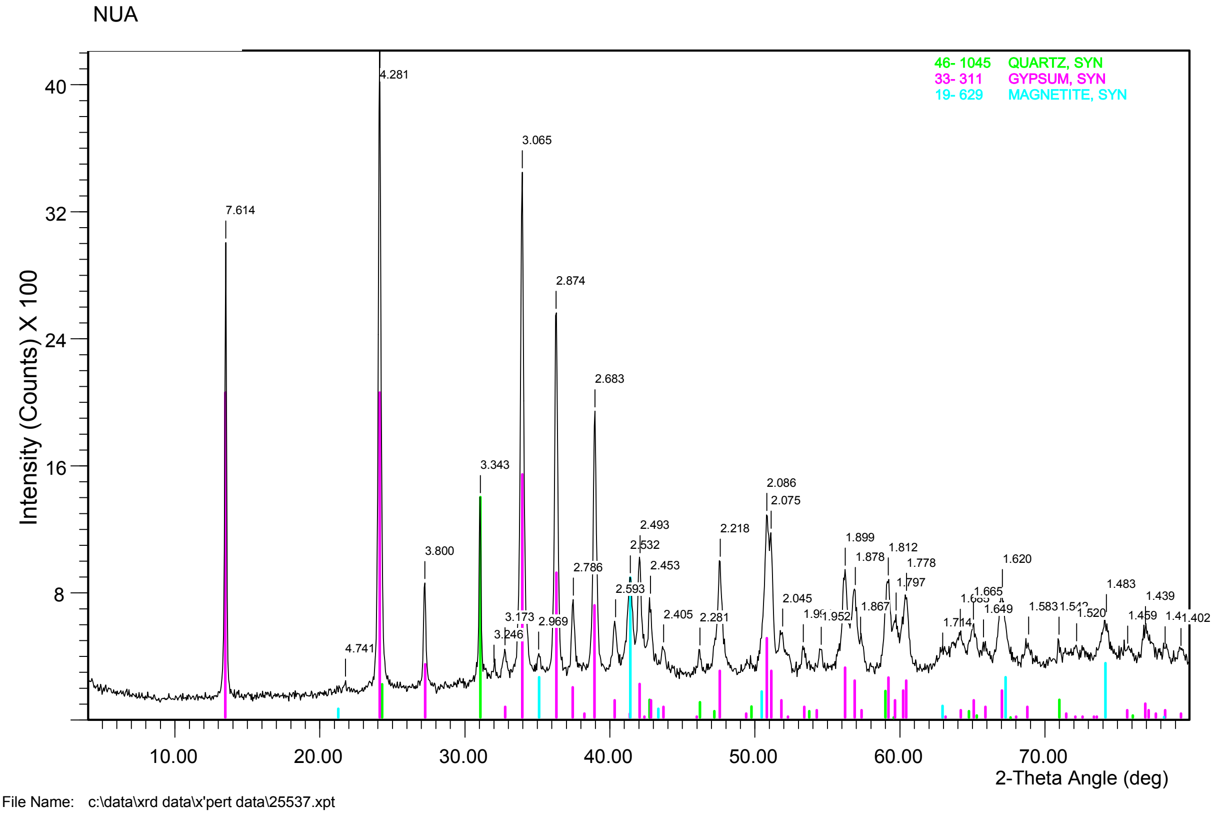

Figure 4. Powder X-ray diffraction (XRD) spectra of neutralised unused acid (NUA).

3.2.3. NUA Major and Trace Element Analysis

X-ray fluorescence analysis showed that the NUA was primarily comprised of CaO and Fe_2O_3, (Table 14) principally as gypsum, magnetite hematite and amorphous Fe oxyhydroxide phases. Six major elements (expressed as oxides) including Fe_2O_3, CaO, SO_3 and to a lesser extent MnO, TiO_2 and SiO_2 (Table 14) collectively constituted nearly 88% of the total mass of the NUA.

Table 14. Fusion X-ray fluorescence (XRF) major elemental composition of neutralised unused acid (NUA).

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
NUA	4.3	1.0	1.7	22.7	2.7	1.8	25.1	0.2	0.08	0.1	31.0	550	90.7

Trace elements that displayed some enrichment (≥2 times) in the NUA when compared to Bassendean Sand included V, Ni, Cu, Zn, Ga, As, Se, Sr, Y, Nb, Ce, Tl, Pb, Bi and Th (Table 15). Elements in the NUA depleted relative to Bassendean Sand included Cr, Mo, Sn, Ba and Nd. A small uncertainty exists in the robustness of Zr and the LREE measurements due to matrix effects in the XRF analysis. Additionally, Co contamination of NUA may have occurred during grinding in the WC ring mill.

Table 15. Pressed powder X-ray fluorescence (XRF) trace elemental composition of neutralised unused acid (NUA). All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
NUA	0.3	10	38	0.03	<2	<0.1	95	172	80	1
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
NUA	44	26	<0.4	1	<0.01	1	35	ND†	3	17
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
NUA	<7	90	21	6	0.4	<7	5.4	<8	3	725
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
NUA	<5	<0.1	112	0.07	6	71	19	1	30	16

†ND = not determined.

3.2.4. NUA U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of NUA is given in Table 16. NUA had relatively high mean activities of ^{232}Th, ^{228}Ra, and ^{228}Th which were derived from the ^{232}Th decay chain.

The calculated absorbed dose rate (D) for NUA was 263 nGy h^{-1}, similar to D values for Darling Scarp soils (35 to 378 nGy h^{-1}, average 195 nGy h^{-1}) (Toussaint, 2005).

Table 16. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of neutralised unused acid (NUA).

Radionuclide	NUA (Bq kg^{-1})
^{238}U	55
^{234}U	71
^{230}Th	112
^{226}Ra	12.8
^{210}Pb	14.4
^{232}Th	360
^{228}Ra	128
^{228}Th	187
^{40}K	28.8
^{137}Cs	0.3

3.2.5. Ecotoxicity of NUA

3.2.5.1. Algal Growth Rate Test

The NUA leachate and method blank for the 72-hour chronic algal growth rate toxicity test were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. The NUA leachate was slightly higher in pH than the method blank and control water (Table 17).

Table 17. Characteristics of filtered neutralised used acid (NUA) leachate used in chronic 72-hour algal growth rate toxicity tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO† (% sat.)
NUA leachate	8.32	1.5	2.9	98
Method blank	7.64	0.2	0.34	103
Synthetic softwater	7.51	0.2	0.32	102

†DO = dissolved oxygen, expressed as percent saturation.

There was a slight but significant decrease in algal growth in the method blank, as compared to the quality assurance (QA) control. Thus, the method blank was used in all statistical calculations for the NUA leachate. The NUA leachate was of low toxicity to algal growth, with an IC50 value of >100% (Table 18). There was, however, significant inhibition of algal growth in test concentrations of 33% and higher. At both 33% and 100% concentrations of NUA leachate, algal growth was significantly less than the method blank. The NOEC value for algal growth inhibition in NUA leachate was 11% and the LOEC value was 33%.

Table 18. Results of neutralised used acid (NUA) chronic 72-hour algal growth rate toxicity tests.

	Growth Rate (doublings per day)	% of Control	CV (%)
Controls			
QA Control	2.02	100	5.0
Method blank	1.87	92	2.4
NUA Leachates			
Method blank	1.87	100	2.4
0.1%	2.18	117	0.7
1.2%	1.79	96	3.6
3.7%	1.92	103	7.8
11%	1.78	95	6.2
33%	1.61	86	5.9
100%	1.47	79	12

3.2.5.2. Cladoceran Immobilisation Test

The NUA leachate and method blank for the 48-hour acute cladoceran immobilisation toxicity test were prepared as described previously, using synthetic softwater in place of acetic acid. All cladocerans in the DMW control, method blank, and softwater control were mobile after 48 hours. For statistical calculations, values for the synthetic softwater control and method blank were pooled. The NUA leachate was not toxic to *Ceriodaphnia dubia*, with no immobile cladocerans in any concentration of leachate tested (Table 19). The EC50 and LOEC values for cladoceran immobilisation in NUA leachate were both >100%, and the NOEC value was 100%.

Table 19. Results of neutralised used acid (NUA) acute 48-hour cladoceran immobilisation toxicity tests.

	Mean mobile (%)	% of pooled control	% inhibition
Controls			
DMW Control	100	100	0
Synthetic softwater	100	100	0
Method blank	100	100	0
NUA Leachates			
0.1%	100	100	0
1.2%	100	100	0
3.7%	100	100	0
11%	100	100	0
33%	100	100	0
100%	100	100	0

3.2.5.3. Microtox® Test

The NUA leachate and method blank for the Microtox® test were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. The pH and salinity of the NUA leachate were slightly higher than those of the method blank (Table 20). The salinity and dissolved oxygen content of the MOAS-amended NUA leachate and method blank were similar.

Table 20. Characteristics of filtered neutralised used acid (NUA) leachate used in Microtox® tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO (% sat.)
NUA leachate	8.37	1.5	2.9	98
NUA leachate + MOAS	7.79	21	34	98
Method blank	7.77	0.1	0.28	98
Method blank + MOAS	7.72	20	32	99

The NUA leachate was not toxic to *Vibrio fischeri*, with no significant inhibition of light output observed for any concentration tested after both a 5- and 15-minute exposure time. In the highest dilution of NUA leachate (82%), however, there was significant stimulation (14-16% stimulation) of light output after a 5-minute exposure. After 15 minutes of exposure to the NUA leachate, significant stimulation was observed in leachate concentrations of 9.1-82%, with up to 24% stimulation of light output. The ecological relevance of stimulation of light output in the Microtox® test system is not well understood.

3.2.5.4. Leachate Chemistry

Trace elements that displayed some enrichment (≥2 times) in the NUA leachate when compared to the softwater control (method blank) included Ba, Ca, Cl, Cr, F, K, Mg, N (primarily as NO_x-N), Na, Rb, S, Si, Sr and U (Table 21). The increase in Ca, Sr and S content of NUA leachate relative to the method blank is likely due to gypsum dissolution during leachate preparation. No elements in the NUA leachate were depleted relative to the method blank.

Table 21. Chemical composition of method blank and neutralised unused acid (NUA) leachates used in toxicity tests.

Analyte (mg L^{-1})	Method blank	Method Blank+MOAS	NUA	NUA+MOAS
Al	<0.005	<0.005	<0.005	<0.005
As	<0.001	<0.01	<0.001	<0.01
B	<0.02	<0.02	<0.02	0.04
Ba	<0.002	<0.002	0.009	0.008
Be	<0.0001	<0.001	<0.0001	<0.001
CO_3 (mg $CaCO_3$/L)	<1	<1	<1	<1
Ca	10.8	9.8	600	593
Cd	<0.0001	<0.001	<0.0001	<0.001
Ce	<0.0005	<0.005	<0.0005	<0.005
Cl	4	11100	80	11200
Co	<0.0001	<0.001	<0.0001	<0.001
Cr	<0.001	<0.001	0.024	0.023
Cu	<0.002	<0.002	<0.002	<0.002
F	0.06	<0.05	1.5	1.3
Fe	0.006	0.012	<0.005	<0.005
HCO_3 (mg $CaCO_3$/L)	61	82	46	92
Hg	<0.0001	<0.001	<0.0001	<0.001
K	1.9	2	9.2	9.8
La	<0.0001	<0.001	<0.0001	<0.001
Mg	9.3	8.8	71.3	71.1
Mn	<0.001	<0.001	0.001	0.001
Mo	<0.001	<0.01	<0.001	<0.01
NH_3-N	<0.01	0.02	0.02	0.03
NO_x-N	0.09	0.08	2.1	2.1
Total N	0.14	0.15	2.6	2.1
Na	21	7870	57.3	7690
Ni	<0.01	<0.01	<0.01	<0.01
OH (mg $CaCO_3$/L)	<1	<1	<1	<1
Total P	<0.1	<0.1	<0.1	<0.1
PO_4-P	<0.01	<0.01	<0.01	<0.01
Pb	<0.0001	<0.001	<0.0001	0.0011
Rb	<0.0001	<0.001	0.02	0.019
S	21	20	560	570
SO_4	62.6	59.3	1680	1710
Sb	<0.0001	<0.001	<0.0001	<0.001
Sc	<0.0005	<0.005	<0.0005	<0.005
Se	<0.001	<0.01	<0.001	<0.01
Si	0.06	0.08	0.55	0.56
Sr	0.004	0.004	11	10
Te	<0.0001	<0.001	<0.0001	<0.001
Th	<0.0001	<0.001	<0.0001	<0.001
Ti	<0.002	<0.002	<0.002	<0.002
Tl	<0.0001	<0.001	<0.0001	<0.001
U	<0.0001	<0.001	0.0023	0.0021
V	<0.005	<0.005	<0.005	<0.005
Y	<0.0005	<0.005	<0.0005	<0.005
Zn	<0.005	<0.005	<0.005	<0.005
Zr	<0.0001	<0.001	0.0002	<0.001

3.3. Steelmaking By-product

Steelmaking by-products (SS), or slags, are the non-metallic residues of metal processing. The most common slags are those resulting from iron and steel production. Slag composition is dependent upon the type of steelmaking process by which it is produced.

3.3.1. Steelmaking By-product General Characteristics

The steelmaking by-product exhibited low EC and circumneutral pH (Table 22).

Table 22. Electrical conductivity (EC) and pH of steelmaking by-product (SS).

	EC (µS cm^{-1})	**pH**
Steelmaking by-product	127.0	7.5

Based on the 50% breakthrough volume of Br, a pore volume of 45% was determined for the ground steelmaking by-product (Figure 5, Table 23). Bulk densities of the steelmaking by-product varied depending on the method of determination, between 1.99 and 1.81 g cm^{-1}.

Table 23. Steelmaking by-product (SS) porosity, bulk density and saturated hydraulic conductivity.

Parameter	**SS**
Porosity by Br^- breakthrough	0.45
Porosity by gravimetric measurement	0.47
Bulk Density by measuring cylinder (g cm^{-3})	1.81
Bulk Density by gravimetric measurement (g cm^{-3})	1.99

The ground steelmaking by-product had a high bulk density (*ca.* 1.9 g cm^{-3}, Table 23); however, the bulk density is highly dependent on how finely ground the by-product is. If a lower bulk density were desired, the by-product could be used as received (gravel sized solid material) or crushed to achieve a smaller size fraction without grinding. The material used for by-product characterisation was finely ground for analysis.

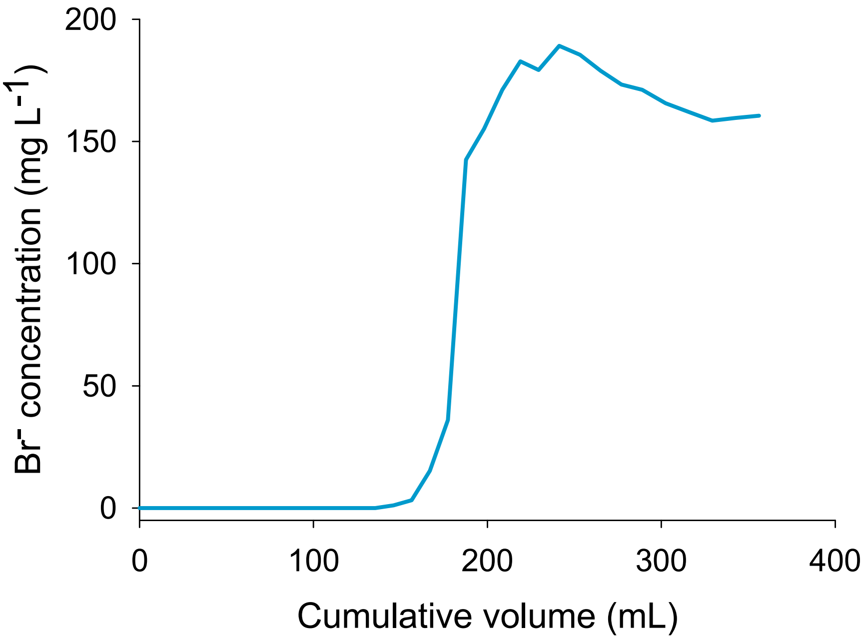

Figure 5. Bromide (as NaBr) breakthrough for a column containing steelmaking by-product (SS).

3.3.2. Steelmaking By-product Mineralogy

X-ray diffraction analysis of the steelmaking by-product (Figure 6) indicated the presence of the melilite group mineral gehlenite ($Ca_2Al_2SiO_7$). Minor pyroxene, such as diopside/augite [$CaMgSi_2O_6$/(Ca,Na)(Mg,Fe,Al,Ti)(Si,Al)$_2$O$_6$], spinel (ideal formula $MgAl_2O_4$) and quartz (SiO_2) were also present.

Quantitative XRD analysis showed that the steelmaking by-product was primarily (90%) comprised of gehlenite, with approximately 5% pyroxene, 3% spinel and 1% quartz. Gehlenite, pyroxene and spinel minerals are all produced via paragenesis at high temperatures consistent with the smelting process.

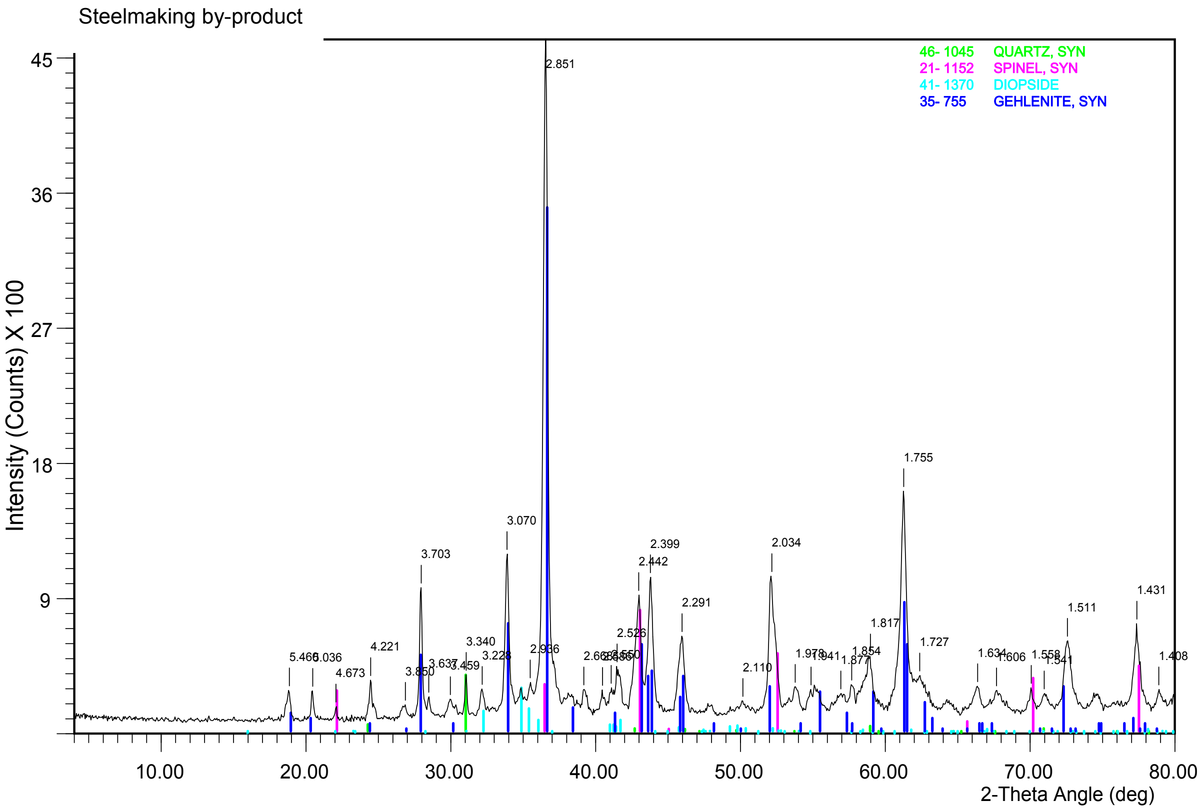

Figure 6. Powder X-ray diffraction (XRD) spectra of steelmaking by-product (SS).

3.3.3. Steelmaking By-product Major and Trace Element Analysis

More than 95% of the steelmaking by-product was accounted for by oxides of Si, Fe, Al Ca and Mg (Table 24).

Table 24. Fusion X-ray fluorescence (XRF) major elemental composition of steelmaking by-product (SS).

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
SS	29.5	0.6	14.2	4.6	0.7	9.1	35.6	0.1	0.03	1.1	0.3	168	95.7

Trace elements that displayed some enrichment (≥2 times) in the steelmaking by-product when compared to Bassendean Sand included As, Ba, Ce, Mn, Rb, Sr, Th, Tl, U, V, Y and Zr (Table 25). Elements in the steelmaking by-product that were depleted relative to Bassendean Sand included Br, Cr, Cu, Mo, and Ni (Table 25).

Table 25. Pressed powder X-ray fluorescence (XRF) trace elemental composition of steelmaking by-product (SS). All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
SS	<4	5	468	<4	<1	<5	125	<7	118	<13
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
SS	<2	<2	<2	<10	<16	<9	50	5232	<1	11
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
SS	37	<2	<3	8	<9	<7	2	<14	<4	1307
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
SS	<8	<8	19	10	12	117	64	<12	<3	164

Detection limits using NAA are generally lower than those for XRF, as can be seen by comparison of Tables 25 and 26. Trace element values obtained for the steelmaking by-product using NAA were in good agreement with XRF results with few exceptions (Table 26). The As, Th and U values determined by NAA were substantially less than those determined using pressed powder XRF. In contrast, the 14.5 mg kg^{-1} value obtained for Sc using NAA was more than twice the concentration determined by XRF analysis.

Table 26. Elemental composition of steelmaking by-product (SS) as determined by neutron activation analysis (NAA).

Element	Units	Steelmaking by-product
Antimony, Sb	mg kg^{-1}	<0.1
Arsenic, As	mg kg^{-1}	<0.5
Barium, Ba	mg kg^{-1}	480
Bromine, Br	mg kg^{-1}	<0.5
Calcium, Ca	% w/w	26
Cerium, Ce	mg kg^{-1}	101
Caesium, Cs	mg kg^{-1}	<1
Chromium, Cr	mg kg^{-1}	86
Cobalt, Co	mg kg^{-1}	<1
Europium, Eu	mg kg^{-1}	2
Iron, Fe	% w/w	4.3
Gold, Au	µg kg^{-1}	<2
Hafnium, Hf	mg kg^{-1}	3
Iridium, Ir	µg kg^{-1}	<5
Lanthanum, La	mg kg^{-1}	46.3
Lutetium, Lu	mg kg^{-1}	0.54
Mercury, Hg	mg kg^{-1}	<1
Molybdenum, Mo	mg kg^{-1}	<1
Neodymium, Nd	mg kg^{-1}	31
Nickel, Ni	mg kg^{-1}	<20
Rubidium, Rb	mg kg^{-1}	<15
Samarium, Sm	mg kg^{-1}	7.7
Scandium, Sc	mg kg^{-1}	14.5
Selenium, Se	mg kg^{-1}	<3
Silver, Ag	mg kg^{-1}	<5
Sodium, Na	% w/w	0.15
Strontium, Sr	% w/w	0.1
Tantalum, Ta	mg kg^{-1}	<0.5
Terbium, Tb	mg kg^{-1}	1.1
Thorium, Th	mg kg^{-1}	8.2
Tin, Sn	% w/w	<0.02
Tungsten, W	mg kg^{-1}	<1
Uranium, U	mg kg^{-1}	7.2
Ytterbium, Yb	mg kg^{-1}	7
Zinc, Zn	mg kg^{-1}	<50

3.3.4. Steelmaking By-product U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of steelmaking by-product is given in Table 27 . The steelmaking by-product exhibited moderate activities of the radioisotopes examined. The calculated absorbed dose rate for steelmaking by-product was 65 nGy h^{-1}.

