



A Review of Mining and Industrial By-Product Use as Environmental Amendments

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August 2009

A Report to the Water Foundation of Western Australia

Water for a Healthy Country Flagship Report series ISSN: 1835-095X

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Citation: Wendling, L. and G. Douglas. A Review of Mining and Industrial By-Product Use as Environmental Amendments. CSIRO: Water for a Healthy Country National Research Flagship Report. August 2009. CSIRO: Perth, Western Australia. 64 pp.

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ACKNOWLEDGMENTS

The authors gratefully acknowledge Iluka Resources, Ltd., Rio Tinto Hismelt and the Western Australian Government for support provided through the Water Foundation and the Department of Water.

EXECUTIVE SUMMARY

Effective removal of nutrients and trace metals from industrial, agricultural and domestic wastewater is pivotal to efficient water re-use. Utilisation of abundant, low-cost mining and industrial by-products as treatment media potentially offers a cost-effective wastewater treatment option. Mineral-based by-products may be effective for the treatment of wastewater previously discarded or treated by less efficient or more costly means. The primary advantages to using by-products as environmental amendments are economic viability (low cost) and waste reduction.

One of Western Australia's most pressing environmental concerns involves the highly acidic, hypersaline drainage waters within the WA wheatbelt. In terms of remediation, the acidic waters of the WA wheatbelt are broadly analogous to acid mine drainage (AMD). Feasible management options for treatment of WA wheatbelt drainage waters may include the use of by-products with inherent acid-neutralising capacity as surface water amendments, within-drain filtration/treatment systems, and/or permeable reactive barriers.

Excess nutrient accumulation due to the mobilisation and leaching of fertilizers, urban development, the use of P-containing detergents, and disposal of untreated human and animal wastes also poses a threat to Western Australia's aquatic systems. The rapid depletion of dissolved oxygen, a consequence of excessive growth and subsequent decay of aquatic plants and algae, negatively impacts freshwater aquatic systems. The use of by-products in constructed wetlands, permeable reactive barriers, drain liners, or other intervention schemes may provide a cost-effective means of reducing nutrient inputs to freshwater systems.

In Western Australia, re-use of industrial by-products is currently considered on a case-by-case basis rather than regulated according to established standards. Use of by-products may be justified where nominally benign materials contain significant quantities of nutrients or provide a source of alkalinity (e.g., a lime substitute). Mining and industrial by-products, particularly those products with large acid neutralisation capacity, may be useful for the amelioration and neutralisation of acid sulfate soils (ASS), now recognised as a major issue on the Swan Coastal Plain.

Additional by-product characteristics with a potential environmental benefit may include improvements in soil physico-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. Mining, mineral-processing and industrial by-products which possess characteristics indicative of potential benefit as soil or surface water amendments, and that are generated in large quantities in WA, include: red mud, flue gas desulfurisation gypsum, cement kiln dust, steelmaking by-products, heavy mineral processing residues, fly ash, calcined magnesite and water treatment residues.

As the world's largest producer of bauxite, each year the Australian mining industry generates thousands of tonnes of red mud and red sand, by-products of the production of alumina from bauxite via the Bayer process. In laboratory studies, red mud has demonstrated a substantial capacity for sorption of metals and metalloids. In addition, neutralised red mud has been demonstrated to successfully adsorb P in both laboratory and field-based studies.

Gypsum is present in Western Australia as both a mined natural mineral and as a gypsum slurry by-product generated during power generation in the post-combustion limestone-gypsum wet flue gas desulfurisation. Some studies indicate that gypsum may be suitable as a surface water

amendment for the reduction of soluble P. Soil amendment with flue gas desulfurisation gypsum has been shown to reduce subsoil acidity.

Iron-rich heavy mineral processing residues are generated in large quantities in Western Australia and exhibit high P and N sorption capacity. These heavy mineral processing residues have substantial potential for both water treatment and soil amendment.

Cement kiln dust has potential applications for neutralisation of acidity due to its alkalinity. Studies demonstrate the removal of metals from solution by cement kiln dust via precipitation as metal hydroxides, and phosphate precipitation as hydroxyapatite. Cement kiln dust contains relatively high levels of some metals, presenting a potential limitation of cement kiln dust use as an environmental amendment. The primary concern associated with the use of cement kiln dust for treatment of AMD or similar acidic solutions is the possible release of potentially toxic metals.

Steelmaking by-products may also be useful for the neutralisation of acidity. As part of the steel-making process the by-products are enriched in minerals containing mostly Mg, Ca and Si. Consequently, these materials have an inherently high capacity to neutralize acidity. Some steelmaking by-products have been shown to have a rapid and substantial trace element or nutrient uptake capacity, particularly when the adsorbate was an oxyanion such as phosphate or chromate.

The presence of a large-scale magnesia industry in Australia means distinct advantages in both cost and supply of calcined magnesia (MgO). Calcined magnesia possesses considerable chemical and operational advantages over other alkalis such as $\text{Ca}(\text{OH})_2$ in the neutralisation of acidic wastes. In addition, results of some laboratory studies show a substantial reduction in metal concentration in effluents following passage through columns containing MgO. These results suggest that MgO may be suitable for treatment of AMD or other acidic, metal-containing liquid waste streams.

Fly ash is the fine-textured mineral residue generated during the combustion of coal to generate electricity. Given the inherent alkalinity of fly ash, numerous studies have examined its use to neutralize AMD in surface or subsurface environments. Fly ash composition varies as a function of the coal source, but is generally enriched in a number of trace elements which may potentially become bio-available in environmental applications.

In metropolitan Perth, Western Australia, selected residues from treatment of groundwater are currently re-used as soil amendments at Gngangara Mound and Jandakot Airport. Compositions and characteristics of water treatment residues are variable due to differences in treatment processes at the industrial level, and the different minerals and feed waters involved. A number of studies have documented the effectiveness of water treatment residues, particularly those derived from treatment processes utilising alum as a coagulant, in P sorption.

Activated carbon is widely used in applications including gas and water purification, gold recovery, and sewage treatment. In Western Australia, large quantities of activated carbon are generated during the processing of mallee eucalyptus trees.

Natural minerals which may be contained within mine overburden such as carbonates or carbonate derivatives, clay minerals, zeolites and/or hydrotalcites also have potential applications as water or soil amendments. Mine overburden is of intrinsically low value, and if in close proximity to sources of acidity could potentially be used as a long-term neutralizing agent. The use of limestone (CaCO_3) as a soil or surface water amendment to neutralise acidity is in

common practice. Dolomite ($\text{Mg,Ca}(\text{CO}_3)_2$), CaCO_3 and lime ($\text{Ca}(\text{OH})_2$), have been used for centuries as amendments to neutralise acidic agricultural soils.

Under appropriate conditions, clay minerals can play a significant role in the sorption or sequestration of contaminants. Clay minerals exhibit both pH-dependent charge at edge sites and permanent (pH-independent) charge due to isomorphic substitution of cations in the mineral structure. Clay minerals have long been employed in environmental applications such as liners for landfills, in radioactive waste disposal sites, and in water clarification.

Zeolites are aluminosilicate minerals with a cage-like structure and may be either naturally-occurring or synthetically produced, for instance from fly ash. Natural zeolites have many uses, including: sorption of organic molecules, radionuclides, metals and ammonium from waters, soils and sediments; application as slow-release fertilisers; use as plant growth media; and as dietary supplements or metal sequestering agents in animal nutrition. Zeolites have also been synthesized for catalytic or ion-sieving applications that may also have potential in a wider environmental context.

Hydrotalcites are a class of layered double hydroxide minerals commonly formed via the co-precipitation of divalent and trivalent metal ions from solution at moderate to high pH. Laboratory investigations using Mg-Al hydrotalcites have demonstrated substantial phosphate sorption capacities. Hydrotalcite-like compounds have also demonstrated an ability to absorb a suite of other anions, including arsenate, selenite and borate.

Extensive study is required to quantify the efficacy of acid neutralisation and removal of nutrients and/or potentially toxic elements from waters, to fully characterise the geochemical interactions between mineral-based materials and contaminants, and to analyse resultant waters for ecotoxicity. Research undertaken within the Water Foundation project “Wastewater purification and re-use: Mineral-based sorbents for contaminant removal” (PWF 009-05) has characterised the nutrient, trace element uptake and acid neutralising capacity of a range of low-cost by-products with a view to the productive use of by-products to address a range of environmental challenges.

1. INTRODUCTION

Effective removal of nutrients and trace metals from industrial, agricultural and domestic wastewater is pivotal to efficient water reuse. Utilisation of abundant, low-cost mining, mineral processing and industrial by-products as treatment media potentially offers a cost-effective wastewater treatment option. By-products may have potential for use in water purification and reuse for a suite of applications as diverse as managed aquifer recharge, industrial, and agricultural wastewaters. In addition, some solid by-product materials may be beneficial 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 reuse of previously unused or underutilised materials as low-cost contaminant sorbents or neutralising agents.

2. BY-PRODUCTS AS SOIL AMENDMENTS

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 efficacy or 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 CFR 257-268) which specifies regulatory limits for disposal of industrial by-products based on flammability, corrosiveness and toxicity. Toxicity is generally assessed using the US Environmental Protection Agency's (US EPA) toxicity characteristic leaching procedure (TCLP) (EPA, 1992). 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.

Industrial by-products nominally identified or classified as non-hazardous according to regulations or guidelines are not necessarily beneficial to the environment or even safe as environmental amendments if used inappropriately. Considerable research is required to identify potential hazards associated with land application, including surface and groundwater contamination, plant uptake and transport or bioaccumulation 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).

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 reuse 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. 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 reuse 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 (Table

1). Untested materials or concentrations higher than C2 are classified as C3. The contaminant grade of a product determines its suitability for reuse, 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.

Table 1. 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.

The total metal or metalloid content of a material or site is an important measure used to assess risk from contamination; however, total metal or metalloid content, however, does not provide information on the bioavailability, mobility or fate of a metal contaminant. Metal or metalloid 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 (Cr³⁺), which generally exists in aqueous solution as either [Cr(H₂O)₆]³⁺ or [Cr(H₂O)₅OH]²⁺, is far less toxic than hexavalent Cr (Cr⁶⁺), or CrO₄²⁻. This is due to the ability of the chromate oxyanion to cross cellular membranes using phosphate/sulfate transporters, whereas Cr³⁺ is unable to cross cell membranes (Duffus, 2005).

In addition, the chemical speciation of elements significantly influences their toxicity, bioavailability, lability, biogeochemical behaviour and potential risk. From an initial 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 ($\text{PbS}_{(s)}$; $K_{sp} = 10^{-28.1}$) and the other contained Pb mainly in the form of cerussite ($\text{PbCO}_{3(s)}$; $K_{sp} = 10^{-13.13}$) the soil with galena Pb would pose significantly less threat due to the 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. If the soils were heavily oxidising, however, it might be expected that galena may, with sufficient time and the absence of sufficient inherent buffering capacity in the soil, be the more reactive mineral. 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 also 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 during possible reuse.

Naturally-occurring soils containing sulfidic minerals, primarily iron sulfides in the form of pyrite, that have undergone oxidation are referred to as acid sulfate soils (ASS). These soils generally have $\text{pH} < 4$ and may exhibit yellow and/or red mottling in the soil profile due to the formation of secondary minerals such as jarosite. Acid sulfate soils are widespread in Western Australia and are normally found in coastal regions, or associated with freshwater wetlands or saline, sulfate-rich groundwater in some agricultural areas such as the Wheatbelt. Under reduced (anoxic) conditions, ASS do not present a substantial risk to human health or to the environment. Soils containing sulfidic materials that have not been oxidised are referred to as potential acid sulfate soils (PASS). Exposure of PASS to oxygen by activities such as excavation or drainage may result in adverse changes to soil and water quality. Exposure of sulfidic materials to oxygen leads to the production of sulfuric acid. In addition to direct effects, such as corrosion of metallic and concrete structures, acidification mobilises potentially toxic elements such as Al from the soil solid phase. Application of limestone or lime (CaCO_3 or CaO) is the conventional method of acid neutralisation in soils; however, the use of by-products with substantial acid neutralisation capacity and in particular those which have a low trace element concentrations and form a stable secondary (post-neutralisation) mineralogy may provide a cost-effective alternative.

Industrial, mining and mineral-processing by-products may also be applicable to the reduction of nutrient loss from urban and agricultural areas. Leaching of applied nutrients, particularly phosphorous, presents a major problem in the largely unretentive soils in coastal regions of South West Western Australia. Off-site transport of nutrients is not only costly in terms of increased fertiliser requirements to maintain agricultural productivity, but is detrimental to adjoining or regional and coastal aquatic systems. Excess bioavailable nutrients, P in particular, is a major factor leading to the eutrophication of natural waters and the resultant degradation in water quality. Application of materials with the capacity to sorb excess nutrients and reduce nutrient loads to local water bodies has the potential to improve or protect the ecological integrity of freshwater systems impacted by fertiliser use.

In Western Australia, reuse of industrial by-products is currently considered on a case-by-case basis rather than regulated according to established standards. Land application of industrial by-products may be justified where environmentally benign by-products contain significant quantities of nutrients or provide a source of alkalinity (e.g., a lime substitute). 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), organic carbon (OC) content. In addition to

physicochemical characteristics and potential toxicity, local availability, source variability and the annual quantity of by-product generated or existing inventory will significantly influence the applicability of various by-products as environmental amendments.

3. BY-PRODUCT USE IN WATER TREATMENT

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. The productive reuse of these by-products is currently considered on a case-by-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 rapid population growth and associated development, has Australia's highest rates of climate change, manifested in a substantial decrease in winter rainfall since 1975 (Swan River Trust, 2007). This reduction in rainfall has led 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, thus facilitating its productive reuse. 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 further reduce pressure on water resources.

The composition of wastewater is dependent upon its source and level, if any, of treatment. For example, agricultural wastewaters may be expected to contain elevated concentrations of nutrients such as N and P, and sometimes herbicides and/or pesticides, whereas urban wastewater may also contain chlorides, metals and hydrocarbons in addition to nutrients. Industrial effluents in particular may be comprised of complex mixtures of contaminants (Table 2). Processes as diverse as the manufacture of catalysts, electrical equipment, antibacterial agents, fertilisers, insecticides and fungicides, pyrotechnics, metal alloys, piping, pigments and stabilisers, petroleum 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 potentially toxic elements such as 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 sulfate soils (ASS). Acid mine drainage occurs when sulfide-bearing minerals in rock are oxidised, transforming the sulfur in metal sulfides to sulfuric 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, given the same composition, the more surface area of rock exposed, the greater the amount of acid produced. During the mining process, hundreds or sometimes thousands of tons of rock are unearthed, crushed and subjected to extractive metallurgical techniques 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 sulfide 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 (Figure 1). 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 2. Major contaminants in effluents from food, chemical and materials industries (McKay, 1996).

| <i>Origin of contaminants</i> | | <i>Components and characteristics of contaminants</i> |
|-------------------------------|---|---|
| Food Industry | | |
| 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 | | |
| Acids | Wash waters, spillage | Low pH |
| Detergents | Purifying surfactants | Surfactants |
| Starch | Evaporation, washing | Starch |
| Explosives | Purifying and washing cartridges | TNT, 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 | | |
| 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, sulfur, phenol, oil |
| Rubber | Washing, extracting impurities | Suspended solids, chloride, odour, variable pH |
| Glass | Polishing, cleaning | Suspended solids |

Unless continued dry climactic conditions impede rates of groundwater rise, the new hydrological equilibrium established by current agronomic practices is expected to facilitate the salinisation of 3-5 million ha of the WA Wheatbelt (Ali et al., 2004a; Clarke et al., 2002). Revegetation of cleared

areas with deep-rooted, perennial plants to manage salinity in parts of the WA Wheatbelt has met with mixed success; as a result, there is an increased emphasis on the use of engineering options to combat rising saline groundwaters (Clarke et al., 2002) and associated contaminants, particularly in acidic environments. 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 open 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. Concerns have been raised about the potential for increased flooding and adverse water quality effects from transported contaminants and acidity occurring at landscape scales arising from such drainage schemes.

Initial investigation of major drainage schemes near Narembeen in the WA Wheatbelt found that the deep open 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). These drainage waters can contain elevated concentrations for a range of elements including Al, Mn, Co, Ni U, Pb and the rare earth elements (Ali et al., 2004b; Degens et al., 2008a, 2008b; 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 (Degens et al., 2008a, 2008b; Lee and Gilkes, 2005; Mann, 1983). The large areal extent 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.

Surveys of drainage waters and shallow groundwaters in the Avon River Basin indicate that acidity is widespread in the northern, north-eastern, eastern and south-eastern Avon River catchment (Fitzpatrick et al., 2005; Rogers and George, 2005). Ferrollysis, or Fe hydrolysis, may be the dominant cause of surface water acidity in the Avon River catchment (Fitzpatrick et al., 2008; Mann, 1983; McArthur et al., 1991). In ferrollysis, reduced Fe in groundwater is oxidised upon exposure to oxygen (O) in air or infiltrating water, generating acidity in the form of protons (H⁺) and Fe oxyhydroxide precipitates (Mann, 1983):



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 over their life cycle on both a local and regional scale.

In terms of remediation, the acidic waters of the WA Wheatbelt can be categorised as broadly analogous to AMD waters (Degens et al., 2008b; Douglas and Degens, 2006). Although the primary source of acidity may be different, predominantly ferrollysis with some authigenic pyrite oxidation in drain sediments for the WA Wheatbelt (Fitzpatrick et al., 2005; Mann, 1983; McArthur et al., 1991) versus primary sulfide oxidation in AMD, the resultant acidity and high trace element burden present a similar remediation challenge of amelioration of acidity and concurrent trace element reduction. Similarly, the mineral suite present within the drainages of the WA Wheatbelt

(Fitzpatrick et al., 2005) is similar to that often observed in AMD (Ashley et al., 2004; Harris et al., 2003) or due to the disturbance of acid sulfate soils (Sullivan and Bush, 2004). A key difference between AMD and drainage waters of the WA Wheatbelt is the saline to hypersaline waters often present in the Wheatbelt relative to the often less saline waters encountered in AMD remediation scenarios (Degens et al., 2008b; Douglas and Degens, 2006).



