



Review

Alkaline residues and the environment: a review of impacts, management practices and opportunities



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ABSTRACT

Around two billion tonnes of alkaline residues are produced globally each year by industries such as steel production, alumina refining and coal-fired power generation, with a total production estimate of 90 billion tonnes since industrialisation. These wastes are frequently stored in waste piles or landfills, and can be an environmental hazard if allowed to generate dust, or if rainwater infiltrates the waste. This review will focus on the environmental impacts associated with alkaline residues, with emphasis on the leachates produced by rainwater ingress. Many alkaline industrial wastes can produce leachates that are enriched with trace metals that form oxyanions (e.g. As, Cr, Mo, Se, V), which can be very mobile in alkaline water. The management options for the residues and their leachates are also discussed, distinguishing active and passive treatment options. Potential reuses of these materials, in construction materials, as agricultural amendments, and in environmental applications are identified. The mechanisms of carbon sequestration by alkaline residues are assessed, and the potential for enhancing its rate as a climate change off-setting measure for the industry is evaluated. The potential for recovery of metals critical to e-technologies, such as vanadium, cobalt, lithium and rare earths, from alkaline residues is considered. Finally research needs are identified, including the need to better understand the biogeochemistry of highly alkaline systems in order to develop predictable passive remediation and metal recovery technologies.

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Contents

1. Introduction	3572
2. Methods	3572
3. Types of alkaline waste	3572
4. Environmental impacts	3574
4.1. Acute and chronic episodes	3574
4.2. Pollutant pressures	3574
4.3. Biological impacts	3575
5. Management	3575
6. Environmental and industrial applications	3576
7. Opportunities	3576
7.1. Carbon sequestration	3576
7.2. Recovery	3577
7.3. Biological resource	3579

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8. Summary of research needs	3579
Funding sources	3579
Supplementary data	3579
References	3579

1. Introduction

Many industrial processes, such as coal combustion (Cabrera et al., 1986; Heidrich et al., 2013; Moreno et al., 2005; Yao et al., 2015), lime production (Steinhauser, 2008), chromium ore processing (Darrie, 2001; Freese et al., 2015; Geelhoed et al., 2002), cement production (Adaska and Taubert, 2008), alumina extraction (Burke et al., 2012b; Power et al., 2011), iron and steel manufacture (Mayes and Younger, 2006; Motz and Geiseler, 2001; Piatak et al., 2015), and waste incineration (Astrup et al., 2006; Bogush et al., 2015; De Boom and Degrez, 2012; Ferreira et al., 2003; Johnson et al., 1999; Quina et al., 2008) produce alkaline residues, representing a large and increasing global flux (Table 1) (Power et al., 2011; USGS, 2015a). While there are significant differences in bulk mineralogical composition among these residues, all are characterised by the presence of Na, Ca or Mg oxides that rapidly hydrate to produce soluble hydroxides. A large range of Ca and Na silicate, aluminate and aluminosilicate phases are also present, hydrating and dissolving to generate alkalinity. Finally, any Ca and Mg carbonates present provide a stable (low solubility) alkaline phase. Initially, dissolution of soluble Na or Ca hydroxides tends to dominate ($\text{pH} > 12$) (Gräfe et al., 2011; Mayes et al., 2008; Roadcap et al., 2005). Over time, the more slowly reacting phases [e.g. Ca silicates, Na aluminosilicates, $\text{Mg}(\text{OH})_2$] control leachate quality ($9 < \text{pH} < 12$). On long timescales, carbonate dissolution prevails ($\text{pH} < 9$). Therefore, despite the differences in composition, there are clear similarities in terms of the environmental hazards posed by leaching processes and in opportunities for valorisation of their by-products. The aim of this review is to assess the environmental impacts of alkaline residues and best-practices in terms of management. Research needs will be identified, highlighting the value of integrated production and management in a resource-constrained future where CO_2 sequestration is also necessary.

2. Methods

A comprehensive search on the Web of Science database was conducted, using as key words “alkaline residues AND” “impact”, “management”, “production”, “alkalinity”. The search was restricted initially to literature later than 2005, but older works were also considered as important references.

3. Types of alkaline waste

The main types of alkaline residues, their amounts and primary source of alkalinity are listed in Table 1. Aluminium production by the Bayer process generates bauxite processing residue (red mud). Bauxite is digested in a hot NaOH solution that converts the alumina to dissolved aluminium hydroxide. The solid impurities that are filtered from the liquor are called red mud (Binnemans et al., 2013). The mineralogical composition of bauxite residues has been recently reviewed and depends on bauxite source and process methods (Gräfe et al., 2011), but typically comprises residual iron oxides, quartz, sodium aluminosilicates, titanium dioxide, calcium carbonate/aluminate (Lehoux et al., 2013). These residues generate aqueous alkalinity associated with NaOH in red

mud suspension, and solid alkalinity from hydroxides, carbonates, aluminates and aluminosilicates (Table 1) (Gräfe et al., 2011).

Steelworks slags are produced in various stages of steelmaking through the reaction of process impurities (primarily silica) with CaO (Bobicki et al., 2012; Eloneva et al., 2010). The slag is named after the process where they are generated: basic oxygen furnace (BOF), electric arc furnace (EAF) and ladle furnace (LF) (Bobicki et al., 2012; De Windt et al., 2011; Navarro et al., 2010; Wang et al., 2010). A recent review presents a summary of major, minor, and trace element chemistry of the slag by type from 70 studies (Piatak et al., 2015). Alkalinity generation from steel slags arises from two processes: the rapid hydration and subsequent dissociation of Ca and Mg oxides, alongside the slower dissolution of Ca-silicates minerals, such as rankinite, larnite and akermanite (Mayes et al., 2008; Roadcap et al., 2005) (Table 1).

Fly ashes are one of the residues generated by coal combustion for electricity production and are captured by electrostatic precipitators or bag filters before the flue gases are emitted (Cabrera et al., 1986; Heidrich et al., 2013; Moreno et al., 2005). Fly ashes can be siliceous or calcareous, depending on the coal type, and consist primarily of glassy spheres with some crystalline matter and unburn carbon (Heidrich et al., 2013; Moreno et al., 2005). Silicon, aluminium and iron oxides account for 75–85% (Heidrich et al., 2013). Lime content is usually less than 10%, but higher in calcareous ashes (>10%) (Heidrich et al., 2013). Leachate alkalinity is generated in a similar manner to steel slags.