Table 27. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of steelmaking by-product (SS).

Radionuclide	Steelmaking by-product (Bq kg^{-1})
^{238}U	73
^{230}Th	75
^{226}Ra	79
^{210}Pb	3.1
^{232}Th	50
^{228}Ra	49
^{228}Th	50
^{40}K	8.6
^{137}Cs	<DL[†]

[†] DL = detection limit.

3.3.5. Ecotoxicity of Steelmaking By-product

3.3.5.1. Algal Growth Rate Test

The SS leachate and method blank for use in all toxicity tests were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. Following centrifugation, the SS leachate had a pH of 10.6, which was higher than acceptable for algal growth (acceptable pH range: 6-9). Thus, the pH of the SS leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. The pH-adjusted SS leachate was slightly higher in pH than the method blank and control water (Table 28).

Table 28. Characteristics of filtered steelmaking by-product (SS) leachate used in chronic 72-hour algal growth rate toxicity tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO (% sat.)
SS leachate	10.64	0.2	0.39	99
SS leachate, pH adj.	8.06	0.2	0.44	98
Method blank	7.65	0.2	0.31	100
Synthetic softwater	7.58	0.1	0.31	101

Algal growth was significantly higher in the method blank than the QA control; therefore, the method blank was used in all statistical calculations for SS leachate. The leachate was of low toxicity to algal growth, with a small but significant inhibition of algal growth (9%) only observed in undiluted leachate (100%) (Table 29). The IC50 value was >100%, while the LOEC and NOEC values were 100 and 33%, respectively.

Table 29. Results of steelmaking by-product (SS) chronic 72-hour algal growth rate toxicity tests.

	Growth Rate (doublings per day)	% of Control	CV (%)
Controls			
QA Control	1.75	100	12
Method blank	2.16	124	2.8
SS Leachates			
Method blank	2.16	100	2.8
0.1%	2.08	96	4.2
1.2%	2.45	113	1.6
3.7%	2.24	104	5.3
11%	2.32	107	0.7
33%	2.23	103	2.1
100%	1.96	91	2.3

At its natural pH (10.6), the SS leachate may have been more toxic to algal growth, since the pH was higher than that acceptable for algal growth. If the leachate was tested at its original pH it is estimated that dilution in synthetic softwater to a concentration of 11% leachate would be required to eliminate toxic effects due to high pH alone. In laboratory tests, 100, 33, 11, 3.7, 1.2 and 0.1% Ss leachate concentrations resulted in pH values of 10.6, 9.9, 9.0, 8.2, 8.0 and 8.0, respectively. This estimated no effect concentration is below the NOEC value obtained testing the pH-adjusted leachate sample.

3.3.5.2. Cladoceran Immobilisation Test

Following centrifugation, the SS leachate had a pH of 10.6, which was higher than acceptable for cladoceran survival (acceptable pH range: 7-9). Thus, the pH of the SS leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. The pH-adjusted SS leachate (pH 8.1) had a similar pH to the DMW control (pH 8.3), but was slightly higher in pH than the method blank (pH 7.7) and synthetic softwater control (pH 7.6).

The proportions of mobile cladocerans in the DMW control, method blank and synthetic softwater control after 48 hours were 95, 100 and 100%, respectively, all above the acceptability criteria of 90%. The pH-adjusted SS leachate was not toxic to cladocerans, with no significant immobilisation observed for any concentration of SS leachate tested (Table 30). The EC50 and LOEC values for cladoceran immobilisation in SS leachate were both >100%, and the NOEC value was 100%.

Table 30. Results of steelmaking by-product (SS) acute 48-hour cladoceran immobilisation toxicity tests.

	Mean mobile (%)	% of pooled DMW and method blank	% inhibition
Controls			
DMW Control	95		
Synthetic softwater	100		
Method blank	100		
SS Leachates			
0.1%	100	103	0
1.2%	95	97	3
3.7%	95	97	3
11%	100	103	0
33%	95	97	3
100%	100	97	3

At its natural pH (10.6), the SS leachate may have been more toxic to *Ceriodaphnia dubia*, since the pH was higher than that acceptable for cladoceran survival (pH 7-9).

3.3.5.3. Microtox® Test

Following centrifugation, the SS leachate had a pH of 10.6, which was higher than acceptable for Microtox® (acceptable pH range: 6-9). Thus, the pH of the SS leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. Because the Microtox® test used a marine bacterium, the method blank and SS leachate were also adjusted to a salinity of 20% with MOAS prior to use in toxicity tests. The pH and salinity of the pH-adjusted SS leachate with added MOAS were similar to those of the method blank (Table 31).

Table 31. Characteristics of filtered steelmaking by-product (SS) leachate used in Microtox® tests.

Sample	pH	Salinity (%)	EC (ms cm^{-1})	DO (% sat.)
SS leachate	10.64	0.2	0.39	99
SS leachate pH adj.	8.06	0.2	0.44	98
SS leachate pH adj. + MOAS	7.80	20	32	94
Method blank	7.65	0.2	0.31	100
Method blank + MOAS	7.44	20	32	90

The method blank was not toxic to *Vibrio fischeri* after 5- and 15-minute exposures. There was, however, a small but significant stimulation (approximately 5%) of bacterial light output for some concentrations tested (5-41%). The SS leachate was of low toxicity to the bacteria with significant inhibition, *ca.* 3-6%, of light output only observed in the highest concentration tested (82%). In both 5- and 15-minute exposures, the EC50 for inhibition of light output by the marine bacterium *Vibrio fischeri* in SS leachate was >82%; the LOEC was 82% and the NOEC was 41%.

3.3.5.4. Leachate Chemistry

Trace elements that displayed some enrichment (≥2 times) in the steelmaking by-product leachate when compared to the softwater control (method blank) included Al, B, Ba, Ca, Cl, Fe, Mn, P, Rb, Si, Sr, Ti, U, V and Zr (Table 32). The increase in the concentration of these elements in SS leachate relative to the method blank is likely due to the dissolution of a small amount of by-product during leachate preparation. In the SS leachate, only N was depleted relative to the method blank (Table 32).

Table 32. Chemical composition of method blank and steelmaking by-product (SS) leachates used in toxicity tests.

Analyte (mg L^{-1})	Method blank	Method Blank+MOAS	SS	SS, pH adjusted to 8	SS+MOAS
Al	<0.005	<0.005	3.2	3.4	2.5
As	<0.001	<0.01	0.001	<0.001	<0.01
B	<0.02	0.04	0.09	0.08	0.12
Ba	<0.002	<0.002	0.13	0.14	0.12
Be	<0.001	<0.001	<0.001	<0.001	<0.001
CO_3 (mg $CaCO_3$/L)	<1	<1	48	<1	<1
Ca	13.2	11.5	34.2	35	30.4
Cd	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Ce	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Cl	10	11400	12	47	11700
Co	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Cr	<0.001	<0.001	<0.001	<0.001	<0.001
Cu	<0.002	<0.002	<0.002	<0.002	<0.002
F	0.15	0.12	0.17	0.18	0.12
Fe	0.012	0.026	0.13	0.14	0.14
HCO_3 (mg $CaCO_3$/L)	104	85	<1	104	110
Hg	<0.0001	<0.001	<0.0001	<0.0001	<0.001
K	2.6	2.6	4.1	4.1	4.1
La	<0.005	<0.005	<0.005	<0.005	<0.005
Mg	12.5	10.8	12.1	13.1	10.8
Mn	<0.001	<0.001	0.017	0.018	0.016
Mo	<0.001	<0.01	<0.001	<0.001	<0.01
NH_3-N	0.01	0.02	<0.01	<0.01	0.01
NO_x-N	0.03	0.02	0.02	0.02	0.02
Total N	0.1	0.1	0.05	0.04	0.1
Na	28.7	8630	29.2	31.5	8040
Ni	<0.001	<0.01	<0.001	<0.001	<0.01
OH (mg $CaCO_3$/L)	<1	<1	17	<1	<1
Total P	<0.1	<0.1	0.2	0.2	0.2
PO_4-P	<0.01	<0.01	0.08	<0.01	<0.01
Pb	<0.0001	<0.001	<0.0001	<0.0001	0.0011
Rb	0.0001	<0.001	0.0036	0.0035	0.004
S	29	26	30	33	29
SO_4	61.2	52	87.3	63.1	74.7
Sb	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Sc	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Se	<0.001	<0.01	<0.001	<0.001	<0.01
Si	0.08	0.28	3.8	3.8	3.6
Sr	0.005	0.005	0.18	0.18	0.16
Te	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Th	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Ti	<0.002	<0.002	0.004	0.004	0.004
Tl	<0.0001	<0.001	<0.0001	<0.0001	<0.001
U	<0.0001	<0.001	0.0003	0.0004	<0.001
V	<0.005	<0.005	0.013	0.015	0.013
Y	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Zn	<0.005	<0.005	<0.005	<0.005	<0.005
Zr	<0.0001	<0.001	0.0003	0.0003	<0.001

3.4. Red Mud

Red mud (RM) is generated during the production of alumina from bauxite via the Bayer process. In aluminium production, bauxite ore is crushed then dissolved in caustic soda (sodium hydroxide, NaOH) at high pressure and temperature. The amphoteric character of aluminium oxide causes it to move into solution as soluble sodium aluminate during caustic digestion. Dissolved alumina is recovered by cooling the alkaline liquor. The fine white crystals are calcined at high temperature to produce alumina. Undissolved materials and bauxite residues are separated from the aluminium-containing liquor by settling and the insoluble mud is thickened then washed to recover the caustic soda, which is recycled for further use in the Bayer process. The insoluble by-product of the Bayer process, known as RM due to its brick-red colour, is comprised primarily of the Fe, Ti and Si portion of the bauxite ore. In Western Australia, at current production rates approximately 36,000 tonnes of by-product from alumina refining are generated annually (Jamieson et al., 2006).

The RM used in these experiments was a Darling Range bauxite residue red mud.

3.4.1. Red Mud General Characteristics

The EC of RM was high, indicating a relatively high concentration of dissolved salts in the aqueous RM extract (Table 33). In addition, RM exhibited a high (alkaline) pH of 9.7 (Table 33).

Table 33. Electrical conductivity (EC) and pH of red mud (RM).

	EC (mS cm^{-1})	**pH**
Red Mud	5.88	9.7

Based on the 50% breakthrough volume of Br, a pore volume of 53% was determined for the ground RM (Figure 7, Table 34). Porosity results based on Br breakthrough data and gravimetric analysis were in general agreement, varying between 43% and 53%.

Table 34. Red mud (RM) porosity, bulk density and saturated hydraulic conductivity.

Parameter	**RM**
Porosity by Br$^-$ breakthrough	0.53
Porosity by gravimetric measurement	0.43
Bulk Density by measuring cylinder (g cm^{-3})	1.74
Bulk Density by gravimetric measurement (g cm^{-3})	1.98

Bulk density determined for the RM varied depending on the method employed, between 1.74 and 1.98 g cm^{-1}.

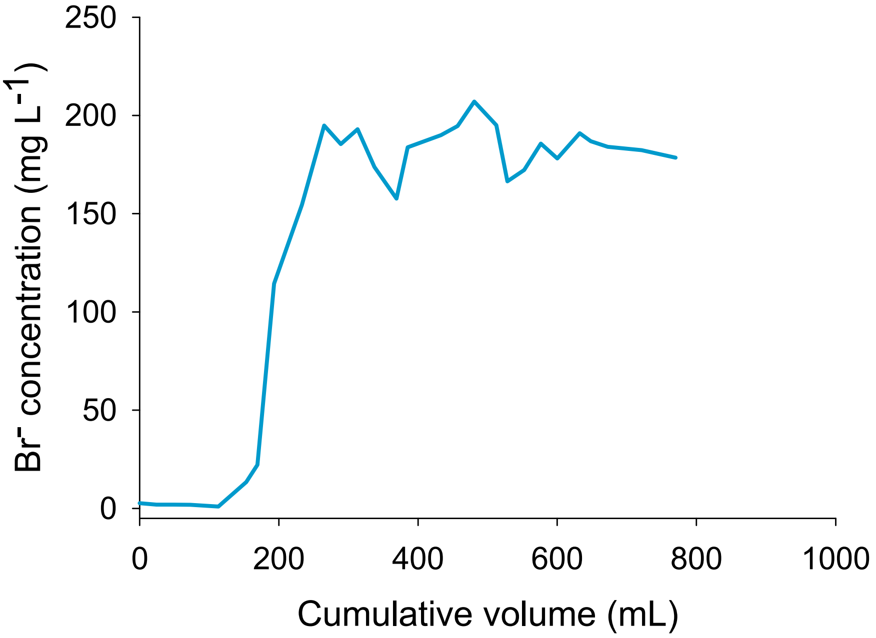

Figure 7. Bromide (as NaBr) breakthrough for a column containing red mud (RM).

3.4.2. Red Mud Mineralogy

X-ray diffraction analysis of the RM (Figure 8) showed the expected dominance by goethite (α-FeOOH) and hematite (α-Fe_2O_3) with some quartz (SiO_2), anatase (TiO_2), calcite ($CaCO_3$) and spinel ($MgAl_2O_4$) present.

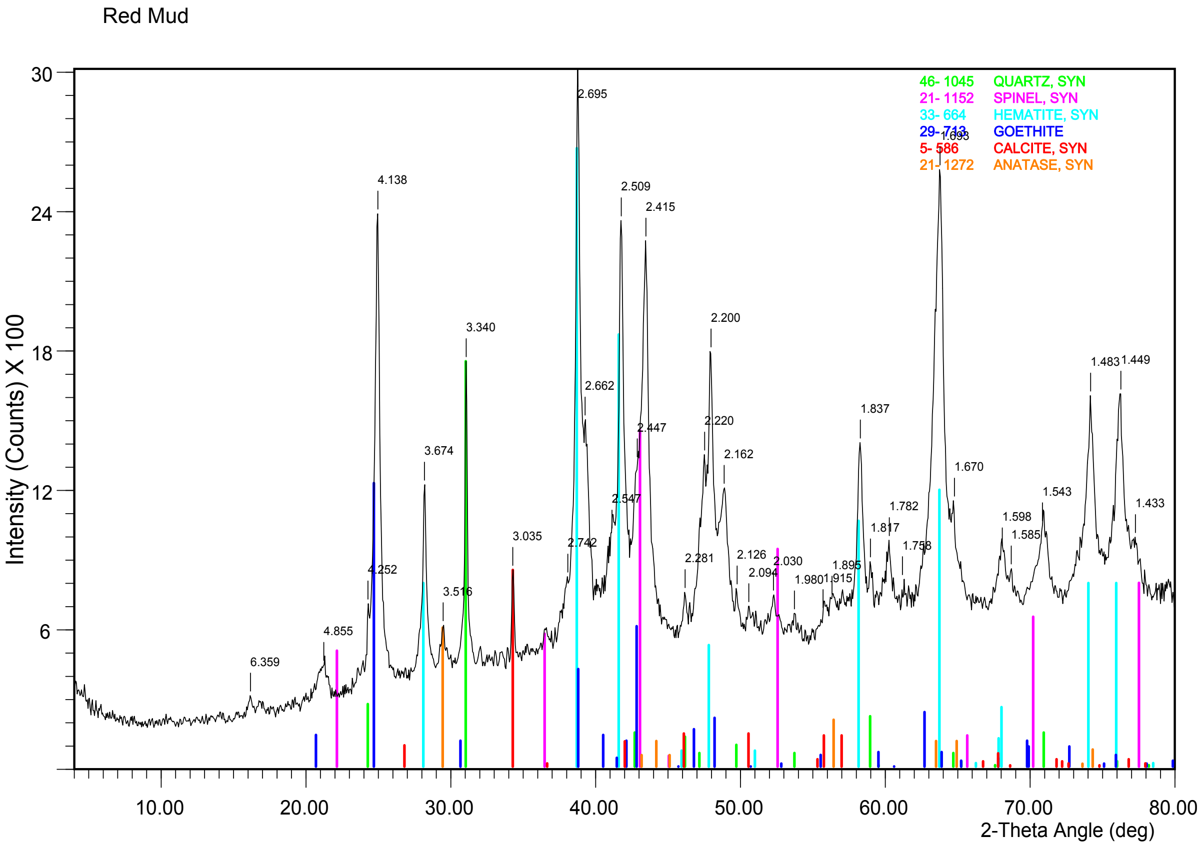

Figure 8. Powder X-ray diffraction (XRD) spectra of red mud (RM).

Quantitative XRD analysis indicated that the composition of the RM ordered phase was 62% goethite, 30% hematite, 4% quartz, 2% anatase and 2% spinel.

3.4.3. Red Mud Major and Trace Element Analysis

The red mud was analysed for most elements by XRF an “as received” basis. The XRF analysis showed that nearly 90% of the RM could be accounted for by Fe, Al Si and Ti (all expressed as oxides, Table 35).

Table 35. Fusion X-ray fluorescence (XRF) major elemental composition of red mud (RM).

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
RM	4.8	4.6	15.9	57.6	0.04	0.14	2.0	3.0	0.06	0.12	0.44	638	88.8

Nearly all trace elements displayed some enrichment (≥2 times) in the RM when compared to Bassendean Sand, including Ag, As, Ba, Bi, Br, Cd, Co, Cs, Cu, Ga, Hf, I, Mn, Nb, Pb, Sb, Se, Sn, Sr, Th, Tl, U, V, Yb, Zn and Zr (Table 36). Only La and Ni were depleted in RS relative to Bassendean Sand (Table 36).

Table 36. Pressed powder X-ray fluorescence (XRF) trace elemental composition of red mud (RM). All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
RM	17	26	38	5	17	9	58	12	496	7
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
RM	67	59	<6	8	ND[†]	71	7	205	8	20
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
RM	6	5	24	<9	8	55	4	16	21	101
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
RM	18	35	21	6	4	1112	6	11	29	519

[†] ND = not determined.

3.4.4. Red Mud U-Th Series, ^{40}K and ^{137}Cs Analysis

Table 37 gives a summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of RM. The RM exhibited moderate activities of the radioisotopes examined with highest activities from the ^{232}Th decay chain. The calculated absorbed dose rate for RM was 112 nGy h^{-1}.

Table 37. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of red mud (RM).

Radionuclide	Red mud (Bq kg^{-1})
^{238}U	64
^{230}Th	62
^{226}Ra	68
^{210}Pb	66
^{232}Th	127
^{228}Ra	136
^{228}Th	143
^{40}K	24.1
^{137}Cs	<DL[†]

[†] DL = detection limit.

3.4.5. Ecotoxicity of Red Mud

3.4.5.1. Algal Growth Rate Test

The RM leachate and method blank for all toxicity tests were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. Following centrifugation, the RM leachate had a pH of 10.7, which was higher than acceptable for algal growth (acceptable pH range: 6-9). Thus, the pH of the RM leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. The pH-adjusted RM leachate was slightly higher in pH than the method blank and control water (Table 38).

Table 38. Characteristics of filtered red mud (RM) leachate used in chronic 72-hour algal growth rate toxicity tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO (% sat.)
RM leachate	10.66	1.5	2.8	103
RM leachate, pH adj.	8.05	n.m.[†]	2.9	102
Method blank	7.50	0.2	0.32	102
Synthetic softwater	7.59	0.2	0.32	103

[†] n.m. = not measured.

The RM leachate was orange in colour, with very fine particles (0.22 µm < d < 0.45 µm) suspended in solution after filtration, based on direct observation after filtration through 0.22 µm and 0.45 µm membrane filters. These particles did not interfere with algal cell density measurements using flow cytometry; however, a colour control was prepared to determine the potential contribution of colour/turbidity to toxicity. Colour controls were prepared by placing control flasks on Petri dished filled with undiluted RM leachate.

There was no significant difference between the growth of algae in the QA controls and that in the method blank. Thus, the data were pooled for use in statistical calculations. The RM leachate was toxic to algal growth, with an IC50 of 60%. All concentrations of leachate caused significant inhibition of algal growth (Table 39). The NOEC for inhibition of algal growth in RM leachate was <0.1%. There was also a slight but significant inhibition (22% inhibition) of algal growth in the colour control, indicating that in undiluted leachate, the colour/turbidity of the sample may have made a minor contribution to the toxicity observed due to the reduced light available for algal growth. As the sample was diluted in colourless diluent water, it is unlikely that reduced light (e.g., colour) contributed to the toxicity of RM leachate to algal growth in lower concentrations (0.1 to 50%) of RM leachate.

Table 39. Results of red mud (RM) chronic 72-hour algal growth rate toxicity tests.

	Growth Rate (doublings per day)	% of Control	CV (%)
Controls			
QA Control	2.00	100	7.1
Method blank	2.00	100	6.3
Colour control	1.57	78	14
RM Leachates			
Pooled controls	2.00	100	6.0
0.1%	1.53	76	1.7
6.3%	1.43	71	6.6
13%	1.43	71	2.1
25%	1.26	63	3.5
50%	1.26	63	1.5
100%	0.00	0	0.0

At its natural pH (10.7), the RM leachate may have been more toxic to *Chlorella* sp. 12, since the pH was higher than that acceptable for algal growth

3.4.5.2. Cladoceran Immobilisation Test

The RM leachate and method blank for the 48-hour acute cladoceran immobilisation toxicity test were prepared as previously described. Following centrifugation, the RM leachate had a pH of 10.7, which was higher than acceptable for cladoceran survival (acceptable pH range: 7-9). Thus, the pH of the RM leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. The pH-adjusted RM leachate (pH 8.5) was slightly higher in pH than the method blank (pH 8.1) and DMW control (pH 8.2) (Table 40). The RM leachate was orange in colour, with very fine particles (0.22 µm < d < 0.45 µm) suspended in solution after filtration, based on observation after filtration through 0.22 µm and 0.45 µm membrane filters.

Table 40. Characteristics of filtered red mud (RM) leachate used in acute 48-hour cladoceran immobilisation toxicity tests.