Figure 1. The Avon River Basin, which contains part of the Western Australian Wheatbelt, south west Western Australia (Douglas and Degens, 2006).

The ionic strength of AMD is generally much less than that of seawater, while many of the WA Wheatbelt waters are orders of magnitude more hypersaline, often 2-3 times seawater salinity. Efforts have been made to understand acidification and related processes in saline to hypersaline waters (Bowell and Parshley, 2005; Bowman et al., 2000; Fitzpatrick et al., 1998; Harris et al., 2003; Lee and Gilkes, 2005) and natural attenuation mechanisms, such as secondary mineral precipitation (Biggam and Nordstrom, 2000; Buck et al., 2006; Gunsinger et al., 2006; Hammarstrom et al., 2005; Lee et al., 2002). Some of the techniques frequently employed to combat AMD (Akcil and Koldas, 2006; Bowman et al., 2000; Gazea et al., 1996; Johnson and Hallberg, 2005; Kuyucak, 2001; Sasowsky et al., 2000; Skousen, 1991; Skousen et al., 2006) and/or manage acid sulfate soils (Thomas et al., 2003a; Thomas et al., 2003b) may be relevant to the remediation of the acidic, saline waters of the WA Wheatbelt. Feasible management options for treatment of WA Wheatbelt drainage waters may include the use of industrial by-products to ameliorate acidity and/or trace element concentrations as surface water amendments, within-drain filtration/treatment systems, and/or permeable reactive barriers.

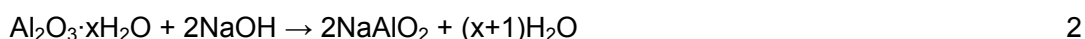
Acidification is not the only threat to Western Australian aquatic ecosystems. Excess nutrient concentrations in aquatic ecosystems can be attributed to the mobilisation and leaching of fertilizers, urban development, the use of P-containing detergents, and disposal of untreated human and animal wastes. The depletion of dissolved oxygen due to eutrophication as a consequence of excessive growth of aquatic plants and algae, negatively impacts these aquatic ecosystems. The use of by-products in constructed wetlands, permeable reactive barriers, drain liners, or other intervention schemes may provide a cost-effective means of reducing nutrient inputs to these ecosystems.

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, however, required to quantify the efficacy of acid neutralisation and removal of nutrients and/or 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. In addition, the ultimate fate and secure disposal of spent by-products in a suitable repository also has to be considered.

4. BY-PRODUCTS OF MINING AND MINERAL PROCESSING

4.1. Red Mud

One of the most characterised mining by-products is red mud (RM), generated during the production of alumina from bauxite via the Bayer process. The term bauxite refers to a naturally-occurring mixture of minerals rich in hydrated aluminium oxides, principally gibbsite, boehmite and diaspore. 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. The insoluble mud is thickened then washed to recover the caustic soda, which is recycled for reuse in the Bayer process. Traditionally, the RM by-products have been disposed via discharge to the ocean or storage in disposal ponds from which the excess water can be recycled to the alumina plant for partial recovery of additional alkali after the RM solids have settled.

The insoluble by-product of the Bayer process, known as RM due to its brick-red colour, is comprised primarily of the iron (Fe), titanium (Ti) and silica (Si) remnants of the bauxite ore. Red mud average particle diameter is <10 µm. The physical and chemical characteristics of RM are largely dependent upon the bauxite ore from which it was generated. The composition of RM residues varies widely: 20-60% ferric iron oxide (Fe₂O₃); 10-30% alumina (Al₂O₃); 2-20% silica (SiO₂); 2-10% sodium superoxide (NaO₂); 2-8% calcium oxide (CaO); and trace-28% titanium dioxide (TiO₂) (Paramguru et al., 2005). The variability in composition of RM generated during alumina production around the world is illustrated in Table 3 (Paramguru et al., 2005). Due to residual caustic alkalinity the untreated RM is highly alkaline, with pH generally > 11.

Australia is the world's largest producer of bauxite, mining 64 million tones in 2006 (AAC, 2007). In addition, Australia accounted for approximately 28% of world alumina production in 2006, producing 18.4 million tones (AAC, 2007). Approximately 50% of the RM generated worldwide each year comes from Australia (Paramguru et al., 2005); thus, the treatment and disposal of RM is a significant concern. In Western Australia alone, at current production rates approximately 36,000 tonnes of by-product from alumina refining are generated annually (Jamieson et al., 2006).

Until the early 1980's bauxite residues were disposed of as low-density slurries in impoundment areas, where solids settled into discrete zones of fine and coarse materials. Any remaining liquor was separated from the settled materials and recycled to the Bayer process. Several problems were encountered with this disposal practice, including the retention of large volumes of caustic soda within the waste stream, the escape of leachates from impoundments under high hydraulic gradients, and difficulties adequately dewatering the residues.

Table 3. Composition of red mud generated in alumina processing plants worldwide (Paramguru et al., 2005).

| Country | Producer | Major constituents (wt %) | | | | |
|-----------|--------------|--------------------------------|--------------------------------|------------------|------------------|-------------------|
| | | Fe ₂ O ₃ | Al ₂ O ₃ | TiO ₂ | SiO ₂ | Na ₂ O |
| India | Al. Corp. | 20.3 | 19.6 | 28.0 | 6.7 | 8.1 |
| | MALCO | 45.2 | 27.0 | 5.1 | 5.7 | 3.6 |
| | HINDALCO | 35.5 | 23.0 | 17.2 | 5.0 | 4.9 |
| | BALCO | 33.8 | 15.6 | 22.5 | 6.8 | 5.2 |
| | NALCO | 52.4 | 14.7 | 3.3 | 8.4 | 4.0 |
| Hungary | | 38.5 | 15.2 | 4.6 | 10.2 | 8.1 |
| Jamaica | | 50.9 | 14.2 | 6.9 | 3.4 | 3.2 |
| Surinam | | 24.8 | 19.0 | 12.2 | 11.9 | 9.3 |
| USA | ALCOA Mobile | 30.4 | 16.2 | 10.1 | 11.1 | 2.0 |
| | Arkansas | 55.6 | 12.2 | 4.5 | 4.5 | 1.5-5.0 |
| | Sherwon | 50.5 | 11.1 | Tr. | 2.6 | 9.0 |
| Germany | | 38.8 | 20.0 | 5.5 | 13.0 | 8.2 |
| Taiwan | | 41.3 | 20.2 | 2.9 | 17.9 | 3.8 |
| Australia | | 40.5 | 27.7 | 3.5 | 19.9 | 1.0-2.0 |

One current management strategy for alumina residue involves pumping the residue slurry to a storage area where solids are separated into two size fractions: sand (>150 µm particle diameter) and mud (<150 µm particle diameter). Sands can easily be stockpiled as they readily de-water. The drained sands can be utilized for construction purposes and will be discussed further in the following section. The fine fraction, or RM, is pumped into a thickening facility where it undergoes dewatering by consolidation aided by chemical flocculants to approximately 50% water content (w/w). As RM slurries thicken they are discharged from outlets at the perimeter of drying beds and spread over red sands in a uniform layer up to several hundred metres from the outlet and up to a metre in depth. Gravimetric drainage and solar drying combine to increase the slurry to 65-70% solids (w/w), whereupon a new slurry layer is applied. Liquors draining through and layers are recovered and recycled to the Bayer process. When the RM slurry has dried sufficiently and machinery are able to traverse the mud fields, the materials may be recovered for alternative use.

Several alumina refineries including Queensland Alumina Limited (QAL) near Gladstone employ seawater neutralisation to treat residual alkalinity in RM residues. After separation of RM from alumina-containing liquor, the mud is separated from the more coarse fraction (red sands, RS), then washed prior to pumping to a RM dam for storage. Residual NaOH in the RM is reacted with

seawater to neutralize alkalinity (e.g., seawater is used to decrease RM pH to ~9). Magnesium (Mg) and calcium (Ca) cations in seawater react with hydroxide (OH⁻), carbonate (CO₃²⁻) and bicarbonate (HCO₃⁻) anions to form magnesium hydroxide (Mg(OH)₂) and calcium carbonate (CaCO₃) precipitates:



Seawater contains approximately 1290 ppm Mg and 412 ppm Ca (Stumm and Morgan, 1996). Supernatant water following the addition of seawater to RM slurry is clear, total suspended solids (TSS) < 80 ppm, and suitable for discharge (Graham and Fawkes). Seawater neutralisation results in alterations to RM mineralogy, as well as enhanced acid neutralisation capacity (Lin et al., 2004, Thornber and Hughes, 1986). Other methods of RM neutralisation include treatment with sulfuric acid (H₂SO₄), or mixing with gypsum (CaSO₄).

A number of potential uses for RM have been suggested, including: fill material for mine voids and quarries; landfill cover; roadbed and levee materials; amendments for agricultural soils; soil filter mix for residential septic systems; production of iron oxide-based pigments for the construction industry; use as a component in ceramic products; and use in building materials or inorganic chemicals. One of the earliest proposed uses of RM was as an amendment to agricultural soils. Barrow (1982) investigated the use of RM as an agricultural amendment both in pot studies of plant growth and column studies of pH effects on the chemical characteristics of RM. Medic species (e.g. *Medicago polymorpha*, *M. littoralis*, *M. minima*, *M. tornata*, etc.) grown in RM neutralised with CaSO₄ and leached to remove excess Na exhibited good growth, which was limited by nutrient application (Barrow, 1982). As characteristic of a material with predominantly variable charge, RM exhibited decreased CEC and increased phosphate (PO₄³⁻) sorption as pH decreased. Barrow (1982) concluded that there was significant potential for the application of RM amended with gypsum to the acidic sandy soils of the Swan Coastal Plain to improve water and nutrient retention and thus agricultural productivity.

The sandy soils of the Swan River Coastal Plain are particularly susceptible to nutrient leaching due to their low sorption capacity. Irrigated vegetable production on the Swan Coastal Plain has the potential to introduce large quantities of the nutrients P and N into the Swan River system. Column studies have demonstrated that the addition of neutralised (CaSO₄-amended) RM to sandy soil from the Swan Coastal Plain significantly increased both the soil pH and CEC (McPharlin et al., 1994). Addition of the neutralised RM at rates equivalent to 64, 128 and 256 t ha⁻¹ inhibited P leaching by 49%, 49% and 85%, respectively (McPharlin et al., 1994). Neutralised RM addition did not affect nitrate (NO₃-N) leaching, but significantly reduced ammonium (NH₄-N) leaching as compared to untreated sand (McPharlin et al., 1994). Field investigation demonstrated that neutralised RM increased soil P fertiliser retention by as much as ca. 65% as compared to untreated control plots, with no yield reduction to carrots grown in RM-amended soils (Robertson et al., 1997).

Concerns have been raised about elevated levels of thorium (Th) and uranium (U) in neutralised RM, and the potential transfer of radioactivity from RM amended to soil via leaching to underlying water bodies or transfer to food crops grown on amended soils. McPharlin (1994) examined leachates from columns amended with neutralised RM for radium (Ra) isotopes; results indicated that soil amendment with neutralised RM posed little risk of an increase in radioactivity in underlying water bodies. A field investigation of the uptake of radionuclides of the U and Th series by vegetable crops showed no significant increase in radionuclide levels in vegetables grown on soils amended with neutralised RM (Cooper et al., 1995). In addition, study has shown that the

gamma (γ) radiation flux from sandy soils of the Swan Coastal Plain amended with red mud bauxite residue at rates below 1500 t ha^{-1} do not exceed UNSCEAR standards (Summers et al., 1993). At red mud amendment rates between 20 and 200 t ha^{-1} , Summers et al. (1993) report substantial P retention and γ activity little different from that of the unamended soil.

A number of studies have examined the use of RM and RM derivatives as adsorbents for metals such as arsenic (As) (Altundoğan et al., 2000; Altundoğan et al., 2002; Genç-Fuhrman et al., 2004a; Genç-Fuhrman et al., 2004b; Genç et al., 2003; Lombi et al., 2004), boron (B) (Cengeloglu et al., 2007), cadmium (Cd) and other metals (Apak et al., 1998; Barrow, 1982; Bhattacharya and Venkobachar, 1984; Brunori et al., 2005; Huang and Ostovic, 1978; Lombi et al., 2003; Lombi et al., 2002; López et al., 1998), radionuclides (Apak et al., 1995b) and nutrients (Akhurst et al., 2006; Cheung et al., 1994; Ho et al., 1992; Koumanova et al., 1997; McPharlin et al., 1994; Robertson et al., 1997; Shiao and Akashi, 1977; Summers and Pech, 1997; Summers et al., 1996; Ward and Summers, 1993). Neutralised RM has been demonstrated to successfully adsorb P in both laboratory and field-based studies. Although RM amendment effectively minimises P leaching and/or runoff, the suitability of RM for application to agricultural areas is dependent upon whether P sorbed to RM is readily available for plant uptake. Studies indicate that addition of RM to soil can reduce sodium bicarbonate extractable phosphorous (P) by 40-60% (Snars et al., 2003; Snars et al., 2004); however, no significant differences in plant yield were detected despite large differences in P concentration within plants grown in soils amended with RM at various rates (Snars et al., 2004). Snars et al. (2004) also observed that the addition of RM decreased both the availability of applied (fertiliser) P and the existing soil P. Additional study is required to quantify the effects of aging on P availability in RM amended soils, and to determine optimal P fertilisation rates for agricultural crops grown in soils amended with RM and RM derivatives.

The use of RM as an adsorbent for As has also been examined. In aqueous solution, untreated RM adsorbed 48 and 26% of initial As(III) and As(V), respectively (Altundoğan et al., 2000). Red mud was a better adsorbent of As(III) under alkaline conditions (pH \sim 9.5), but As(V) sorption decreased sharply above pH 3.2 (Altundoğan et al., 2000). Seawater-neutralised RM has been demonstrated to efficiently remove As(V) from aqueous solution; however, high amendment rates (e.g., $\geq 10 \text{ g L}^{-1}$) were required for effective water treatment (Genç et al., 2003). Recent work has shown that acid or acid and heat treatment of seawater-neutralised RM can increase As(V) sorption from 89% to 95% or approximately 100%, respectively (Genç-Fuhrman et al., 2004b). Acid treatment of RM is however, a detailed and costly process and is unlikely to be suitable for large-scale application. As has been reported for As, acid- and heat-treated RM was more successful in the removal of caesium (Cs) from aqueous solution than untreated RM; however, acid and heat treatment reduced the ability of RM to sorb strontium (Sr) (Apak et al., 1995b).

A later study determined that As(V) is more effectively removed from aqueous solution by modified calcined bauxite (MCB), which removed \sim 99% of the As(V) from aqueous solution at $\text{pH} \leq 7.5$, 88% at pH \sim 10 and 49% at pH \sim 12 (Bhakat et al., 2006). In addition, MCB is effective in the adsorption of As(III); MCB removed up to 99% of As(III) from aqueous solution in laboratory studies (Ayoob et al., 2007). Both refractory grade bauxite and feed bauxite have also been shown to effectively remove As(V) from contaminated groundwater (Mohapatra et al., 2007).

Although RM can be modified or the system pH adjusted to facilitate oxyanion sorption to RM, elements that exist as oxyanions such as arsenate (AsO_4^{3-}) or arsenite (AsO_3^{3-}) are less likely to be removed effectively from contaminated water by RM. The primary constituents of RM, Fe oxides/oxyhydroxides, are characterised by predominantly pH-dependent charge. At low pH, RM will exhibit a net positive or circumneutral charge; at high pH, RM will possess a net negative charge, which facilitates cation sorption. Pot studies of soils amended with RM showed a

significant decrease in Cu concentration in porewater as compared to untreated controls, but no significant effect of RM amendment on As porewater concentration (Lombi et al., 2004). Comparisons between Cd, Cu, Pb, Ni, and zinc (Zn) concentrations in porewater extracts of soils amended with RM, lime or beringite (a modified aluminosilicate mineral) indicated that pH increase is a significant mechanism involved in metal removal from soil solution (Lombi et al., 2002). Induced acidification following Cd, Zn and Cu sorption to RM indicated that both pH-dependent adsorption and pH-independent mechanisms, such as solid-phase diffusion, specific chemisorption or migration into micropores, may be involved in metal fixation to RM (Lombi et al., 2003; Lombi et al., 2002).

Red mud has demonstrated a high capacity for metal sorption in batch experiments, with sorption in the order $\text{Cu} > \text{Pb} \geq \text{Cd}$ (Apak et al., 1998). Apak et al. (1998) observed that metal sorption to RM was essentially irreversible; sorbed metals were not leached in either carbonic acid or bicarbonate buffered solutions. Column studies have also shown that neutralised RM is effective in the removal of the divalent metals Pb, Zn, Cd and Cu from contaminated water (Ciccu et al., 2003). In addition, the potential exists to reuse RM that has previously been utilised as a metal sorbent. Examination of the potential reuse of metal-bearing RM in cement indicated that up to 20% metal-loaded RM could be incorporated into cement mortars, and the sorbed metals were not leachable (Kilinçkale et al., 1997).