Within the broad class of materials that fall into the category of construction and demolition waste, concrete crusher fines can pose disposal issues through their composition and leaching properties (Butera et al., 2014). The CaO content of demolition wastes varies from 2.6% in masonry to 28.6% in concrete, blocks and aggregate (Renforth, 2011; Renforth et al., 2011). With concrete crusher fines leachate alkalinity is generated predominantly by the remaining CaO and the hydrolysis of calcium-silica phases (Table 1).

Flue gas desulfurisation wastes are the result of SO_x removal from exhaust flue gases of fossil-fuel power plants and other sulphur oxide emitting processes with an alkali sorbent such as CaO or $\text{Ca}(\text{OH})_2$ in the dry processes, and CaCO_3 or $\text{Ca}(\text{OH})_2$ in the wet processes (Córdoba, 2015; Khatib et al., 2013). Air pollution control (APC) residues are the solid output of flue gas treatment, comprising the fly ash and the reagents (mainly CaO and activated carbon) used in the flue gas treatment (Quina et al., 2008). The remaining CaO and $\text{Ca}(\text{OH})_2$ in the residues and calcium-silica phases generate alkalinity (Table 1).

Solvay process waste results from the production of sodium carbonate, one of the most important inorganic chemicals (37 million tonnes globally in 2014) (Steinhauser, 2008; USGS, 2015b). The process uses salt brine as source of NaCl and limestone, generating distillation sludges and solid wastes from brine purification, both of which contain CaO and $\text{Mg}(\text{OH})_2$ as main sources of alkalinity (Steinhauser, 2008).

Highly alkaline chromite ore processing residue (COPR) results primarily from the obsolete high lime process, where chromite ore is mixed with alkali carbonate and lime or dolomite, heated to 1150 °C to oxidise Cr(III) to Cr(VI), and the soluble Cr(VI) is then extracted by leaching with water (Geelhoed et al., 2003). The high

Table 1

Classification of alkaline residues, annual production and primary sources of alkalinity.

Type	Dominant mineral matrix	Production (t a ⁻¹)	Primary sources of alkalinity
Bauxite residues or red mud (Bayer process in aluminium production)	Iron oxides, Na(Ca)-aluminosilicates, Ti(Fe) oxides, natrite (Na ₂ CO ₃), calcite (CaCO ₃) and NaOH (Gräfe et al., 2011; Xue et al., 2015)	120 million (Power et al., 2011)	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{NaOH}$; $\text{NaOH} \rightleftharpoons \text{Na}^+ + \text{OH}^-$ $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{NaOH} + 24\text{H}_2\text{O} \rightleftharpoons 8\text{Na}^+ + 8\text{OH}^- + 6\text{Al}(\text{OH})_3 + 6\text{H}_4\text{SiO}_4$ $\text{Na}_6[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{CaCO}_3 + 26\text{H}_2\text{O} \rightleftharpoons 6\text{Na}^+ + 2\text{Ca}^{2+} + 8\text{OH}^- + 2\text{HCO}_3^- + 6\text{Al}(\text{OH})_3 + 6\text{H}_4\text{SiO}_4$ $\text{Ca}_4\text{Al}_2(\text{OH})_{12} \cdot \text{CO}_3 \cdot 6\text{H}_2\text{O} + 7\text{H}_2\text{O} \rightleftharpoons 4\text{Ca}^{2+} + 2\text{Al}(\text{OH})_3(\text{aq}) + \text{HCO}_3^- + 7\text{OH}^- + 6\text{H}_2\text{O}$ $\text{Ca}_3\text{Al}_2[(\text{OH})_{12-4n}(\text{SiO}_4)_n(\text{s}) + \text{H}_2\text{O} \rightleftharpoons 3\text{Ca}^{2+} + 2\text{Al}(\text{OH})_3 + 6\text{OH}^-$ $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}(\text{s}) + \text{H}_2\text{O} \rightleftharpoons 2\text{Na}^+ + \text{HCO}_3^- + \text{OH}^- + 10\text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$ $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $\text{Ca}_3\text{Si}_2\text{O}_7 + 7\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+} + 2\text{H}_4\text{SiO}_4 + 6\text{OH}^-$ $\text{Ca}_2\text{SiO}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 4\text{OH}^-$ $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7 + 5\text{H}_2\text{O} \rightleftharpoons \text{SiO}_2 + 2\text{Al}(\text{OH})_3 + 2\text{Ca}^{2+} + 4\text{OH}^-$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$ $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{H}_2\text{O} \rightleftharpoons 2\text{SiO}_2 + \text{Ca}^{2+} + 2\text{Al}^{3+} + 8\text{OH}^-$
Steelworks slags	Free lime (CaO) and periclase (MgO), Ca-silicates, Ca-Fe(Al)-oxides and refractory Mg-Fe(Mn)-oxide phases (Piatak et al., 2015)	170–250 million (USGS, 2015a)	$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$ $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $\text{Ca}_3\text{Si}_2\text{O}_7 + 7\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+} + 2\text{H}_4\text{SiO}_4 + 6\text{OH}^-$ $\text{Ca}_2\text{SiO}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + \text{H}_4\text{SiO}_4 + 4\text{OH}^-$ $\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7 + 5\text{H}_2\text{O} \rightleftharpoons \text{SiO}_2 + 2\text{Al}(\text{OH})_3 + 2\text{Ca}^{2+} + 4\text{OH}^-$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$ $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{H}_2\text{O} \rightleftharpoons 2\text{SiO}_2 + \text{Ca}^{2+} + 2\text{Al}^{3+} + 8\text{OH}^-$
Fly ashes (coal combustion)	Quartz (SiO ₂), magnesioferrite (MgFeO ₄), anorthite (CaAl ₂ Si ₂ O ₈), anhydrite (CaSO ₄), haematite (Fe ₂ O ₃), mullite (Al ₆ Si ₂ O ₁₃) and lime (CaO) (Yilmaz, 2015)	415 (Heidrich et al., 2013)–600 million (Bobicki et al., 2012)	$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$ $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{CaAl}_2\text{Si}_2\text{O}_8 + 4\text{H}_2\text{O} \rightleftharpoons 2\text{SiO}_2 + \text{Ca}^{2+} + 2\text{Al}^{3+} + 8\text{OH}^-$
Concrete crusher fines	Quartz (SiO ₂), calcite (CaCO ₃), Na(Ca)-aluminosilicates, albite (NaAlSi ₃ O ₈) and portlandite Ca(OH) ₂ (Somasundaram et al., 2014)	497–2095 million (Renforth et al., 2011)	$\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{Ca}_3\text{Al}_2(\text{OH})_{12} \rightarrow 3\text{Ca}^{2+} + 2\text{AlO}_2^- + 4\text{OH}^- + 4\text{H}_2\text{O}$ $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_{0.8}(\text{OH})_{8.8} \rightarrow 3\text{Ca}^{2+} + 2\text{AlO}_2^- + 0.8\text{HSiO}_3^- + 3.2\text{OH}^- + 2.4\text{H}_2\text{O}$ $\text{Ca}_4\text{Al}_2(\text{SO}_4)(\text{OH})_{12} \cdot 6\text{H}_2\text{O} \rightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{SO}_4^{2-} + 4\text{OH}^- + 10\text{H}_2\text{O}$ $\text{Ca}_2\text{Al}_2\text{SiO}_2(\text{OH})_{10} \cdot 3\text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{HSiO}_3^- + \text{OH}^- + 7\text{H}_2\text{O}$ $\text{Ca}_4\text{Al}_2(\text{CO}_3)(\text{OH}) \cdot 5\text{H}_2\text{O} \rightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{CO}_3^{2-} + 4\text{OH}^- + 9\text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} \rightarrow 6\text{Ca}^{2+} + 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 12\text{OH}^- + 26\text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$
Flue gas desulphurisation waste	Hannebachite (CaSO ₃ ·0.5H ₂ O), calcite (CaCO ₃), lime (CaO), mullite (Al ₆ Si ₂ O ₁₃) quartz (SiO ₂), haematite (Fe ₂ O ₃), magnetite (Fe ₃ O ₄), and ettringite [Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O] (NERC, 1980)	11 million (Córdoba, 2015)	$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O} \rightarrow 6\text{Ca}^{2+} + 2\text{Al}^{3+} + 3\text{SO}_4^{2-} + 12\text{OH}^- + 26\text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$
Air pollution control (APC) residues	Calcite (CaCO ₃), gypsum (CaSO ₄), CaClOH, portlandite [Ca(OH) ₂], lime (CaO), ettringite [Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ ·26H ₂ O], Quartz (SiO ₂) (Bogush et al., 2015)	1.2 million ^a	$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{CaClOH} \rightleftharpoons \text{Ca}^{2+} + \text{Cl}^- + \text{OH}^-$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$ $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$; $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CrO}_4 \cdot 6\text{H}_2\text{O} \rightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{CrO}_4^{2-} + 2\text{OH}^- + 10\text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$
Solvay process waste	Calcite (CaCO ₃), lime (CaO), gypsum (CaSO ₄ ·2H ₂ O), brucite [Mg(OH) ₂] (Steinhauser, 2008)	15.5 thousands ^b	$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$ $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$ $\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$; $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CrO}_4 \cdot 6\text{H}_2\text{O} \rightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{CrO}_4^{2-} + 2\text{OH}^- + 10\text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$
Chromite ore processing residue (COPR)	Free lime (CaO), portlandite [Ca(OH) ₂], brucite [Mg(OH) ₂], calcite (CaCO ₃), hydrocalumite [Ca ₄ Al ₂ (OH) ₁₂ CrO ₄ ·6H ₂ O], periclase (MgO) (Geelhoed et al., 2003)	6 million ^c (Wu et al., 2015)	$\text{CaO} + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2$; $\text{Ca}(\text{OH})_2 \rightleftharpoons \text{Ca}^{2+} + 2\text{OH}^-$ $\text{MgO} + \text{H}_2\text{O} \rightleftharpoons \text{Mg}(\text{OH})_2$; $\text{Mg}(\text{OH})_2 \rightleftharpoons \text{Mg}^{2+} + 2\text{OH}^-$ $\text{Ca}_4\text{Al}_2(\text{OH})_{12}\text{CrO}_4 \cdot 6\text{H}_2\text{O} \rightarrow 4\text{Ca}^{2+} + 2\text{AlO}_2^- + \text{CrO}_4^{2-} + 2\text{OH}^- + 10\text{H}_2\text{O}$ $\text{CaCO}_3 + \text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + \text{H}_2\text{CO}_3$