Sample	pH	EC (mS cm^{-1})	DO (% sat.)
RM leachate	10.66	2.8	103
RM leachate, pH adj.	8.50	2.9	102
Method blank	8.06	0.32	101
Synthetic softwater	7.92	0.31	102
DMW control	8.18	0.29	100

There were 100% mobile cladocerans in each the DMW control, method blank and synthetic softwater control after 48 hours, well above the acceptability criteria of 90% (Table 41). The DMW control and method blank data were pooled for use in statistical calculations.

The RM leachate was toxic to cladocerans, with an EC50 of 47% and a NOEC value of 25%. The LOEC for cladoceran mobility in RM leachate was 50%. The fine particles in test solutions of RM leachate settled over the course of the 48-hour test to form a film of sediment at the base of test vials. This was particularly evident in the 50% and 100% RM leachate concentration test vials. Cladocerans are filter feeders, and it is possible that the particles interfered with both their feeding and respiration. It is also possible that elevated conductivity contributed to the toxicity observed in unfiltered leachate, as the conductivity in this test solution (2.8 mS) was above that know n to have adverse effects of cladocerans (2.0 mS).

Table 41. Results of red mud (RM) acute 48-hour cladoceran immobilisation toxicity tests.

	Mean mobile (%)	% of pooled DMW and method blank	% inhibition
Controls			
DMW Control	100		
Synthetic softwater	100		
Method blank	100		
RM Leachates			
1.0%	100	100	0
6.3%	100	100	0
13%	95	95	5
25%	90	90	10
50%	55	55	45
100%	0	0	100

At its natural pH (10.7), the RM leachate may have been more toxic to *Ceriodaphnia dubia*, since the pH was higher than that acceptable for cladoceran survival (pH 7-9).

3.4.5.3. Microtox® Test

Following centrifugation, the RM leachate had a pH of 10.7, which was higher than acceptable for Microtox® (acceptable pH range: 6-9). Thus, the pH of the RM leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. Because the Microtox® test used a marine bacterium, the method blank and RM leachate were also adjusted to a salinity of 20% with MOAS prior to use in toxicity tests. The pH and salinity of the pH-adjusted RM leachate with added MOAS were higher than those of the method blank (Table 42).

Table 42. Characteristics of filtered red mud (RM) leachate used in Microtox® tests.

Sample	pH	Salinity (%)	EC (ms cm^{-1})	DO (% sat.)
RM leachate	10.66	1.5	2.8	103
RM leachate pH adj.	8.05	n.m.[†]	2.9	102
RM leachate pH adj. + MOAS	8.32	20	33	91
Method blank	7.50	0.2	0.32	102
Method blank + MOAS	7.76	20	32	92

[†] n.m. = not measured.

The RM leachate had very fine particles (0.22 µm < d < 0.45 µm) suspended in solution after filtration, based on observation after filtration through 0.22 µm and 0.45 µm membrane filters. Colour/turbidity correction procedures were carried out for the RM leachate.

The method blank was not toxic to *Vibrio fischeri* after 5- and 15-minute exposures. The RM leachate was not toxic to bacteria, with no significant inhibition of light output observed for any concentration tested, i.e. the NOEC value for light output by *Vibrio fischeri* in RM leachate was 82%. Both the EC50 and LOEC values were >82%.

3.4.5.4. Leachate Chemistry

Trace elements that displayed some enrichment (≥2 times) in the pH 10.7 RM leachate when compared to the softwater control (method blank) included Al, As, B, Ba, CO_3, Cd, Ce, Cl, Co, Cr, F, Fe, HCO_3, Hg, Mo, N, Na, P, Rb, S, Se, Si, Sr, Ti, U, V, Zn and Zr (Table 43). The increase in the concentration of these elements in RM leachate relative to the method blank is likely due to the dissolution of a small amount of by-product during leachate preparation. In the RM pH 10.7 leachate, only Ca and Mg were depleted relative to the method blank (Table 43).

Trace elements that displayed some enrichment (≥2 times) in the pH 8 RM leachate when compared to the softwater control (method blank) included Al, As, Cd, Ce, Cl, Co, Cr, F, Fe, HCO_3, Mo, N, Na, P, Rb, S, Sc, Se, Si, Sr, Ti, U, V, Y and Zr (Table 43). In the pH 8 RM leachate, Ca, K and Mg were depleted relative to the method blank (Table 43).

Table 43. Chemical composition of method blank and red mud (RM) leachates used in toxicity tests.

Analyte (mg L^{-1})	Method blank	Method Blank+MOAS	RM	RM, pH adjusted to 8	RM+MOAS
Al	<0.005	<0.005	14	14	13
As	<0.001	<0.01	0.051	0.033	0.027
B	<0.02	<0.02	0.05	<0.02	0.04
Ba	<0.002	<0.002	0.05	0.003	<0.002
Be	<0.001	<0.001	<0.001	<0.001	<0.001
CO_3 (mg $CaCO_3$/L)	<1	<1	570	<1	24
Ca	13.9	13.3	1.9	1.9	1.2
Cd	<0.0001	<0.001	0.0005	0.0004	<0.001
Ce	<0.0005	<0.005	0.0016	0.0046	0.0052
Cl	9	11100	110	403	11600
Co	<0.0001	<0.001	0.0003	0.0003	<0.001
Cr	<0.001	<0.001	0.046	0.049	0.046
Cu	<0.002	<0.002	0.002	0.003	<0.002
F	<0.05	<0.05	17	16	13
Fe	<0.005	<0.005	0.6	0.19	0.18
HCO_3 (mg $CaCO_3$/L)	67	64	214	793	714
Hg	<0.0001	<0.001	0.0009	<0.0001	<0.001
K	2.2	2.4	1.4	1.1	1.3
La	<0.005	<0.005	<0.005	<0.005	<0.005
Mg	12	10.7	0.4	0.4	0.2
Mn	<0.001	<0.001	<0.001	<0.001	<0.001
Mo	<0.001	<0.01	0.46	0.37	0.36
NH_3-N	0.03	0.03	0.01	<0.01	0.01
NO_x-N	0.07	0.23	0.11	0.09	0.09
Total N	0.21	0.33	0.89	0.9	0.97
Na	26.5	8260	684	687	8030
Ni	<0.001	<0.01	0.001	0.001	<0.01
OH (mg $CaCO_3$/L)	<1	<1	<1	<1	<1
Total P	<0.1	<0.1	0.4	0.4	0.4
PO_4-P	<0.01	<0.01	0.38	0.03	0.03
Pb	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Rb	<0.0001	<0.001	0.0007	0.0004	<0.001
S	27	26	61	61	56
SO_4	66.7	71.5	170	174	166
Sb	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Sc	<0.0005	<0.005	0.0007	0.001	<0.005
Se	<0.001	<0.01	0.35	0.36	0.27
Si	0.06	0.24	0.66	0.63	0.76
Sr	0.005	0.005	0.015	0.016	0.015
Te	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Th	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Ti	<0.002	<0.002	0.07	0.2	0.22
Tl	<0.0001	<0.001	<0.0001	<0.0001	<0.001
U	<0.0001	<0.001	0.52	0.52	0.44
V	<0.005	<0.005	0.56	0.78	0.73
Y	<0.0005	<0.005	0.0007	0.001	<0.005
Zn	<0.005	<0.005	0.059	<0.005	<0.005
Zr	<0.0001	<0.001	0.035	0.039	0.04

3.5. Red Sand

Worldwide, red sands (RS) generally comprise *ca.* 20% of the total bauxite residues generated during alumina production; however, in Western Australia approximately half of the by-product resulting from alumina production has a mean particle diameter >90 µm and can be classified as RS. The greater proportion of RS produced by WA alumina refineries is due to the high quartz content of bauxite from the Darling Range. Western Australian alumina refineries generate approximately 18,000 tonnes of RS each year (Jamieson et al., 2006). Red sand for use in these experiments was prepared by wet sieving a Darling Range bauxite residue red mud through a 355 µm sieve.

3.5.1. Red Sand General Characteristics

The RS exhibited a mid-range EC of approximately 1 mS cm^{-1} (Table 44). The measured pH of RS in 1:5 0.01 M $CaCl_2$ solution was slightly acidic at 6.3 (Table 44).

Table 44. Electrical conductivity (EC) and pH of red sand (RS).

	EC (mS cm^{-1})	**pH**
Red Sand	1.08	6.3

Based on the 50 % breakthrough volume, RS porosity was determined to be 46% (Figure 9). Porosity results based on bromide breakthrough data and gravimetric analysis are given in Table 45. The results for both methods of porosity determination were in good agreement, providing greater confidence in the porosity values.

Table 45. Red sand (RS) porosity, bulk density and saturated hydraulic conductivity.

Parameter	**RS**
Porosity by gravimetric measure	0.48
Porosity by Br^- breakthrough	0.46
Bulk Density by measuring cylinder (g cm^3)	1.66
Bulk Density by gravimetric measurement (g cm^3)	1.70
Saturated hydraulic conductivity by head pressure differential (cm min^{-1})	4.00

Bulk density of the RS was consistent with sands on the Swan Coastal Plain of Perth, in the range from 1.40 to 1.80 g cm^{-1} (Table 45) (Pollock et al., 2002; Rümmler et al., 2005).

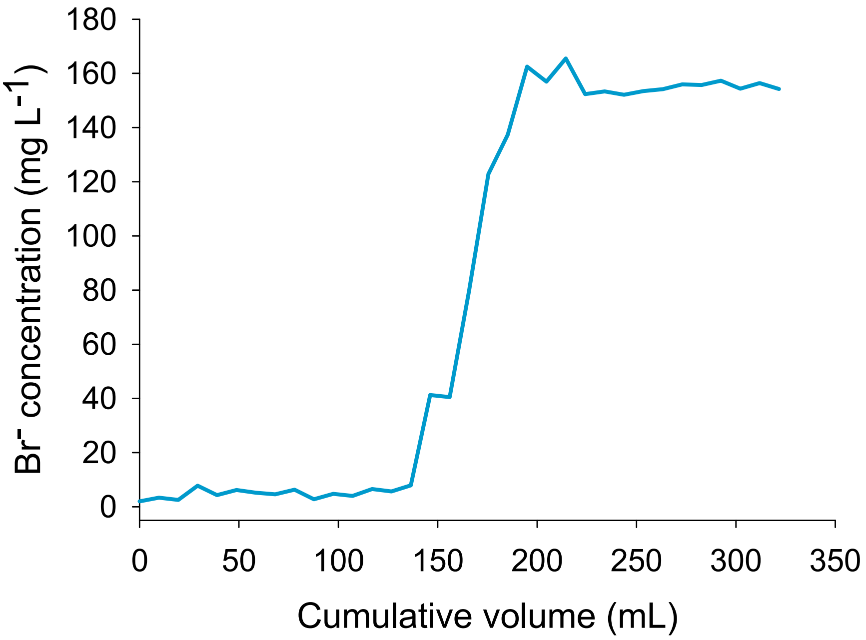

Figure 9. Bromide breakthrough (as NaBr) for a column containing red sand (RS).

The sieve analysis (Table 46) showed that the majority of the RS had a particle size in the range 250 to 1000 µm, which explains its high hydraulic conductivity.

Table 46. Red sand (RS) particle size distribution by sieve analysis.

Size fraction (µm)	RS composition (%)
> 1000	0.22
500 - 1000	3.51
355 -500	60.26
250 - 355	28.98
180 - 250	6.14
125 - 180	0.03
90 - 125	0.34
63 -90	0.14
< 63	0.39

3.5.2. Red Sand Mineralogy

X-ray diffraction analysis of RS indicated the expected dominance by hematite (α-Fe_2O_3), goethite (α-FeOOH) and quartz (SiO_2) with some anatase (TiO_2) and gibbsite [$Al(OH)_3$] present (Figure 10). Quantitative XRD analysis was not performed on RS.

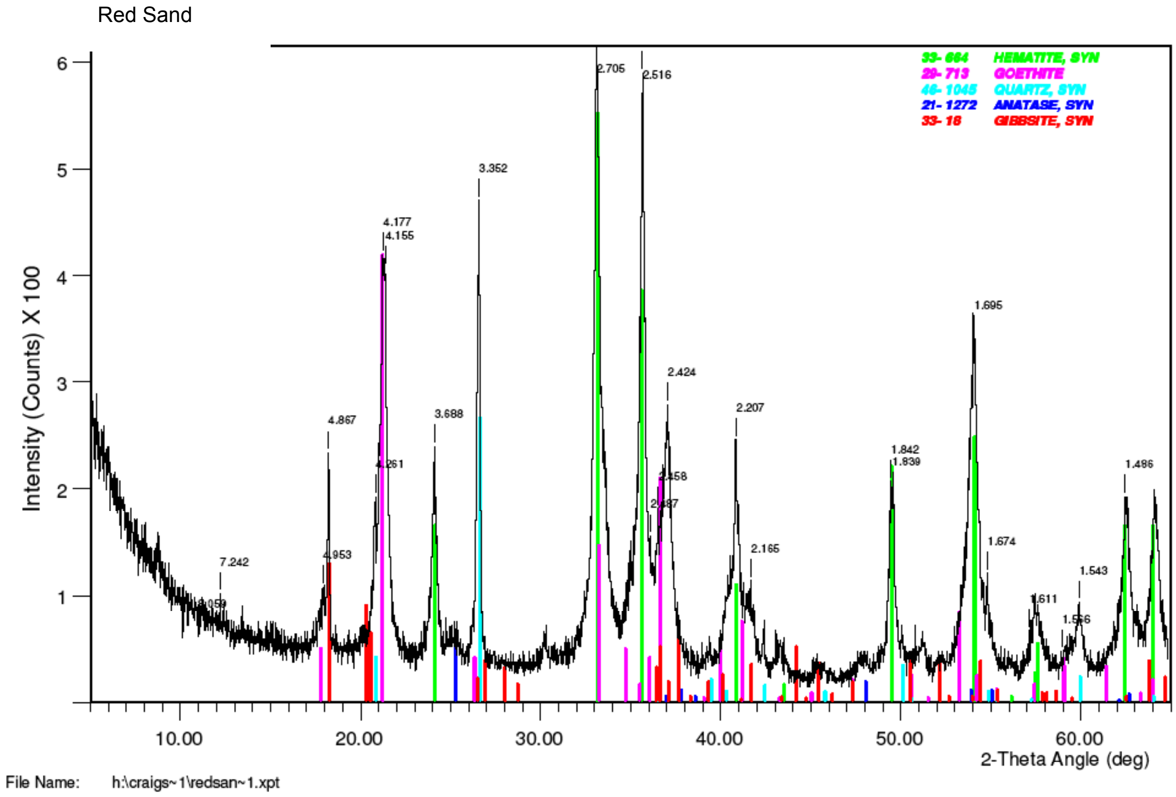

Figure 10. Powder X-ray diffraction (XRD) spectra of red sand (RS).

3.5.3. Red Sand Major and Trace Element Analysis

The red sand was analysed for most elements by XRF an “as received” basis. For those elements that the XRF method could not readily detect due to low abundance (Ca, Mg, Ni and Zn) ICP-AES was used. In the later case, 0.1 gram of each of sample was digested in a concentrated HF/HCl/HNO_3 mixture, made up to 100 mL volume and analysed on a Varian Vista ICP-AES for content. Fusion XRF indicated that >95% of the RS is accounted for by Fe, Al and Ti (Table 47).

Table 47. Fusion X-ray fluorescence (XRF) major elemental composition of red sand (RS).

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
RS	2.6	1.9	20.7	73.0	0.06	0.01	0.3	0.9	0	0.07	0.07	0	99.6

Of the trace elements determined for RS, none displayed enrichment in the RS when compared to Bassendean Sand (Table 48). Elements in the RS depleted relative to Bassendean Sand included Cr, Cu, Ni, V, Zn and Zr (Table 48).

Table 48. Pressed powder X-ray fluorescence (XRF) trace elemental composition of red sand (RS). All elements are expressed on a percent basis (%).

	Ag	As	Ba	Bi	Br	Cd	Ce	Co	Cr	Cs
RS	ND†	ND	ND	ND	ND	ND	ND	<0.01	0.07	ND
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
RS	0.02	ND	ND	ND	ND	ND	ND	0.02	ND	ND
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
RS	ND	<0.01	ND	ND	ND	ND	ND	ND	ND	ND
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
RS	ND	ND	ND	ND	ND	0.09	ND	ND	<0.01	0.04

†ND = not determined.

3.5.4. Red Sand U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of RS is given in Table 49. The RS had moderate to high mean activities of ^{232}Th, ^{228}Ra, and ^{228}Th which were derived from the ^{232}Th decay chain. The calculated absorbed dose rate (D) for RS was 79 nGy h^{-1}, lower than the D of 112 calculated for RM.

Table 49. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of red sand (RS).

Radionuclide	Red sand (Bq kg^{-1})
^{238}U	35.0
^{230}Th	45.5
^{226}Ra	41.7
^{210}Pb	42.4
^{232}Th	96
^{228}Ra	104
^{228}Th	104
^{40}K	8.1
^{137}Cs	<DL†

†DL = detection limit.

3.5.5. Ecotoxicity of Red Sand

3.5.5.1. Algal Growth Rate Test

The RS and method blank leachates for all toxicity tests were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. Following centrifugation, the RS leachate had a pH of 10.2, which was higher than acceptable for algal growth (acceptable pH range: 6-9). Thus, the pH of the RS leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. The pH-adjusted RS leachate was slightly higher in pH than the method blank and control water (Table 50).

Table 50. Characteristics of filtered red sand (RS) leachate used in chronic 72-hour algal growth rate toxicity tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO (% sat.)
RS leachate	10.24	0.3	0.67	104
RS leachate, pH adj.	8.06	n.m.[†]	0.67	103
Method blank	7.50	0.2	0.32	102
Synthetic softwater	7.59	0.2	0.32	103

[†] n.m. = not measured.

There was no significant difference between the growth of algae in the QA controls and that in the method blank. Thus, the data were pooled for use in statistical calculations. The RS leachate was not toxic to the alga, with no significant inhibition of algal growth observed for any concentration of leachate tested (Table 51). At lower concentrations of RS leachate, (6.3 and 13%) there was also a slight but significant stimulation (26-27%) of algal growth.

Table 51. Results of red sand (RS) chronic 72-hour algal growth rate toxicity tests.

	Growth Rate (doublings per day)	% of Control	CV (%)
Controls			
QA Control	2.00	100	7.1
Method blank	2.00	100	6.3
Colour control	1.57	78	14
RS Leachates			
Pooled controls	2.00	100	6.0
6.3%	2.52	126	2.9
13%	2.54	127	0.8
25%	2.04	102	5.3
50%	2.02	101	2.4
100%	1.93	97	6.7

At its natural pH (10.2), the RS leachate may have been more toxic to *Chlorella* sp. 12, since the pH was higher than that acceptable for algal growth

3.5.5.2. Cladoceran Immobilisation Test

The RS leachate for the 48-hour acute cladoceran immobilisation toxicity test was prepared as previously described. Following centrifugation, the RS leachate had a pH of 10.2, which was higher than acceptable for cladoceran survival (acceptable pH range: 7-9). Thus, the pH of the RS leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. The pH-adjusted RS leachate (pH 8.5) was slightly higher in pH than the method blank (pH 8.1) and DMW control (pH 8.2) (Table 52).

Table 52. Characteristics of filtered red sand (RS) leachate used in acute 48-hour cladoceran immobilisation toxicity tests.

Sample	pH	EC (mS cm^{-1})	DO (% sat.)
RS leachate	10.24	0.67	104
RS leachate, pH adj.	8.50	0.72	103
Method blank	8.06	0.32	101
Synthetic softwater	7.92	0.31	102
DMW control	8.18	0.29	100

There were 100% mobile cladocerans in each the DMW control, method blank and synthetic softwater control after 48 hours, well above the acceptability criteria of 90% (Table 53). The DMW control and method blank data were pooled for use in statistical calculations.

The RS leachate was not toxic to cladocerans, with no significant immobilisation observed for any concentration tested, i.e. the NOEC value for cladoceran mobility in RS leachate was 100% (Table 53). Both the EC50 and LOEC were >100%.

Table 53. Results of red sand (RS) acute 48-hour cladoceran immobilisation toxicity tests.

	Mean mobile (%)	% of pooled DMW and method blank	% inhibition
Controls			
DMW Control	100		
Synthetic softwater	100		
Method blank	100		
RS Leachates			
1.0%	100	100	0
6.3%	100	100	0
13%	80	80	20
25%	95	95	5
50%	90	90	10
100%	80	80	20

At its natural pH (10.2), the RS leachate may have been more toxic to *Ceriodaphnia dubia*, since the pH was higher than that acceptable for cladoceran survival (pH 7-9).

3.5.5.3. Microtox® Test

Following centrifugation, the RS leachate had a pH of 10.2, which was higher than acceptable for Microtox® (acceptable pH range: 6-9). Thus, the pH of the RS leachate was adjusted to 8.0 via the dropwise addition of 0.1, 1.0 or 3.0 M HCl prior to use in the toxicity test. Because the Microtox® test used a marine bacterium, the method blank and RS leachate were also adjusted to a salinity of 20% with MOAS prior to use in toxicity tests. The pH and salinity of the pH-adjusted RS leachate with added MOAS were higher than those of the method blank (Table 54).

Table 54. Characteristics of filtered red sand (RS) leachate used in Microtox® tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO (% sat.)
RS leachate	10.24	0.3	0.67	104
RS leachate pH adj.	8.06	n.m.†	0.67	103
RS leachate pH adj. + MOAS	8.04	21	33	98
Method blank	7.50	0.2	0.32	102
Method blank + MOAS	7.76	20	32	92

†n.m. = not measured.

The method blank was not toxic to *Vibrio fischeri* after 5- and 15-minute exposures. The RS leachate was of low toxicity to the bacteria, with significant inhibition (21-29% inhibition) of light output only observed in the highest concentration tested (82%). The 5- and 15-minute LOEC for light output by *Vibrio fischeri* in RS leachate was 82%, while the NOEC was 41%. The EC50 was >82%.

3.5.5.4. Leachate Chemistry

Trace elements that displayed some enrichment (≥2 times) in the pH 10.2 RS leachate when compared to the softwater control (method blank) included Al, CO_3, Cr, F, Fe, Na, Rb, Se, Si, Ti, U and V (Table 55). The increase in the concentration of these elements in RS leachate relative to the method blank is likely due to the dissolution of a small amount of by-product during leachate preparation. In the RS pH 10.2 leachate, Ca, Mg and Sr were depleted relative to the method blank (Table 55).

Trace elements that displayed some enrichment (≥2 times) in the pH 8 RS leachate when compared to the softwater control (method blank) included Al, B, Cl, Cr, HCO_3, F, Fe, Na, Rb, Se, Si, Ti, U, V and Zr (Table 55). In the pH 8 RS leachate, Ca, Mg and Sr were depleted relative to the method blank (Table 55).

Table 55. Chemical composition of method blank and red sand (RS) leachates used in toxicity tests.