Brunori et al. (2005) investigated the environmental compatibility of RM reuse through a series of ecotoxicological tests on untreated and seawater-neutralised RM, and characterisation of metal leaching behaviour using the Italian leaching test, which analyses leachates produced at a material's natural pH over a period of 16 days (Brunori et al., 2005). The Italian leaching test, which uses eight sequential extractions with deionised water, indicated that leachates from both the untreated and neutralised RM contained vanadium (V), fluorides (F^-) and sulfates (SO_4^{2-}) at levels exceeding the Italian regulatory limits; however, results indicated that additional washing of RM with water prior to use would eliminate the high levels of F^- and SO_4^{2-} observed in leaching tests (Brunori et al., 2005). Both untreated and neutralised RM effectively removed As, Cd, Co, Cu, Mn, Ni and Zn from aqueous solution, with little release of sorbed metals in subsequent leaching tests and less release from the neutralised than the untreated RM (Brunori et al., 2005). Ecotoxicological tests using RM leachates indicated no significant ecotoxicological effects resulting from neutralised RM (Brunori et al., 2005).

Douglas et al. (2007) conducted a series of laboratory column sorption experiments using RM. The column sorption investigation involved saturated up-flow of an acidic metal test solution of 0.01 M H_2SO_4 containing 20 mg L^{-1} Cu, Co, Cd, Mn, Ni and Zn as chloride salts and the subsequent monitoring of those metal species as well as Al, Fe, S, Mn and Si along with pH in the column eluent. Empirical column data were used as inputs for solute geochemical modelling to establish saturation indices for a suite of minerals covering five main groups of Al, Fe, Mn, Ca (carbonates/sulfates) and clay minerals. The RM displayed good broad range metal attenuation in column trials up to 105-185 pore volumes, depending on the metal, but exhibited sharp capacity limitation. Results indicated that one cubic metre of RM could contain the metal content from ~53-92 m^3 of polluted acidic water containing 20 mg L^{-1} of a suite of metals. The geochemical modelling indicated that a range of mineral systems were present where RM reached metal sorption capacity. Gibbsite and ferrihydrite were identified as the key metal ion sorbents in the RM system (Douglas et al., 2007).

4.2. Red Sand

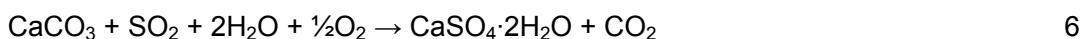
Worldwide, red sands (RS) generally comprise ca. 20% of the total bauxite residues generated during alumina production; however, in Western Australia approximately half of the by-product resulting from alumina production has a mean particle diameter $>90\ \mu\text{m}$ and can be classified as RS. The 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). There are a number of uses for sand residues as construction material for drainage layers, embankments and capping of land surfaces. The coarse texture facilitates the removal of alkali residue from the sand by washing and recovery by gravity draining. Recovered residue sand is frequently utilized as construction material by the refinery where it originated (Glenister et al., 1992). Few studies have examined the potential reuse of RS due to its relatively low volume in worldwide alumina production and its utility as general fill within the construction industry and for road construction.

In one study of RS re-use for environmental applications, a series of detailed column sorption experiments were conducted using RS and reduced red sand (RRS) (Douglas et al., 2006). The laboratory column sorption trial involved saturated up-flow of an acidic metal test solution of $0.01\ \text{M}\ \text{H}_2\text{SO}_4$ containing $20\ \text{mg}\ \text{L}^{-1}$ Cu, Co, Cd, Mn, Ni and Zn as chloride salts and the subsequent monitoring of those metal species as well as Al, Fe, S, Mn and Si along with pH in the column outflow. The empirical column data were used as inputs for solute geochemical modelling to establish saturation indices for a suite of minerals covering four main groups of Al, Fe, Mn and Ca (carbonates/sulfates) minerals. The RS exhibited good broad range metal attenuation up to approximately 40 pore volumes; however, once the residual RS alkalinity was consumed a large release of previously adsorbed metals was observed. Reduced red sand, containing metallic or zero valent iron, generally performed poorly in terms of metal attenuation with the exception of Cu containment. The large capacity for Cu sorption by RRS was attributed to reduction of the Cu cation to metallic copper by zero valent iron in the RRS and subsequent Cu cementation within the experimental column (Douglas et al., 2006). The investigators concluded that one cubic metre of RS could contain the metal content from $\sim 19\ \text{m}^3$ of polluted acidic water containing $20\ \text{mg/L}$ of a suite of metals. Geochemical modelling indicated that the mineral systems that become most undersaturated (negative saturation index) at the point where RS reached metal sorption capacity were amorphous gibbsite, ferrihydrite, gypsum and gypsum anhydrite. Amorphous gibbsite and ferrihydrite were identified as the key metal ion sorbents in the red sand system (Douglas et al., 2006).

4.3. Gypsum

Gypsum, or calcium sulfate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), is a common mineral with extensive deposits present in sedimentary rocks worldwide. In Western Australia, gypsum deposits are present within salt lakes or playas, coastal basins, and sedimentary rock sequences. The largest gypsum reserves are associated with coastal basins and sedimentary deposits, but the majority of the mined gypsum deposits in WA are associated with salt lakes (Hamblin, 2001). Western Australia's largest gypsum producing area is near Lake McLeod, 70 km north of Carnarvon, which accounts for approximately 74% of the State's gypsum production (Fetherston and Abeysinghe, 2000). Gypsum has a number of uses, including that as a soil conditioner or fertiliser. Gypsum is frequently mixed with red mud to neutralise alkalinity. In addition to mining of natural minerals, gypsum slurry is produced via power generation in the post-combustion limestone-gypsum wet flue gas desulfurisation (FGD) process. In this process ground limestone is used to absorb sulfur dioxide ($\text{SO}_{2(g)}$) and other acid gases resulting from fossil fuel combustion. In the limestone-gypsum wet FGD process, limestone is mixed with water and flue gases to produce a slurry

which absorbs $\text{SO}_{2(g)}$. The resulting slurry is oxidised to CaSO_4 , which can then be reused in suitable applications. The chemical reaction is as follows:



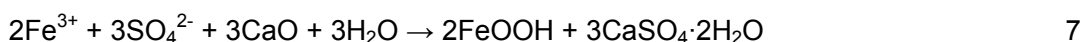
Gypsum has been studied as a potential surface water amendment for the reduction of soluble phosphorus and restoration of eutrophic lakes. In one study, gypsum was found to be unsuitable for removal of P from eutrophic lake waters because gypsum was not effective in P removal at $\text{pH} < 10$ (Higgins et al., 1976). The efficacy of gypsum as a P sorbing material for application to high-P containing soils on or near streambanks was recently examined. Gypsum applied to the soil surface at a rate equivalent to 100 t ha^{-1} resulted in an 83% reduction in soluble P contained in soil runoff (Penn and Bryant, 2006). In a similar study, gypsum applied at a rate of 15 t ha^{-1} only slightly reduced P concentration in soil runoff (Cox et al., 2005); however, the authors observed that gypsum amendment improved soil structure, thereby altering the relative proportions of P transported in soil runoff and in interflow through the subsoil.

Examination of FGD gypsum as a soil amendment showed that surface application of gypsum reduced subsoil acidity via significant reduction of soluble Al concentrations (Stout and Priddy, 1996). In addition, gypsum amendment increased soil Ca concentrations and raised the Ca:Al ratio, contributing to increases in alfalfa (*M. sativa* L.) yields of approximately 14% (Stout and Priddy, 1996). In Malawi, gypsum has been investigated as a water defluoridation agent. Dental fluorosis due to high levels of F is common in Malawi. Comparison between untreated gypsum and samples that were calcined at 200, 300, 400 or 500°C showed that gypsum calcined at 400°C, which removed ca. 68% of the F, was the most effective at F removal from aqueous solution (Masamba et al., 2005).

4.4. Heavy Minerals Processing Residue

Heavy minerals processing residue (HMPR) is generated during the production of rutile from mineral sands. One such residue is a material produced by Iluka Resources Ltd., a global miner and processor of mineral sands with large operations in Western Australia. Iluka Resources Ltd. is the world's largest producer of zircon, synthetic rutile, natural rutile and chloride ilmenite. Millions of tonnes per annum of NUA and similar residues are currently produced in Australia; approximately 20,000 tpa NUA are presently generated at the Iluka Resources Ltd. North Capel facility in Western Australia alone. Similar mineral sands mining and processing facilities are located elsewhere in Western Australia including Chandala (Tiwest Joint Venture) Bunbury (Bemax Resources Ltd. Cable Sands Group), and in the Murray Basin Region of South Australia (Australian Zircon, Iluka Resources Ltd., Rio Tinto).

The Fe-rich HMPR is a by-product of the production of synthetic rutile (TiO_2) from ilmenite (FeTiO_3), where sulfuric acid is used to leach impurities from the reduced ilmenite. The used acid from the leach is neutralised with lime to produce a gypsum-based solid residue containing Fe and Mn. The main chemical reaction involved in the generation of HMPR is:



which forms an intimate mixture of ferrihydrite (and related Fe minerals) and gypsum. 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 main ordered mineral phase contained in HMPR is bassanite ($2\text{CaSO}_4 \cdot \text{H}_2\text{O}$), a partially dehydrated form of gypsum, and the material is primarily comprised of Fe, Ca and S.

The HMPR is normally disposed of in lined storage systems but recent work indicates that it may be useful in a variety of environmental applications (e.g. Douglas et al., 2008; MERIWA Projects M122, M208, M230 and M344 www.doir.wa.gov.au/meriwa). Long-term field trials at a turf farm have demonstrated excellent P removal by HMPR; over the course of more than three years, total P in HMPR-amended plots was reduced by more than 97% as compared to control (non-amended) sites (Douglas et al., 2008). Nitrogen leaching was reduced by ca. 82%, and carbon retention in the upper soil profile approximately doubled due to DOC complexation with HMPR (Douglas et al., 2008). The high nutrient retention, in particular the P sorption capacity, of HMPR may be useful in situations where fertilizers are used extensively on soils which are largely unretentive for P (e.g. Ellen Brook and Peel/Harvey catchments) to prevent or diminish the rate of nutrient export to adjacent waterways.

In addition to retention of nutrients and DOC, field trials demonstrated that a wide range of trace elements applied within fertilizer were retained within the HMPR-amended soil profiles (Douglas et al., 2008). The few elements enriched in HMPR-treated plots as compared to unamended controls included Ca, Mg, SO₄-S and Sr, primarily due to the dissolution of gypsum in the HMPR material over time. Douglas et al. (2008) showed that a further benefit of HMPR amendment was a ca. 50% reduction in leaching of applied water.

4.5. Cement Kiln Dust

Cement is formed when CaCO₃ is reacted with silica-bearing minerals at high temperatures to form calcium silicates. Cement kiln dust (CKD) is the fine-textured (ash-like) particulate material removed from cement kiln exhaust gas by air pollution control systems. The non-combusted CKD may be recycled back into the kiln for cement production; however, most CKD is land disposed or marketed for secondary reuse. Millions of tons of CKD are generated annually in North America alone (Smith and Campbell, 2000). Cockburn Cement Ltd., with production sites in Munster, Dongara, Kemerton, Kwinana and Forrestfield, is Western Australia's largest producer of cement and lime products. Cement kiln dust is an alkaline material comprised primarily of lime (CaO), CaCO₃ and Ca(OH)₂ (Table 4). As such, CKD has potential as an environmental amendment for the neutralisation of acidity, and sorption/removal of aqueous metals and nutrients.

Phosphate removal from aqueous solution by CKD proceeds via the precipitation of hydroxyapatite:



The reaction rate is limited by low (1-5%) CKD solubility in aqueous solution (Smith and Campbell, 2000). The supersaturation and precipitation of hydroxyapatite solids from aqueous solution proceeds as shown in the generalised precipitation scheme in Figure 2. Addition of CKD was found to remove approximately 10% of the soluble P in processed effluent from a paper and pulp mill; however, re-acidification of the effluent solution indicated that phosphate removal was partially reversible (Smith and Campbell, 2000). Soil amendment of CKD has been shown to reduce the quantity of bioavailable P in manure-amended soils (Peters and Basta, 1996). The EC in CKD-treated soils was significantly ($p < 0.05$) elevated as compared to control soils and some concerns were raised that a potential increase in salinity due to CKD amendment could negatively impact salt-sensitive crops (Peters and Basta, 1996).

Table 4. Mean reported percent composition of some fresh and aged (landfilled) CKD.

| | Suez Cement Co. ¹ | North Star Cement Co. ² | CockburnGP Grey Cement ³ | CockburnGP Blended Cement ⁴ | CockburnGP Coarse Cement ⁵ |
|--------------------------------|------------------------------|------------------------------------|-------------------------------------|--|---------------------------------------|
| SiO ₂ | 12.6 | 14.5 | 20.2 | 24.9 | 21.5 |
| Al ₂ O ₃ | 3.5 | 3.5 | 4.9 | 8.3 | 5.2 |
| Fe ₂ O ₃ | 2.7 | 2.1 | 2.8 | 2.2 | 2.9 |
| CaO ^a | 40.7 | 48.5 | 63.9 | 56.5 | 64.0 |
| MgO | 1.8 | 3.2 | 2.0 | 2.5 | 2.3 |
| K ₂ O | 3.1 | 4.7 | | | |
| Na ₂ O | | 0.3 | 0.5 | 0.5 | 0.5 |
| TiO ₂ | | 0.1 | | | |
| SO ₃ ²⁻ | 6.2 | 7.1 | 2.4 | 2.6 | 2.5 |
| Cl ⁻ | 5.4 | 0.2 | 0.0015 | 0.035 | 0.01 |

^aCaO represents all Ca containing species, including CaCO₃

¹Zaki et al., 2007

²Smith and Campbell, 2000

³CCL-LAB-STD-Product General Specification 21-02-08: <http://www.cockburncement.com.au/>

⁴CCL-LAB-STD-Product General Specification 25-09-07: <http://www.cockburncement.com.au/>

⁵CCL-LAB-STD-Product General Specification 21-02-08: <http://www.cockburncement.com.au/>

Industrial waste streams, such as those resulting from electroplating, metal finishing, or leather tanning, are frequently contaminated with potentially toxic metals such as Cd, chromium (Cr), Pb, mercury (Hg), Ni and Zn. Amendment of tannery effluent with CKD at 20 g L⁻¹ resulted in the removal of nearly 100% of the Cd, Cr, Cu, Fe, Pb, Mn and Zn, and approximately 80% removal of Ni from the tannery effluent (El-Awady and Sami, 1997). Consistent with these results, CKD added to aqueous solution removed nearly 100% of the Cd, Co, Cu, Pb and Ni in solution and the capacity of CKD for these divalent metals decreased in the order Pb > Cu > Cd > Co > Ni (Pigaga et al., 2005). The highly alkaline (pH > 12) leachate of CKD has been demonstrated to remove nearly 100% of Cu, Ni and Zn from solution (Zaki et al., 2007). Removal of each cation was pH-dependent, as metals were moved from solution via precipitation as metal hydroxides; Cu was removed from solution at pH > 5.5, Ni removal from solution was initiated at pH > 7, and Zn removal from solution began at pH > 7.3 (Zaki et al., 2007).

Cement kiln dust has successfully been used to raise the pH of acid soils. Field studies demonstrated that amendment of CKD to Australian acid soils significantly increased soil pH with no negative effect on herbage yield (Dann et al., 1989). Soil neutralisation field trials in Canada using lime or CKD as soil amendments showed that CKD was a more effective neutralising agent, possibly due to its fine texture (Rodd et al., 2004). The fine texture of CKD also caused some handling issues, however, including clogging air filters and damaging bearings of equipment (Rodd et al., 2004). Of note, in addition to mechanical issues associated with CKD handling, there are human health hazards associated with exposure to CKD. Cement kiln dust is corrosive and can cause severe burns if dry CKD comes into contact with moist areas of the human body, including serious tissue (skin, eye, respiratory tract) damage due to chemical (caustic) burns (Mantus et al., 1992). Because CKD contains silica, prolonged or repeated inhalation of CKD may also lead to lung silicosis.

The acid neutralising capability of CKD has led to examination of its potential use as a control technique for sulfidic mine tailings. Stabilisation has been nominated as the “best demonstrated available technology” for treatment of potentially hazardous wastes due to the low cost, ease of application and ability to contain waste materials (Nehdi and Tariq, 2007). Solidification of waste from the metal-plating and dye industries exhibited very low Cr, Cu, Fe, Pb, Ni and Zn leachability as examined using the TCLP test (Fatta et al., 2004). Some research indicates that use of CKD-

amended cement is particularly beneficial for stabilisation of waste containing metals and metalloids, as the CKD accelerated hydration reactions of cementitious materials (Park, 2000); however, further work is required to fully characterise the effectiveness of CKD as a partial replacement for ordinary Portland cement in stabilisation techniques.

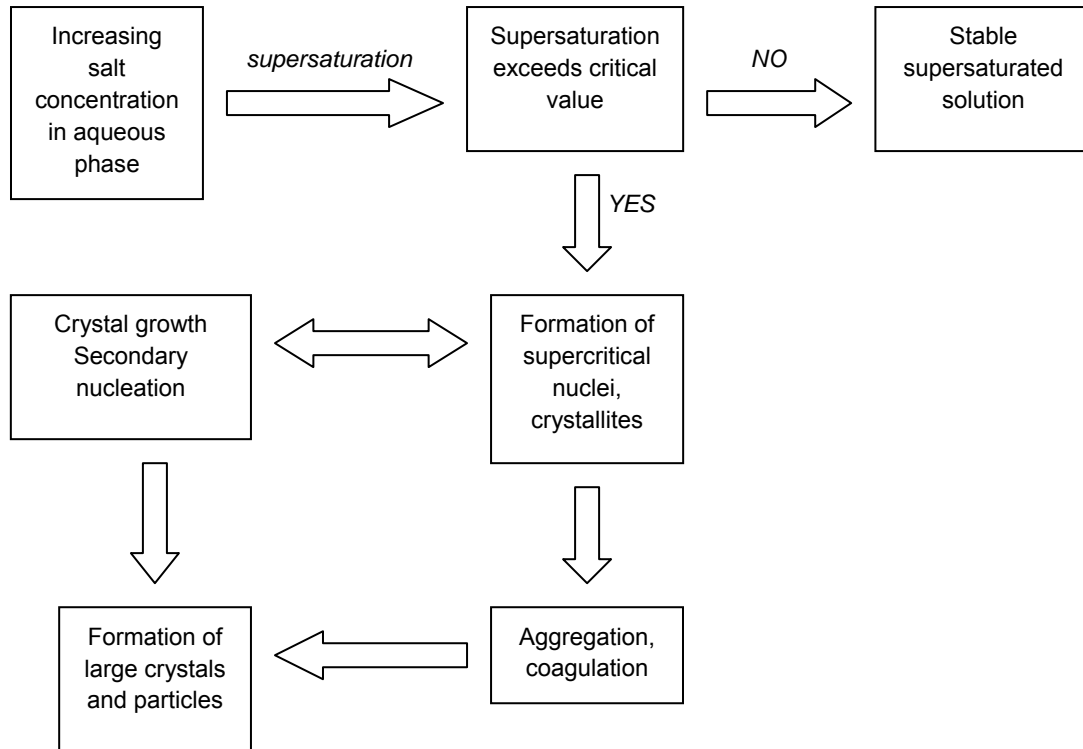


Figure 2. Schematic representation of the process of solid precipitation from solutions (Koutsoukos and Valsami-Jones, 2004).