^a Calculated for EU28 considering 2.54% (Brunner and Rechberger, 2015) of waste incinerated (EUROSTAT, 2015).^b Calculated with the USGS soda ash production data (USGS, 2015b) and the amount of wastes produced with the BREF (CEFC, 2004).^c Residue produced in China only.

lime process was discontinued in the USA and Europe in the 1960s after concerns of adverse health effects for workers (Freese et al., 2015). This phase-out continues globally, but facilities in Russia, China, India and Pakistan still use it, accounting for 40% of global chromate production in 2007 (Freese et al., 2015; Wang et al., 2007). Chromite ore processing residue generates alkalinity from the remaining CaO, but the dissolution of Ca–Al–Cr oxides also generates aqueous Cr(VI) and hydroxide (Chrysochoou et al., 2009).

4. Environmental impacts

4.1. Acute and chronic episodes

The environmental impacts of alkaline residues can be locally severe (Roadcap et al., 2005) and long-lived (Mayes et al., 2008), and can affect terrestrial and aquatic environments. Negative impacts can result from both accidental releases and from reuse of the residue, e.g. as construction material. These impacts can be divided into: (a) relatively brief but acute episodes, associated with residue repository failure, and (b) chronic problems associated with improper management of waste (poor control of dust, surface water run-off and leachate) (Burke et al., 2012b). There have been recent comprehensive reviews of tailings/residue repository failures, including alkaline residues (Alonso Pérez de Agreda and Gens Solé, 2006; Azam and Li, 2010; Kossoff et al., 2014). These include three major coal ash failures this century (Table 1, Supplementary information), alongside one of the most high profile episodes (Bednar et al., 2013; Dennis Lemly, 2015; Otter et al., 2015) – the red mud repository failure in Ajka (Hungary) in 2010 (Ádám et al., 2011; Anton et al., 2014; Burke et al., 2012a; Mayes et al., 2011). This accident released about one million m³ of red mud, which was transported over 120 km downstream, inundating 40 km² of agricultural and urban land, killing ten people and causing severe injuries (Ádám et al., 2011; Burke et al., 2012a).