Analyte (mg L^{-1})	Method blank	Method Blank+MOAS	RS	RS, pH adjusted to 8	RS+MOAS
Al	<0.005	<0.005	1.9	1.9	1.7
As	<0.001	<0.01	<0.001	<0.001	<0.01
B	<0.02	<0.02	<0.02	0.27	0.32
Ba	<0.002	<0.002	<0.002	<0.002	<0.002
Be	<0.001	<0.001	<0.001	<0.001	<0.001
CO$_3$ (mg CaCO$_3$/L)	<1	<1	90	<1	<1
Ca	13.9	13.3	1.7	1.7	1.7
Cd	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Ce	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Cl	9	11100	9	80	12000
Co	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Cr	<0.001	<0.001	0.003	0.003	0.003
Cu	<0.002	<0.002	<0.002	<0.002	<0.002
F	<0.05	<0.05	0.26	0.31	0.15
Fe	<0.005	<0.005	0.037	0.04	0.038
HCO$_3$ (mg CaCO$_3$/L)	67	64	92	183	366
Hg	<0.0001	<0.001	<0.0001	<0.0001	<0.001
K	2.2	2.4	1.3	1.3	1.4
La	<0.005	<0.005	<0.005	<0.005	<0.005
Mg	12	10.7	0.2	0.2	0.3
Mn	<0.001	<0.001	<0.001	<0.001	<0.001
Mo	<0.001	<0.01	0.001	0.001	<0.001
NH$_3$-N	0.03	0.03	0.01	<0.01	0.03
NO$_x$-N	0.07	0.23	0.02	0.17	0.19
Total N	0.21	0.33	0.14	0.25	0.24
Na	26.5	8260	134	151	8590
Ni	<0.001	<0.01	<0.001	<0.001	<0.01
OH (mg CaCO$_3$/L)	<1	<1	<1	<1	<1
Total P	<0.1	<0.1	<0.1	<0.1	<0.1
PO$_4$-P	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Rb	<0.0001	<0.001	0.0005	0.0005	<0.001
S	27	26	28	27	27
SO$_4$	66.7	71.5	57	78.5	70
Sb	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Sc	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Se	<0.001	<0.01	0.007	0.007	<0.01
Si	0.06	0.24	0.12	3.4	3.3
Sr	0.005	0.005	<0.002	<0.002	<0.002
Te	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Th	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Ti	<0.002	<0.002	0.008	0.007	0.007
Tl	<0.0001	<0.001	<0.0001	<0.0001	<0.001
U	<0.0001	<0.001	0.0006	0.0004	0.0069
V	<0.005	<0.005	0.009	0.008	0.016
Y	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Zn	<0.005	<0.005	<0.005	<0.005	<0.005
Zr	<0.0001	<0.001	<0.0001	0.0012	0.0022

3.6. Reduced Red Sand

Reduced red sand (RRS) was generated by mixing red sand with charcoal and roasting the mixture at 1050ºC within a rotary pot-holder. Un-reacted charcoal was then sieved out and the resultant metallic or zero-valent iron (ZVI) content determined using a Satmagan device to determine ZVI on the basis of magnetic saturation.

On the original assumption that the RS used to produce RRS was 60% by weight Fe oxide, (i.e., 600 g or 3.76 moles Fe_2O_3 per 1000 g sand), a 3:1 molar excess of charcoal to Fe oxide was added. Assuming that 100% of the C becomes CO_2 the nominal reaction is:

$$2Fe_2O_3 + 3C \rightarrow 4Fe + 3CO_2$$

In all, three reduction tests were carried out: one of 2 hours and two of 3 hours. Actual XRF of the RS indicated that the Fe oxide content was lower than assumed but the C was still in substantial excess.

The Satmagan was calibrated with known samples, the roasted samples were sieved, weighed and an extrapolation obtained to estimate the ZVI content for the RRS samples which varied from 46 to 53% w/w. Note that the calibration is dependent on no magnetic oxides being present. Likely accuracy, without correction for non-metallic magnetic materials would be approximately ±2-3%, *e.g.* unreacted RS was found to contain 2.4% Fe which would relate to the magnetic Fe oxide phases rather than to metallic Fe.

3.6.1. Reduced Red Sand General Characteristics

The RRS exhibited a relatively low EC and circumneutral pH (Table 56).

Table 56. Electrical conductivity (EC) and pH of reduced red sand (RRS).

	EC (µS cm^{-1})	pH
Reduced Red Sand	109.5	7.1

Based on the 50 % breakthrough volume, RRS porosity was determined to be 51% (Figure 11). Porosity results based on bromide breakthrough data and gravimetric analysis are given in Table 57. The results for both methods were in good agreement, providing greater confidence in the porosity values.

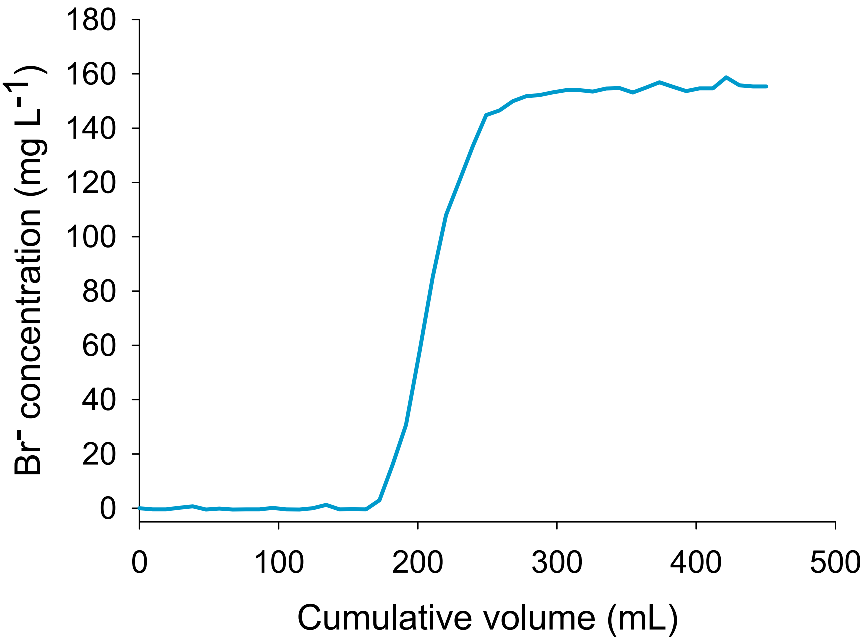

Figure 11. Bromide (as NaBr) breakthrough for a column containing reduced red sand (RRS).

The measured bulk density of the RRS was slightly higher than sands on the Swan Coastal Plain of Perth (1.40 - 1.80 g cm^{-1}) (Table 57).

Table 57. Reduced red sand (RRS) porosity, bulk density and saturated hydraulic conductivity.

Parameter	RRS
Porosity by gravimetric measure	0.50
Porosity by Br- breakthrough	0.51
Bulk Density by measuring cylinder (g cm^3)	1.89
Bulk Density by gravimetric measurement (g cm^3)	1.91
Saturated hydraulic conductivity by head pressure differential (cm min^{-1})	1.28

The sieve analysis (Table 58) showed that the majority of RRS had a particle size in the range 250 to 1000 µm.

Table 58. Reduced red sand (RRS) particle size distribution by sieve analysis.

Size fraction (μm)	RRS composition (%)
> 1000	0.00
500 - 1000	34.97
355 -500	44.86
250 - 355	18.44
180 - 250	1.01
125 - 180	0.22
90 - 125	0.12
63 -90	0.08
< 63	0.30

3.6.2. Reduced Red Sand Mineralogy

The dramatic change in the reduction of the RS to RRS is evident in the powder XRD in Figure 12. As expected, the RRS was dominated by metallic Fe. Ferrian [$Mg(Al,Fe)_2O_4$] was unexpected due to the low concentration of Mg from the XRF, both before and after reduction. The presence of ferrian in the XRD pattern of RRS may be indicative of contamination during the reduction process. The maganochromite or $(Mn,Fe)(Cr,V)_2O_4$ is however plausible due to the Mn, Cr and V levels. Similarly, the formation of hercynite ($FeAl_2O_4$) is plausible due to large quantities of Fe and Al in the solid phase.

Quantitative XRD analysis was not performed on RRS.

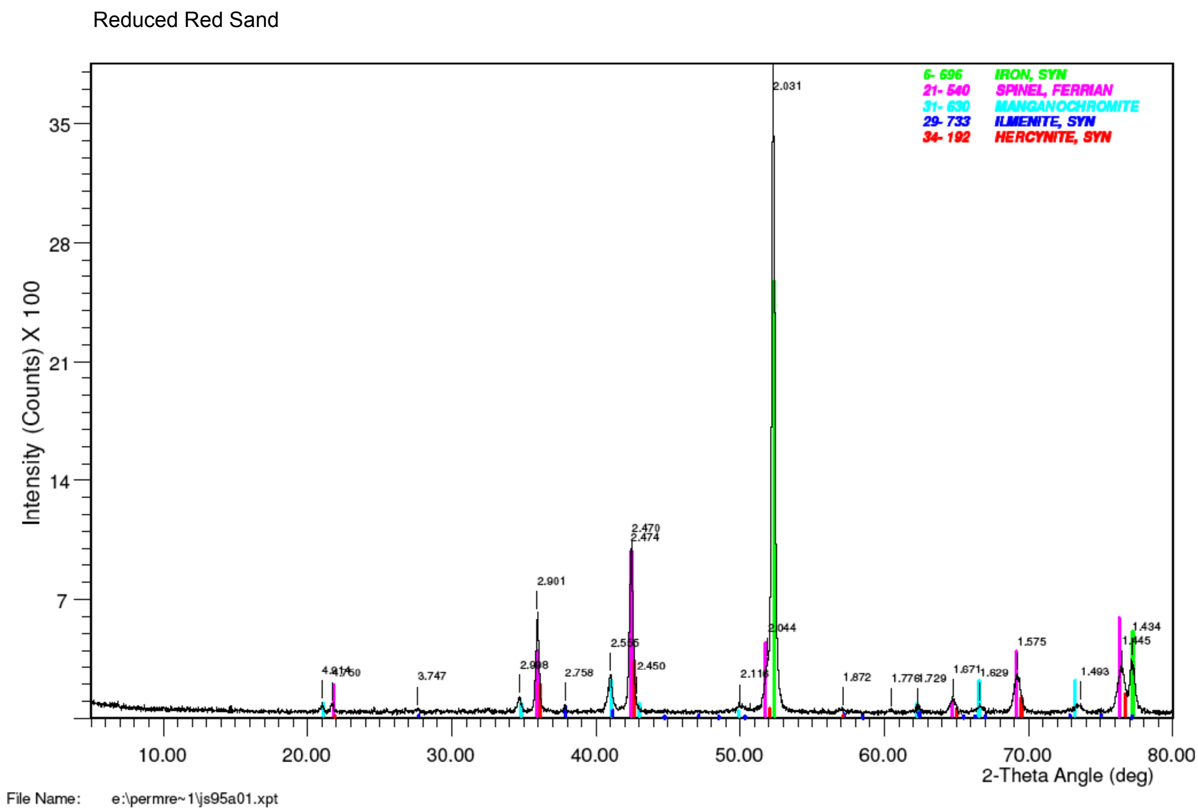

Figure 12. Powder X-ray diffraction (XRD) spectra of reduced red sand (RRS).

3.6.3. Reduced Red Sand Major and Trace Element Analysis

The RRS was analysed for most elements by XRF an “as received” basis. For those elements that the XRF method could not readily detect due to low abundance (Ca, Mg, Ni and Zn) ICP-AES was used. In the later case, 0.1 gram of each of sample was digested in a concentrated HF/HCl/HNO_3 mixture, made up to 100 mL volume and analysed on a Varian Vista ICP-AES for content. Fusion XRF indicated that nearly 90% of the RRS can be accounted for by Fe_2O_3 (Table 59).

Table 59. Fusion X-ray fluorescence (XRF) major elemental composition of reduced red sand (RRS).

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
RRS	2.3	4.1	21.0	89.5	0.05	<0.01	0.5	<0.01	0.02	0.1	0.2	<50	117.8

Of the trace elements determined for RRS, none displayed enrichment in the RRS when compared to Bassendean Sand (Table 60). Elements in the RRS depleted relative to Bassendean Sand included Cd, Cr, Cu, Ga, Mo, Ni, Pb, Sn, Sr, V, Zn and Zr (Table 60).

Table 60. Pressed powder X-ray fluorescence (XRF) trace elemental composition of reduced red sand (RRS). All elements are expressed on a percent basis (%).

	Ag	As	Ba	Bi	Br	Cd	Ce	Co	Cr	Cs
RRS	ND[†]	<DL[‡]	<DL	ND	ND	0.006	ND	<DL	0.127	ND
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
RRS	0.014	0.009	ND	ND	ND	ND	ND	0.037	0.003	ND
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
RRS	ND	0.036	0.018	ND	ND	ND	ND	ND	0.032	0.002
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**W**	**Y**	**Zn**	**Zr**
RRS	ND	ND	ND	ND	ND	0.179	<DL	ND	0.004	0.05

[†] ND = not determined.
[‡] DL = detection limit.

3.6.4. Reduced Red Sand U-Th series, ^{40}K and ^{137}Cs Analysis

A summary of U-Th series, ^{40}K and ^{137}Cs isotopic composition of RRS is given in Table 61. The RRS had moderate to high mean activities of ^{232}Th, ^{228}Ra and ^{228}Th which were derived from the ^{232}Th decay chain. The calculated absorbed dose rate (D) for RRS was 120 nGy h^{-1}, greater than the absorbed dose rates determined for both RS and RM.

Table 61. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of reduced red sand (RRS).

Radionuclide	RRS (Bq kg^{-1})
^{238}U	64
^{230}Th	63
^{226}Ra	62
^{210}Pb	19.3
^{232}Th	139
^{228}Ra	145
^{228}Th	152
^{40}K	13.1
^{137}Cs	<DL[†]

[†] DL = detection limit.

3.7. Laterite

Across the Yilgarn Craton of WA, laterite is present as a hard weathered crust (duricrust) or pisolitic gravel. Laterite is formed in situ by chemical weathering processes and usually enriched in iron and aluminium oxides. Darling Range laterites are generally comprised of the minerals gibbsite, goethite, quartz, hematite, kaolin and muscovite (Anand and Gilkes, 1987). Laterite has been investigated for its use as substrate material for the adsorption of phosphorus and heavy metals from wastewater (Wood and McAtamney, 1996).

3.7.1. Laterite General Characteristics

The laterite exhibited a low EC and slightly acidic pH (Table 62). The bulk density of laterite, as determined by measuring cylinder, was 1.69 g cm^{-3} (Table 62).

Table 62. Electrical conductivity (EC), pH and bulk density (ρ_B) of laterite.

	EC (µS cm^{-1})	pH	ρ_B (g cm^{-3})
Laterite	33.8	6.4	1.69

3.7.2. Laterite Mineralogy

X-ray diffraction analysis of laterite showed the presence of substantial hematite (α-Fe_2O_3), gibbsite [$Al(OH)_3$] and quartz (SiO_2), with minor goethite (α-FeOOH), kaolinite [$Al_2Si_2O_5(OH)_4$], maghemite (γ-Fe_2O_3) and anatase (TiO_2) (Figure 13).

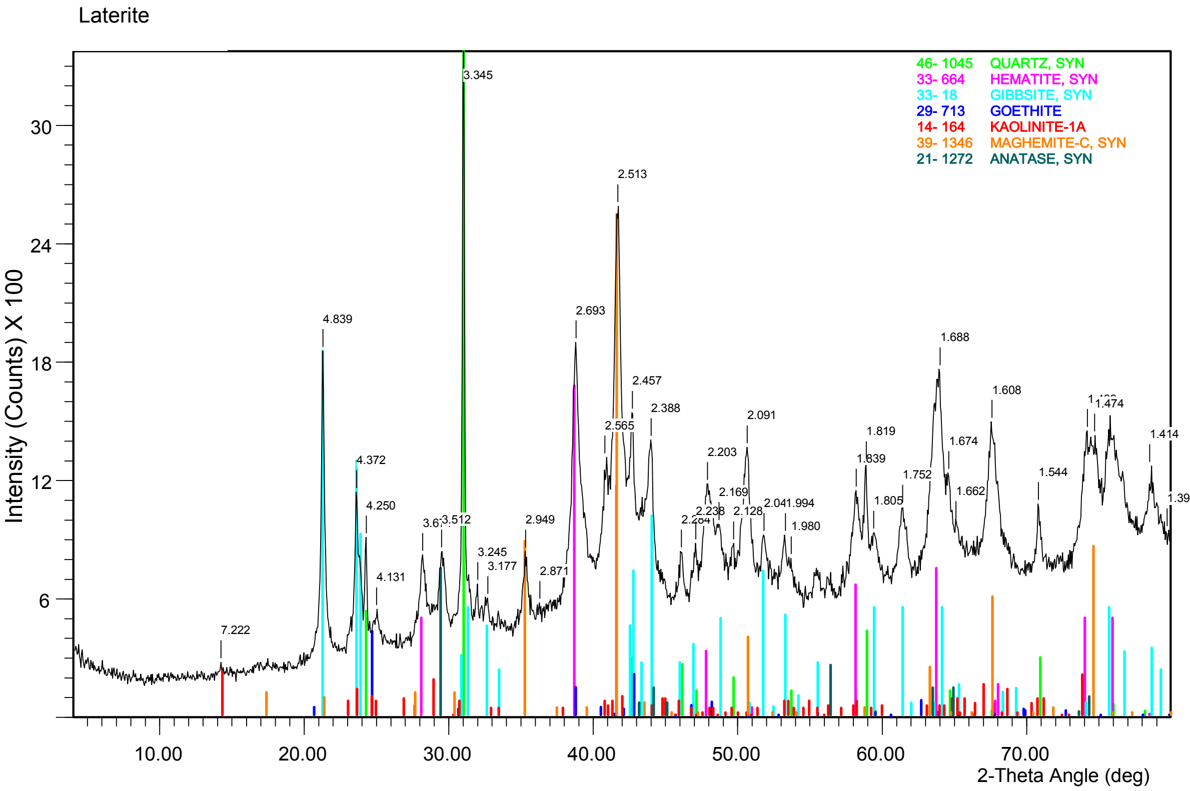

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Figure 13. Powder X-ray diffraction (XRD) spectra of laterite.

Quantitative XRD of laterite indicated that the laterite ordered phase was comprised of 9% quartz, 23% hematite, 35% gibbsite, 6% goethite, 12% kaolin, 12% maghemite and 4% anatase.

3.7.3. Laterite Major and Trace Element Analysis

Fusion XRF indicated that nearly 90% of the laterite could be accounted for by Al_2O_3, Fe_2O_3, SiO_2 and TiO_2 (Table 63).

Table 63. Fusion X-ray fluorescence (XRF) major elemental composition of laterite.

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
Laterite	6.8	2.9	42.7	36.2	0.004	0.03	0.03	<0.006	0.02	0.05	0.05	181	88.8

Trace elements that displayed some enrichment (≥2 times) in the laterite when compared to Bassendean Sand included As, Br, Co, Ga, I, Nb, Pb, Th, Tl, U, V, Y and Zr (Table 64). No elements were depleted in the laterite relative to Bassendean Sand reference material (Table 64).

Table 64. Pressed powder X-ray fluorescence (XRF) trace elemental composition of laterite. All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
Laterite	<8	28	<32	<8	5	<8	47	16	513	<17
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
Laterite	5	70	<4	<22	<35	19	<30	63	8	32
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
Laterite	<22	30	29	<6	<18	22	<4	<23	<7	6
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
Laterite	<19	<16	47	9	7	577	12	<29	<7	575

3.7.4. Laterite U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of laterite is given in Table 65. The laterite had relatively high mean activities of ^{232}Th, ^{228}Ra, and ^{228Th}, mostly derived from the ^{232}Th decay chain.

The calculated absorbed dose rate (D) for laterite was 133 nGy h^{-1}, similar to D values for Darling Scarp soils (35 to 378 nGy h^{-1}, average 195 nGy h^{-1}) (Toussaint, 2005).

Table 65. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of laterite.

Radionuclide	Laterite (Bq kg^{-1})
^{238}U	51
^{230}Th	64
^{226}Ra	78
^{210}Pb	72
^{232}Th	167
^{228}Ra	190
^{228}Th	201
^{40}K	18.8
^{137}Cs	<DL[†]

[†] DL = detection limit.

3.8. Calcined Magnesia

The ongoing development of a large-scale magnesia industry in Australia will facilitate distinct advantages in both cost and supply of calcined magnesia (MgO). Magnesite ($MgCO_3$) is formed via the replacement of Ca by Mg in calcareous rocks such as limestone ($CaCO_3$) or dolomite ($CaMgCO_3$), by alteration of olivine or serpentine by waters containing CO_2, or through precipitation from Mg-rich waters upon reaction with sodium carbonate (Na_2CO_3). It is commonly associated with serpentinite rock, either as a secondary mineral or a nearby sedimentary deposit. When magnesite is heated during magnesia production, magnesite is converted to MgO. Both raw magnesite and calcined magnesia are used in fertilisers, as well as a number of other products.

The calcined magnesia (CM) used in these experiments is principally composed of MgO; however, CM may also contain some CaO depending on the source material.

3.8.1. Calcined Magnesia General Characteristics

The CM exhibited a mid-range EC of approximately 1.7 mS cm^{-1} (Table 66). The measured pH of CM in 1:5 0.01 M $CaCl_2$ solution was highly alkaline, at 10.2 (Table 66). The bulk density of CM, as determined by measuring cylinder, was 0.90 g cm^{-3}.

Table 66. Electrical conductivity (EC) and pH of calcined magnesia (CM).

	EC (mS cm^{-1})	pH	ρ_B (g cm^{-3})
Calcined magnesia	1.66	10.2	0.90

3.8.2. Calcined Magnesia Mineralogy

X-ray diffraction analysis of CM showed the presence of substantial periclase (MgO) and brucite [$Mg(OH)_2$], with minor calcite ($CaCO_3$) and quartz (SiO_2) (Figure 14).