The use of CKD in barriers has also been examined for treatment of AMD. Doye and Duchesne (2003) reported that use of 5-10% CKD in a permeable reactive barrier significantly reduced Al, Fe, Cu, Zn and SO_4^{2-} concentrations in leachate from reactive mine tailings. In addition, pH of tailings leachate solutions passed through barriers containing CKD was maintained at near neutral values over the one-year course of the investigation (Doye and Duchesne, 2003). The primary concern associated with the use of CKD for treatment of AMD or similar acidic solutions is the potential for the release of potentially toxic metals. Cement kiln dust contains relatively high levels of some metals (Table 5) and the potential exists for these metals to be released to solution due to chemical weathering of CKD, as occurs when the material is introduced to a highly acidic environment. Doye and Duchesne (2003) noted that although the CKD utilised in the reactive barrier was particularly high in Pb, concentrations of Pb remained below limits of detection throughout the investigation. Similarly, examination of extractable metals in CKD-amended soils (Peters and Basta, 1996) and in soils amended with CKD-stabilised biosolids (Dinel et al., 2000) remained below USEPA regulatory limits.

Table 5. Some trace element contaminants (mg kg⁻¹) in cement kiln dust (CKD) samples.

| Element (mg kg ⁻¹) | CKD A [†] | CKD B [‡] | CKD C [*] |
|--------------------------------|--------------------|--------------------|--------------------|
| As | | 104.3 | |
| Cd | 3.0 | | |
| Cr | | 18.7 | 61.0 |
| Co | | 20.0 | 4.0 |
| Cu | 7.5 | 27.3 | 10.0 |
| Mo | 0.7 | | |
| Ni | 14.4 | 22.3 | |
| Pb | 29.7 | 43.5 | 344 |
| Zn | 36.8 | 26.2 | 708 |

[†]Peters and Basta, 1996

[‡]Dinel et al., 2000

^{*}Doye and Duchesne, 2003

Despite reports of low trace metal leachability in CKD-amended soils (e.g. Peters and Basta, 1996; Dinel et al., 2000), caution is advisable when considering potential wide-scale application of CKD as an environmental amendment. Goats kept within 5 km of a cement factory in Nigeria exhibited significantly ($p < 0.05$) elevated blood Pb levels as compared to more distant herds (Oluokun et al., 2007). Goats within the test location displayed clinical signs consistent with Pb poisoning, including locomotor disturbances ranging from stiff gait to complete posterior paralysis and depressed blood haemoglobin levels (Oluokun et al., 2007). Deposition of CKD on surface soils resulted in high EDTA (ethylenediaminetetraacetic acid)-extractable Pb and Cd in soils near the cement factory, and forage crops grown ≤ 5 km from the factory possessed elevated concentrations of Pb and Cd (Oluokun et al., 2007). These results indicate that trace metal constituents of CKD have the potential to accumulate in the environment as a result of long-term exposure/application of CKD, and these potentially toxic elements exhibit the potential for soil-plant-animal transfer. Caution should be exercised in designing environmental treatment options that include widespread or long-term use of CKD without prior elemental characterization.

5. BY-PRODUCTS OF METAL REFINING AND PROCESSING

5.1. Metal Slags

Industrial by-products are a ubiquitous legacy of the mineral processing industry. A potentially promising material for the neutralisation of acidity is steel-making by-product derived from the reduction of iron ore into crude iron. In the United States alone approximately 21 million tonnes of steel industry by-products are produced annually (Proctor et al., 2000). In general, approximately 300 kg of by-products are generated for every 1000 kg of steel. In Western Australia, the newly commissioned HIs melt steel-making plant in Kwinana, south of Perth will produce in the order of 200,000 tonnes of steel smelting by-products per annum in full operation.

Slags are the non-metallic by-products of metal processing, and the most common slags are those resulting from iron and steel production. There are three basic steps in steel production: generation of the heat source used to melt the ore; melting of the iron ore in a furnace; and processing of the molten iron to make steel. Slag composition is dependent upon the type of steelmaking process by which it is produced. Coke, a solid carbon fuel and carbon source produced by heating pulverised, bituminous coal to high temperatures, is used to melt and reduce

iron ore. Iron ore, coke, and limestone or other flux materials are heated in a blast furnace. The fluxing agents react with and remove acidic impurities from the iron ore. There are three types of slag produced by the steel industry: blast furnace (BF) iron slag, basic oxygen furnace (BOF) steel slag and electric arc furnace (EAF) steel slag. The main components of these slags are fluxing agent, generally lime, and molten impurities of iron or steel. The BF slag is comprised primarily of SiO_2 and Al_2O_3 from the iron ore, with Ca and Mg from the added flux. The BOF and EAF steel slags usually contain substantially more Ca and Mg than BF iron slag.

Major chemical constituents of iron and steel slag include Al, Ca, Fe, Mg, manganese (Mn), phosphate (PO_4^{3-}), Si and sulfur (S) (Proctor et al., 2000). As part of the steel-making process the by-products are enriched in a range of elements, in particular oxides or more complex minerals containing mostly Mg, Ca and Si. Consequently, these materials may have an inherently high capacity to neutralize acidity, often similar to that of calcium carbonate (Bayless and Schulz, 2003; Bayless et al., 2004; Ochola and Moo-Young, 2004; Proctor et al., 2000; Simmons et al., 2002). Although trace element contents may be high in some steel-making by-products, extensive testing suggests that they are not readily leachable (e.g. using US EPA TCLP testing protocol, Proctor et al., 2000). Some slags have been shown to have a rapid and substantial trace element uptake capacity, particularly when the adsorbate was present as an oxyanion such as PO_4^{3-} (Agyei et al., 2000) or CrO_4^{2-} (Ochola and Moo-Young, 2004). An investigation of long-term field disposal sites of steel slags indicated that the steelmaking by-products were influential in limiting the mobility of trace elements, primarily through the precipitation of secondary minerals such as gypsum (Bayless and Schulz, 2003).

In batch experiments, blast furnace slag demonstrated a particularly high P adsorption capacity of 44.2 g P kg^{-1} slag (Sakadevan and Bavor, 1998). Similarly, column studies indicated that both crystalline and amorphous metal slag treatments removed >95% of total P from simulated wastewater (Johansson, 1999). Some experimental evidence suggests that the dominant mechanism of PO_4^{3-} removal from aqueous solution by metal slags may be hydroxyapatite precipitation, due to the alkaline pH and excess Ca in slag-amended environments (Johansson and Gustafsson, 2000). Examination of P interactions with metal slag from an exhausted (saturated) effluent filter indicated that mechanisms for P removal from wastewater by metal slags include: P adsorption onto metal oxides/oxyhydroxides throughout the metal slag matrix and amorphous Fe oxide/oxyhydroxide surface films; precipitation of P, mainly as Fe-phosphates, on amorphous Fe oxide/oxyhydroxide surface films; and P sequestration by an amorphous organic resin formed on the slag surface (Pratt et al., 2007). These results show that the duration of the reaction and other materials present in the system will significantly affect the mechanism of interaction between P and metal slags.

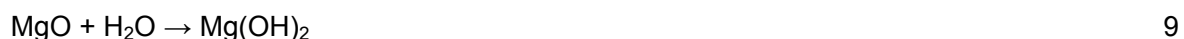
At high pH, metal slags exhibit a net negative charge and can readily adsorb cations from solution. Amendment of metal-contaminated dredged sediments with 4% w/w blast furnace slag resulted in a reduction in the leachability of some metals, including barium (Ba), Ni, and Zn; however, Cu leachability increased following slag amendment (Barth et al., 2007). Conversely, assessment of metal slag as a potential component for a reactive permeable barrier to treat landfill leachate showed that 60-95% of the metals examined were removed from solution by metal slag (Chung et al., 2007). The system pH significantly influenced metal sorption to slag, with $\text{pH } 7 > \text{pH } 5 > \text{pH } 9$; in addition, divalent metals were removed in the order $\text{Cd}^{2+} > \text{Pb}^{2+} > \text{Cr}^{2+} > \text{Cu}^{2+}$ (Chung et al., 2007). In laboratory leaching trials, steel slag sequestered Fe, Cd, beryllium (Be), Zn, and antimony (Sb) from solution, whereas Ba and V concentrations were higher in effluent than in source water, indicating a net enrichment in these elements following slag treatment (Simmons et al., 2002). These results indicate that steel slag may be most effective as an environmental amendment when used in a mixture with other materials.

Researchers have recently devised a method to easily granulate the molten by-product from steel manufacture (Xie, 2007). The end product resembles small porous marbles which possess a high internal surface area. This granulated slag product could be used as channel lining or within wetlands as a reactive substrate to attenuate acidity in WA Wheatbelt waters. Wetlands incorporating steel making by-products in combination with limestone pre-treatment wetlands have previously been studied as a method to treat AMD (Simmons et al., 2002).

5.2. 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 (MgCO₃) is formed via the replacement of Ca by Mg in calcareous rocks such as limestone (CaCO₃) or dolomite (CaMgCO₃), by alteration of olivine or serpentine alteration of by waters containing CO₂, or through precipitation from Mg-rich waters upon reaction with sodium carbonate (Na₂CO₃). 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 for agriculture and industry.

Calcined magnesia (MgO) or its derivative, Mg(OH)₂, possess considerable advantages over other alkalis such as Ca(OH)₂ in the neutralisation of acidic wastes. One of the most important advantages of MgO use in acid neutralisation is the relatively small amount of MgO or Mg(OH)₂ required. For the neutralisation of 1 tonne of 98% H₂SO₄, only 424 kg of 96% solid MgO, 613 kg of 96% solid Mg(OH)₂ or 1005 kg of a 58% slurry of Mg(OH)₂ are required, in comparison to a requirement of 1599 kg of a 50% NaOH solution, 1645 kg of a 45% solution of Ca(OH)₂, 3210 kg of a 33% slurry of Na₂CO₃ or 975 kg of CaCO₃ (assuming 100% effectiveness). Additional advantages of MgO are related to its chemistry (Cortina et al., 2003; García et al., 2004; Teringo, 1987). Alkalis such as caustic soda or lime neutralise acidity via a one-step dissociation reaction which results in the formation of OH⁻ and an increase in solution pH that is frequently difficult to control. In contrast, the neutralisation of acidic solutions by MgO is a two-step reaction as Mg(OH)₂, the intermediate product in the neutralisation process is only sparingly soluble in water. As a consequence neutralisation occurs as soluble OH⁻ ions derived from Mg(OH)₂ are consumed by the acid.



As a result of the production of hydroxide ions from the sparingly soluble Mg(OH)₂, the neutralisation reaction occurs rapidly at low pH and slows appreciably as the pH increases. In addition, varying particle size can change the reactivity of MgO. In contrast, the neutralisation rate of lime and similar products do not vary appreciably as a function of pH. It is the slower reaction rate of MgO that results in the formation of denser slurries (e.g. of mineral precipitates) relative to lime, thus reducing handling and disposal costs. An additional feature of MgO is the potential for the efficient, and often simultaneous, removal of a range of metals. Removal efficiency is related to the presence of a high pH immediately adjacent to the particle surface that can provide an ideal region for the precipitation of metal hydroxides, which may cement onto the surface of the MgO substrate.

In the presence of mixed metal solutions, which are common in industrial effluents and also within WA Wheatbelt drain waters, MgO also may interact with Fe and/or Al to form a range of mixed layer hydroxide materials generally known as layered double metal hydroxides or in the predominantly Mg-Al form as hydrotalcites (Albiston et al., 1996; Shin et al., 1996; Taylor, 1984; Vucelic et al., 1997). A unique property of layered double hydroxides such as hydrotalcites is that a range of metals of widely varying speciation and concentrations may be simultaneously co-precipitated, hence forming a polymetallic hydrotalcite. This has particular relevance to acidic groundwaters (e.g. derived from oxidation of acid sulfate soils) and waste streams which may contain a suite of divalent and trivalent metals.

Amendment of MgO to soil columns at rates between 5-10% w/w has been shown to reduce the concentration of metals in leachates by more than 80% (García et al., 2004). Soils stabilised with MgO, irrespective of rate of amendment, exhibited pH near 9.2 and only SO_4^{2-} concentrations in leachates exceeded regulatory limits (García et al., 2004). Separate investigation indicated that soil columns amended with MgO at a rate of 50% w/w maintained both reactivity and permeability for more than 10 months (Cortina et al., 2003). These results suggest that MgO may be a suitable material for remediation technology such as a permeable reactive barrier.

6. BY-PRODUCTS OF PUBLIC UTILITIES

6.1. Fly Ash

The fine-textured mineral residue generated during the combustion of coal to generate electricity, normally about 10% of the original material by weight, is called fly ash (FA). 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. 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 Berggaut, 1995). As a consequence of the large volume of FA generated annually and the cost of disposal, there is increasing interest in the beneficial reuse of FA. Given the inherently alkaline properties of many types of FA, numerous studies have examined its use to neutralize acid mine drainage in either surface (Potgieter-Vermaak et al., 2006; Scheetz and Earle, 1998; Xenidis et al., 2002) or subsurface (Canty and Everett, 2006) environments. In WA, FA is produced at the Kwinana, Muja, and Collie power stations.

The non-combustible material in coal is fused during combustion to produce a material with a glassy, amorphous structure. Mineral phases in FA commonly include (in order of decreasing importance): glass, mullite, quartz, char, hematite-magnetite, anhydrite-gypsum, feldspars, lime-portlandite, clay and mica minerals, cristobalite-tridymite, calcite-ankerite, corundum, jarosite, and some Ca and Ca-Mg silicate minerals (Vassilev and Vassileva, 2007).

Although FA 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 sulfur (Singer and Berggaut, 1995). Specific types of fly ash, and in particular Class C which is produced from the burning of sub-bituminous coals and lignite have a relatively high calcium content, principally present as CaO , $\text{Ca}(\text{OH})_2$ or CaCO_3 and thus have substantial neutralization capacity. Trace element abundances are generally high with concentrations of elements such as As, Pb, Cu, Zn, Cd, Cr and Hg typically 1-100 times above average crustal abundances (Theis, 1975). The

principal mineralogical constituents of fly ash are impure aluminosilicate glasses (ca. 60-90%), with smaller amounts of quartz, mullite, residual coal and ore minerals (Singer and Berggaut, 1995).

The pH and trace element content of FA also varies as a function of the coal source. An early investigation of trace element content of FA from a coal-fired power plant in Arizona, USA, showed that the FA contained higher concentrations of As, B, Cd, Cr, Co, molybdenum (Mo), Ni, Pb and selenium (Se) than typically found in soils (Phung et al., 1979). With the exception of Cd, Co and Pb, the trace elements were more concentrated in the <63 μm size fraction as compared to the coarser >250 μm fraction (Phung et al., 1979). This is consistent with a previous study which reported that the concentration of a number of trace elements in FA increased with decreasing particle size (Davison et al., 1974). A more recent examination of trace elements in FA derived from Spanish coal indicated that the FAs were enriched in a number of trace elements such as Ag, As, Ba, Cr, Cs, Li, P, Sb, Sc, Sn, Sr, Ti, V, Zn and Zr relative to mean trace element content reported for FA worldwide (Vassilev et al., 2003).

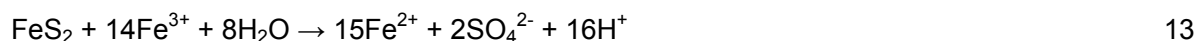
The primary concern related to trace element content of FA and environmental application of FA is the potential for the release of undesirable elements as the ash weathers. Phung et al. (1979) reported that trace element release from FA was strongly associated with the pH of the FA suspension. Solubility of all trace elements was low at the original (unadjusted) pH of 12.3, but increased significantly as the equilibrium pH was lowered (Phung et al., 1979). Soil amendment of FA at rates equivalent to up to 1% by weight did not result in elevated water-soluble trace element concentrations in soil, with the exception of B (Phung et al., 1979).

Significant effort has been expended investigating P sorption by FA. Over three decades ago, Higgins et al. (1976) examined the use of FA for the removal of P from eutrophic lakes. Results indicated that in some cases, application of a quantity of FA sufficient to cover lake sediments to a depth of 5 cm would reduce the P concentration of lake water to desired levels; however, in other cases the addition of a cation (e.g., Ca, Fe or Al salts) to promote P precipitation was also necessary (Higgins et al., 1976). This result differs from those obtained in more recent laboratory studies; batch experiments yielded P removal rates >99.8% in the presence of 20 g L⁻¹ FA, and the quantity of P sorbed was primarily dependent upon solution pH (Ugurlu and Salman, 1998). Approximately 94% of solution P was sorbed by FA at application rates as low as 4 mg L⁻¹ (Ugurlu and Salman, 1998).