The most widespread chronic impact of alkaline wastes is that of the leachate on receiving waters, especially with old and abandoned disposal sites. The geochemical behaviour of the alkaline leachate depends on the chemistry of the infiltrating water; the physicochemical composition and age of the residue; the nature of any co-deposited wastes; the hydrogeological setting (e.g. flow rates, redox status, residence time of water); the properties of the native ground, and the receiving water chemistry (Mayes et al., 2008). Impacts of alkaline leachates include increased water pH, high chemical oxygen demand and oxygen depletion in the water column, high sulphate loadings, salinity, and increase of metal concentrations (Mayes and Younger, 2006; Mayes et al., 2008). These issues are coupled with extremely rapid rates of mineral precipitation (mostly calcite), making leachate streams analogous to natural travertine deposits (through CO₂ vigorously in-gassing into the leachate waters) (Andrews et al., 1997; Rogerson et al., 2008). The precipitates can smother macroinvertebrate communities and reduce light penetration amplifying the ecological cost of leachate release (Hull et al., 2014). Steel slag leachate altered the alkalinity, pH, and calcium, and magnesium concentrations in a small Pennsylvania stream, Nine Mile Run, and fish were absent in the water course where pH > 10 (Koryak et al., 2002). The impact of former steel mills in the UK is also well documented, showing the same issues already described (Hull et al., 2014; Mayes and Younger, 2006; Mayes et al., 2008; Riley and Mayes, 2015). Hyperalkaline waters have been reported at Lake Calumet (Chicago, Illinois, USA) where a wetland was infilled with steel slag (Roadcap et al., 2005), and at Gorka Lake (Poland) (Czop et al., 2011) and Kinghorn Loch (Scotland) where red mud was deposited (Edwards, 1986). There are relatively few studies on the longevity of the pollution from alkaline residues. However, leachates from steel mill

sites can continue for over 30 years after closure (Mayes et al., 2008), while residual releases from Solvay waste beds impacted negatively surface waters >15 years after operations cease (Effler and Matthews, 2003). Hyperalkaline water (pH > 12) has leached from an abandoned COPR waste tip for more than 100 years after the disposal (Whittleston et al., 2011). As such, closure plans for alkaline residue repositories should incorporate multi-decadal legacy plans.

4.2. Pollutant pressures

The alkalinity generating reactions detailed in Table 1 raise leachate pH above typical regulatory thresholds for discharge to water bodies (usually 9) (Mayes et al., 2008), and also have a major influence on the mobility of common contaminants (Fig. 1). Many ore bodies and waste streams contain trace quantities of metals such as arsenic, beryllium, cadmium, chromium, lead, manganese, mercury, molybdenum, nickel, selenium, thorium and uranium (De Boom and Degrez, 2012; Klauber et al., 2011; Piatak et al., 2015;

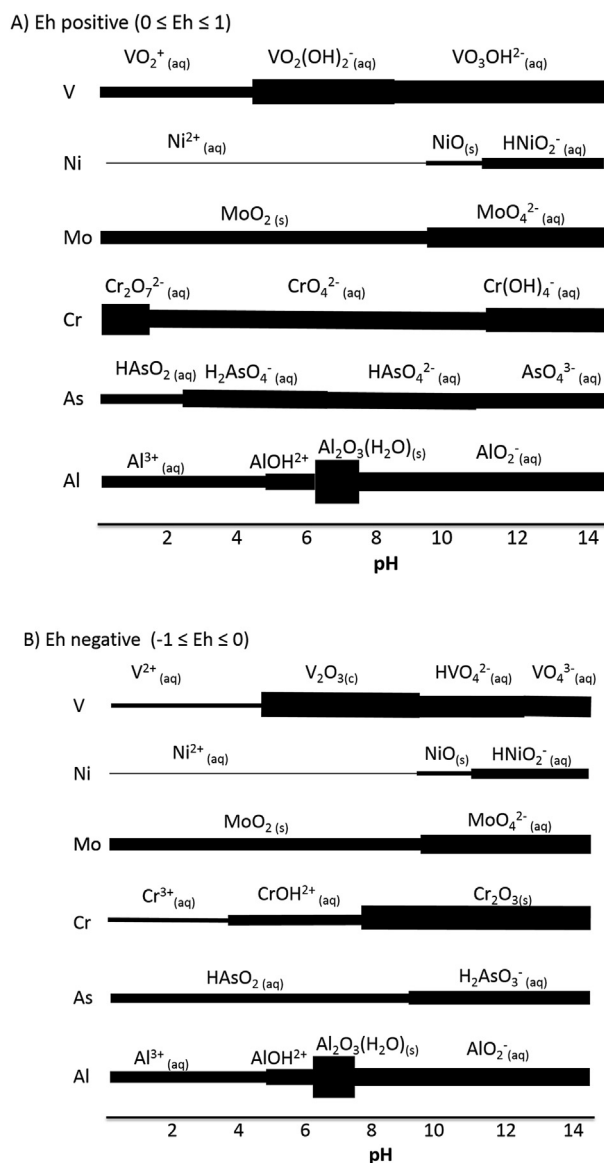


Fig. 1. Main species present in aqueous solution at different pH values in aerobic (A; 0 ≤ Eh ≤ 1) and anaerobic (B; -1 ≤ Eh ≤ 0) media.

Somasundaram et al., 2014; Yao et al., 2015). The trace metals of most environmental concern are those potentially soluble at high pH, because they form oxyanions (e.g. As, Cr, Mo, Se and V), which can be very mobile as they sorb weakly to soils and sediments (Cornelis et al., 2008; Mayes et al., 2011). High concentrations of As (0.6–5.2 mg L⁻¹), Cr (0.2–4.9 mg L⁻¹), V (1.2–5.4 mg L⁻¹), Mo (0.3–2.6 mg L⁻¹), and Ga (0.3–1.5 mg L⁻¹) were found in Gorka Lake, Poland, where red mud was deposited (Czop et al., 2011). After the Ajka spill in Hungary similar patterns with elevated Al, V, As, and Mo were observed in the Marcal and Rába river systems, and elevated Cr, Ga, and Ni concentrations were observed in aqueous (filtered at 0.45 µm) and particulate phases within 2 km of the source (Mayes et al., 2011). By 2013, the geochemical signal of the red mud was largely absent from the previously affected river systems, indicating that the impact on river quality was limited by this time (Anton et al., 2014). However, arsenic and nickel levels were moderately raised in the Marcal River two years after the spill compared with the pre-disaster period (Nagy et al., 2013).

Oxyanions can also be found in other alkaline residue leachates. Waters draining steel slag mounds (Mayes et al., 2008) and fly ash disposal sites (Cornelis et al., 2008) showed environmentally significant concentrations of various oxyanions including As, Cr and V. Chromium concentrations of up to 91 mg L⁻¹ [>90% as Cr(VI)] have been found in the porewater at a COPR landfill in Glasgow (UK), and Cr concentrations of up to 6.7 mg L⁻¹ were measured in a local tributary stream affected by the landfill more than 30 years after its closure in 1968 (Farmer et al., 2002).