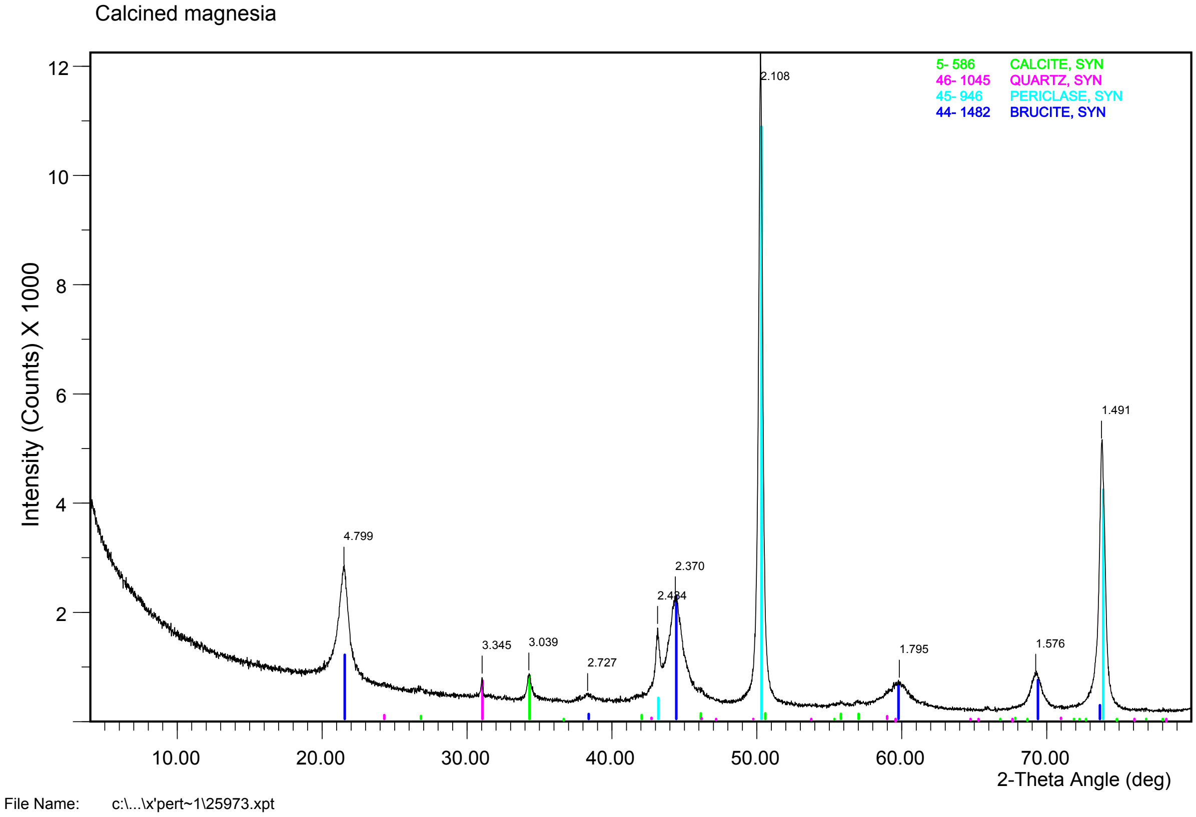

Figure 14. Powder X-ray diffraction (XRD) spectra of calcined magnesia (CM).

Quantitative XRD analysis of calcined magnesia indicated that the composition was 97% periclase (MgO), and approximately 3% portlandite [$Ca(OH)_2$].

3.8.3. Calcined Magnesia Major and Trace Element Analysis

The calcined magnesia re-crystallised upon fusion, so was mixed 50/50 with quartz before fusing. Hence, SiO_2 is not reported in major elemental XRF analysis. Nearly the entire composition of CM can be accounted for by MgO, with minor amounts of CaO (Table 67).

Table 67. Fusion X-ray fluorescence (XRF) major elemental composition of calcined magnesia (CM).

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)
CM	-	0	0.01	0.06	0.13	90.3	3.2	0	0	0.01	0	0

Trace elements that displayed some enrichment (≥2 times) in the CM when compared to Bassendean Sand included As, Co, Cu, I, Ni, Sr, Tl and Yb (Table 68). Several elements were depleted in the CM relative to Bassendean Sand, including Br, Ce, Cr, La, Mo, Nb, Th, V and Zr (Table 68).

Table 68. Pressed powder X-ray fluorescence (XRF) trace elemental composition of calcined magnesia (CM). All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
CM	<2	2	17	<2	<1	<2	<12	15	8	<7
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
CM	15	<1	<1	<6	<9	5	<12	1038	<1	1
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
CM	<7	159	<2	2	<5	5	<1	<8	<2	56
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
CM	<5	<5	3	6	1	4	8	15	2	<1

Detection limits using NAA are generally lower than those for XRF, as can be seen by comparison of Tables 68 and 69. Trace element values obtained for the CM using NAA were generally in good agreement with XRF results with few exceptions (Table 69). The As, Sc, Sr and Th values determined by NAA were substantially less than those determined using pressed powder XRF. In contrast, the value obtained for Ba using NAA was more than three times the concentration determined by XRF analysis.

Table 69. Elemental composition of calcined magnesia (CM) as determined by neutron activation analysis (NAA).

Element	Units	Calcined magnesia
Antimony, Sb	mg kg^{-1}	<1
Arsenic, As	mg kg^{-1}	<0.5
Barium, Ba	mg kg^{-1}	60
Bromine, Br	mg kg^{-1}	<0.5
Calcium, Ca	% w/w	3
Cerium, Ce	mg kg^{-1}	7
Caesium, Cs	mg kg^{-1}	<1
Chromium, Cr	mg kg^{-1}	6
Cobalt, Co	mg kg^{-1}	14
Europium, Eu	mg kg^{-1}	0.3
Iron, Fe	% w/w	0.08
Gold, Au	µg kg^{-1}	<2
Hafnium, Hf	mg kg^{-1}	<1
Iridium, Ir	µg kg^{-1}	<5
Lanthanum, La	mg kg^{-1}	2.6
Lutetium, Lu	mg kg^{-1}	0.08
Mercury, Hg	mg kg^{-1}	<1
Molybdenum, Mo	mg kg^{-1}	<1
Neodymium, Nd	mg kg^{-1}	<5
Nickel, Ni	mg kg^{-1}	170
Rubidium, Rb	mg kg^{-1}	<15
Samarium, Sm	mg kg^{-1}	1.1
Scandium, Sc	mg kg^{-1}	0.2
Selenium, Se	mg kg^{-1}	<3
Silver, Ag	mg kg^{-1}	<5
Sodium, Na	% w/w	0.07
Strontium, Sr	% w/w	<0.05
Tantalum, Ta	mg kg^{-1}	<0.5
Terbium, Tb	mg kg^{-1}	<0.5
Thorium, Th	mg kg^{-1}	<0.2
Tin, Sn	% w/w	<0.02
Tungsten, W	mg kg^{-1}	<1
Uranium, U	mg kg^{-1}	<0.5
Ytterbium, Yb	mg kg^{-1}	0.8
Zinc, Zn	mg kg^{-1}	<50

3.8.4. Calcined Magnesia U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of CM is given in Table 70. The CM exhibited very low activities of the radioisotopes examined. The calculated absorbed dose rate for CM was only 5 nGy h^{-1}, compared to 4 nGy h^{-1} for the Bassendean Sand reference material.

Table 70. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of calcined magnesia (CM).

Radionuclide	CM (Bq kg^{-1})
^{238}U	1.2
^{230}Th	5.9
^{226}Ra	2.5
^{210}Pb	1.3
^{232}Th	7.3
^{228}Ra	0.8
^{228}Th	8.6
^{40}K	0.04
^{137}Cs	<DL†

†DL = detection limit.

3.8.5. Ecotoxicity of Calcined Magnesia

3.8.5.1. Algal Growth Rate Test

Three litres of CM leachate as well as method blank solution for use in all toxicity tests were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. Following centrifugation, the CM leachate had a pH of 12.2, which was higher than acceptable for algal growth (acceptable pH range: 6-9). Previous experiments with CM leachates indicated that very slow adjustment of pH was required to effectively reduce its pH to an acceptable level for algal growth (pH 7-9). Experiments also showed that when left to equilibrate with air for several days, the pH of the leachate decreased naturally by approximately 3 pH units.

Following centrifugation and filtration, the CM leachate and method blank were loosely covered and gently stirred for the next 4 days using magnetic stirrers to facilitate the natural decrease in pH. After three days, the pH of the CM leachate had only decreased to 11.9, so over the course of one day the CM leachate was slowly adjusted to pH 9.0 by the very slow addition of 3.0, 1.0 or 0.1 M HCl. After allowing the method blank and pH-adjusted CM leachate to stir overnight, the pH of the CM leachate had dropped to 8.4 and was ready for use in toxicity tests (Table 71). A fine precipitate had formed in the CM leachate during the four days of leachate preparation; thus, the CM leachate and method blank were centrifuged at 8000*g* for 5 minutes to remove precipitate prior to use in toxicity tests.

Table 71. Characteristics of filtered calcined magnesia (CM) leachate used in chronic 72-hour algal growth rate toxicity tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO (% sat.)
CM leachate	12.2	1.2	2.4	80
CM leachate, pH adj.	8.31	0.5	1.1	97
Method blank	8.46	0.2	0.44	94
Synthetic softwater	7.56	0.1	0.27	103

There was no significant difference between the growth of algae in the QA controls and that in the method blank. Thus, the data were pooled for use in statistical calculations. After a 48-hour exposure, there was complete inhibition of algal growth in undiluted CM leachate (100%); however, over the next 24 hours the algae recovered to achieve a growth rate that was statistically similar to that of the pooled QA and method blank controls. After a 72-hour exposure, there was no significant inhibition of algal growth in any dilution of CM leachate, and in 11 and 33% concentrations of leachate there was significant stimulation of algal growth (approximately 35%) (Table 72). The cause of the sudden and unusual recovery of algal growth in undiluted CM leachate is not known.

The pH in all test treatments was relatively stable. The pH in 100% CM leachate decreased by approximately 0.1 pH unit during the growth rate test, while for all other test treatments and controls there was an increase of *ca.* 0.1-0.2 pH units. A brown precipitate was observed in undiluted (100%) CM leachate on the final day of the algal growth rate test.

Table 72. Results of calcined magnesia (CM) chronic 72-hour algal growth rate toxicity tests.

	Growth Rate (doublings per day)	% of Control	CV (%)
Controls			
QA Control	1.50	100	13
Method blank	1.71	114	3.3
CM Leachates			
Pooled controls	1.60	100	11
0.1%	1.35	84	14
1.1%	1.72	107	16
3.3%	1.66	103	13
11%	2.24	139	8.1
33%	2.14	134	19
100%	1.61	100	16

The IC50 and LOEC values for inhibition of algal growth by CM leachate were >100%, while the NOEC value was 100%. At its natural pH (12.2), however, the CM leachate may have been more toxic to *Chlorella* sp. 12, since the pH was higher than that acceptable for algal growth.

3.8.5.2. Cladoceran Immobilisation Test

The method blank and CM leachate for the 48-hour cladoceran mobility toxicity test were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. Following centrifugation, the CM leachate had a pH of 12.2, which was higher than acceptable for cladoceran survival (acceptable pH range: 7-9). Previous experiments with CM leachates indicated that very slow adjustment of pH was required to effectively reduce its pH to an acceptable level for cladoceran survival. Experiments also showed that when left to equilibrate with air for several days, the pH of the leachate decreased naturally by approximately 3 pH units.

Following centrifugation and filtration, the CM leachate and method blank were loosely covered and gently stirred for the next 4 days using magnetic stirrers to facilitate the natural decrease in pH. After three days, the pH of the CM leachate had only decreased to 11.9, so over the course of one day the CM leachate was slowly adjusted to pH 9.0 by the very slow addition of 3.0, 1.0 or 0.1 M HCl. After allowing the method blank and pH-adjusted CM leachate to stir overnight, the pH of the CM leachate had dropped to 8.4 and was ready for use in toxicity tests (Table 73). A fine precipitate had formed in the CM leachate during the four days of leachate preparation; thus, the CM leachate and method blank were centrifuged at 8000*g* for 5 minutes to remove precipitate prior to use in toxicity tests. The CM leachate, method blank and synthetic softwater control were also supplemented with Se and Vitamin B_{12} prior to toxicity testing.

Table 73. Characteristics of filtered calcined magnesia (CM) leachate used in acute 48-hour cladoceran immobilisation toxicity tests.

Sample	pH	EC (mS cm^{-1})	DO (% sat.)
CM leachate	12.2	2.4	80
CM leachate, pH adj.	8.31	1.1	97
Method blank	8.46	0.44	94
Synthetic softwater	7.56	0.27	103
DMW control	8.13	0.18	101

There were 100% mobile cladocerans in each the DMW control, method blank and synthetic softwater control after 48 hours, well above the acceptability criteria of 90% (Table 74).

The DMW control and method blank data were pooled for use in statistical calculations. The CM leachate was not toxic to cladocerans, with no significant immobilisation observed for any concentration tested, i.e. the NOEC value for cladoceran mobility in CM leachate was 100% (Table 74). Both the EC50 and LOEC were >100%.

At its natural pH (12.2), the CM leachate may have been more toxic to *Ceriodaphnia dubia*, since the pH was higher than that acceptable for cladoceran survival (pH 7-9).

Table 74. Results of calcined magnesia (CM) acute 48-hour cladoceran immobilisation toxicity tests.

	Mean mobile (%)	% of pooled DMW and method blank	% inhibition
Controls			
DMW Control	100		
Synthetic softwater	100		
Method blank	100		
CM Leachates			
1.0%	100	100	0
6.3%	100	100	0
13%	100	100	0
25%	100	100	0
50%	90	90	10
100%	95	95	5

3.8.5.3. Microtox® Test

The method blank and CM leachate for the Microtox® test were prepared according to the TCLP protocol (USEPA, 1986) with synthetic softwater used in place of acetic acid. Following centrifugation, the CM leachate had a pH of 12.2, which was higher than acceptable for *Vibrio fischeri* survival (acceptable pH range: 6-9). Previous experiments with CM leachates indicated that very slow adjustment of pH was required to effectively reduce its pH to an acceptable level for Microtox® testing. Experiments also showed that when left to equilibrate with air for several days, the pH of the leachate decreased naturally by approximately 3 pH units.

Following centrifugation and filtration, the CM leachate and method blank were loosely covered and gently stirred for the next 4 days using magnetic stirrers to facilitate the natural decrease in pH. After three days, the pH of the CM leachate had only decreased to 11.9, so over the course of one day the CM leachate was slowly adjusted to pH 9.0 by the very slow addition of 3.0, 1.0 or 0.1 M HCl. After allowing the method blank and pH-adjusted CM leachate to stir overnight, the pH of the CM leachate had dropped to 8.4 and was ready for use in toxicity tests. A fine precipitate had formed in the CM leachate during the four days of leachate preparation; thus, the CM leachate and method blank were centrifuged at 8000*g* for 5 minutes to remove precipitate prior to use in toxicity tests. Because the Microtox® test used a marine bacterium, the method blank and CM leachate were also adjusted to a salinity of 20% with MOAS prior to use in toxicity tests. The pH and salinity of the pH-adjusted CM leachate with added MOAS were higher than those of the method blank (Table 75).

Table 75. Characteristics of filtered calcined magnesia (CM) leachate used in Microtox® tests.

Sample	pH	Salinity (%)	EC (mS cm^{-1})	DO (% sat.)
CM leachate	12.2	1.2	2.4	80
CM leachate pH adj.	8.31	0.5	1.1	97
CM leachate pH adj. + MOAS	8.55	20	33	97
Method blank	8.46	0.2	0.44	94
Method blank + MOAS	8.35	20	32	98

The CM leachate and two method blanks were not toxic to *Vibrio fischeri* after 5- and 15-minute exposures, with no significant inhibition of light output at any concentration tested after both a 5- and 15-minute exposure. The 5- and 15-minute LOEC for light output by *Vibrio fischeri* in CM leachate was 82%, while the NOEC and EC50 were >82%.

It is possible that at its natural pH (12.2) the CM leachate may have been more toxic to *Vibrio fischeri* than reported here, since the acceptable pH range for Microtox® is pH 6-9.

3.8.5.4. Leachate Chemistry

Trace elements that displayed some enrichment (≥2 times) in the pH 12.2 CM leachate when compared to the softwater control (method blank) included CO_3, Ca, Co, F, La, Mn, OH, Rb and Sr (Table 76). The increase in the concentration of these elements in pH 12.2 CM leachate relative to the method blank is likely due to the dissolution of a small amount of by-product during leachate preparation. In the pH 12.2 CM leachate, HCO_3, Mg, Pb, S and Si were depleted relative to the method blank.

Trace elements that displayed some enrichment (≥2 times) in the pH 8 CM leachate when compared to the softwater control (method blank) included Al, B, CO_3, Ca, Cl, F, La, Mn, Rb, Si, Sr and Zr (Table 76). In the pH 8 CM leachate, HCO_3, Mg, Pb and S were depleted relative to the method blank.

Table 76. Chemical composition of method blank and calcined magnesia (CM) leachates used in toxicity tests.

Analyte (mg L^{-1})	Method blank	Method Blank+MOAS	CM	CM, pH adjusted to 8	CM+MOAS
Al	<0.005	<0.005	<0.005	0.05	0.054
As	<0.001	<0.01	<0.001	<0.001	<0.01
B	<0.02	0.02	<0.02	0.49	0.61
Ba	<0.002	<0.002	0.58	0.78	0.76
Be	<0.0001	<0.001	<0.0001	<0.0001	<0.001
CO_3 (mg $CaCO_3$/L)	<1	<1	90	15	30
Ca	19	17.7	161	112	107
Cd	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Ce	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Cl	9	11100	10	310	11600
Co	<0.0001	<0.001	0.0004	0.0001	<0.001
Cr	<0.001	<0.001	<0.001	0.001	0.002
Cu	<0.002	<0.002	<0.002	<0.002	<0.002
F	0.08	<0.05	0.06	0.06	<0.05
Fe	<0.005	<0.005	<0.005	<0.005	<0.005
HCO_3 (mg $CaCO_3$/L)	107	107	<1	15	<1
Hg	<0.0001	<0.001	<0.0001	<0.0001	<0.001
K	3.6	3.8	3.7	3.8	4.1
La	<0.0001	<0.001	0.0003	0.0002	<0.001
Mg	17.3	16.4	3.4	6.1	6
Mn	<0.001	<0.001	0.017	0.006	0.008
Mo	<0.001	<0.01	<0.001	<0.001	<0.01
NH_3-N	0.01	0.01	<0.01	0.02	0.01
NO_x-N	0.04	0.04	0.04	0.04	0.04
Total N	0.11	0.12	0.09	0.08	0.1
Na	39.3	7710	48.5	65.9	8160
Ni	<0.01	<0.01	<0.01	<0.01	<0.01
OH (mg $CaCO_3$/L)	<1	<1	153	<1	<1
Total P	<0.1	<0.1	<0.1	<0.1	<0.1
PO_4-P	<0.01	<0.01	<0.01	<0.01	<0.01
Pb	0.0002	<0.001	<0.0001	<0.0001	0.0011
Rb	0.0001	<0.001	0.0012	0.0013	0.0013
S	37	39	3.1	2.9	2.9
SO_4	112	115	8.5	8.6	8.6
Sb	<0.0001	<0.001	<0.0001	0.0001	<0.001
Sc	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Se	<0.001	<0.01	<0.001	<0.001	<0.01
Si	0.57	0.58	<0.05	5.1	5.3
Sr	0.007	0.006	1.6	2.2	2.1
Te	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Th	<0.0001	<0.001	<0.0001	<0.0001	<0.001
Ti	<0.002	<0.002	<0.002	<0.002	<0.002
Tl	<0.0001	<0.001	<0.0001	<0.0001	<0.001
U	<0.0001	<0.001	<0.0001	<0.0001	<0.001
V	<0.005	<0.005	<0.005	<0.005	<0.005
Y	<0.0005	<0.005	<0.0005	<0.0005	<0.005
Zn	<0.005	0.006	<0.005	<0.005	<0.005
Zr	0.0001	<0.001	<0.0001	0.0008	<0.001

3.9. Groundwater Treatment Plant Lime Residue

In general, drinking water purification involves treatment with a coagulant to remove colour, turbidity and humic substances (DOC) from source water. The coagulation agents used to treat water can include iron chloride ($FeCl_3$), alum ($Al_2(SO_4)_3 \cdot 14H_2O$), organic polymers (e.g. PDADMAC), calcium oxides and/or $Ca(OH)_2$. Large volumes of water treatment residues are produced annually; for example, the water treatment authority in the Gauteng Province of South Africa alone produces 550 tons of residues each day (Van Rensburg and Morganthal, 2003). Several factors have led to increased interest in re-use of water treatment residues, including the implementation of more restrictive environmental regulations, increasing disposal costs and decreasing landfill capacities. In the Perth, WA, metropolitan area some residues from treatment of groundwater are currently re-used as soil amendments at Gnagara Mound and Jandakot Airport (Foo and Masters, 2007).

The water treatment residues used in these experiments were lime- and $CaCO_3$-based materials used to remove colour and odour from groundwaters at treatment plants (GWTP) in Perth, WA. The lime-based GWTP residue contained a mixture of sediments from the clarifiers, with very low organic matter in lime sediment (9% w/w). Lime-based GWTP residues contained high concentrations of Ca (250,470 mg/kg), $CaCO_3$ (62.5% w/w), and Mg (86,310 mg/kg), all of which are impurities in the lime.

3.9.1. GWTP Lime Residue General Characteristics

The GWTP lime residue was characterised by a very high EC, indicating a large quantity of dissolved salts in the aqueous GWTP lime residue extract (Table 77). In addition, the GWTP lime residue exhibited a highly alkaline pH of 11.8 (Table 77). The bulk density of GWTP lime residue, as determined by measuring cylinder, was 0.64 g cm^{-3}.

Table 77. Electrical conductivity (EC) and pH of groundwater treatment plant (GWTP) lime residue.

	EC (mS cm^{-1})	**pH**	**ρ_B (g cm^{-3})**
GWTP lime residue	5.84	11.8	0.64

3.9.2. GWTP Lime Residue Mineralogy

X-ray diffraction analysis of GWTP lime residue showed the presence of substantial calcite ($CaCO_3$) and portlandite [$Ca(OH)_2$], with minor quartz (SiO_2), brucite [$Mg(OH)_2$] and a magnesium aluminium compound (Figure 15). Quantitative XRD indicated that the GWTP lime residue was comprised of 12% quartz, 39% calcite, 12% brucite, 34% portlandite and 3% hydrotalcite [ideal formula $Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$].