Addition of FA to agricultural soils may reduce P in soil runoff without decreasing plant-available P below levels required for plant growth. Soil amendment with fluidised bed combustion FA at 8% w/w reduced water-soluble P by approximately 72% (Stout et al., 1998). Stout et al. (1999) also observed that amendment of FA to agricultural soils increased soil pH and stimulated the transformation of P from water-soluble forms to sparingly soluble Ca phosphates. The researchers concluded that the neutralising capacity and Ca content of FA are the primary characteristics responsible for P sorption (Stout et al., 1999). Laboratory studies showed that application of FA to soil at 1% w/w reduced the water-soluble P concentration by 60% (Stout et al., 1999). Both dissolved P and total P (TP) are important factors in managing surface water eutrophication, as P loss from soil in surface runoff contains both a dissolved P (water-soluble) component and a particulate-sorbed P component. Stout et al. (2000) found that on grassed soil, FA effectively reduced dissolved P concentration in runoff by approximately 20%; however, on bare soils FA application had no effect on P concentration in runoff. Other results indicated that the application of FA to grassed soils did not affect As, Cd or Pb concentrations in runoff, nor did FA amendment affect P, As, Cd, or Pb uptake by canola (*Brassica napus* L.) grown in amended soils (Stout et al., 2000).

Fly ash has also been investigated for use in infiltration beds to remove P from subsurface water. Comparison of the P removal capabilities of unweathered FA obtained directly from the electrostatic precipitator at an electric power plant and weathered FA from the storage lagoon at the same facility showed that although the weathered FA sorbed a significant quantity of P in column leaching studies, the unweathered FA exhibited a significantly higher attenuation capacity for P (Cheung and Venkitachalam, 2000). The untreated FA was judged suitable for amendment to sand at up to 15% w/w for use in infiltration beds for wastewater treatment.

Experimental evidence indicates that FA may be beneficial for the treatment of AMD. Sulfide-rich mine waste generates acidity via the oxidation of pyrite (FeS₂):



Other elements present as minor metallic sulfides can also be released via oxidation, and the highly acidic leachates generated catalyse the release of metals from surrounding minerals through chemical weathering processes. The use of FA, an inherently alkaline material, has been proposed to neutralise acidity both in acidic surface waters and in sulfide-bearing mineral residues. The addition of alkaline substrate to AMD neutralises acidity and decreases metal solubility. Precipitates formed at alkaline pH can form coatings on sulfide grains and hinder the further dissolution and release of contaminants to solution (Nehdi and Tariq, 2007; Perez-Lopez et al., 2007a; Perez-Lopez et al., 2007b).

Column studies using FA to neutralise leachate from sulfide-rich waste rock showed that FA addition increased leachate pH and reduced the aqueous concentration of potentially toxic metals (Perez-Lopez et al., 2007b). Under some conditions, FA cementation due to aragonite precipitation decreased column permeability and hindered oxygen diffusion, thereby providing a physical barrier that led to diminished AMD production (Perez-Lopez et al., 2007b). Fly ash addition raised solution pH, causing precipitation of metals released from sulfide-bearing minerals under oxidising conditions which formed coatings on pyrite surfaces, successfully halting pyrite oxidation (Perez-Lopez et al., 2007b).

Lime is traditionally employed in the treatment of AMD to neutralise acidity and facilitate the precipitation of metals in solution. Less expensive alternatives such as limestone, dolomite, and fly ash have been examined and found to show promise as environmental amendments. Batch experiments indicated that 500 g L⁻¹ FA was required to remove Fe²⁺ and SO₄²⁻ from AMD and neutralise the solution to pH ~7.9 (Potgieter-Vermaak et al., 2006). As compared to limestone and dolomite, even at the relatively high amendment rate required for AMD treatment FA was the least costly of the materials investigated (Potgieter-Vermaak et al., 2006).

Column leaching studies have demonstrated the applicability of FA to removal of metals from aqueous solution. Soil columns amended with FA exhibited good percolation rates and significant reduction of Pb, Cu, Zn and Cd concentrations in soil leachates (Ciccu et al., 2003). Cadmium sorption to FA has been found to be dependent upon Cd concentration, temperature, and solution pH (Yadava et al., 1987). Sorption of Cd by FA removed approximately 12% of the Cd from solution at 4.0 and approximately 90% Cd was removed from solution at pH 8.5; however, above pH 10, soluble Cd hydroxide complexes were formed, which reduced sorption to FA (Yadava et al., 1987). Examination of Cu sorption on FA exhibited up to 100% removal of Cu from aqueous solution and indicated that the process is likely diffusion controlled, as rate constants for diffusion and adsorption were nearly equal (Panday et al., 1985). Apak et al. (1998) used batch experiments to demonstrate the ability of FA to remove Cd, Cu and Pb from contaminated water,

and to retain the cations following leaching with carbonic acid or bicarbonate solution. Fly ash has also been shown to be a good sorbent of the radionuclides ^{137}Cs and ^{90}Sr (Apak et al., 1995a).

A potential drawback to the use of FA as an environmental amendment is the possibility of the introduction and release of additional metals contained in the FA due to dissolution or weathering. Untreated FA does not meet US EPA standards as an environmental amendment as its application introduces new contaminants to the environment (Apak et al., 1998). Soils where FA has been applied frequently exhibit elevated levels of As, and FA leachate has been shown to contain as much as $800\ \mu\text{g L}^{-1}$ where calcium phosphate ($\text{Ca}(\text{H}_2\text{PO}_4)_2$) was used as a leaching agent (Qafoku et al., 1999). Results indicated that phosphate and sulfate compete with arsenate for sorption sites on FA; thus, in gypsum and phosphorus amended soils FA amendment is likely unsuitable due to the increased potential for As release (Qafoku et al., 1999). The benefit of FA use as a soil amendment requires careful examination to ensure that FA amendment results in a net improvement to soil and water quality.

Elements that form anionic species in solution, such as B, Cr and Mo, and SO_4^{2-} are often present at elevated concentrations in FA leachate. The addition of lime, Portland cement, or a lime/dolomite mixture to FA has been shown to induce the formation of anionic clays, which remove anions from solution through sorption to interlayer sites (Duchesne and Reardon, 1999; Reardon and Della Valle, 1997). Lime/dolomite addition to FA resulted in the formation of hexagonal crystals $\leq 100\ \mu\text{m}$ in diameter, identified as hydrotalcite ($\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$) and/or hydrocalumite ($\text{Ca}_4\text{Al}_2\text{CO}_3(\text{OH})_{12}\cdot 5\text{H}_2\text{O}$) (Reardon and Della Valle, 1997). Lime addition to Class F FA, in which $(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 70\%$, results in the formation of the anionic clay hydrocalumite; however, lime addition to a Class C FA $[(\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3) \geq 50\%]$ generates hydrogarnet and ettringite, which have fewer surface sites for anion substitution and a lower preference for chromate (CrO_4^{2-}) and molybdate (MoO_4^{2-}) than hydrocalumite, respectively (Duchesne and Reardon, 1999).

Despite the large volume of FA produced each year by the electric power utilities there has been little success in using FA as a soil amendment, due in part to its low nutrient value, low CEC and the potential for the release of toxic elements. Hydrothermal treatment of FA converts $\sim 50\%$ of the ash to zeolite minerals, which have a high CEC and high surface area (Singer and Berggaut, 1995). Heat and alkali treatment of FA also results in the formation of zeolite materials with high CEC (Table 6), but that are relatively unstable at acidic pH (Amrhein et al., 1996). Microwave techniques have been employed in the synthesis of zeolite from FA. The type and yield of zeolite produced using microwave-assisted zeolite synthesis from FA are very similar to those obtained using conventional hydrothermal techniques, but far less time is required for zeolite formation (Querol et al., 1997).

Zeolite synthesised from FA, or zeolitised fly ash (ZFA), is effective in the removal of ammonium (NH_4^+) and PO_4^{2-} from wastewater, particularly following treatment to transform Na-ZFA to Al-ZFA, which removed 80-98% of NH_4^+ and nearly 100% of PO_4^{2-} from solution (Wu et al., 2006). Acid treatment of ZFA is less successful at promoting NH_4^+ and PO_4^{2-} sorption. Treatment of ZFA with 0.01 M H_2SO_4 improved the removal efficiency of NH_4^+ at low initial concentrations, and PO_4^{2-} at all initial concentrations (Zhang et al., 2007). Treatment of ZFA with more concentrated acid solution (e.g., $> 0.9\ \text{M H}_2\text{SO}_4$) has been shown to cause deterioration of zeolite structure and reduction in CEC, as well as reduce the sorption capacity for both NH_4^+ and PO_4^{2-} (Zhang et al., 2007).

Table 6. Zeolites produced from fly ash subjected to heat, pressure and alkalinity (Amrhein et al., 1996; Singer and Berggaut, 1995).

| Treatment | °C | Pressure (atm) | CEC (mmol _c kg ⁻¹) | Zeolites formed |
|-------------------------|-----------|----------------|---|--|
| Untreated ¹ | | 1 | <100 | |
| 3 M NaOH ¹ | 100 | 1 | ~2850 | Zeolite Na-PI, Na-Al silicate hydrate |
| 3.5 M NaOH ² | 100 | 1 | 2500 - 3000 | Zeolite P, Hydroxysodalite |
| 3 M NaOH ¹ | 100 | High | 3030 | Zeolite Na-PI, P-C, Na-Al silicate hydrate |
| 3 M NaOH ¹ | 150 - 200 | High | 460 | Zeolite X, Pectolite |
| 3 M KOH ¹ | 100 | 1 | >3000 | Zeolite K-G |

¹Amrhein et al., 1996

²Singer and Berggaut, 1995

6.2. Water Treatment Residues

Characteristics of water treatment residues (WTR) are highly variable due to differences in treatment processes at the industrial level, and the different minerals and waters involved. In general, drinking water purification involves treatment with a coagulant to remove colour, turbidity and humic substances from source water (Figure 3). The coagulation agents used to treat water can include iron chloride (FeCl₃), alum (Al₂(SO₄)₃·14H₂O), organic polymers, calcium oxides and/or Ca(OH)₂. Large volumes of WTR 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 Morgenthal, 2003). Several factors have led to increased interest in reuse of WTR, 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 reused as soil amendments at Gnagara Mound and Jandakot Airport (Foo and Masters, 2007).

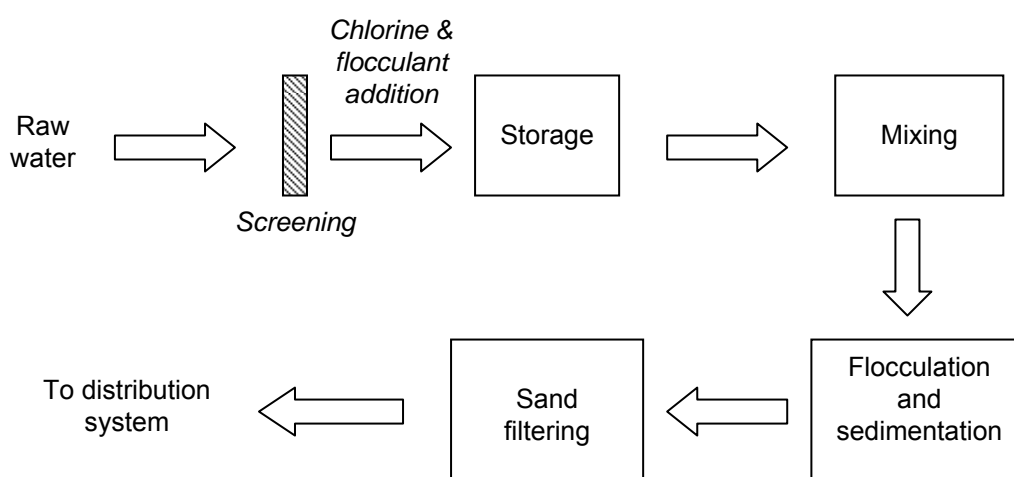


Figure 3. Generalised diagram of a conventional water treatment system (Neely and Isacoff, 1982).

Examination of the ability of a high-Fe WTR to reduce the potential bioavailability of Cu and As in contaminated soil showed significant reduction in both labile Cu and As resulting from WTR amendment at a rate of 2% w/w (Lombi et al., 2004). The reduction in labile Cu appeared to be primarily pH-dependent; re-acidification of WTR-amended soils resulted in a linear increase in

labile Cu as pH decreased (Lombi et al., 2004). Re-acidification of WTR-amended soil resulted in an increase in isotopically-exchangeable As; however, As solubility in WTR-amended soil remained relatively constant as pH decreased, likely due to the balance between the increased lability of As and the increased number of exchange sites on Al and Fe oxides at lower pH (Lombi et al., 2004). Some WTR, particularly those produced using lime as a coagulating agent, may be suitable for treatment of AMD or soil acidity due to their alkaline pH (>8.0) and high CEC. Van Rensburg and Morganthal (2003) observed that addition of WTR produced using activated silica, lime and FeCl₃ as coagulating agents to gold mine tailings significantly increased the pH of tailings leachate and reduced the solubility of metals.

A number of studies have documented the effectiveness of WTR, particularly those derived from treatment processes utilising alum as a coagulant, in P sorption (e.g., Razali et al. 2007, Mortula and Gagnon 2007, and references therein). Alum-based WTR has been reported to remove up to 98% of P from aqueous solution (Mortula et al., 2007; Mortula and Gagnon, 2007). Phosphorous binding capacities between 10.4 and 37.0 g P kg⁻¹ have been reported for a range of WTR (Dayton and Basta, 2001). Investigations of P removal from simulated wastewater showed that P sorption by WTR was most effective at acid pH and followed the order orthophosphate (KH₂PO₄) > polyphosphate (Na(PO₃)₆) > organic P (C₁₀H₁₄N₅O₇PH₂O) (Razali et al., 2007; Zhao et al., 2007). In a continuous flow scenario, an alum-based WTR removed >80% P, regardless of P species, in 30 days and the WTR bed was not saturated with P following 60 days continuous operation (Razali et al., 2007). The high capacity of WTR for P indicates strong potential for removal of excess P from wastewater or agricultural runoff, but may make WTR application unsuitable where establishment or re-establishment of vegetation is an objective, in particular where sorbed P is present in tightly-bound forms.

Application of WTR to degraded soils can improve soil structure, neutralise pH and add nutrients required for plant growth. These same amendments, however, have the potential to increase soil metal concentration via sorption/precipitation reactions and to reduce the concentration of plant-available P and essential micronutrients (Teixeira et al., 2007). Whereas some studies have reported positive effects (Lombi et al., 2004) or no significant effect (Codling et al., 2007) on plant growth as a result of WTR amendment to soil, others have demonstrated decreased plant yield (Teixeira et al., 2007; Titshall et al., 2007), possibly resulting from micronutrient or P deficiency. Excess Al and Fe can both exhibit phytotoxic effects and as such, it is possible that WTR generated using FeCl₃ or alum as coagulating agents could have detrimental effects on plant growth. An additional concern is that as compared to other types of WTP residues, those in which FeCl₃ was used as a coagulant appear more likely to contain high concentrations of metals such as Ni (Elliott et al., 1990). Due to the heterogeneity of WTR extensive characterisation and careful examination of individual residues is required to determine suitability for specific environmental applications.

6.3. Carbonised Wood Products

Carbonised wood products are generated by the temperature-driven chemical combustion of biomass, usually under oxygen-limited conditions. A wide range of carbonised materials are produced industrially, including:

- Char – the solid material generated by the thermal decomposition of any organic material.
- Charcoal – the solid material produced by thermal decomposition of wood, generally at high temperatures and in the absence of oxygen. Primarily used for cooking, heating and industrial purposes.

- Activated carbon – generated by heating carbonaceous material at high temperatures over a long period of time. Characterised by large surface area and high sorptive capacity.
- Black carbon – refractory organic material produced by incomplete combustion of fossil fuels, biofuels and biomass.

Activated carbon is widely used in gas and water purification, gold recovery, metal extraction sewage treatment, and numerous other applications. In Western Australia, large quantities of activated carbon are generated during the integrated processing of Mallee Eucalyptus trees. The WA Department of Environment and Conservation (DEC) is promoting the planting of Mallee Eucalypts in Western Australia's Wheatbelt region to combat rising groundwater tables and subsequent salinity. Integrated processing of the harvested Mallee tree biomass generates eucalyptus oil from the leaves, charcoal and activated carbon from the wood, and electricity via combustion of gasification of the biomass (Figure 4). The 1 MW demonstration integrated tree processing facility in Narrogin, WA, designed to process 20,000 tpa whole trees (fresh weight) generated 690 t of activated carbon, 7500 MWh of electricity and 210 t of eucalyptus oil in 2008 (McHenry, 2009).

The granular activated carbon generated from Mallee Eucalyptus trees has demonstrated effective sorption of methylisoborneol (MIB), a small organic molecule frequently used to assess the ability of a substance to remove taste and odour from water (Enecon, 2001). Additional testing showed 86% removal of microcystin, a toxin associated with contamination by blue-green algae, and 96% removal of the herbicide atrazine (2-chloro-4-ethylamine-6-isopropylamine-s-triazine) from water (Enecon, 2001). Activated carbon is widely used for the removal of contaminants from water. Numerous studies have documented the removal of metals (*e.g.*, Chen and Wang, 2000; Chen and Lin, 2001; Huang and Ostovic, 1978; Huang and Wu, 1975; Kobya, 2004; Rao et al., 2009), nutrients (*e.g.*, Helal Uddin et al., 2007; Hussain et al., 2006; Sison et al., 1996) and organic and inorganic compounds (*e.g.*, Dash et al., 2009; Dosoretz and Bøddeker, 2004; Lua and Jia, 2009; Palomar et al., 2009; Xing and Hickey, 1994) from water using activated carbon.