Interactions with the surrounding geochemical environment can be critical in determining the risk posed by alkaline residues after environmental release or in after-uses. After the Ajka red mud spill, at floodplain locations where only a thin layer of red mud was deposited (<5 cm), the material was ploughed into the subsoil to prevent dust formation and further dispersal (Ádám et al., 2011; Lockwood et al., 2014). However, it was found that abundant competing ions such as carbonate and phosphate could enhance arsenate release (Lockwood et al., 2014). Furthermore, the mixing of red mud into organic-rich soils can potentially mobilise Cu and Ni as organically bound complexes, via soil alkalinisation (Lockwood et al., 2015). Similar mobilisation of vanadium through complexation with low molecular weight carboxylic acids after organic amendment has also been documented (Karsson et al., 2011; Sjöberg et al., 2011). Such processes have a bearing not just of accidental release, but also in repository rehabilitation where organic materials are introduced to aid revegetation (Courtney and Kirwan, 2012).

4.3. Biological impacts

Alkaline pH (pH 8.5–10) can cause severe physiological disturbance to most fish, inhibiting the rate of ammonia excretion, leading to its accumulation and toxicity (Saha et al., 2002). The precipitation of calcite from alkaline leachates smother benthic and littoral aquatic habitats, and reduces light penetration to primary benthic producers (Mayes and Younger, 2006). Data from a former steel slag disposal site in Consett, UK shows a stream receiving leachate from the slag heap highly impacted at source, but ~500 m downstream, where the pH lowers to 9, complex biological communities become established and there is a rapid recovery of benthic invertebrate communities (Hull et al., 2014). Reduced diversity and abundance of zooplankton assemblages have also been recorded, alongside suppression in macrophyte growth at Solvay waste impacted waters in Onondaga Lake, NY, USA with excess rates of carbonate precipitation (Effler and Matthews, 2003).

Red mud toxicity tests showed the most pronounced effects in *Vibrio fischeri* bioluminescence inhibition, *Lemna minor* bioassay

and *Sinapis alba* root and shoot growth (Klebercz et al., 2012). Red mud was also found to inhibit the root growth of *S. alba* and affected the shoot yield in barley (*Hordeum vulgare*) (Klebercz et al., 2012; Ruyters et al., 2011). Sodium was identified as the principal cause of restricted plant growth (Ruyters et al., 2011). Other studies showed genotoxic effects of red mud in plants, namely chromosomal damage in tetrads of *Tradescantia* and root cells of *Alliomascepa*, as well as root growth retardation, due to the presence of vanadate in high concentrations (Mišik et al., 2014). However, after the accident in Ajka, a stimulatory effect on aerobic and facultative anaerobic bacterial communities was observed, and the red mud impact on aquatic biota was only visible at few sites (Klebercz et al., 2012).

To date, no data has been published that indicates that a chronic low-level dietary V intake poses a direct lethal hazard to wildlife, but point sources have been more problematic, especially to water birds (Rattner et al., 2006). A Canada goose (*Branta canadensis*) died at a petroleum refinery fly ash pond in 2003, in Delaware, was attributed to vanadium toxicity (Rattner et al., 2006). Acute vanadium toxicity was also implicated in the death of cattle grazing on land amended with basic steel slag (as fertiliser and lime substitute) in Sweden, highlighting potential risks (Frank et al., 1996). Vanadium pentoxide was classified as a possible human carcinogen (group 2B) by the International Agency for Research on Cancer in 2006 (IARC, 2006), but there are limited studies on the biological response to V, so further research is needed.

A coal fly ash spill in Kingston, Tennessee, USA has been linked to reduced reproductive success and growth of tree swallows (*Tachycineta bicolor*) (Beck et al., 2015). Higher concentrations of Hg, Se, Sr, and Tl were found in the eggs in colonies impacted by the spill (Beck et al., 2015). Several years after the spill, Se in nestling blood and Hg in eggs remained relatively high and stable (Beck et al., 2015). A further study reported that grackle birds (*Quiscalus quiscula*) nesting around coal fly ash basins had accumulated Se, As, Cd and Sr in their offspring via dietary exposure (Bryan et al., 2012). Such studies show that there are many potential biological stressors [e.g. ionic strength, salinity, elevated metal(loid) concentration, physical smothering], but determining specific causal relationships between contaminant exposure and biological response can be problematic under field conditions.

5. Management

Power et al. (2011) reviewed the current management practices for disposal and amendment for red mud (addition of seawater, mineral acid, CO₂, SO₂), and discussed how each step in the Bayer process influences residue properties. Bauxite residues have a total inventory of 2.7 billion of tonnes (Binnemans et al., 2013), mainly stored in large holding ponds with high maintenance costs, risk of caustic exposure for living organisms, leakage of alkaline compounds into the groundwater, overflow of materials during storm events and the loss of fugitive dusts from dry surfaces (Sahu et al., 2010). Since 1980, lagoon-type impoundments have increasingly been replaced by “dry” stacking; this reduces the potential for leakage and the physical footprint, improving NaOH and alumina recoveries (Power et al., 2011). The addition of gypsum to red mud allows a significant decrease in plant available Al (Courtney and Kirwan, 2012), which can increase the rate of surface revegetation during site restoration. This practice in Aughinish Alumina BRDA (Ireland) allowed a 10-fold increase in microbial biomass in only one year (Courtney et al., 2014). The ecological restoration of red mud repositories is challenging (highly alkaline, saline, sodic, low water retention, no organic matter and numerous nutrient deficiencies), but recent results showed the potential for surface revegetation with bermudagrass (*Cynodon dactylon*) together with

arbuscular mycorrhizal fungi (Giridhar Babu and Sudhakara Reddy, 2011) and giant reed (*Arundo donax* L.) (Alshaal et al., 2013). Bio-augmentation with extremophile microorganisms in combination with biostimulation (addition of organic C and N) can be a good target for future research (Santini et al., 2015).

Air pollution control residues have currently two management practices: landfill after adequate treatment or recycling as ceramics and glass–ceramic materials (Quina et al., 2008). A review on the management of these residues focused on several treatment methods (separation, solidification/stabilization, thermal and combined methods) (Quina et al., 2008). The commonly adopted solution for these wastes is landfill disposal after treatment, usually solidification/stabilization (Quina et al., 2008).