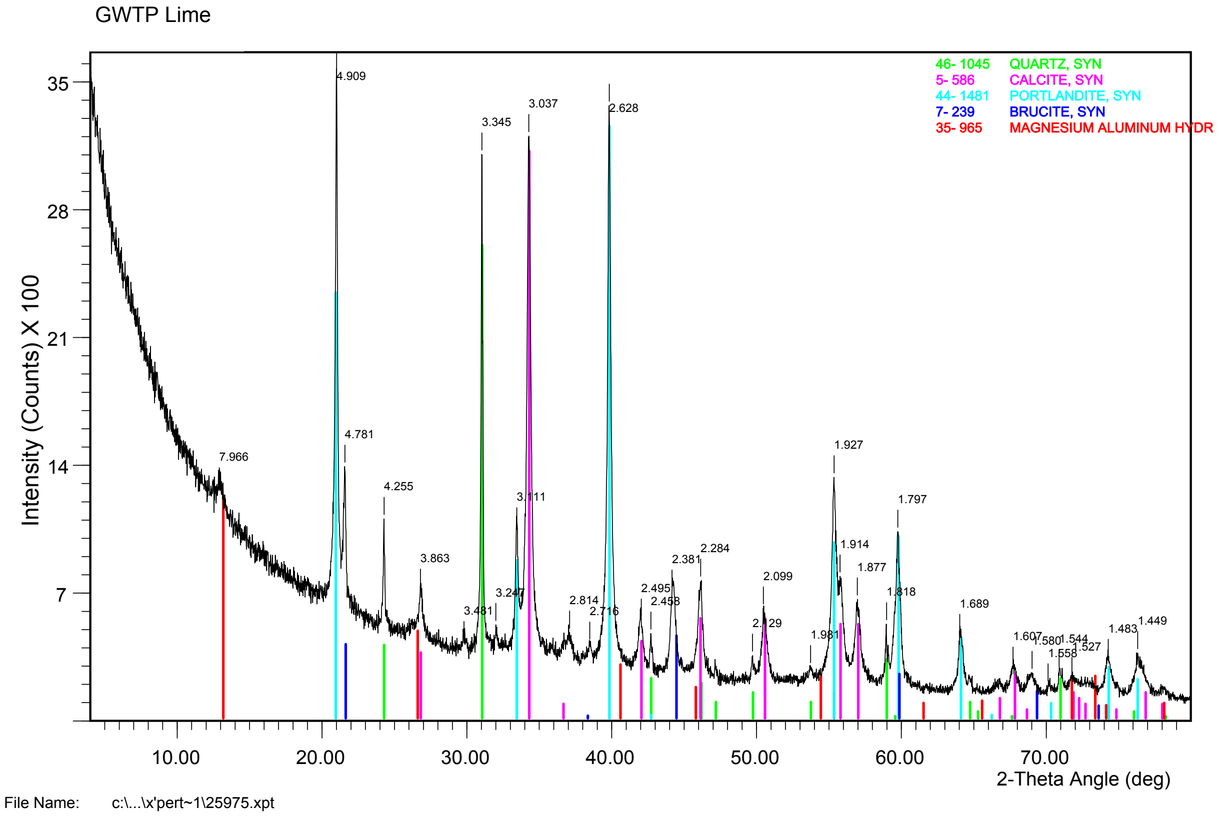

Figure 15. Powder X-ray diffraction (XRD) spectra of groundwater treatment plant (GWTP) lime residue.

3.9.3. GWTP Lime Residue Major and Trace Element Analysis

Fusion XRF indicated that more than 45% of the GWTP lime residue could be accounted for by CaO (Table 78).

Table 78. Fusion X-ray fluorescence (XRF) major elemental composition of groundwater treatment plant (GWTP) lime residue.

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
GWTP Lime	11.6	0.04	0.9	0.3	0.001	6.8	45.4	0.03	0.3	0.2	0.5	672	66.2

Trace elements that displayed some enrichment (≥2 times) in the GWTP lime residue when compared to Bassendean Sand included As, Ba, Ga, Ge, Rb, Sr, Tl, U, Y and Zn (Table 79). Several elements were depleted in the GWTP lime residue relative to Bassendean Sand, including Br, Ce, Cr, Mo, Nb, Ni and Zr (Table 79).

Table 79. Pressed powder X-ray fluorescence (XRF) trace elemental composition of groundwater treatment plant (GWTP) lime residue. All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
GWTP Lime	<4	8	77	<3	<1	<4	<20	<5	66	<11
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
GWTP Lime	2	3	1	<8	<13	<8	<18	57	1	4
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
GWTP Lime	<11	<2	<3	15	<8	<7	<2	<11	<3	1411
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
GWTP Lime	9	<7	9	7	16	8	10	<10	9	32

Analysis of the chemical composition of GWTP lime residue by ICP-OES indicated that the residue contained high levels of Al, Ca, Fe, Mg, Na and P (Table 80). The relatively high concentration of P in GWTP lime residue may be an indication that the GWTP lime residue is an effective sorbent for P, as these residues were previously used to treat groundwater. Further study is required to determine whether the GWTP lime residue has any remaining capacity for P uptake, or conversely, if the GWTP lime residue will release sorbed P.

Table 80. Chemical composition of groundwater treatment plant (GWTP) lime residue as determined by acid digest and ion-coupled plasma-optical emission spectroscopic (ICP-OES) analysis.

Parameter	Units	GWTP Lime residue
Aluminium, Al	mg kg^{-1}	3,000
Arsenic, As	mg kg^{-1}	8
Barium, Ba	mg kg^{-1}	25
Beryllium, Be	mg kg^{-1}	<1
Boron, B	mg kg^{-1}	65
Cadmium, Cd	mg kg^{-1}	<0.4
Calcium, Ca	mg kg^{-1}	250,469
Chromium, Cr	mg kg^{-1}	51
Cobalt, Co	mg kg^{-1}	<5
Copper, Cu	mg kg^{-1}	<5
Iron, Fe	mg kg^{-1}	3,900
Lead, Pb	mg kg^{-1}	<10
Magnesium, Mg	mg kg^{-1}	86,309
Manganese, Mn	mg kg^{-1}	85
Mercury, Hg	mg kg^{-1}	<0.05
Molybdenum, Mo	mg kg^{-1}	<5
Nickel, Ni	mg kg^{-1}	<4
Potassium, K	mg kg^{-1}	340
Selenium, Se	mg kg^{-1}	<1
Silver, Ag	mg kg^{-1}	<5
Sodium, Na	mg kg^{-1}	1,000
Zinc, Zn	mg kg^{-1}	<5
Total phosphorous, P	mg kg^{-1}	1,449
Calcium carbonate, $CaCO_3$	% w/w	62.5
Acid insoluble material	% w/w	25.5
LOI 105-550°C	% w/w	9
LOI 550-950°C	% w/w	41.1
Total Solids	% w/w	24

3.9.4. GWTP Lime Residue U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of GWTP lime residue is given in Table 81. The GWTP lime residue exhibited relatively low activities of the radioisotopes examined. The calculated absorbed dose rate for GWTP lime residue was 31 nGy h^{-1}.

Table 81. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of groundwater treatment plant (GWTP) lime residue.

Radionuclide	GWTP Lime (Bq kg^{-1})
^{238}U	47.6
^{230}Th	20.7
^{226}Ra	4.0
^{210}Pb	15.8
^{232}Th	10.6
^{228}Ra	4.7
^{228}Th	9.8
^{40}K	85
^{137}Cs	<DL†

†DL = detection limit.

3.10. Groundwater Treatment Plant Calcium Carbonate Residue

The water treatment residues used in these experiments were a $CaCO_3$-based material used to treat groundwater at a groundwater treatment plant (GWTP) in Perth, WA. The GWTP $CaCO_3$ residue was comprised of sediments from clarifiers, and had low organic matter content (9.5% w/w). The GWTP $CaCO_3$ residues contained high levels of Ca (310,000 mg/kg), $CaCO_3$ (77% w/w), and Fe (101,500 mg/kg).

3.10.1. GWTP $CaCO_3$ Residue General Characteristics

The GWTP $CaCO_3$ residue was characterised by a low EC, indicating few dissolved salts in the aqueous GWTP $CaCO_3$ residue extract (Table 82). The GWTP $CaCO_3$ residue exhibited an alkaline pH of 9.0 (Table 82). The bulk density of GWTP $CaCO_3$ residue, as determined by measuring cylinder, was 1.77 g cm^{-3}.

Table 82. Electrical conductivity (EC) and pH of groundwater treatment plant (GWTP) $CaCO_3$ residue.

	EC (μS cm^{-1})	pH	ρ_B (g cm^{-3})
GWTP $CaCO_3$ residue	48.0	9.0	1.77

3.10.2. GWTP $CaCO_3$ Residue Mineralogy

X-ray diffraction analysis of GWTP $CaCO_3$ residue showed the presence of substantial calcite ($CaCO_3$), with minor for quartz (SiO_2), periclase (MgO) and brucite [$Mg(OH)_2$] (Figure 16). Quantitative XRD of GWTP $CaCO_3$ residue indicated that the ordered phase was comprised of 1% quartz, 95% calcite, and 4% garnet [$(Mg,Fe,Ca)_3(Al,Fe,Cr)_2Si_3O_{12}$], the latter used as a nucleation agent for carbonate crystallisation.

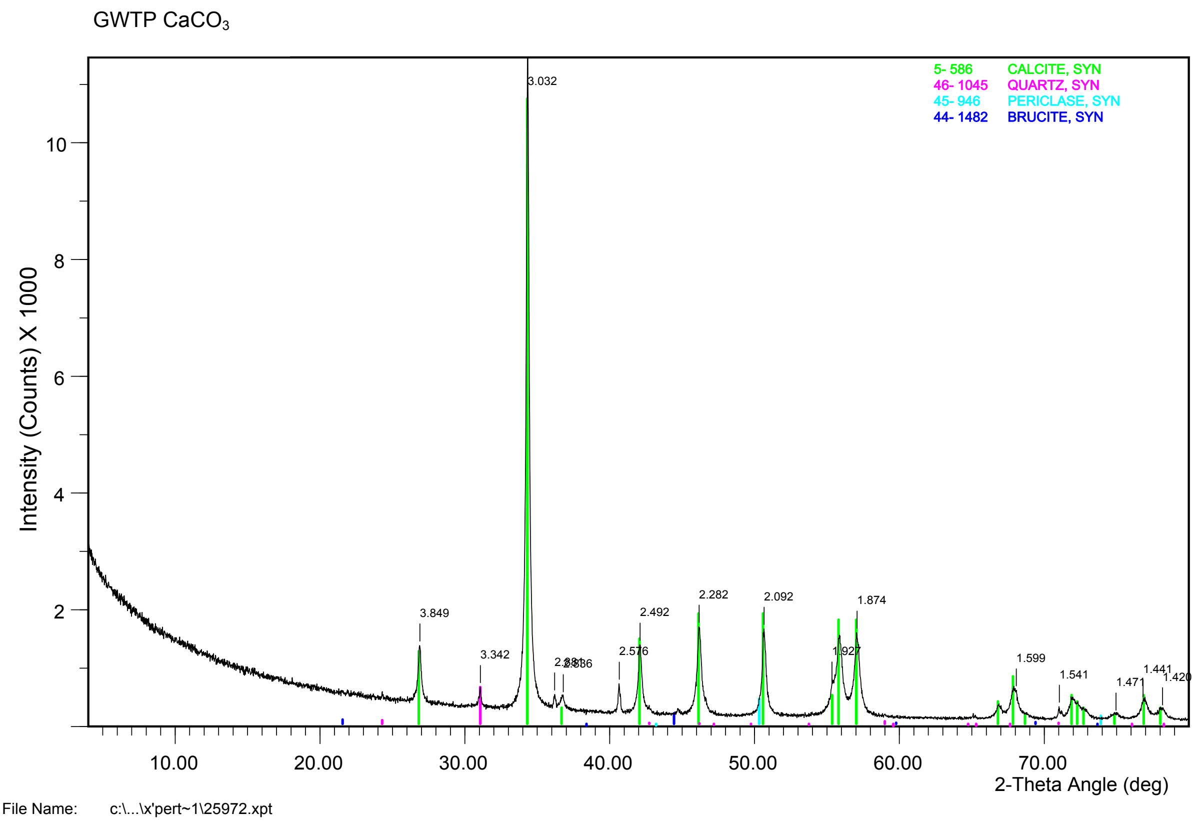

Figure 16. Powder X-ray diffraction (XRD) spectra of groundwater treatment plant (GWTP) $CaCO_3$ residue.

3.10.3. GWTP $CaCO_3$ Residue Major and Trace Element Analysis

Fusion XRF indicated that nearly 50% of the GWTP $CaCO_3$ residue could be accounted for by CaO (Table 83).

Table 83. Fusion X-ray fluorescence (XRF) major elemental composition of groundwater treatment plant (GWTP) $CaCO_3$ residue.

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
GWTP $CaCO_3$	0.5	<0.003	0.3	0.5	<0.001	0.6	49.7	<0.002	<0.002	0.03	0.09	275	51.8

Trace elements that displayed some enrichment (≥2 times) in the GWTP $CaCO_3$ residue when compared to Bassendean Sand included As, Ba, Rb, Sr, Tl and U (Table 84). Several elements were depleted in the GWTP $CaCO_3$ residue relative to Bassendean Sand, including Br, Ce, Cr, Cu, Mo, Nb, Ni and Zr (Table 84).

Table 84. Pressed powder X-ray fluorescence (XRF) trace elemental composition of groundwater treatment plant (GWTP) $CaCO_3$ residue. All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
GWTP $CaCO_3$	<4	5	237	<3	<1	<4	<20	<5	9	<11
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
GWTP $CaCO_3$	<1	<1	<1	<8	<13	<8	<18	118	<1	2
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
GWTP $CaCO_3$	<11	<2	<3	5	<8	<7	<2	<11	<3	935
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
GWTP $CaCO_3$	9	<7	7	8	7	<7	5	<10	<2	19

Analysis of the chemical composition of GWTP $CaCO_3$ residue by ICP-OES indicated that the residue contained high levels of Al, Ca, Fe, Mg, Na, P and $CaCO_3$ (Table 85). The relatively high concentration of P in GWTP $CaCO_3$ residue may be an indication that this by-product is an effective sorbent for P, as these residues were previously used to treat groundwater. Further study is required to determine whether the GWTP $CaCO_3$ residue has any remaining capacity for P uptake, or conversely, if the $CaCO_3$ residue will release P.

Table 85. Chemical composition of groundwater treatment plant (GWTP) lime residue as determined by acid digest and ion-coupled plasma-optical emission spectroscopic (ICP-OES) analysis.

Parameter	**Units**	**GWTP $CaCO_3$ residue**
Aluminium, Al	mg kg^{-1}	2,700
Arsenic, As	mg kg^{-1}	44
Barium, Ba	mg kg^{-1}	590
Beryllium, Be	mg kg^{-1}	<1
Boron, B	mg kg^{-1}	100
Cadmium, Cd	mg kg^{-1}	1.8
Calcium, Ca	mg kg^{-1}	311,621
Chromium, Cr	mg kg^{-1}	96
Cobalt, Co	mg kg^{-1}	<5
Copper, Cu	mg kg^{-1}	8
Iron, Fe	mg kg^{-1}	105,474
Lead, Pb	mg kg^{-1}	<10
Magnesium, Mg	mg kg^{-1}	6,300
Manganese, Mn	mg kg^{-1}	190
Mercury, Hg	mg kg^{-1}	<0.05
Molybdenum, Mo	mg kg^{-1}	<5
Nickel, Ni	mg kg^{-1}	<4
Potassium, K	mg kg^{-1}	170
Selenium, Se	mg kg^{-1}	<1
Silver, Ag	mg kg^{-1}	<5
Sodium, Na	mg kg^{-1}	2,100
Zinc, Zn	mg kg^{-1}	20
Total phosphorous, P	mg kg^{-1}	7,099
Calcium carbonate, $CaCO_3$	% w/w	77.8
Acid insoluble material	% w/w	4.4
LOI 105-550°C	% w/w	9.6
LOI 550-950°C	% w/w	35.8
Total Solids	% w/w	20.2

3.10.4. GWTP $CaCO_3$ Residue U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of GWTP $CaCO_3$ residue is given in Table 86. The GWTP $CaCO_3$ residue exhibited low activities of the radioisotopes examined. The calculated absorbed dose rate for GWTP $CaCO_3$ residue was 3 nGy h^{-1}.

Table 86. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of groundwater treatment plant (GWTP) $CaCO_3$ residue.

Radionuclide	GWTP $CaCO_3$ (Bq kg^{-1})
^{238}U	2.8
^{230}Th	1.2
^{226}Ra	35.6
^{210}Pb	<DL[†]
^{232}Th	2.7
^{228}Ra	56
^{228}Th	27.5
^{40}K	3.1
^{137}Cs	<DL

[†] DL = detection limit.

3.11. Fly Ash

Fly ash (FA) is a fine-textured predominantly mineral residue generated during the combustion of coal to generate electricity, normally 60-88% of the original material by weight. In excess of 140 million tonnes of FA is produced annually as a residue from fossil fuel combustion in coal-fired power stations around the world. It has long been recognised that at least half of this by-product is not utilised in a meaningful way, resulting in its disposal in landfills, which has the potential to cause major environmental problems (Higgins et al., 1976; Singer and Berkgaut, 1995), particularly from often alkaline fly ash leachates. As a consequence of the large volume of fly ash generated annually and the cost of disposal, there is increasing interest in the beneficial re-use of fly ash.

Although fly ash composition varies depending on the type of coal and the technological process from which the product is derived, the principal constituents of fly ash are typically silica (*ca.* 30-60% as SiO_2), aluminium (*ca.* 10-30% as Al_2O_3) and lesser amounts of iron and sulphur (Singer and Berkgaut, 1995). A major barrier to fly ash resue, however, is the often substantial enrichment of a range of potentially toxic trace elements remaining in the residue after coal combustion.

3.11.1. Fly Ash General Characteristics

The fly ash was characterised by a moderate EC of 0.7 mS cm^{-3} (Table 87). In addition, the fly ash exhibited a slightly alkaline pH of 8 (Table 87). The bulk density of fly ash, as determined by measuring cylinder, was 0.74 g cm^{-3}.

Table 87. Electrical conductivity (EC) and pH of fly ash (FA).

	EC (µS cm^{-1})	pH	ρ_B (g cm^{-3})
Fly Ash	697.0	8.0	0.74

3.11.2. Fly Ash Mineralogy

X-ray diffraction analysis of fly ash showed the presence of quartz (SiO_2) and mullite ($3Al_2O_3{\cdot}2SiO_2$), with minor hematite (α-Fe_2O_3) (Figure 17). Quantitative XRD indicated that the fly ash was approximately 65% amorphous, and that the ordered phase was comprised of 17% quartz, 13% mullite, 3% hematite and 3% spinel (possibly maghemite, γ-Fe_2O_3).

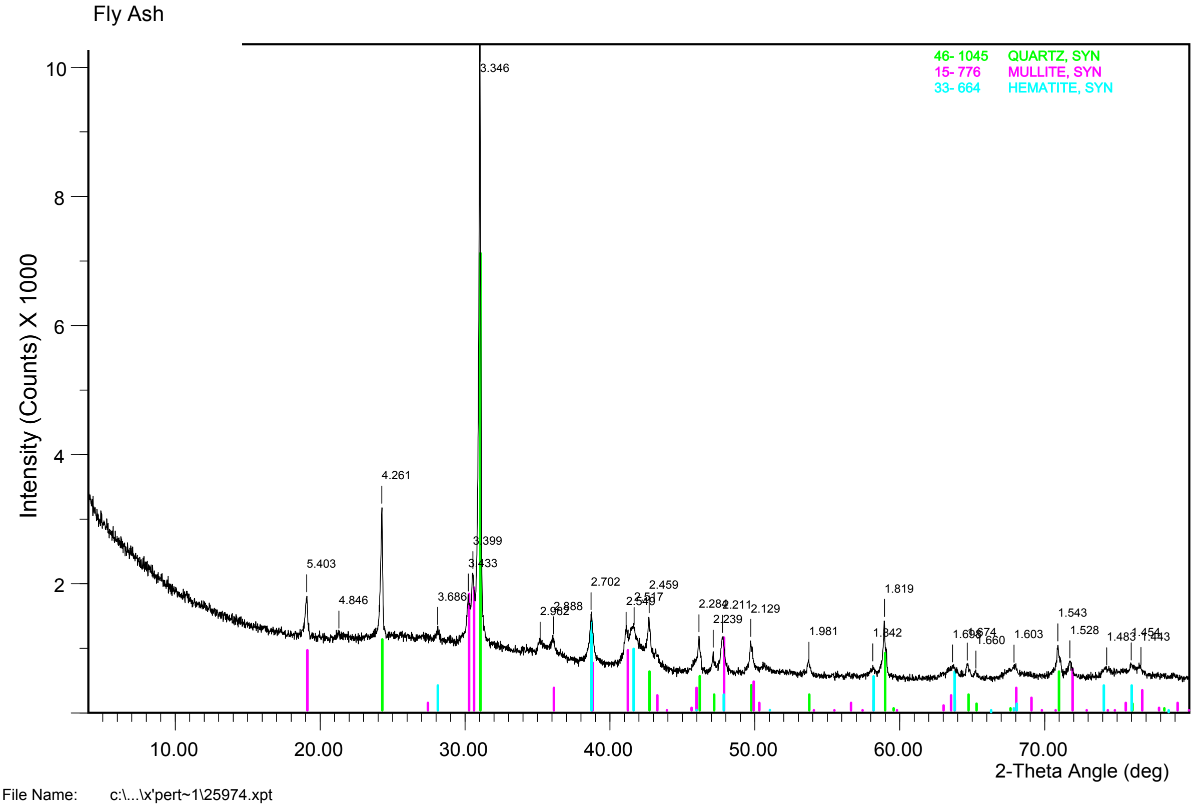

Figure 17. Powder X-ray diffraction (XRD) spectra of fly ash (FA).

3.11.3. Fly Ash Major and Trace Element Analysis

Fusion XRF indicated that nearly 50% of the fly ash could be accounted for by SiO_2, and that SiO_2, Al_2O_3 and Fe_2O_3 together comprised over 80% of the fly ash solid phase (Table 88).

Table 88. Fusion X-ray fluorescence (XRF) major elemental composition of fly ash (FA).

	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
FA	49.6	1.2	22.4	9.7	0.1	1.1	1.6	0.3	0.8	1.2	0.3	149	88.3

Trace elements that displayed some enrichment (≥2 times) in the fly ash when compared to Bassendean Sand included As, Ba, Bi, Br, Cd, Ce, Co, Cs, Cu, Ga, Ge, Hf, La, Nb, Ni, Pb, Rb, Se, Sn, Sr, Th, Tl, U, V, Y, Zn and Zr (Table 89). A range of trace elements including As, Cr, Cu, Mn, Nb, Ni, Pb, Zn, Th Tl, V, Uand Zr and the rare earth elements (La, Ce, Nd Sm and Y) were particularly enriched (*ca.* >5 to >10 times or more) relative to Bassendean Sand.

There were no major or trace elements depleted in the fly ash relative to Bassendean Sand (Table 89).

Table 89. Pressed powder X-ray fluorescence (XRF) trace elemental composition of fly ash (FA). All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
FA	<4	17	3741	3	4	4	407	183	170	19
	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
FA	100	45	12	12	<13	<8	229	1035	16	66
	Nd	**Ni**	**Pb**	**Rb**	**Sb**	**Sc**	**Se**	**Sm**	**Sn**	**Sr**
FA	158	283	53	62	<8	30	11	15	9	2062
	Ta	**Te**	**Th**	**Tl**	**U**	**V**	**Y**	**Yb**	**Zn**	**Zr**
FA	<7	<7	57	29	28	156	142	<10	353	443

3.11.4. Fly Ash U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition of fly ash is given in Table 90. The Fly ash exhibited moderate activities for the majority of radioisotopes examined. The calculated absorbed dose rate for fly ash was 170 nGy h^{-1}.