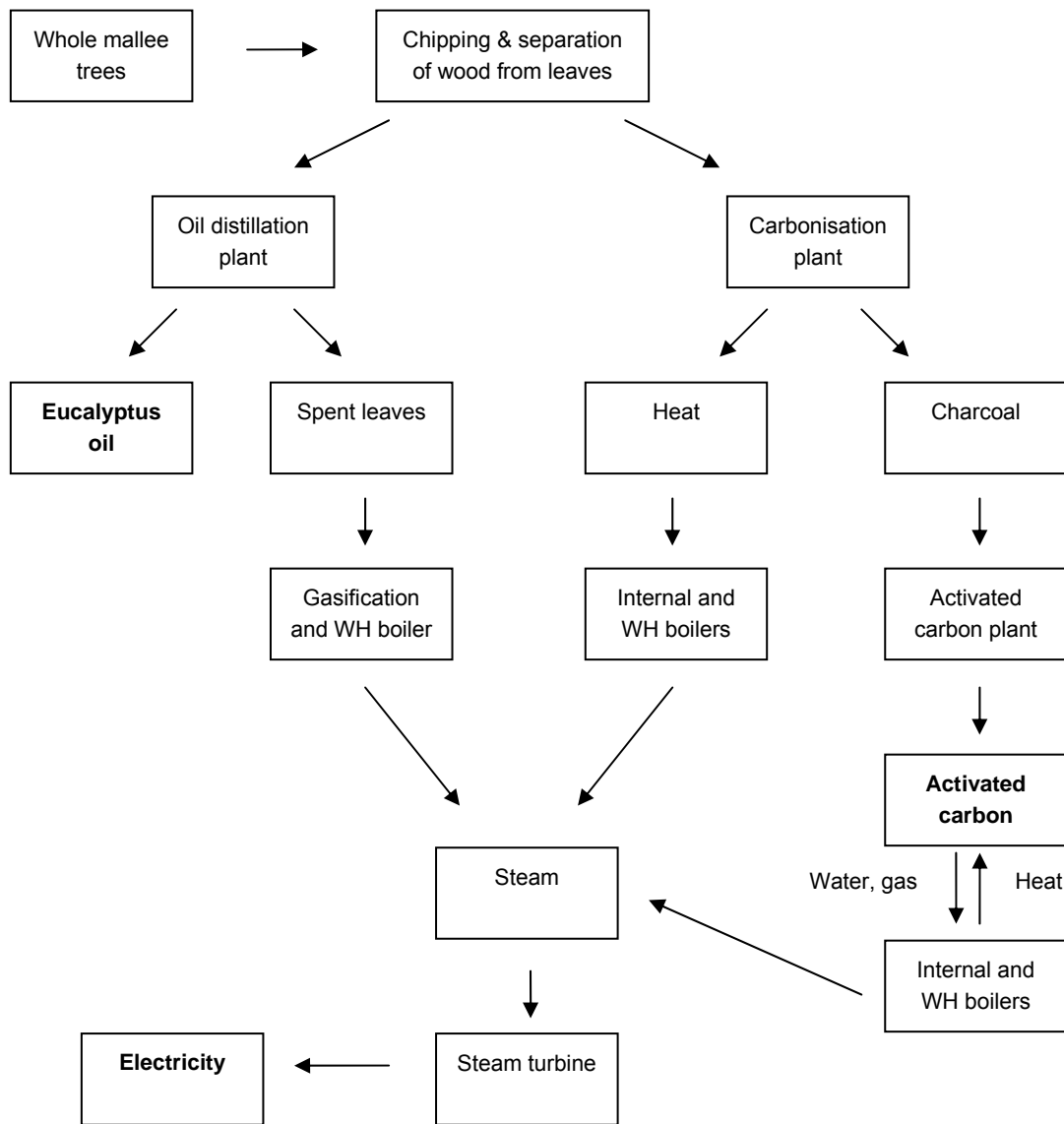


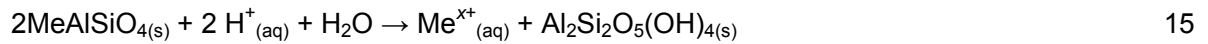
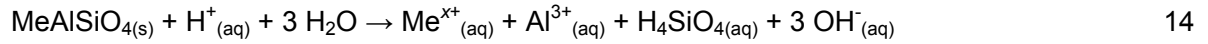
Figure 4. Schematic diagram of activated carbon production via integrated processing of Mallee Eucalyptus trees. WH boilers = waste heat boilers. Adapted from *Integrated Tree Processing of Mallee Eucalypts* (Enecon Pty Ltd, 2001).

7. WIDELY DISTRIBUTED NATURAL MINERALS

7.1. Primary Minerals/Mine Overburden

Some natural minerals such as those contained in mine overburden possess characteristics indicative of potential benefit as soil or surface water amendments, such as the ability to neutralise acidity or strongly sorb nutrients or potentially toxic elements. Montmorillonite, bentonite, glauconite, kaolin, calcite, zeolite, ozocerite, opoka, sepiolite, volcanic tuff and saposel have all demonstrated potential for the removal of metals from industrial wastewaters (Pigaga et al., 2005). As silicate, carbonate and hydroxide minerals undergo weathering, these minerals consume hydrogen ions through buffering reactions. Minerals in mine overburden, or

gangue minerals, dissolve at different pH. Silicate minerals such as olivines, pyroxenes, amphiboles, garnets, feldspars, feldspathoids, clays and micas comprise the majority of the minerals in the earth's crust and are the major reservoir of acid buffering capacity in the environment. As silicate minerals weather, hydrogen ions are consumed, dissolved cations and silicic acid are released, and secondary minerals are formed. Acid neutralisation by silicates can occur either through congruent weathering (12) in which the mineral is completely dissolved, or through incongruent weathering (13) whereby the primary silicate mineral is altered to a secondary mineral phase (Lottermoser, 2007):



(Me = Ca, Na, K, Mg, Mn or Fe)

Carbonate minerals such as calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), ankerite ($\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$), and magnesite (MgCO_3) are extremely important in acid neutralisation reactions. Calcite is arguably the most significant acid neutralising mineral due to its relative ubiquity in the environment and its rapid rate of reaction as compared to other minerals, such as dolomite. In the presence of acid, CaCO_3 dissolves and complexes with free hydrogen ions to form bicarbonate (HCO_3^-) in weakly acidic to alkaline environments (14), or carbonic acid (H_2CO_3) in strongly acidic environments (15):



Calcite dissolution occurs most rapidly in an open system where the aqueous phase is in contact with a gas phase and carbon dioxide (CO_2) is available for gas exchange. Dissolution of calcite can also occur under saturated conditions where there is no $\text{CO}_{2(g)}$ present; however, CaCO_3 is less soluble in the absence of $\text{CO}_{2(g)}$. Although slower than calcite, dolomite, ankerite and magnesite dissolution also result in the consumption of free hydrogen ions, the formation of bicarbonate and carbonic acid, and the release of Ca^{2+} and Mg^{2+} ions.

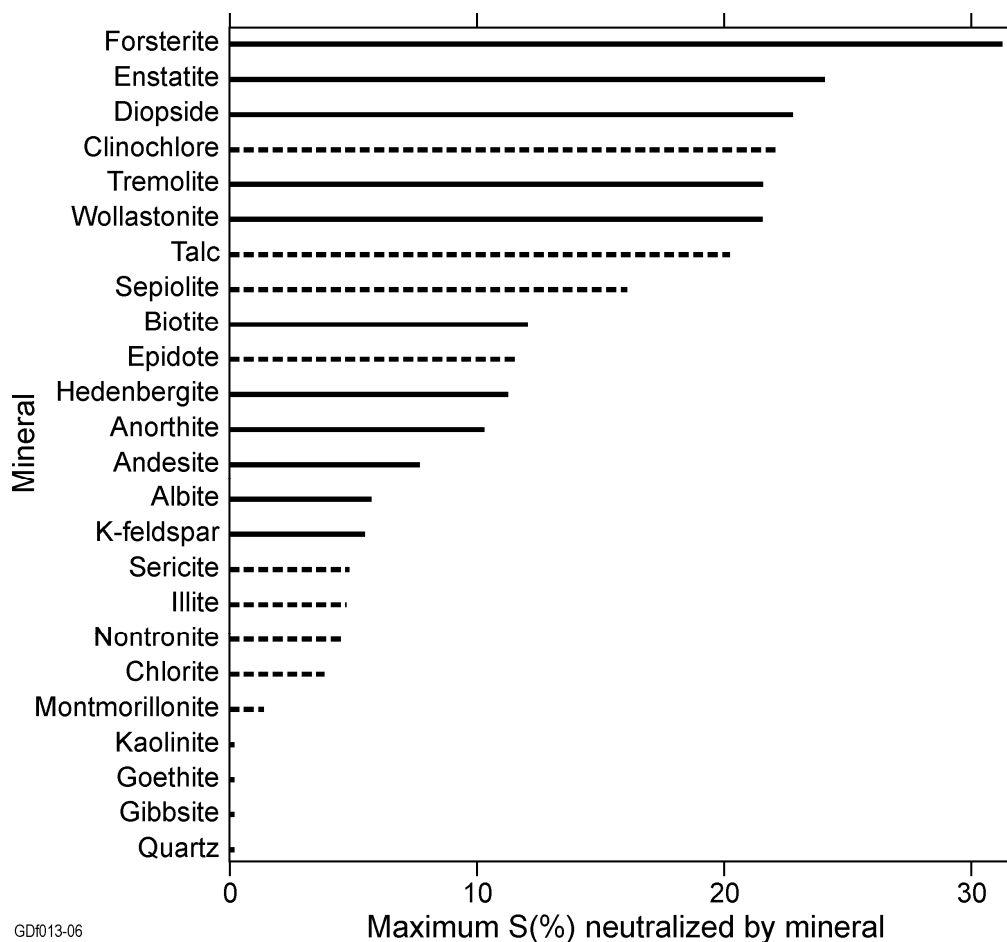
The rate at which minerals weather (weathering kinetics) is a function of physicochemical characteristics such as mineral composition, crystal shape, size and degree of crystallinity, and mineral surface area; the pH and dissolved CO_2 content of the weathering solution, and access of the weathering solution to the mineral surface; and temperature and redox conditions (Lottermoser, 2007).

Base cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) in the subsurface comprise an additional source of acid neutralising capacity. Through cation exchange reactions, base cations present on exchange sites of micas, clay minerals and organic matter can be replaced by H^+ and Fe^{2+} ions released during sulfide oxidation.

Table 7. Relative reactivity of minerals at pH 5 (from Lottermoser, 2007).

| Mineral Group | Relative reactivity at pH 5 | Typical minerals |
|-------------------------|------------------------------------|---|
| Dissolving | 1.00 | Calcite, aragonite, dolomite, magnesite, brucite, halite |
| Fast weathering | 0.60 | Anorthite, nephelite, olivine, garnet, jadeite, leucite, spodumene, diopside, wollastonite |
| Intermediate weathering | 0.40 | Ortho and ring silicates (epidote, zoisite), chain silicates (enstatite, hypersthene, hornblende, glaucophane, tremolite, actinolite, anthophyllite), sheet silicates (serpentine, chrysotile, chlorite, biotite, talc) |
| Slow weathering | 0.02 | Framework silicates (albite, oligoclase, labradorite), sheet silicates (vermiculite, montmorillonite, kaolinite), gibbsite |
| Very slow weathering | 0.01 | K-feldspar, muscovite |
| Inert | 0.004 | Quartz, rutile, zircon |

In WA, the Yilgarn Craton underlying the Wheatbelt region is dominated by granite and granitic gneiss rocks with a significantly lesser quantity of basic/ultrabasic rocks such as greenstone and komatiites (Anand and Paine, 2002). Unaltered basic/ultrabasic rocks are generally comprised of olivine, pyroxene and plagioclase feldspar. Olivines and pyroxenes in particular have an inherently high, long-term acid neutralisation capacity (Figure 5). Minerals formed during physical and chemical weathering processes and known to be present in the Yilgarn regolith include a range of carbonates within the lower weathering profile, which may only be uncovered during mining activities. Mine overburden has an intrinsically low value and if in physical proximity to sources of acidity could be used as a long-term neutralizing agent. There are however some potential drawbacks to the use of mine overburden, including processing the overburden to increase its effective surface area and reactivity (*i.e.* crushing), transport and the filling of drains, construction of appropriate filter structures (*e.g.* permeable barriers) or receiving environments. In addition, the neutralising capacity of mine overburden will be dependent upon factors such as the effective rate of mineral weathering and the availability of fresh reaction surfaces.



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Figure 5. Buffering capacity of a range of common minerals (solid lines) and their alteration products (dashed lines) in circumneutral solution. Estimated buffer capacity is the maximum percentage of sulfur that can be neutralized by the mineral assuming an infinite amount of time for reactions or containment of net-acidic materials with net-alkaline minerals (Risacher et al., 2002)

7.2. Carbonates/Carbonate Derivatives

7.2.1. Limestone

The sedimentary rock commonly referred to as limestone is comprised primarily of calcite, or CaCO_3 , derived from marine organisms or chemical precipitation. The use of limestone as a soil and/or surface water amendment to neutralise acidity is in common practice (Cravotta, 2003; Hammarstrom et al., 2003; Potgieter-Vermaak et al., 2006; Sasowsky et al., 2000; Skousen, 1991; Skousen et al., 2006). Limestone dissolves in water at $\text{pH} < 6.4$ to form dissolved CO_2 (denoted as H_2CO_3^*):



The H_2CO_3^* continues to react with the limestone to produce calcium and bicarbonate alkalinity:



If solution pH increases > 9.5 , carbonate alkalinity (CO_3^{2-}) may also become significant; however, as caustic alkalinity (OH^-) is converted to bicarbonate alkalinity (HCO_3^-) the pH declines to between 6 and 8. This is generally sufficient to remove trivalent metals (eg Al^{3+}) as hydroxides,

but insufficient to facilitate the precipitation of many divalent metal ions which may require a higher pH. The effectiveness of limestone is frequently reduced by precipitated Fe-oxyhydroxides armouring the surface of the limestone, thereby inhibiting its effective reactivity (Sasowsky et al., 2000; Skousen et al., 2006). Considerable work has been devoted to overcoming the problem of Fe armouring with the most frequent solution being the use of limestone under anaerobic conditions to reduce ferric iron (Fe³⁺) to its ferrous (Fe²⁺) state (Skousen, 1991). Some long-term studies suggest that despite anoxic conditions, where high (>10 mg L⁻¹) Al concentrations are present, a rapid reduction in permeability leading to wetland failure can occur (Watzlaf et al., 2000). Many acidic drainage and groundwaters in the WA Wheatbelt contain Al concentrations in excess of the 10 mg L⁻¹ threshold (Degens et al., 2008b).

In the presence of CaCO₃, metal ions in solution are immobilised either through precipitation reactions as solution pH increases, or by sorption reactions. Sorption of metals to limestone occurs through surface exchange reactions as Ca²⁺ is replaced by divalent metal ions in specific surface sites. The order of selectivity of divalent metal sorption to CaCO₃ has been reported as Cd²⁺ > Zn²⁺ > Mn²⁺ > Co²⁺ > Ni²⁺ >> Ba²⁺ = Sr²⁺ (Zachara et al., 1991).

A recent study of the available limestone deposits on the South Coast of WA suggests that sufficient deposits are available for >100 years if the primary use of these materials is to ameliorate soil acidification (Anderson, 1999). Use of these limestone deposits to treat acidic drainage waters would reduce the lifespan of this resource. Additional carbonate resources in inland areas, principally calcrete, are available in WA (Anand and Paine, 2002). A portion of current limestone/calcrete reserves could likely be utilized for the treatment of acidic Wheatbelt waters, particularly if effective means of combating Fe-armouring are overcome and the carbonate source could be efficiently crushed to create a larger surface area and higher reactivity.

7.2.2. Lime

Lime has traditionally been used worldwide as a treatment for AMD (Akcil and Koldas, 2006; Feng et al., 2000; Kalin et al., 2006; Kuyucak, 2001; Skousen et al., 2006; Vachon et al., 1994). Similarly, lime may also be used in the stabilization of mine tailings with actual acidity and/or acid forming potential (Davis et al., 1999) or in natural soils with potential or actual acidity (Thomas et al., 2003a). The term “lime” generally refers to quicklime (CaO) or hydrated lime (Ca(OH)₂). Neutralisation of acidic solution by limestone can be limited by slow rates of limestone dissolution; however, the dissolution of quicklime results in the rapid formation of hydrated lime and increase in pH:



The application of CaO results in the rapid formation of Ca(OH)₂ in the presence of water as opposed to the often exceedingly slow dissolution (depending primarily on pH) that occurs with limestone in natural waters.

In addition to providing surface sites for the sorption of metal cations in solution, the increase in pH due to lime amendment can immobilise metal contaminants via precipitation reactions. Following dissolution of the hydrated lime, the pH increases and metal ions precipitate as metal hydroxides. Specific metals will precipitate at specific pH values with for instance hydroxides of Fe³⁺, Al³⁺, Ni²⁺, Fe²⁺ and Zn²⁺ beginning to precipitate at pH 3, 3.7-4.5, 8, 8-9 and >9 respectively (Kalin et al., 2006). In addition, due to the amphoteric nature of some of the metal hydroxides,

maximum removal efficiency cannot be achieved at a single pH (Feng et al., 2000). Reliably effective precipitation can be achieved in a multi-reagent and multi-stage intensive process; however, this would be unlikely to be feasible in the context of the treatment of polymetallic acid waters such as those found in the WA Wheatbelt. In addition to pH, a number of other factors such as ionic strength, temperature, and redox potential can all influence mineral saturation states. In addition, precipitated solids may be influential in trace element removal (Uhlmann et al., 2004).