Leachate generation from alkaline residues is inevitable, given the difficulties in preventing rainfall infiltration when dry stacking large volumes, and the extensive use of wet processing. Remediation options for alkaline leachates usually require intensive and sustained capital input, such as active aeration (to promote carbonation), recirculation of drainage waters over stockpiled or lagooned residues, and acid dosing (Mayes et al., 2009). The use of strong acids (HCl, H₂SO₄) to neutralise pH can be successful and is often used at active processing plants, but the effluent can remain toxic to aquatic environments (Roadcap et al., 2005). Wetlands are a low-cost, passive approach to remediating alkaline leachates (Mayes et al., 2009; Mayes and Younger, 2006). They can improve water quality parameters such as pH, TDS, salinity, and sulfates (Banks et al., 2006). The success of wetlands was shown in various pilot studies (Banks et al., 2006; Mayes et al., 2009; Mayes and Younger, 2006), but data on the long-term performance under a range of alkalinity loadings remains scarce.

6. Environmental and industrial applications

Considerable effort has been made to find after-uses for most alkaline residues, particularly as construction materials, but reuse is still limited to avoid stockpiling and landfilling. Concrete demolition waste is crushed and reused as granular fill and as recycled concrete aggregates (RCA), but RCA currently produced are considered to be of a lower quality than primary aggregates, which restricts their usage (Akbarnezhad et al., 2013). Approximately half of coal fly ash is recycled, predominantly as cementitious material in concrete (Heidrich et al., 2013). Coal fly ash is also reused on smaller scales in soil amelioration; the ceramics industry; catalysis; recovery of cenospheres, unburnt carbon and magnetic spheres; and in zeolite synthesis (Yao et al., 2015). Where flue gas desulfurisation waste is predominantly gypsum it can be used to make building products, such as plasterboard (Khatib et al., 2013), while research is on-going into the use flue gas desulfurisation waste with a higher fly ash content in other cement-based prefabricated building materials (Khatib et al., 2013; Telesca et al., 2013). APC residues may be incorporated into lightweight aggregates for construction (at 3%) after a washing pre-treatment (Quina et al., 2014). Aggregate made from municipal solid waste incinerator bottom ash and APC fly ash have been tested at lab scale for use as embankment fill in applications where high mechanical properties are not needed (del Valle-Zermeño et al., 2013).

Steel slags are widely used as aggregates for road construction (e.g. as road base and sub-base for high-trafficked roads, and also in hot mix asphalt concrete and bituminous paving mixtures) (Ahmedzade and Sengoz, 2009; Das et al., 2007; Pasetto and Baldo, 2010; Shen et al., 2009; Sorliini et al., 2012; Wei et al., 2014); railroad grade ballast (Banks et al., 2006) earthworks; armour stones for hydraulic structures (e.g. stabilisation of shores) (Motz and Geiseler, 2001); as an additive to cement clinker production (Tsakiridis et al., 2008), and as phosphate fertiliser (Motz and

Geiseler, 2001). However, steel slag requires extensive weathering before after-uses in construction to remove CaO through carbonation (Schwab et al., 2006). During weathering, they produce highly alkaline (pH 9–13) leachates that requires management (Chaurand et al., 2007). Such weathering takes time, requires large storage areas and can produce fine-grained slag that may not be suitable for use as a construction material (Motz and Geiseler, 2001).

The reuse of alkaline residues in construction can sometimes be a concern if there are elevated levels of naturally occurring radioactive materials (NORM). Fly ash from coal combustion, metallurgical slags, and other by-products have an enhanced content of natural radionuclides (Nuccetelli et al., 2015). The reuse of red mud is more limited than the other alkaline residues (Klauber et al., 2011), due in part to the potential of increased radon emissions. Based on the radionuclide concentration, red mud is not allowed as a building material, but mixing of a maximum 20% red mud and 80% clay meets the EU requirements (Jobbágy et al., 2009). Other cementitious material made with red mud and coal industry by-products also complied with ASTM requirements and the EPA regulation on the environmental metal leaching (Yao et al., 2013).

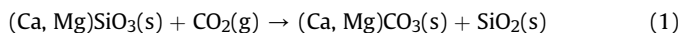
Other uses for red mud are as a surface treatment for carbon steel prior painting (Collazo et al., 2005), and potentially to catalyse reactions such as hydrogenation and liquefaction, hydrodechlorination, and exhaust gas clean/up, although it cannot compete with the available commercial catalysts (Kastner et al., 2015; Samal et al., 2013; Sushil and Batra, 2008). Liu et al. (2011) produced a comprehensive review on the use of red mud as an amendment for pollutants, and Wang et al. (2008) reviewed its use as a coagulant, adsorbent and catalyst. There are also an increasing number of patents for new uses of red mud, from construction to metallurgical applications (Klauber et al., 2011), but most of them are not implemented because raw materials from virgin sources are cheaper and without the perceived risks associated with bauxite residue.

Table 2 in Supplementary information summarises the main environmental applications of alkaline wastes. Most of them are still in an initial development phase, and a very limited number of full-scale applications are in place, despite the potential identified for these materials in the removal of different pollutants.

7. Opportunities

7.1. Carbon sequestration

Mineral carbonation is an increasingly promising concept that may play a significant role in management strategies and climate change mitigation options (Doucet, 2010). It involves the reaction of calcium and magnesium with gaseous CO₂ to form stable mineral carbonates (Doucet, 2010), mimicking natural weathering processes:



This mineralisation can be a safe storage option as either acidic conditions or high temperatures (~900 °C) would be required to release CO₂ (Eloneva et al., 2010). Carbon sequestration can be performed in the aqueous phase in two ways: (a) direct – CO₂ and alkaline metal dissolution and carbonation occur in one step; (b) indirect – first the residue is lixiviated with acids or bases to extract the alkaline metal from the silicate matrix and then afterwards CO₂ is dissolved and precipitates as a carbonate (Kunzler et al., 2011; Zingaretti et al., 2014). Comprehensive reviews on the mechanisms and techniques for alkaline wastes carbonation can be found in the literature (Bobicki et al., 2012; Bodor et al., 2013). The rate and extent of carbonation can be affected by the solid to liquid ratio

(Dri et al., 2014), particle size and reaction temperature (Huijgen and Comans, 2005), and processes like: (a) transport mechanisms such as CO₂ and Ca²⁺ diffusion to/from reaction sites; (b) boundary layer effects (diffusion across precipitate coatings on particles); (c) dissolution of Ca(OH)₂ at the particle surface; (d) pore blockage; and (e) precipitate coating (Pan et al., 2012).