Table 90. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of fly ash (FA).

Radionuclide	FA (Bq kg^{-1})
^{238}U	109
^{230}Th	148
^{226}Ra	169
^{210}Pb	164
^{232}Th	174
^{228}Ra	180
^{228}Th	204
^{40}K	198
^{137}Cs	<DL†

†DL = detection limit.

3.12. Granular Activated Carbon

Granular activated carbon (GAC) is produced when tree biomass, typically Mallee Eucalyptus, is carbonized to charcoal and then activated with steam to produce activated carbon. As outlined in publication number 01/160, *Integrated Tree processing of Mallee Eucalypts,* from the Rural Industries Research and Development Corporation (Enecon, 2001), GAC of the type characterised in this study compares well with other commercially available sources of activated carbon (*e.g.* Norit ROW 0.8 Supra, Calgon Filtrasorb 300 – granules, Calgon WPL – powder) in removing taste and odours from drinking water.

3.12.1. GAC General Characteristics

The GAC was characterised by a moderate EC of 1.1 mS cm^{-3} (Table 91). In addition, the fly ash exhibited an alkaline pH of 9.2 (Table 91). The bulk density of fly ash, as determined by measuring cylinder, was 0.22 g cm^{-3}.

Table 91. Electrical conductivity (EC) and pH of granular activated carbon (GAC).

	EC (mS cm^{-1})	**pH**	**ρ_B (g cm^{-3})**
Granular activated carbon	1.14	9.2	0.22

3.12.2. GAC Mineralogy

X-ray diffraction analysis of GAC showed that the GAC solid phase was almost entirely amorphous (e.g., little identifiable ordered structure), exhibiting only a small calcite ($CaCO_3$) peak (Figure 18). Quantitative XRD on GAC indicated that the material was >95% amorphous.

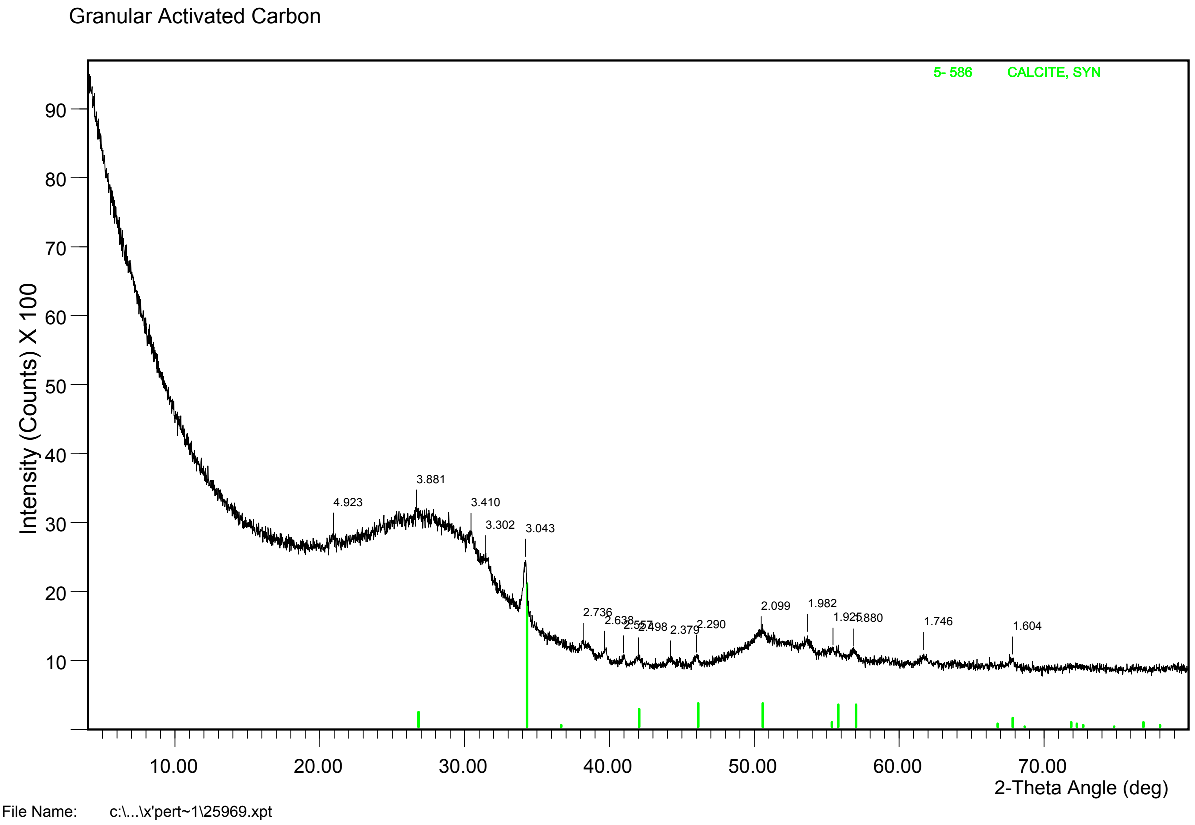

Figure 18. Powder X-ray diffraction (XRD) spectra of granular activated carbon (GAC).

3.12.3. GAC Major and Trace Element Analysis

Fusion XRF of GAC indicated that the measureable oxides were primarily Al_2O_3 and CaO (constituting only 3% of the total mass), with minor quantities of MgO, K_2O, TiO_2, MnO and P_2O_5 (Table 92).

Table 92. Fusion X-ray fluorescence (XRF) major elemental composition of granular activated carbon (GAC).

	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	P_2O_5	SO_3	Cl	Sum
GAC	<0.005	0.1	1.3	0.08	0.1	0.4	1.7	0.03	0.2	0.1	0.05	32	4.1

It was not possible to conduct pressed powder XRF on the GAC to examine trace element contents, as the material was not amenable to analysis. Other analytical techniques including NAA or ICP-MS could be undertaken if a potential end use for GAC was identified.

3.12.4. GAC U-Th Series, ^{40}K and ^{137}Cs Analysis

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition GAC is given in Table 93. The GAC exhibited low activities of the radioisotopes examined. The calculated absorbed dose rate for GAC was 3 nGy h^{-1}.

Table 93. Summary of U-Th series, ^{40}K and ^{137}Cs mean isotopic composition of granular activated carbon (GAC).

Radionuclide	GAC (Bq kg^{-1})
^{238}U	<DL†
^{230}Th	0.1
^{226}Ra	3.6
^{210}Pb	0.2
^{232}Th	1.8
^{228}Ra	6.3
^{228}Th	9.6
^{40}K	46.1
^{137}Cs	<DL

†DL = detection limit.

4. DISCUSSION

4.1. Potential for By-Product Reuse in Environmental Applications

Results of chemical and mineralogical characterisation of a variety of industrial by-products, Bassendean Sand reference material, laterite and some commercially-available materials suggest some potential for the productive reuse for a range of materials or material combinations. Applications of specific by-products or by-product mixtures could be as diverse as surface water or soil amendments, or in permeable reactive barriers to neutralise acidity or sequester excess nutrients from agricultural drainage such as Ellen Brook and potentially toxic metals from acid-saline drainage prevalent in the WA Wheatbelt.

Land application of industrial by-products as soil amendments may be justified where nominally environmentally benign by-products may contain significant quantities of bio-available nutrients or provide a source of alkalinity (*e.g.*, a lime substitute) or alternatively, have a strong nutrient-binding capacity. Additional characteristics indicating environmental benefit may include improvements in soil physical or chemical characteristics such as water holding capacity, structural stability, porosity and permeability, cation or anion exchange capacity (CEC or AEC) or organic carbon (OC) content.

On the basis of the characterisation studies undertaken in this study, a number of industrial by-products produced on a commercial scale in WA possess characteristics indicative of potential benefit as soil or surface water amendments (Table 94), including:

- heavy minerals processing residue,
- red mud,
- red sand,
- cement kiln dust,
- steelmaking by-products,
- fly ash,
- calcined magnesia and
- water treatment residues.

Natural mineral amendments such as:

- mine overburden or laterite,
- carbonates or carbonate derivatives (*e.g.* limestone, lime, dolomite),
- phyllosilicate (clay) minerals,
- zeolite minerals and/or
- hydrotalcite minerals

could also potentially be used in conjunction with low-cost industrial by-products to ameliorate acidity and attenuate potentially toxic metals and excess nutrients in effluent waters (Table 94).

Table 94. Summary of potential soil and surface water amendments and some pertinent characteristics.

Material	**Chemistry**	**Mineralogy**	**Occurrence**	**Modification**	**ANC**[†]	**Potential Applications**[‡]
Carbonates and derivatives						
Limestone/ calcrete/limesand	$CaCO_3$	Primarily calcite & aragonite	Common throughout coastal and inland WA	May require crushing	High	CW, SW, DL, PRB
Lime	Quicklime (CaO) or hydrated lime ($Ca(OH)_2$)	Portlandite	Commercially available from calcination of limestone	Available in powder form	High	SA, CW, SW, DL, PRB
Calcined magnesia (CM)[§]	MgO	Periclase & brucite	By-product of magnesia industry	May require crushing	Very high	SA, CW, SW, DL, PRB
Magnesium hydroxide	$Mg(OH)_2$	Brucite	By-product of magnesia industry	May require crushing	Very high	CW, SW, DL, PRB
Dolomite	$CaMg(CO_3)_2$	Dolomite, with minor magnesite, calcite	Common throughout coastal and inland WA	May require crushing	Mid-high	CW, SW, DL, PRB
Mineral processing by-products						
Red mud (RM)[§]	Complex Fe & Al oxides/oxyhydroxides	Primarily goethite & hematite	By-product of alumina refining (Bayer process)	Neutralisation, as by seawater or gypsum addition	High	SA, CW, SW, DL, PRB
Red sand (RS)[§]	Complex Fe & Al oxides/oxyhydroxides	Hematite, goethite & quartz	By-product of alumina refining (Bayer process)	Neutralisation, as by seawater or gypsum addition	Moderate	SA, CW, SW, DL, PRB
Reduced red sand (RRS)[§]	Complex Fe & Al oxides/oxyhydroxides	Primarily metallic Fe, some $(Mn,Fe)(Cr,V)_2O_4$ and $FeAl_2O_4$	By-product of alumina refining (Bayer process)	Generated by mixing red sand with charcoal and roasting the mixture at high temperature	Mid-high	SA, CW, SW, DL, PRB
Gypsum	$CaSO_4$	Gypsum, bassanite	Naturally-occurring or by-product of power generation	May require drying prior to application	Mid-high	SA, DL
Steelmaking by-product (SS)[§]	Primarily SiO_2 and CaO with lesser quantities of Al_2O_3, MgO & Fe_2O_3	Gehlenite ($Ca_2Al_2SiO_7$), minor pyroxene, spinel & quartz	By-product of steel manufacturing	Requires pelletisation or crushing prior to use	High	SA, CW, SW, DL, PRB
Neutralised unused acid (NUA)[§]	Primarily CaO, SO_4 and Fe_2O_3	Gypsum, Fe oxyhydroxides, minor magnetite & quartz	By-product of heavy mineral processing.	None	Moderate	SA, CW, SW, DL, PRB

[†] ANC = acid neutralisation capacity.

[‡] Applications dependent upon particle size, design of treatment scheme, end use of resource, combination with other materials to buffer pH where necessary, etc. SA=soil amendment; CW=constructed wetland; SW=soak well; DL=drain liner; PRB=permeable reactive barrier.

[§] Characteristics of materials examined in this study; by-products sourced from different localities may exhibit different physicochemical characteristics.

Table 94 (continued). Summary of potential soil and surface water amendments and some pertinent characteristics.

Material	**Chemistry**	**Mineralogy**	**Occurrence**	**Modification**	**ANC**[†]	**Potential Applications**[‡]
Industrial by-products						
Cement kiln dust	Largely CaO and $Ca(OH)_2$	Portlandite	By-product of cement production	None	High	CW, SW, PRB – low bulk density
Fly ash (FA)[§]	SiO_2, Al_2O_3	Primarily quartz & mullite	By-product of electricity production (coal combustion)	None	High	SA, CW, SW, PRB – low bulk density
Water treatment residues	Variable due to different treatment processes and source water; generally high in Fe and/or Al	Variable – carbonates, hydroxides, crystalline & amorphous	Produced in large volumes in water treatment plants	Dewatering may be required for use	Variable, but generally moderate	SA, CW, SW, DL, PRB – wet, low bulk density
Carbonised wood products (GAC)[§]	Primarily Al_2O_3 & CaO	>95% amorphous carbon or charcoal	Produced in large volumes from integrated tree processing	None	Moderate	SW, PRB – low bulk density
Other materials						
Mine overburden	Variable	Variable, generally soils or saprock	Widely available	Requires crushing	Low to high	CW, SW, DL, PRB
Laterite[§]	Primarily Al_2O_3 & Fe_2O_3	Hematite, gibbsite & quartz	Widely available	Requires crushing	Moderate	CW, SW, DL, PRB
Hydrotalcites	Variable, usually Mg, Al, Fe hydroxides	Layered double hydroxide minerals	Present in soils & sediments or may be synthesized	None or possibly purification	Low	SA, CW, SW, DL, PRB
Zeolites	Variable	Framework silicates formed by SiO_4^{4-} & AlO_4^{5-} tetrahedra	Components of mafic igneous & sedimentary rocks, also commercially available	None necessary, although saturation of exchange sites with Na^+/Ca^{2+} may improve ion exchange	Low	SA, CW, SW, DL, PRB
Phyllosilicate clay minerals (i.e., illite, smectite, vermiculite)	Variable, usually Na, K, Ca, Fe, Mg aluminosilicates	Variable mineralogy; layer silicate structure formed by stacking of tetrahedral and octahedral layers	Ubiquitous weathering products of primary minerals, also commercially available	Dehydration, calcination, hydration surface adsorption, cation exchange, acid activation, intercalaction e.g. organo-composites or pillaring	Low to moderate	SA, CW, SW, DL, PRB – swelling clays not suitable where infiltration is required

[†] ANC = acid neutralisation capacity.

[‡] Applications dependent upon particle size, design of treatment scheme, end use of resource, combination with other materials to buffer pH where necessary, etc. SA=soil amendment; CW=constructed wetland; SW=soak well; DL=drain liner; PRB=permeable reactive barrier.

[§] Characteristics of materials examined in this study; by-products sourced from different localities may exhibit different physicochemical characteristics.

The by-products investigated herein exhibited a range of pH from *ca.* 5.3 to nearly 12.0, and EC from 34 to nearly 6 mS cm^{-1} (Table 95). These results, in combination with XRF major (Table 96) and trace elemental analyses (Table 97) provide critical information regarding the potential utility of individual by-products in acid attenuation. The pH of a material that may be used as an environmental amendment is of particular importance, as pH in soil environments strongly influences ion exchange, dissolution/precipitation, reduction/oxidation, adsorption, and complexation reactions. The pH provides an indication of potential of direct or indirect effects of extreme H$^+$ or OH$^-$ activities. A pH of 2-3 generally indicates the presence of free acid and at pH less than 5.0-5.5, high concentrations of soluble (and phytotoxic) metals such as Al may be present (Thomas, 1996). Conversely, soil pH greater than 8.5 is generally indicative of soluble or exchangeable Na at concentrations detrimental to soil structure and plant growth (Thomas, 1996). Total metal solubility in soils frequently displays a two-stage trend, high at low pH and decreasing to pH 6-7 then increasing again at higher pH as soluble ligands (e.g., organic acids, OH$^-$) bind to and remobilise metals (e.g., $Al(OH)_4^-$) (McBride, 1994).

Table 95. Summary of electrical conductivity and pH of Bassendean Sand reference material and by-products examined for potential re-use as environmental amendments ranked by increasing pH.

By-product	EC (mS cm^{-1})	pH
Bassendean Sand reference	0.03	4.8
Neutralised unused acid (NUA)	2.5	5.3
Red sand (RS)	1.1	6.3
Laterite	0.03	6.4
Reduced red sand (RRS)	0.1	7.1
Steelmaking by-product (SS)	0.1	7.5
Fly ash (FA)	0.7	8.0
GWTP $CaCO_3$ residue	0.05	9.0
Granular activated carbon (GAC)	1.1	9.2
Red mud (RM)	5.9	9.7
Calcined magnesia (CM)	1.7	10.2
GWTP lime residue	5.8	11.8

The high pH and high CaO content of both the lime- and $CaCO_3$-based GWTP residues indicate that these materials may be particularly suitable for acid neutralisation either as a soil amendment, for instance in acid sulfate soils, or to neutralise acid waters. Similarly, CM exhibits high acid neutralisation potential with a pH of 10.2 and extremely high MgO content (Table 95, Table 96). Although the measured pH of SS and NUA by-products are not as alkaline as those obtained for the CM or either of the GWTP residues, both SS and NUA may, depending on mineralogy and grain size, also be effective to neutralise acidity. Both SS and NUA possess a relatively high CaO content, indicating that these by-products may have a moderate acid neutralisation capacity (Table 96). The GAC, FA and RM by-products may also merit further investigation of acid attenuation, as these by-products exhibit alkaline pH (Table 95). High trace element concentrations of FA including Cu, Pb and Zn may, however, preclude its widespread application.

Electrical conductivity is the measure of total soluble salt concentration, in this case measured in by-product extracts, and is an indication of soil salinity. Saline soils are unsuitable for plant growth due to low permeability and the toxic effects of Na accumulation in plants; an EC greater than 4 mS cm^{-1} is generally indicative of a saline soil (McBride, 1994). Of the by-products examined, RM and GWTP lime reisude both exhibit EC greater than 4 mS cm^{-1}. Thus, particular attention should be paid to Na concentration if these by-products were utilised as, for instance, a soil amendment.

Those by-products containing a relatively large proportion of Fe and/or Mn oxide minerals may be particularly well-suited to the sorption of nutrients such as P (Table 96). As such, the nutrient and DOC sorption capacity of these by-products, including NUA, RM, RS, RRS and laterite, should be investigated further. In particular, mixtures of by-products may be suitable as environmental amendments. The characterisation results presented herein yield critical information for the generation of potentially suitable by-product mixtures for various environmental applications.

A summary of trace element content of the materials examined, with the exception of granular activated carbon which was not suitable for trace element analysis by XRF is given in Table 97. Trace elements have numerous biological functions and display a diversity of toxicities to both plants and animals. Trace elements essential to plant growth include Fe, Mn, Zn, B, Cu, Mo and Cl; however, at high concentrations these elements can also be toxic to plants and microorganisms while some metals are considered highly toxic including Hg, Pb, Cd, Cu, Ni and Co (McBride, 1994). Based on toxicity, the metals/metalloids Sb, As, Be, Cd, Cr, Cu, Pb, Hg, Ni, Se and Zn are included in the USEPA 1998 Draft RCRA Waste Minimization Persistent, Bioaccumulative and Toxic (PBT) Chemical List of priority pollutants (USEPA, 1998). This list has since been modified to include only Cd, Pb and Hg as "priority metals" (USEPA, 2009).

Soils with Cd concentrations greater than 0.5 ppm are generally considered polluted (McBride, 1994). Australian guidelines for land application of biosolids limit Cd and Hg concentrations in soil to 1 ppm, and Pb concentration to 150 ppm (DEHP, 2002). Cadmium concentrations in RRS, RM and FA are substantially greater than 1 ppm at 60, 9 and 4 ppm, respectively (Table 97). Reduced red sand also exhibits an elevated concentration of Pb (180 ppm). Based on contaminant acceptance concentration threshold values for biosolids (DEHP, 2002), recommended interim sediment quality guidelines (ANZECC/ARMCANZ, 2000), and maximum permissible metal concentrations in soil (Crommentuijn et al., 1997), metal concentrations in soils and waters should be closely monitored following use of some by-products, including RM and FA. It is important to note, however, that the total concentration of an element in a material is not necessarily equivalent to the concentration element that is biologically available. The total concentrations of trace elements reported in Table 97 provide an indication of elements of potential concern, but further testing is required to quantify the extent to which each element may be released from the solid material in an environmental application.

A summary of the U-Th series, ^{40}K and ^{137}Cs isotopic composition, and absorbed dose rate (D), which equates to an intergral of activities for a range of radionuclides, for each by-product is given in Table 98. A comparison of the calculated absorbed dose rates (D) indicates that the NUA (263 nGy h^{-1}) was the highest, followed by FA (170 nGy h^{-1}) and laterite (131 nGy h^{-1}) (Table 98). The Bassendean Sand had a D of 4 nGy h^{-1}. Western Australia's Darling Scarp soils exhibit D values between 35 and 378 nGy h^{-1} (average 195 nGy h^{-1}) (Toussaint, 2005). In comparison, phosphogypsum fertiliser, widely used in agricultural applications, has D values ranging from 273 to 320 nGy h^{-1} (average 297 nGy h^{-1}) (Bolivar et al., 1998; Douglas et al., 2007; Mourad et al., 2009; Yücel et al., 2004).

Calculated absorbed dose rates indicate that some by-products such as NUA and FA would likely need to be diluted prior to application, and the mobility of radionuclides in the intended application would require investigation and monitoring. In the case of soil application, by-products could be diluted by mixing with native soils such as the Bassendean Sands which have very low activity. The radioactivity of by-products is dependent upon sources of original material and processes by which by-products are generated. For example, the mean D of FA produced in Hungary is reported to be 421 nGy h^{-1}, as compared to the D of 171 nGy h^{-1} determined here for FA generated in WA (Somlai et al., 2008). The radioisotope concentrations and resultant radioactivities of RM and RS determined in this study are also low as compared to other investigations, which report radionuclide concentrations equivalent to D values for RM ranging from 206 to 1524 nGy h^{-1} (Akinci and Artir, 2008; Cooper, 2005; Somlai et al., 2008). Red mud generated in Western Australia during alumina production via the Bayer process has reported ^{238}U and ^{232}Th concentrations of 150-600 Bq kg^{-1} and 1000-1900 Bq kg^{-1}, respectively; reported ^{238}U and ^{232}Th concentrations for RS generated in WA via the Bayer process are 5-200 Bq kg^{-1} and 300-800 Bq kg^{-1}, respectively (Cooper, 2005).

Based on the results of geochemical, mineralogical and radiological analyses and the potential for field application, leachates of NUA, steelmaking by-product, red mud, red sand, and calcined magnesia were subjected to ecotoxicity testing. Ecotoxicity testing indicated that with the exception of RM, the by-product leachates tested were of low toxicity to *Chlorella* sp. 12 algae, the cladoceran *Ceriodaphnia dubia*, or the marine bacterium *Vibrio fischeri* (Table 99). Of note, only the NUA leachate was tested at its natural pH. The leachates of SS (pH 10.6), RM (pH 10.7), RS (pH 10.2) and CM (pH 12.2) had pH higher than acceptable for algal growth, cladoceran survival or Microtox® testing. Thus, the pH of these leachates was adjusted to 8.0 prior to use in the toxicity tests. At their natural pH (10.2-12.2), the SS, RM, RS and CM leachates may have exhibited greater toxic effects on algal growth, cladoceran mobility, and light output by the marine bacterium *Vibrio fischeri*.