A consequence of applying lime to ameliorate acidity is the production of water with high Ca^{2+} content, which can also result in precipitated gypsum where sulfate concentrations are also sufficiently high. The ensuing hardness of waters after lime treatment has the potential to be detrimental to receiving environments (Kalin et al., 2006). In terms of treating saline and hypersaline waters in the WA Wheatbelt, however, the potential formation of gypsum is not likely to be problematic as gypsum is frequently at saturation or oversaturation in drains and streams. A further problem with lime can be high residual pH (ca. 12) when over-application occurs. This can result in a range of deleterious effects including to endemic micro- and macro-biota, with possible reneutralization of any discharged water required, particularly in sensitive environmental areas. The highly caustic nature of many dry lime products also raises the need to implement additional occupational health and safety precautions while transporting and handling these products.

7.2.3. Dolomite

Dolomite, or $\text{MgCa}(\text{CO}_3)_2$, is one of the most abundant carbonate minerals in soil. It has been used for centuries, along with CaCO_3 and $\text{Ca}(\text{OH})_2$, as an amendment to neutralise acidic agricultural soils. Comparison between limestone and dolomite amendment to treat simulated AMD showed that the neutralisation reaction rate of dolomite was slower than that of limestone, and that a greater quantity of dolomite was required for solution neutralisation as compared to limestone (Potgieter-Vermaak et al., 2006). Examination of the neutralisation efficiency of dolomite indicated that $\text{MgCa}(\text{CO}_3)_2$ could be used in place of limestone for AMD treatment at considerable cost savings (Potgieter-Vermaak et al., 2006). Although dolomite exhibits a slower rate and capacity for acid neutralisation, in areas where $\text{MgCa}(\text{CO}_3)_2$ is readily available it may provide a suitable source of alkalinity for remediation of acid soils or surface waters. Additional work is required to characterise the acid neutralisation capacity of dolomite and its effects on the behaviour of potentially toxic metals in aqueous solution.

7.3. 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. A common feature of the Darling Ranges, laterite generally comprises 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), though there are disadvantages. Lateritic gravel requires crushing to increase surface area and hence reactivity and thorough washing prior to use.

7.4. Phyllosilicate Minerals

Phyllosilicate, or layer silicate, clay minerals comprise the majority of the reactive solid phase in low-organic matter temperate soils. Clay minerals are ubiquitous in soils and a number of clays are mined for commercial applications. In Western Australia, the hydrated magnesium silicate clay attapulgite is mined primarily from the Lake Nerramynne deposit, approximately 165 km north of Geraldton (Fetherston and Abeysinghe, 2000). A limited quantity (ca. 3380 t y⁻¹) of kaolinite is mined in southwest WA (Fetherston and Abeysinghe, 2000). Magnesium-rich Western Australian bentonite clay is produced from a series of claypans north of Watheroo (Fetherston and Abeysinghe, 2000).

Under appropriate conditions clay minerals can play a significant role in the sorption/sequestration of a suite of elements. Clay minerals exhibit both pH-dependent charge at edge sites and permanent (pH-independent) charge due to isomorphic substitution of cations in the mineral structure. Common isomorphic substitutions in clay minerals resulting in a net negative charge include Al³⁺ substitution for Si⁴⁺ tetrahedral layers, and Mg²⁺ or Fe²⁺ for Al³⁺ in octahedral layers. The pH-dependent charge exhibited by clay minerals due to edge aluminol (AlO₂) and silanol (SiO₂) groups of phyllosilicate mineral structures enables clays to sorb negatively charged ions at pH < pK_a of aluminol or silanol groups (e.g., where AlO₂ or SiO₂ exhibit a net positive charge). Although the AEC of clay minerals increases with decreasing pH, it is generally low compared to CEC. For example, the AEC of smectite minerals < 5 cmolc kg⁻¹ while the CEC may be > 100 cmolc kg⁻¹ (Tiller, 1996).

Clay minerals have long been employed in environmental applications such as liners for landfills and radioactive waste disposal sites, and in water clarification (Churchman et al., 2006; Lange et al., 2007). Clays can be utilised for the management of cationic contaminants, either through surface complexation, cation exchange or surface precipitation reactions. Metals exhibit a strong tendency to form covalent bonds with clay minerals; the relative affinities between metals and clay minerals vary, but generally follow the sequence Cu²⁺ > Zn²⁺ > Co²⁺ > Ni²⁺ ≈ Mn²⁺, which approximates the hydrolysis constants of these metal cations (Tiller, 1996). In general the relative affinities of common clay minerals for selected divalent metal cations are as follows (Jackson, 1998):

| | | |
|-----------------|---|----|
| Kaolinite | Pb ²⁺ > Ca ²⁺ > Cu ²⁺ > Mg ²⁺ > Zn ²⁺ > Cd ²⁺ | 22 |
| Illite | Pb ²⁺ > Cu ²⁺ > Zn ²⁺ > Ca ²⁺ > Cd ²⁺ > Mg ²⁺ | 23 |
| Montmorillonite | Ca ²⁺ > Pb ²⁺ > Cu ²⁺ > Mg ²⁺ > Cd ²⁺ > Zn ²⁺ | 24 |

Kaolinite [Al₂Si₂O₅(OH)₄] is a 1:1 clay mineral, with one tetrahedral layer and one octahedral layer per unit cell. Kaolinite typically exhibits a CEC of 1 to 5 cmolc kg⁻¹. Kaolinite minerals exhibit a net positive charge at low pH, making them a significant source of AEC under acidic conditions. As such, kaolinite sorption of PO₄³⁻ and NO₃²⁻ can decrease leaching of these nutrients, particularly in tropical agricultural systems where soils are frequently highly weathered and kaolinite-rich (White and Dixon, 2002). The clay mineral gibbsite [Al(OH)₃], which has a structure comprised of a single octahedral sheet, also has an affinity for anions at pH < pH_{pznpc} (the pH at which point the mineral exhibits zero net proton charge, pH ~9.0). Depending upon pH and PO₄³⁻ concentration, the sorption of PO₄³⁻ to both gibbsite and kaolinite results from a combination of surface complexation and surface precipitation (Van Emmerik et al., 2007).

Illite is a 2:1 clay mineral in which isomorphic substitution of Al for Si results in a layer charge of 0.6 to 0.8 mol per formula unit and CEC of 10 to 40 cmolc kg⁻¹. An ideal unit cell formula for illite can be written K_{0.75}(Al_{1.75}M²⁺_{0.25})(Si_{3.5}Al_{0.5})O₁₀(OH)₂. Illite minerals exhibit a strong affinity for large, weakly hydrated cations such as K⁺, Cs⁺ and rubidium (Rb⁺), and as such have important

implications in radioactive waste disposal. Cations with low hydration energy such as K^+ , Rb^+ , Cs^+ and NH_4^+ can shed their hydration shell in clay interlayers. Dehydration of these ions permits a close approach to the tetrahedral silicate sheets and formation of polar bonds with structural oxygen atoms. Cations bound to dehydrated ('collapsed') interlayer sites are not readily exchanged and usually considered 'fixed'. Potassium is generally the cation present in illite interlayers. Recent study indicates that illite can be used for effective in situ remediation of surface waters contaminated with the radionuclide ^{137}Cs (Hinton et al., 2006).

Smectites are another class of 2:1 clay minerals which possess layer charge ranging from 0.2 to 0.6 mol per formula unit and CEC of 80 to 150 cmolc kg^{-1} . Montmorillonite $[M^{+}_{0.33}(Si_4)(Al_{1.67}Mg_{0.33})O_{10}(OH)_2]$ is one of the most common smectite minerals. Bentonite is a soft, clayey rock that contains primarily smectite minerals and is used extensively in the construction of liners for landfills or mine waste, industrial waste and sewage treatment lagoons, and other waste treatment or storage facilities. Smectite clays are particularly useful as liners due to their ability to disperse when hydrated and fill voids between larger soil particles, thereby impeding hydraulic conductivity. Smectites also possess a high adsorptive capacity for metals, and thus an ability to attenuate cationic contaminants in wastes and leachates (Lange et al., 2007).

Vermiculite is a hydrous 2:1 clay mineral structurally similar to illite, but with layer charge ranging from 0.6 to 0.9 mol per formula unit and containing hydrated exchangeable cations in the mineral interlayer. The chemical formula of an ideal vermiculite is $(nH_2O, Mg_z)(Al_xSi_{4-x})Mg_3O_{10}(OH)_2$, where $z=0.6 - 0.9$ and $x = 0.6 - 1.5$. The CEC of vermiculite clays is 130 to 210 cmolc kg^{-1} . Vermiculite clays can sorb both weakly hydrated cations such as K^+ , Cs^+ , Rb^+ and NH_4^+ , and strongly hydrated cations such as Ca^{2+} , Mg^{2+} and Sr^{2+} . Sorption of weakly hydrated cations causes interlayer dehydration and layer collapse, whereas sorption of strongly hydrated cations leads to layer expansion. Vermiculite is particularly suitable for sorption and removal of potentially toxic cations such as Cu^{2+} , Pb^{2+} , Cd^{2+} , Zn^{2+} and Ni^{2+} from aqueous solution. The greater the quantity of negative charge localised in the tetrahedral layers of vermiculite, the greater the selectivity for cations such as Zn^{2+} and Cd^{2+} (Malla, 2002).

7.5. Zeolite minerals

Zeolites are a class of aluminosilicate minerals with a cage-like structure, called tectosilicates, and may be either naturally-occurring or synthetic. Synthetic zeolites can be tailored to produce specific pore size distributions, and are sometimes referred to as molecular sieves. Numerous zeolite materials have been synthesized for specific catalytic or ion-sieving industrial applications (Figure 6). Zeolite minerals are characterised by high CEC, high cation selectivities and surface areas of several hundred thousand $m^2 kg^{-1}$. In general, zeolites consist of polyhedra formed by silica (SiO_4^{4-}) and alumina (AlO_4^{5-}) tetrahedral which form a framework containing exchangeable alkali and alkaline earth cations and adsorbed water. Like phyllosilicate minerals, zeolites are able to exchange cations and undergo reversible hydration-dehydration reactions; however, a significant difference between zeolites and phyllosilicate minerals is that due to its rigid but porous framework, zeolite structure is not altered as a result of reversible cation exchange or hydration-dehydration reactions (Boettinger and Ming, 2002). Natural zeolites have many uses, including: sorption and removal of organic molecules, radionuclides, metals and ammonium from waters, soils and sediments; application as slow-release fertilisers; use as plant growth media; and as dietary supplements or metal sequestering agents in animal nutrition.

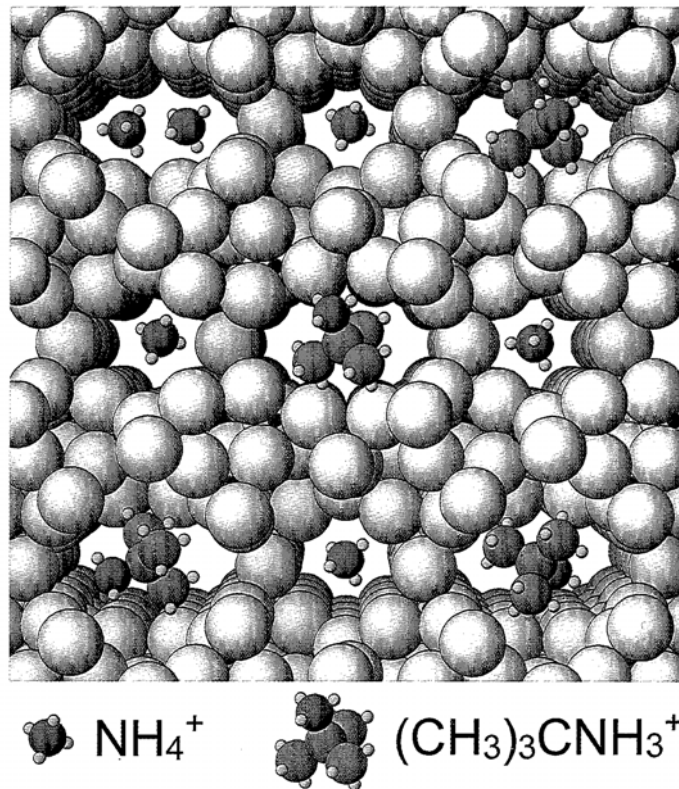


Figure 6. Illustration of ion-sieving principle in clinoptilolite. Ammonium (NH_4^+) can enter channels and sorb to negatively charged sites in the zeolite interior. Tert-butyl ammonium [$(\text{CH}_3)_3\text{CNH}_3^+$] cannot access interior cation exchange sites due to its large size (Boettinger and Ming, 2002).

Naturally-occurring zeolites are sometimes found as secondary minerals in the cavities of mafic igneous rocks (*e.g.*, basalt) and as components of sedimentary rocks, particularly those of volcanic origin. Clinoptilolite [$(\text{Na}_3\text{K}_3)(\text{Al}_6\text{Si}_{30}\text{O}_{72}) \cdot 24\text{H}_2\text{O}$], heulandite [$(\text{Ca}_4(\text{Al}_8\text{Si}_{28}\text{O}_{72})) \cdot 24\text{H}_2\text{O}$], analcime [$(\text{Na}_{16}(\text{Al}_{16}\text{Si}_{32}\text{O}_{96})) \cdot 16\text{H}_2\text{O}$], chabazite [$(\text{Na}_2\text{Ca})_6(\text{Al}_{12}\text{Si}_{24}\text{O}_{72}) \cdot 40\text{H}_2\text{O}$], laumontite [$(\text{Ca}_4(\text{Al}_8\text{Si}_{16}\text{O}_{48})) \cdot 16\text{H}_2\text{O}$], erionite [$(\text{Na}, \text{Ca}_{0.5}\text{K})_9(\text{Al}_9\text{Si}_{27}\text{O}_{72}) \cdot 27\text{H}_2\text{O}$], phillipsite [$(\text{Na}, \text{K})_5(\text{Al}_5\text{Si}_{11}\text{O}_{32}) \cdot 20\text{H}_2\text{O}$] and mordenite [$(\text{Na}_8(\text{Al}_8\text{Si}_{40}\text{O}_{96})) \cdot 24\text{H}_2\text{O}$] are common zeolite minerals occurring in sedimentary deposits. The potential CEC of these minerals based on representative unit cell formulae ranges from 220–460 $\text{cmol}_c \text{ kg}^{-1}$ and is related to the extent of isomorphic substitution of Al^{3+} for Si^{4+} in tetrahedral structures; phillipsite (380 $\text{cmol}_c \text{ kg}^{-1}$), chabazite (420 $\text{cmol}_c \text{ kg}^{-1}$) and clinoptilolite (220 $\text{cmol}_c \text{ kg}^{-1}$) are the zeolite minerals most commonly used for adsorption of potentially toxic trace metal cations (Boettinger and Ming, 2002). Clinoptilolite exhibits particularly high selectivity for NH_4^+ , and has been utilised in the reduction of N loss from agricultural lands and golf greens, and for the removal of N from agricultural and municipal wastewater systems (Boettinger and Ming, 2002). Within Australia zeolite deposits, comprised principally of clinoptilolite, primarily lie within the Carboniferous rocks of the Tamworth Belt in NSW (Holmes and Pecover, 1987). The two zeolite mines currently operating in the Tamworth Belt are The Escott mine near Werris Creek and the Bindawalla mine, near Quirindi (Hughes, 2006).

Natural clinoptilolite has been reported to remove NH_4^+ from solution via cation exchange at rates between 8.12 and 11.5 mg g^{-1} (Karadag et al., 2006; Saltalı et al., 2007; Wang et al., 2007). Ammonium removal is dependent upon factors such as pH, temperature, Initial solution concentration and sorption time. Saltalı et al. (2007) reported maximum NH_4^+ uptake by natural clinoptilolite at pH 8 and 21°C, most likely due to deprotonation of NH_4^+ at alkaline pH and to the

exothermic nature of NH_4^+ exchange on clinoptilolite, respectively. The reaction rate was rapid, with maximum sorption reached within 30 min (Saltalı et al., 2007). Modifications to the zeolite mineral, such as saturation of exchange sites with Na^+ or Ca^{2+} , can increase NH_4^+ sorption capacity to 19.3 or 14.8 mg g^{-1} , respectively (Ji et al., 2007; Wang et al., 2007). Phosphate sorption by zeolitic materials is low as compared to NH_4^+ ; laboratory investigation indicated a P sorption capacity of 2.15 mg g^{-1} clinoptilolite (Sakadevan and Bavor, 1998).

Its high selectivity for some potentially toxic metal cations makes clinoptilolite a promising material for the remediation of industrial waste streams or drainage waters with high metal content. The selectivity series of natural clinoptilolite for various cations has been given as $\text{Pb}^{2+} > \text{NH}_4^+ > \text{Ba}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Cd}^{2+} \approx \text{Sr}^{2+} > \text{Co}^{2+}$ (Blanchard et al., 1984) and as $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Cs}^+ > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Cr}^{3+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Hg}^{2+}$ (Zamzow et al., 1990). The order of adsorption efficiency for some common divalent metal contaminants by clinoptilolite has been determined as $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Cd}^{2+} > \text{Ni}^{2+}$, with maximum adsorption capacity of 4.2 mg g^{-1} for Cd^{2+} at an initial solution concentration of 80 mg L^{-1} , and for Pb^{2+} , Cu^{2+} and Ni^{2+} of 27.7, 25.7, and 13.0 mg g^{-1} at initial solution concentrations of 800 g L^{-1} respectively (Sprynskyy et al., 2006). Under different environmental conditions, clinoptilolite capacity for Pb^{2+} has been reported as 80.9 mg g^{-1} at an initial solution concentration of 400 mg L^{-1} (Günay et al., 2007). An additional characteristic of clinoptilolite beneficial for the removal of metals from acid drainages is that the mineral is stable under acidic conditions; clinoptilolite dissolution has been observed only at $\text{pH} < 2.0$ (Wingenfelder et al., 2005).