The theoretical annual carbon sequestration potential of silicate materials, such as aggregate and mine waste, cement kiln dust, construction and demolition waste, iron and steel slag, and fuel ash is 697–1218 Mt CO₂ a⁻¹, based on their estimated global production of 7–17 Gt a⁻¹ and assuming that the divalent cation content is completely converted to carbonate (Renforth et al., 2011). Recent work focussing only on fly ash, cement kiln dust, and iron and steel slag in the USA and assuming 75% conversion to carbonate, estimates a carbonation potential of 7.6 Mt CO₂ a⁻¹, of which 7.0 Mt CO₂ a⁻¹ are captured through carbonation and 0.6 Mt CO₂ a⁻¹ are emissions avoided through reuse as synthetic aggregate (replacing sand and gravel) (Kirchofer et al., 2013). Mineral waste resources (pulverised fuel ash, municipal solid waste ash, cement kiln dust, biomass and paper sludge ash, and sewage sludge ash) have the theoretical potential to capture 1 Mt CO₂ a⁻¹ in the UK, considering the materials currently sent to landfill (Sanna et al., 2012).

Global steel industry CO₂ emissions are estimated to be 1500–1600 Mt CO₂, including emissions from coke manufacture and indirect emissions from power consumption, corresponding to 6–7% of global anthropogenic emissions (IPCC, 2007). Although the global theoretical CO₂ emissions reduction potential of steelmaking slag carbonation is 170 Mt CO₂ a⁻¹ (Eloneva et al., 2008), the reduction could be a significant offset on a site-by-site basis (Pan et al., 2012). However, these estimates have to be considered carefully as the steel slags CO₂ sequestration capacity can be lower than the 'theoretical' capacity (considering total calcium and magnesium content) under ambient conditions. A study showed that it was 25.2% lower for three basic oxygen and one electric arc furnace slags (Doucet, 2010). The 'real' sequestration capacity can be expected to be even lower as the Ca and Mg conversion to carbonated products is also possibly an incomplete process (Doucet, 2010).

The red mud global inventory is 2600 Mt (Power et al., 2011), so there is a carbon capture potential of 572 Mt CO₂ (Renforth et al.,

2012). Annually, 3–4% of the CO₂ emissions could be carbonated, with considerable implications for the aluminium industry (Renforth et al., 2012). At present red mud storage is not optimised for carbon capture, but it was estimated that its natural weathering unintentionally sequestered 100 Mt CO₂ worldwide from the late 19th century to 2008 (Si et al., 2013). If appropriate carbonation technologies are applied to red mud, an additional 6 Mt CO₂ can be potentially captured and stored annually, simultaneously reducing the hazardousness of the red mud (Si et al., 2013). A SWOT (Strengths, Weaknesses, Opportunities and Threats) analysis of carbonation of alkaline residues is presented in Table 2, highlighting the internal and external factors that affect its implementation.

7.2. Recovery

The recovery of metals from alkaline residues has increasingly raised interest, as these residues routinely contain high concentrations of elements considered of *importance* or *critical importance* to green technologies (La, Li, Co, V, Te, Ga, Se) (Naden, 2013). Table 3 summarises the potential amount of elements that could be recovered from the alkaline residues along with the amounts typically present in the leachates.

Many of the toxic trace elements that are problematic during the disposal alkaline wastes (e.g. vanadium) are also valuable commodities. Some are highly soluble at high pH (Mayes et al., 2011), and so potentially recoverable from leachates. Consequently, alkaline leachates have attracted considerable attention as secondary sources of e-tech elements with potentially globally significant reserves (Qu and Lian, 2013). Recovery of these resources would be important for addressing the security of supply of e-tech elements highlighted in various strategic reviews (EC, 2014; USDE, 2011; Naden, 2013), while simultaneously reducing the environmental cost of landfilling.

Recent reviews on the recovery of metals from red mud highlighted the difficulty of recovery as the metals are in complex mineral phases and the need to improve leaching, extraction selectivity and efficiency, and to develop processes with low energy requirements and cost (Liu and Naidu, 2014; Liu and Li, 2015). Recovery of Al and Na from red mud using a sinter process (Meher

Table 2
SWOT (Strengths, Weaknesses, Opportunities and Threats) analysis of the carbonation of alkaline residues.

Strengths	Weaknesses
<ul style="list-style-type: none"> Carbonation products are thermodynamically stable under ambient conditions – safe storage of CO₂ (Pan et al., 2012) High availability of alkaline residues deposits and higher reactivity, when compared with natural minerals; transport is not required as they are close to CO₂ sources (Bobicki et al., 2012; Pan et al., 2012) In many cases, these materials present a particle size already suitable for carbonation allowing to reduce or avoid the need for a grinding step (one of the most energy-intensive processes) Carbonation can minimise the release of some metals from alkaline waste materials, stabilising the residue, thus making their reuse or disposal easier (Bobicki et al., 2012; Pan et al., 2012) 	<ul style="list-style-type: none"> Need of optimal conditions for CO₂ reaction (Pan et al., 2012) Use of thermal pre-treatments and high temperature/pressure or strong and weak acids, salts, caustic agents and bioleaching agents High energy intensity, slow reaction kinetics and low reaction conversions of traditional processing routes (Sanna et al., 2012; Santos et al., 2013) Complexities of the production chain and process adaptability (Santos et al., 2013) Economic viability of the technology (Pan et al., 2012) Need for separation/disposal of the reaction products (Sanna et al., 2012)
Opportunities	Threats
<ul style="list-style-type: none"> Energy consumption and costs may be reduced as carbonation is an exothermic reaction (Pan et al., 2012) Further valorisation of the residues, either via reduced waste treatment or landfilling costs or the production of marketable products (Bodor et al., 2013) If alkaline wastewater is used, carbonation can neutralise the pH of the solution as carbonate precipitates are formed (Pan et al., 2012) 	<ul style="list-style-type: none"> Material and energy requirements of accelerated carbonation for the full-scale applicability (Zingaretti et al., 2013) Lack of legislative mandates for carbon capture and a sustainable CO₂ pricing scheme (Santos et al., 2013) Competition with alternative carbon capture technologies (such as geological carbon capture and storage) (Santos et al., 2013) Need for re-evaluation of the residues after carbonation (carbonation as an end-of-waste procedure if the residue has to be handled as waste) (Eloneva et al., 2010)

Table 3
Production of alkaline residues and typical e-tech element composition (mg kg⁻¹). Values in parenthesis give the % of annual global production in the respective residue assuming a 5% metal recovery rate. Values in square brackets are the dissolved concentrations (passed a <0.45 μm filter) in leachates (μg L⁻¹).