The RS and CM leachates were not toxic to the alga *Chlorella* sp. 12, with no significant inhibition of algal growth observed for any concentration of RS or CM leachate tested. The SS leachate was of low toxicity to algal growth, with significant inhibition of algal growth only observed in undiluted leachate. The IC50 value for inhibition of algal growth in SS leachate was >100%, while the LOEC and NOEC values were 100 and 33%, respectively. The NUA leachate also exhibited low toxicity to algal growth, with NOEC and LOEC values of 11% and 33%, respectively. In contrast, the RM leachate was toxic to algal growth, with an IC50 of 60%. All concentrations of RM leachate tested caused significant inhibition of algal growth.

Only the RM leachate inhibited cladoceran mobility in toxicity tests. The NUA, SS, RS and CM leachates were not toxic to *Ceriodaphnia dubia*, with no immobile cladocerans in any concentration of NUA, SS, RS or CM leachates tested. However, the RM leachate was toxic to cladocerans, with an EC50 of 47% and a NOEC value of 25%. The LOEC for cladoceran mobility in RM leachate was 50%.

The NUA, RM and CM leachates were not toxic to *Vibrio fischeri*, with no significant inhibition of light output observed for any concentration tested after both 5- and 15-minute exposure times. The 5- and 15-minute LOEC for light output by *Vibrio fischeri* in NUA, RM and CM leachates was 82%, while NOEC and EC50 were >82%. Both the SS and RS leachates showed low toxicity to the bacteria with significant inhibition of light output only observed in the highest concentration tested (82%). In both 5- and 15-minute exposures, the EC50 for inhibition of light output by the marine bacterium *Vibrio fischeri* in SS and RS leachates was >82%; the LOEC was 82% and the NOEC was 41%.

It is likely that those by-products which generate leachate with pH greater than 9 will require mixing with other materials to buffer pH prior to use as environmental amendments. Further toxicity testing may be required for regulatory purposes; however, results of the toxicity tests undertaken thus far provide a general indication of the degree of toxicity of leachates from these by-products. In addition, the toxicity tests reported herein provide an additional framework by which to evaluate the potential for environmental reuse of selected by-products.

Table 96. Summary of major elemental composition of Bassendean Sand (BS) reference material, neutralised unused acid (NUA), steelmaking by-product (SS), red mud (RM), red sand (RS), reduced red sand (RRS), laterite, calcined magnesia (CM), groundwater treatment plant (GWTP) lime and $CaCO_3$ residues, fly ash (FA) and granular activated carbon (GAC) as determined by fusion X-ray fluorescence (XRF) analysis.

By-product	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	Cl (ppm)	Sum (%)
BS	98.21	0	0.11	0.39	0	0	0.07	0	0	0.07	0.02	0	98.9
NUA	4.3	1.0	1.7	22.7	2.7	1.8	25.1	0.2	0.08	0.1	31.0	550	90.7
SS	29.5	0.6	14.2	4.6	0.7	9.1	35.6	0.1	0.03	1.1	0.3	168	95.7
RM	6.8	2.9	42.7	36.2	0.004	0.03	0.03	<0.006	0.02	0.05	0.05	181	88.8
RS	2.6	1.9	20.7	73.0	0.06	0.01	0.3	0.9	-	0.07	0.07	0	-
RRS	2.3	4.1	21.0	89.5	0.05	<0.01	0.5	<0.01	0.02	0.1	0.2	<50	117.8
Laterite	6.8	2.9	42.7	36.2	0.004	0.03	0.03	<0.006	0.02	0.05	0.05	181	88.8
CM	-	0	0.01	0.06	0.13	90.32	3.21	0	0	0.01	0	0	93.7
GWTP Lime	11.6	0.04	0.9	0.3	0.001	6.8	45.4	0.03	0.3	0.2	0.5	672	66.2
GWTP $CaCO_3$	0.5	<0.003	0.3	0.5	<0.001	0.6	49.7	<0.002	<0.002	0.03	0.09	275	51.8
Fly ash	49.6	1.2	22.4	9.7	0.1	1.1	1.6	0.3	0.8	1.2	0.3	149	88.3
GAC	<0.005	0.1	1.3	0.08	0.1	0.4	1.7	0.03	0.2	0.1	0.05	32	4.1

Table 97. Summary of pressed powder X-ray fluorescence (XRF) trace elemental composition of Bassendean Sand (BS) reference material, neutralised unused acid (NUA), steelmaking by-product (SS), red mud (RM), red sand (RS), reduced red sand (RRS), laterite, calcined magnesia (CM), groundwater treatment plant (GWTP) lime and $CaCO_3$ residues, and fly ash (FA). All elements are expressed as parts per million (ppm).

	Ag	**As**	**Ba**	**Bi**	**Br**	**Cd**	**Ce**	**Co**	**Cr**	**Cs**
BS	0.3	<0.4	21	1	2	0.5	39	<2.0	287[1]	3
NUA	0.3	10	38	0.03	<2	<0.1	95	172[3]	80	1
SS	<4	5	468[3]	<4	<1	<5	125	<7	118[1]	<13
RM	17[2]	26[1]	38	5	17	9[1]	58	12	496[1]	7
RS	ND[†]	ND	ND	ND	ND	ND	ND	<100	700[1]	ND
RRS	ND	<DL[‡]	<DL	ND	ND	60[1]	ND	<DL	1270[1]	ND
Laterite	<8	28[1]	<32	<8	5	<8	47	16	513[1]	<17
CM	<2	2	17	<2	<1	<2	<12	15	8	<7
GWTP Lime	<4	8	77	<3	<1	<4	<20	<5	66	<11
GWTP $CaCO_3$	<4	5	237[3]	<3	<1	<4	<20	<5	9	<11
FA	<4	17	3741[3]	3	4	4[1]	407	183[3]	170[1]	19

	Cu	**Ga**	**Ge**	**Hf**	**Hg**	**I**	**La**	**Mn**	**Mo**	**Nb**
BS	3	1	<0.4	0	1	1	30	ND[†]	14	8
NUA	44	26	<0.4	1	<0.01	1	35	ND	3	17
SS	<2	<2	<2	<10	<16	<9	50	5232	<1	11
RM	67	59	<6	8	ND	71	7	205	8	20
RS	200[1]	ND	ND	ND	ND	ND	ND	200	ND	ND
RRS	140[1]	90	ND	ND	ND	ND	ND	370	30	ND
Laterite	5	70	<4	<22	<35	19	<30	63	8	32
CM	15	<1	<1	<6	<9	5	<12	1038	<1	1
GWTP Lime	2	3	1	<8	<13	<8	<18	57	1	4
GWTP $CaCO_3$	<1	<1	<1	<8	<13	<8	<18	118	<1	2
FA	100[2]	45	12	12	<13	<8	229	1035	16	66

[†] ND = not determined

[‡] <DL = less than detection limit

[1] Exceeds contaminant acceptance threshold value in grade C1 biosolids (Table 2; DEHP, 2002)

[2] Exceeds recommended interim sediment quality guidelines (Table 2; ANZECC/ARMCANZ, 2000)

[3] Exceeds soil maximum permissible concentration (Table 2; Crommentuijn et al., 1997)

Table 97 (continued). Summary of pressed powder X-ray fluorescence (XRF) trace elemental composition of Bassendean Sand (BS) reference material, neutralised unused acid (NUA), steelmaking by-product (SS), red mud (RM), red sand (RS), reduced red sand (RRS), laterite, calcined magnesia (CM), groundwater treatment plant (GWTP) lime and $CaCO_3$ residues, and fly ash (FA). All elements are expressed as parts per million (ppm).

	Nd	Ni	Pb	Rb	Sb	Sc	Se	Sm	Sn	Sr
BS	ND[†]	16	3	2	<0.8	ND	1	ND	2	7
NUA	<7	90[1]	21	6	0.4	<7	5.4[1]	<8	3	725
SS	37	<2	<3	8	<9	<7	2	<14	<4	1307
RM	6	5	24	<9	8[3]	55	4[1]	16	21	101
RS	ND	<100	ND	ND	ND	ND	ND	ND	ND	ND
RRS	ND	360[1]	180[1]	ND	ND	ND	ND	ND	320[3]	20
Laterite	<22	30[2]	29	<6	<18	22	<4	<23	<7	6
CM	<7	159[1]	<2	2	<5	5	<1	<8	<2	56
GWTP Lime	<11	<2	<3	15	<8	<7	<2	<11	<3	1411
GWTP $CaCO_3$	<11	<2	<3	5	<8	<7	<2	<11	<3	935
FA	158	283[1]	53[2]	62	<8	30	11[1]	15	9	2062

	Ta	Te	Th	Tl	U	V	Y	Yb	Zn	Zr
BS	ND[†]	ND	7	3	<0.9	9	5	1	3	72
NUA	<5	<0.1	112	0.07	6	71[3]	19	1	30	16
SS	<8	<8	19	10[3]	12	117[3]	64	<12	<3	164
RM	18	35	21	6[3]	4	1112[3]	6	11	29	519
RS	ND	ND	ND	ND	ND	900[3]	ND	ND	<100	400
RRS	ND	ND	ND	ND	ND	1790[3]	ND	ND	40	500
Laterite	<19	<16	47	9[3]	7	577[3]	12	<29	<7	575
CM	<5	<5	3	6[3]	1	4	8	15	2	<1
GWTP Lime	9	<7	9	7[3]	16	8	10	<10	9	32
GWTP $CaCO_3$	9	<7	7	8[3]	7	<7	5	<10	<2	19
FA	<7	<7	57	29[3]	28	156[3]	142	<10	353[1]	443

[†] ND = not determined

[1] Exceeds contaminant acceptance threshold value in grade C1 biosolids (Table 2; DEHP, 2002)

[2] Exceeds recommended interim sediment quality guidelines (Table 2; ANZECC/ARMCANZ, 2000)

[3] Exceeds soil maximum permissible concentration (Table 2; Crommentuijn et al., 1997)

Table 98. Summary of material U-Th series, ^{40}K and ^{137}Cs mean isotopic composition, and absorbed dose rate (D). All radionuclide units are in Bq kg^{-1}, with standard errors generally 5-10% of the mean.

Material	**^{238}U**	**^{230}Th**	**^{226}Ra**	**^{210}Pb**	**^{232}Th**	**^{228}Ra**	**^{228}Th**	**^{40}K**	**^{137}Cs**	**D (nGy h^{-1})**
BS	2.5	2.7	4.8	5.2	4.3	4.5	4.9	3.2	0.4	4
NUA	55	112	12.8	14.4	360	128	187	28.8	0.3	263
SS	73	75	79	3.1	50	49	50	8.6	<DL[†]	65
RM	64	62	68	66	127	136	143	24.1	<DL	112
RS	35.0	45.5	41.7	42.4	96	104	104	8.1	<DL	79
RRS	64	63	62	19.3	139	145	152	13.1	<DL	120
CM	1.2	5.9	2.5	1.3	7.3	0.8	8.6	0.04	<DL	5
GWTP CaCO$_3$	2.8	1.2	35.6	<DL	2.7	56	27.5	3.1	<DL	3
GWTP Lime	47.6	20.7	4.0	15.8	10.6	4.7	9.8	85	<DL	31
Laterite	51	64	78	72	167	190	201	18.8	<DL	133
GAC	<DL	0.1	3.6	0.2	1.8	6.3	9.6	46.1	<DL	3
FA	109	148	169	164	174	180	204	198	<DL	170

[†] DL = detection limit.

Table 99. Summary of results from algal growth rate, cladoceran mobility and Microtox® toxicity tests using leachates from neutralised unused acid (NUA), steelmaking by-product (SS), red mud (RM), red sand (RS), and calcined magnesia (CM).

	Algal Growth Rate			**Cladoceran Mobility**			**Microtox® 5-minute exposure**			**Microtox® 15-minute exposure**		
Material	NOEC	LOEC	IC50	NOEC	LOEC	EC50	NOEC	LOEC	EC50	NOEC	LOEC	EC50
NUA	11%	33%	>100%	100%	>100%	>100%	82%	>82%	>82%	82%	>82%	>82%
SS†	33%	100%	>100%	100%	>100%	>100%	41%	82%	>82%	41%	82%	>82%
RM†	<0.1%	0.1%	60%	25%	50%	47%	82%	>82%	>82%	82%	>82%	>82%
RS†	100%	>100%	>100%	100%	>100%	>100%	41%	82%	>82%	41%	82%	>82%
CM†	100%	>100%	>100%	100%	>100%	>100%	82%	>82%	>82%	82%	>82%	>82%

†Toxicity testing results of leachate adjusted to pH 8; toxicity may be greater at natural (unadjusted) pH of by-product leachate.

4.2. Assessment of Potential for By-Product Reuse

To aid in the assessment of possible suitability for environmental application, for each of the characteristics investigated the materials have been classified based on available information and existing guidelines for biosolids, soils and sediments (Table 100). In the absence of a specific application scenario and associated environmental background information, this classification scheme is somewhat arbitraty; however, it does provide a general assessment framework for possible by-product reuse. In addition, the classification scheme indicates for each material which characteristics, if any, may be of potential concern and where further investigation, or in the event of field trials, targeted monitoring may be required.

Although some of the materials assessed contain potentially harmful elements, the bio-availability and thus potential risk posed cannot be determined based on composition alone. As a result, none of the materials have been eliminated from further investigation at this time. Additional work may indicate that potentially toxic elements contained in an individual by-product are not likely to be released from the material under specific conditions of use, or that combination with one or more additional materials or dilution in a nominally unreactive solid phase could reduce the concentration of potentially harmful elements and the associated risk to an acceptable level. In addition, physicochemical characteristics of a particular by-product may vary based on both the source material and the process by which the by-product is generated. For example, although the red mud examined here exhibited moderate radioactivity and relatively high concentration of potentially toxic elements, red mud from a different source may have a lower metal content but higher radioactivity.

Additional investigation under controlled conditions such as field or pilot trials is required prior to the field-scale re-use of by-product materials as environmental amendments. Important considerations influencing the potential end-use of any of these products include the character of the waste stream or nature of the issue being addressed, the physical suitability of a material for the designed treatment and/or the degree of processing or pre-processing required for use of a given product in any particular treatment scheme, the projected lifespan of a given material, and any future costs associated with replacement, removal or disposal of spent materials.

The characterisation of by-products and complimentary materials undertaken in this study establishes a basis to undertake laboratory-scale column trials to investigate specific material performance aspects such as acid neutralisation, metal and nutrient attenuation, and DOC removal from water. At the completion of the column trials a further assessment will be made of the potential application of materials for specific problems such as neutralisation of acidity or removal of metals and/or nutrients from wastewaters as outlined in the by-product characterisation scheme in Figure 1. Consideration will also be given to the production of specific blends of by-product materials where there is potential for complementary (*e.g.* removal of two or more contaminants of concern) or synergistic (*e.g.* increased combined removal capacity over individual materials) effects. Where materials with potential benefit have been identified, discussions will be held with both the industry owners of the by-product material(s) to secure sufficient quantities for field trials, and appropriate State government agencies to identify specific testing sites, and to jointly initiate the regulatory and approval processes to conduct the trial(s). The Department of Water is a core participant in the project and will actively participate in site selection and trial planning and approval.

Table 100. Summary of characteristics of materials examined that are pertinent to reuse as soil amendments or in water treatment schemes. A = within acceptable range; L = low; H = high. ND = not determined. Values in red fall outside acceptable ranges.

Material	Chemistry			Radioactivity[4]	Environmental Toxicity			Potential Barriers to Application
	pH[1]	EC[2]	Potentially toxic elements[3]		Algal growth	Cladoceran mobility	Microtox®	
Bassendean Sand	L	A	Cr	A	ND	ND	ND	**N/A**
NUA	A	A	Co, Ni, Se, V	A-H	L	L	L	moderate to high radioactivity, may require dilution
Steelmaking by-product	A	A	Ba, Cr, Tl, V	A-H	L[†]	L[†]	L[†]	moderate to high radioactivity, high leachate pH
Red sand	A	A	Cr, Cu, V	A-H	L[†]	L[†]	L[†]	moderate to high radioactivity, high leachate pH
Reduced red sand	A	A	Cd, Cr, Cu, Ni, Sn, V	A-H	ND	ND	ND	moderate to high radioactivity, may require dilution, processing required
Laterite	A	A	As, Cr, Ni, Tl, V	A-H	ND	ND	ND	moderate to high radioactivity, may require crushing
Fly ash	A	A	Ba, Cd, Co, Cr, Cu, Ni, Pb, Se, Zn, Tl, V	A-H	ND	ND	ND	low density, moderate to high radioactivity, may require dilution, high metal/metalloids
GWTP CaCO$_3$	H	A	Ba, Tl	A	ND	ND	ND	high solid pH
Red mud	H	H	Ag, As, Cd, Cr, Sb, Se, Tl, V	A-H	H	H	L[†]	high solid/leachate pH, moderate to high radioactivity, high EC, moderate - high metal/metalloids
Calcined magnesia	H	A	Ni, Tl	A	L[†]	L[†]	L[†]	high solid/leachate pH
GWTP lime	H	H	Tl	A	ND	ND	ND	may require dewatering, low bulk density, high pH, high EC
GAC	H	A	ND	A	ND	ND	ND	very low density, high pH

[1] A = pH 5.0 - 8.5, acceptable range for plant growth and soil microbial activity (McBride, 1994). Low (L) = <5.0; high (H) = >8.5.

[2] EC > 4 mS cm^{-1} = high (H)/saline (McBride, 1994). Acceptable (A) = <4 mS cm^{-1}.

[3] Elevated concentrations based on existing guidelines for biosolids (DEHP, 2002), soils (Crommentuijn et al., 1997) and sediments (ANZECC/ARMCANZ, 2000).

[4] Acceptable radioactivity (A) = <54 nGy h^{-1} (UNSCEAR guideline radioactivity = 11-54 nGy h^{-1}; UNSCEAR, 1998); Moderate to High (H) = >54 nGy h^{-1} – may require dilution/also dependent on radionuclide speciation and mobility.

[†] Toxicity of leachate adjusted to pH ~8; toxicity of leachate at natural pH may be higher.

Importantly, not all mining, mineral processing and industrial by-products will be suitable for environmental application, and it is unlikely that any single material will remove every contaminant of interest, or be suitable for a full range of potential applications. The objective of this report is to characterise by-products, principally from Western Australia, with the aim of identifying by-products or optimised mixtures of materials suited to specific environmental applications. Both the characteristics of the wastewater or contaminant of interest and the physical design of the treatment scheme will influence the suitability of individual by-products. The physicochemical characterisation of by-products indicates that certain by-products may be restricted in their applications, thus the focus on the identification of by-products that are "fit for purpose". For example, a material with low bulk density such as GAC is unlikely to be suitable for soil amendment due to the resultant destabilisation of the soil surface and susceptibility to erosion. Likewise, an alkaline material such as CM is unlikely to be suitable as the sole material for water filtration in an ecologically sensitive environment.

5. CONCLUSIONS AND FUTURE WORK

The physicochemical and selected toxicological assessments of mining, mineral processing and industrial by-products and complimentary materials reported here provide information essential in the assessment of potential by-product suitability as environmental amendments. Based on their Ca, Fe and/or Al content, red mud, red sand, reduced red sand, steelmaking by-product, NUA, fly ash and lime- or $CaCO_3$-based groundwater treatment plant residues may have a high anion uptake capacity and thus may be suited to the removal of excess P from surface waters or wastewater streams. By-products comprised of substantial quantities of poorly crystalline Fe/Al/Mn (oxy)hydroxide minerals (e.g., ferrihydrite), including red mud, red sand, reduced red sand, NUA and laterite, may be useful for sorption of metals. By-products such as calcined magnesia, red mud, steelmaking by-product, and fly ash exhibit high acid neutralisation capacity and may be suited for remediation of acidic drainage waters.

In future research within this Water Foundation project, by-products and complimentary materials will be evaluated in column studies singly and/or in mixtures. Individual materials or hybrid mixtures will be selected on the basis of geochemical and mineralogical characteristics which may prove useful for the amelioration of acidity and attenuation of metals and/or excess nutrients in surface and/or groundwaters. A series of one metre long stainless steel columns will be packed with homogenised Bassendean sand with the intermediate third of the column comprising a blend of one or more by-product materials and the Bassendean sand. Columns comprised only of Bassendean sand will be used as controls. All columns will be maintained in a bottom-up flow through configuration under ambient conditions. The Bassendean sand and experimental influent water will remain unsterilized to allow the development of endemic microbial flora.

The multi-layer column set-up is designed to simulate the configuration of eventual real-world pilot- or full-scale applications such as:

- a constructed wetland amendment;
- an in-situ groundwater permeable barrier;
- a soil amendment; or
- a water/wastewater filtration system.

Column studies will facilitate examination of characteristics of by-products affecting their suitability as environmental amendments, such as permeability and porosity or changes to permeability or porosity over time, and the limit of effectiveness of each by-product (*e.g.*, breakthrough curves). The column experiments will be conducted over a period of approximately 6-12 months or until contaminant release or breakthrough occurs.

The influent water and column effluents for individual and hybrid materials will be monitored for a range of parameters to evaluate the retention, attenuation and/or transformation of important organic and inorganic species. These parameters are as follows:

- total nitrogen;
- total phosphorus;
- major cations (Na, K, Ca, Mg, Fe, Al, Mn, Si);
- metals (Co, Ni, Pb, Cu, Zn, Cd, Cr, Se, As);
- major anions (Cl, SO_4, HCO_3);
- pH; and
- EC/salinity.

The chemistry of the column effluent will be modelled using geochemical software such as PHREEQC to facilitate an understanding the processes occurring in each of the columns. The results of this study will provide required information for the design of in-field trials using the most appropriate industrial by-product materials.

In a broader context, it is unlikely that a single low-cost industrial by-product possesses all the physicochemical characteristics necessary for a range of applications including the treatment of waters and soils. Combinations of two or more by-product materials, however, may provide the properties necessary for successful amelioration of challenges posed by surface water and soil acidity and sorption of nutrients and potentially toxic metals. Further investigation is required to examine the effects of combining by-products on the characteristics of each material. In some cases mixing by-products may have a synergistic result, as in the mixture of materials with high calcium carbonate equivalent with highly degradable organic material resulting in a material capable of neutralising subsoil acidity (Brown and Chaney, 2000).

In addition to the investigation of contaminant attenuation under controlled conditions, it is necessary to evaluate the risk posed by different materials to the environment based on a comparative risk assessment of each treatment and taking into account relevant pathways of exposure, environmental endpoints, and the sensitivity of such endpoints. This is especially relevant where waters discharge into ecologically-sensitive receiving environments.

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