7.6. Hydrotalcite minerals

Hydrotalcites are a class of layered double hydroxide (LDH) minerals commonly formed via the co-precipitation of divalent (e.g. Mg^{2+} , Fe^{2+}) and trivalent (e.g. Al^{3+} , Fe^{3+}) metal ions from solution at intermediate to high pH. The generalised formula for hydrotalcite-like minerals is $\text{M}_1^{2+} \text{M}_x^{3+} (\text{OH})_2 (\text{A}^{n-})_{x/n} \cdot y \text{H}_2\text{O}$, where M^{2+} and M^{3+} are divalent and trivalent metals, and A^{n-} is an anion with valence n . Hydrotalcite minerals occur naturally in soils and sediments, but can also be synthesised from industrial waste materials such as the reaction of RM with seawater (Thorner and Hughes, 1986) or the reaction of lime with fly ash (Reardon and Della Valle, 1997). Through careful control of reaction temperature and concentrations of reactants, it is possible to synthesise hydrotalcite particles with highly defined mean particle size distributions ranging from approximately 2 to 20 μm (Ogawa and Kaiho, 2002), making hydrotalcite minerals particularly appealing for industrial applications.

Phosphate sorption by hydrotalcite has been shown to occur via anion exchange and to reach a maximum at $\text{pH} \sim 7.0$ (Ookubo et al., 1993). Laboratory investigations using Mg-Al hydrotalcites have demonstrated sorption capacities ranging from 25-30 mg P g^{-1} (Miyata, 1983; Shin et al., 1996) to approximately 60 mg P g^{-1} (Ookubo et al., 1993). Hydrotalcite-like compounds have also demonstrated an ability to sorb arsenate (AsO_4^{3-}) and selenite (SeO_3^{2-}) (Yang et al., 2005) and borate [$\text{B}(\text{OH})_4^-$] (Ferreira et al., 2006) from dilute solutions. A potential obstacle to the use of hydrotalcite for PO_4^{3-} and/or NO_3^- removal from aqueous solution is its selectivity for CO_3^{2-} over PO_4^{3-} and for many common anions over NO_3^- , with selectivities in the order $\text{CO}_3^{2-} > \text{HPO}_4^{2-} \gg \text{SO}_4^{2-} \approx \text{OH}^- > \text{F}^- > \text{Cl}^- > \text{NO}_3^-$ (Douglas et al., 2004 and references therein).

Batch sorption experiments using synthetic hydrotalcites showed nearly complete removal of vanadate (VO_4^{3-}), arsenate, chromate (CrO_4^{2-}), molybdate (MoO_4^{2-}) and selenate (SeO_4^{2-}) from solution (Lim et al., 2009). The monovalent anions borate and perchlorate (ClO_4^-), however, exhibited only about 50% and <10% sorption to hydrotalcite, respectively (Lim et al., 2009). Results of batch sorption experiments indicated that oxyanions with high valence and small ionic

radius, such as chromate, were more readily removed from solution by hydrotalcites. In aqueous solutions containing Cr(VI) as chromate, dichromate ($\text{Cr}_2\text{O}_7^{2-}$) and hydrogen chromate (HCrO_4^-), Li et al. (2009) observed sorption capacities ranging from 105.3 to 112 g Cr(VI) kg^{-1} hydrotalcite, thus demonstrating the potential for hydrotalcite use in treatment of wastewaters containing Cr(VI), such as effluents of electroplating, leather tanning, chromite beneficiation, fertilizer manufacturing and other industries.

Batch experiments indicated hydrotalcite sorption capacities of approximately 18 mg g^{-1} for both Cd^{2+} and Ni^{2+} ; whereas hydrotalcite calcined at 500°C exhibited sorption capacities of 100 mg g^{-1} for Ni^{2+} and Pb^{2+} , and 70 mg g^{-1} for Cd^{2+} (Lazaridis, 2003). Laboratory experiments showed that a Li-Al hydrotalcite was able to sorb Cr^{6+} , a common contaminant in industrial effluents, from aqueous solution at a maximum rate of ca. 197 mg g^{-1} (Hsu et al., 2007). Although these results indicate that hydrotalcite-like compounds could be used to remove metals from solutes such as drainage waters in the WA Wheatbelt, a potential limitation to hydrotalcite use in the sorption of metals or excess nutrients from acidic solution is that hydrotalcite is unstable at $\text{pH} < 5$ and unable to maintain an adequate AEC under acidic conditions (Ookubo et al., 1993). Further investigation of hydrotalcite-like compounds is required to characterise the sorption capacity of these minerals.

8. DISCUSSION

8.1. Potential Barriers to By-Product Reuse

One of the principal and enduring concerns associated with the reuse of industrial by-products from regulatory agencies is the possibility of environmental contamination via the unintentional release of potentially toxic elements, other contaminants or radionuclides. Furthermore, there is a common perception from within a large proportion of the general public that materials designated as waste or by-products of mining or industry are inherently unsafe. While this may be true in many instances, a carefully validated and pragmatic approach subject to independent scientific peer-review that allows for targeted or “fit for purpose” secondary applications of by-products may eventually allow environmentally useful outcomes for previously discarded or stockpiled materials nominally considered as worthless.

In addition to basic characterisation, laboratory and small-scale field trials that are required to establish safety and efficacy in the desired application, there are a number of standard leaching procedures that can be used to assess the toxicity of leachate from solid products as a cornerstone of establishing potential environment impact and safety. The most common leach methods include the extraction procedure (EP), the TCLP and the synthetic precipitation leaching procedure (SPLP) (EPA, 1992; EPA, 1994; EPA, 2004). In addition, the American Society for Testing and Materials has proposed a standard method to investigate leaching of potentially toxic elements using water rather than an acid solution to leach solid material (ASTM-D3987). Both the EP and TCLP are designed to assess leaching behaviour of solid wastes disposed in a municipal landfill, with the assumption that the solid waste will comprise approximately 5% of the total waste in the landfill. The SPLP is designed to simulate a monofill disposal scenario, where there is no mixing of the solid waste with any other waste or fill material. The ASTM shake extraction of solid waste with water method is designed for use where the solid waste is the dominant factor in determining the solution pH of the extract. The method selected for leachate characterisation or assessment of leachate toxicity is highly dependent upon the intended application of the solid material and may span a number of trophic levels, and will also vary depending on the environmental conditions under which the material may be utilised.

Concerns have been raised about the applicability of existing “standard” leaching tests to assess industrial by-products prior to their reuse (van der Sloot et al., 2006). Recent efforts have focused on developing standardised leaching tests that characterise contaminant release in leachates (1) as a function of time, and (2) as a function of the controlling parameters pH, oxidative-reductive potential (redox status) and potential complexation (Gawlik et al., 2004; van der Sloot, 1996). In particular, project HORIZONTAL, supported by the European Committee for Standardisation (CEN), is an interdisciplinary effort to develop standard analytical methods for the characterisation of solid “waste” materials (van der Sloot et al., 2001). Adoption of internationally-recognised analytical methods for the analysis of contaminants in solid materials will seek to resolve the current inability to compare results between different jurisdictions or between disciplines.

Because many sorption and precipitation reactions in soil environments are governed by pH, a pH-dependent leach test is particularly appropriate for characterisation of industrial by-products with the potential for future reuse as environmental amendments. One such leaching protocol is the pH-static leach test (CEN/TC 292 TS 14429), in which crushed material is leached at eight pH values between 2 and 13, each at a liquid to solid ratio of 10 (van der Sloot et al., 2007). After 48 hours equilibration at the designated pH, leachates are analysed for contaminants. A pH-static leaching technique (CEN/TC 292 TS 14497) can also be used to examine contaminant release from solid materials over time by removing aliquots of solution from batch reactors equilibrated at each set pH (2-13) at predetermined times throughout the experiment (*e.g.*, between 3 and 168 h). This method was used by Dijkstra et al. (2006) to analyse leaching from municipal solid waste incineration fly ash, and has also been used on materials as diverse as contaminated soils and sediments, stabilised and mixed landfill wastes, cement and other construction materials, and sewage sludge (van der Sloot et al., 1996, 2006, 2007; van der Sloot, 2000).

8.2. Further Study

A number of mineral-based by-products and other materials produced in large volumes in Western Australia demonstrate potential for reuse as environmental amendments (Table 8). There are, however, issues that must be addressed prior to implementation of any soil remediation or water treatment scheme utilising mining, mineral processing or industrial by-products. Extensive study is required to quantify the efficacy of acid neutralisation and removal of nutrients and/or potentially toxic elements from treated waters, to fully characterise the geochemical interactions between potential receiving waters and each mineral-based by-product sorbent, and to analyse resultant waters/leachate for potential ecological toxicity. Detailed characterisation of locally and regionally available industrial by-product materials is required to develop and critically assess viable remediation options. In addition, 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 to the effective long-term treatment of the highly acidic, hypersaline drainage waters of the WA Wheatbelt and in particular where waters discharge into ecologically-sensitive receiving environments.

In a broader context, it is unlikely that a single low-cost industrial by-product possesses all the physico-chemical characteristics necessary for a range of applications including the treatment of waters and soils of the WA Wheatbelt or removal of nutrients from surface or groundwater in the Swan Coastal Plain. 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/or 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).

Based on existing information, a number of mining, mineral-processing and industrial by-products or low-value materials may be useful as environmental amendments (Table 8). For example, one or more of carbonate materials and their derivatives, cement kiln dust, fly ash, red mud, steelmaking by-products and mine overburden could be useful for the neutralisation of acidity. Alternatively, if the goal were to attenuate excess nutrients from solution, cement kiln dust, fly ash, wastewater treatment residues, red mud, red sand, heavy minerals processing residues, gypsum, or steelmaking by-products may prove particularly useful for PO₄-P removal. Zeolites, red sand, and red mud could potentially be utilised for NH₃-N attenuation. Further investigation is required to comprehensively characterise these and other materials and to assess their suitability for use as soil amendments or water treatment media in environmental remediation schemes.

Contaminant removal from natural and wastewaters, and amelioration of acidity in both water and soils are core environmental management priorities for a sustainable Western Australia. Utilisation of abundant, low-cost industrial by-product materials potentially offers a cost-effective wastewater treatment option. Research is currently underway to examine the productive re-use largely unexploited by-products or low-cost mineral-based materials, primarily from Western Australia, as “designer” contaminant adsorbents (http://portal.water.wa.gov.au/portal/page/portal/PlanningWaterFuture/PremiersWaterFoundation/Content/FundedProjects/CSIRO_wastewater_Purification_00905_details.pdf). 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 mining, mineral processing and industrial by-products with the specific aim of identifying by-product materials “fit for purpose” for specific environmental applications.

Table 8. Summary of potential soil and surface water amendments and some pertinent properties. ANC = acid neutralisation capacity.

| By-product | Chemistry/mineralogy | Occurrence | Modification | Metal uptake | Nutrient uptake | ANC |
|--|--|---|------------------------------------|---|---|----------------------------------|
| Carbonates and derivatives | | | | | | |
| Limestone/calcrete/limesand | CaCO ₃ ; primarily calcite & aragonite | Widely available | May require crushing | Immobilisation via surface sorption &/or precipitation of metal hydroxides; Fe-armouring during use | Effective PO ₄ ³⁻ removal but slow due to rate of mineral dissolution | High |
| Lime | Quicklime (CaO) or hydrated lime (Ca(OH) ₂) | Commercially available | Available in powder form | Primarily immobilisation via precipitation of metal hydroxides. | Highly effective PO ₄ ³⁻ removal via precipitation &/or adsorption, and flocculation of suspended solids | High |
| Calcined magnesia or magnesium hydroxide | Calcined magnesia (MgO) or Mg(OH) ₂ ; periclase & brucite | By-product of magnesia industry | May require crushing | High metal uptake/sorption due to precipitation of metal hydroxides &/or formation of hydrotalcite minerals | Moderate PO ₄ ³⁻ removal & low to moderate NH ₄ ⁺ removal via via struvite precipitation | Very high |
| Dolomite | CaMg(CO ₃) ₂ ; dolomite, with minor magnesite, calcite | Widely available | May require crushing | Primarily immobilisation via precipitation of metal hydroxides | Moderate to high PO ₄ ³⁻ removal via sorption &/or precipitation | Moderate to high |
| Industrial by-products | | | | | | |
| Cement kiln dust | Largely CaO and Ca(OH) ₂ ; portlandite | By-product of cement production | None | Effectively removes metal ions from solution via precipitation as metal hydroxides (pH-dependent) | Effective PO ₄ ³⁻ removal via hydroxyapatite precipitation | High |
| Fly ash | Largely CaCO ₃ and CaO; quartz & mullite | By-product of electricity production (coal combustion) | None | Effectively removes metal ions from solution, primarily via precipitation as metal hydroxides | Effectively removes PO ₄ ³⁻ from aqueous solution; zeolitised FA effectively removes NH ₄ ⁺ and PO ₄ ²⁻ from solution | High |
| Wastewater treatment sludge | Variable due to different treatment processes and source water; generally high in Fe and/or Al | Produced in large volumes in water treatment plants | Dewatering may be required for use | Removes metal ions from solution via sorption and/or precipitation as metal hydroxides | Effective PO ₄ ³⁻ sorbent | Variable, but generally moderate |
| Carbonised wood products | Primarily Al ₂ O ₃ & CaO; amorphous carbon or charcoal | Produced in large volumes from integrated tree processing | None | | | Moderate |

Table 8 (continued). Summary of potential soil and surface water amendments and some pertinent properties. ANC = acid neutralisation capacity.

| By-product | Chemistry/mineralogy | Occurrence | Modification | Metal uptake | Nutrient uptake | ANC [†] |
|---------------------------------------|---|--|--|---|--|------------------|
| Mineral processing by-products | | | | | | |
| Red mud | Complex Fe & Al oxides/oxyhydroxides; primarily goethite & hematite | By-product of alumina refining (Bayer process) | Neutralisation, as by seawater or gypsum addition | Both pH dependent and independent mechanisms responsible for metal fixation; oxyanions can be sorbed under acidic conditions due to pH-dependent charge | Excellent PO ₄ ³⁻ sorbent; effectively sorbs NH ₄ ⁺ ; no effect on NO ₃ -N leaching | High |
| Red sand | Complex Fe & Al oxides/oxyhydroxides; goethite, hematite & quartz | By-product of alumina refining (Bayer process) | Neutralisation, as by seawater or gypsum addition | Both pH dependent and independent mechanisms responsible for metal fixation; oxyanions can be sorbed under acidic conditions | Excellent PO ₄ ³⁻ sorbent; effectively sorbs NH ₄ ⁺ ; no effect on NO ₃ -N leaching | Moderate |
| Heavy minerals processing residue | CaO, SO ₄ and Fe ₂ O ₃ ; gypsum, Fe oxyhydroxides, magnetite & quartz | By-product of heavy mineral processing | Screening and possible mixing with sand to increase permeability | Both pH dependent and independent mechanisms responsible for metal fixation; some oxyanions may be sorbed under acidic conditions | Excellent PO ₄ ³⁻ sorbent. May also remove organic-bound P and N | Moderate |
| Gypsum | CaSO ₄ ; gypsum, bassanite | By-product of power generation | May require drying and crushing prior to application | Moderate metal attenuation via precipitation reactions at alkaline pH | Effectively removes PO ₄ ³⁻ via precipitation of Ca ²⁺ phosphates, best at alkaline pH (e.g. pH 7-12) | Mid-high |
| Steelmaking by-products | SiO ₂ and Al ₂ O ₃ with Ca ²⁺ and Mg ²⁺ ; gehlenite (Ca ₂ Al ₂ SiO ₇), pyroxene, spinel & quartz | By-product of steel manufacturing | Requires pelletisation or crushing prior to use to increase surface area | Effectively removes some metals from solution, sorption is pH-dependent | Effectively removes PO ₄ ³⁻ from aqueous solution via sorption and precipitation reactions | High |

Table 8 (continued). Summary of potential soil and surface water amendments and some pertinent properties. ANC = acid neutralisation capacity.

| By-product | Chemistry/mineralogy | Occurrence | Modification | Metal uptake | Nutrient uptake | ANC [†] |
|---|--|---|---|--|--|------------------|
| Natural minerals | | | | | | |
| Mine overburden | Variable | Widely available | Requires crushing prior to use to increase surface area | Metal attenuation via sorption and/or precipitation as metal hydroxides | Low to high depending on mineralogy and solution pH | Low to high |
| Laterite | Primarily Al ₂ O ₃ & Fe ₂ O ₃ ; hematite, gibbsite & quartz | Widely available | Requires crushing prior to use to increase surface area | Both pH dependent and independent mechanisms responsible for metal fixation; oxyanions can be sorbed under acidic conditions | | Moderate |
| Hydrotalcites | Variable, usually Mg, Al, Fe hydroxides ; layered double hydroxide (LDH) minerals | Present in soils & sediments or may be synthesized | None or possibly purification or stabilisation | High CEC, high metal uptake via sorption or cation exchange | High PO ₄ ³⁻ removal via anion exchange, but strongly pH-dependent | Low |
| Zeolites | Complex mineralogy; cage and channel tectosilicates formed by SiO ₄ ⁴⁻ and AlO ₄ ⁵⁻ tetrahedra | Components of mafic igneous and sedimentary rocks, also commercially available | None necessary, although saturation of exchange sites with Na ⁺ /Ca ²⁺ may improve ion exchange | Effective removal of metal ions from solution via cation exchange | Effective NH ₄ ⁺ removal from solution via ion exchange; some PO ₄ ³⁻ sorption on modified zeolite | Low |
| Phyllosilicates (illite, smectite, vermiculite) | Variable, usually Na, K, Ca, Fe, Mg aluminosilicates ; layer silicate structure | Ubiquitous weathering products of primary minerals, also commercially available | , Intercalation e.g. organo-composites or pillaring, surface adsorption, cation exchange, acid activation, calcination, dehydration | Effective removal of metal ions from solution via cation exchange and adsorption | Low to high depending on mineralogy, modification and solution pH | Low to moderate |

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