Residue	Production (Mt a ⁻¹)	Cobalt	Gallium	Lanthanum	Lithium	Selenium	Vanadium
Steel slag ^a	180 ^b	40–700 (0.3–5.3%) [0.20] ^c	30–60 (96–193%) na	60–75 (4.3–5.4%) na	1–140 (0.03–3.6%) [4.4–822] ^d	<1 (–) [10–150] ^e	100–1500 (1.2–17.8%) [6–120] ^e
Red mud ^f	120 ^g	90–110 (0.5–0.6%) [17] ^f	70–80 (150–171%) [12–2350] ^f	141–282 (6.7–13.5%) na	50–60 (0.9–1.0%) [4–303] ^f	<1 (–) [35–6398] ^f	860–1100 (6.8–8.6%) [35–6398] ^f
Fly ash ^h	415 ⁱ	3–10 (0.1–0.2%) [0.007–0.12] ^j	40–60 (296–445%) [0.001–1.12] ^j	80–100 (13.3–16.6%) na	300–400 (17.8–23.7%) [2.1–23.6] ^j	2–5 (2.1–5.2%) [0.045–3.7] ^j	50–100 (1.4–2.7%) [0.051–4.06] ⁱ
C&D waste ^k	497 ^l	5.4–7.0 (0.1%) [19] ^{k,l,m}	na	na	12–16 (0.9–1.1%) na	<7 (–) [5–33] ^m	30–40 (10–13%) na
APC residue ⁿ	1.2	10–23 (0.1%)	4.2–5.8 (9–12.4%)	5.1–8.9 (0.2–0.4%)	na	1.3–9.6 (0.4–2.9%)	12–36 (0.1–0.3%)
2013 Global production (t a ⁻¹) ^o		120,000	280	12,500 (in 2012)	35,000	2000 (in 2012)	76,000

na – Not available.

^a (Oty et al., 2014).

^b (USGS, 2015a).

^c (Matern et al., 2013).

^d (Hull et al., 2014).

^e (Mayes et al., 2008).

^f (Mayes et al., 2011).

^g (Power et al., 2011).

^h (Dai et al., 2010).

ⁱ (Heidrich et al., 2013).

^j (Moreno et al., 2005).

^k (Butera et al., 2014).

^l (Renforth et al., 2011).

^m (Galvín et al., 2012).

ⁿ (Bogush et al., 2015).

^o (USGS, 2014).

et al., 2011) together with the Bayer process has potential benefits such as NaOH savings, organics removal through liquor drying, increased aluminium extraction, and cheaper waste handling, but it is still not widely used. Attempts have also been made to use red

mud as a source of iron, but the recovery processes were not commercially successful (Binnemans et al., 2013; Samouhos et al., 2013). The enrichment factor of the rare earths in red mud compared with bauxite is about two, and scandium represents

Table 4
Summary of research priorities for improved management of alkaline residues.

Knowledge gap/research requirement	Research outcome/impact
<i>Leaching mechanisms for oxyanion-forming metal(loid)s</i>	
- Constrain geochemical conditions under which oxyanion release is promoted	- Define disposal conditions for minimising release, or conversely process conditions for maximising release of elements of value.
- Understand fate of oxyanion-forming contaminants under residue and leachate neutralisation	- More robust monitoring protocols and regulation regarding residues in disposal and after-use
<i>Environmental impacts of alkaline waters and residues</i>	- Improved monitoring protocols and regulation regarding residues in disposal and after-use
- Determine fate of oxyanion-forming elements in the environment	
- Undertake toxicity testing using appropriate alkaline matrices on a range of trophic levels	
<i>Passive (bio-)remediation</i>	- Robust closure plans for repositories can be formulated not requiring high energy/reagent demands (e.g. acid dosing)
- Full life-cycle evaluation of the effectiveness of passive treatment systems for alkaline waters (e.g. wetlands)	
- Mechanistic understanding of buffering mechanisms in wetlands (biological influence, seasonal variation)	
<i>Recovery technologies</i>	- Develop microbial inocula to ensure consistent and predictable metal release
- Mechanistic understanding of bio-leaching of e-tech metals from alkaline residues.	- Offset some of the costs for long-term remediation
- Trial conventional metal recovery technologies (e.g. ion exchange resins, electrochemical recovery) at the alkaline extreme of the pH spectrum	- Encourage further bulk residue re-use once potential contaminants leached
<i>Bulk reuse of residue</i>	
- Larger scale testing of novel environmental after-uses for alkaline residues (e.g. in wastewater treatment).	- Increased valorisation of residues; more diverse range of after-uses likely to diminish residue quantities to landfill
<i>Carbon sequestration</i>	- Further valorisation of residues
- Quantify potential for offsetting emissions in residue weathering and long-term storage in field scale trials	- Significant industrial offset fully accounted for
<i>Governance and policy issues</i>	
- Critical multi-scale analyses of key stakeholders and external factors influencing long-term residue management decisions	- Identify governance and policy frameworks that need to be engaged with to encourage best-practice
- Multi-scale policy analysis of potential constraints to alternative residue management approaches	- Industry account for environmental benefits of alternative approaches to residue management

more than 95% of the economic value of rare earth elements (REE) in red mud (Binnemans et al., 2013, 2015). A REE maximum extraction ~80% from red mud can be achieved by acid leaching, although it also dissolves iron, sodium and calcium (Borra et al., 2015). Gallium, an important semiconductor for the electronic and computer industries, could also be recovered from Bayer liquors (Radnai et al., 2014). Bioleaching of red mud with *Aspergillus niger* allowed the recovery of over 80% Pb and Zn, 67% Cu, 50% Ni, 44% As, 31% Ba, 26% Cr and about 11% Fe and Zr (Qu et al., 2013). Bioleaching of REE and radioactive elements from red mud with *Penicillium tricolor* showed that the highest extraction yields are achieved under a two-step process with 10% solids percentage (Qu and Lian, 2013).

Different methods can be used to recover metals from alkaline residues. Vanadium can be recovered from steel slag through alkaline roasting (Voglauer et al., 2004), and Fe–Cr–Ni (Shen et al., 2004) can also be potentially recovered from this material. Zinc can be recovered selectively with alkaline leaching (Stefanova et al., 2013). Vanadium bioleaching from basic oxygen converter slag achieved >90% removal, using autotrophic and heterotrophic bacteria, and fungi (Mirazimi et al., 2015).

The potential for recovery of metals from other alkaline residues is also high. Coal combustion ashes, oil shale ashes and ashes of waste incinerators contain significant concentrations of REE (Binnemans et al., 2013), with light REE being dominant (Franus et al., 2015). Aluminium and iron can also be recovered from coal furnace bottom ash (Li et al., 2009). Concentrations of Ag (6–15 mg kg⁻¹) and In (1–13 mg kg⁻¹), as well as Zn (0.26–0.73 wt.%) and Pb (0.05–0.2 wt.%), were found to be enriched in APC residues (Bogush et al., 2015). The recovery of secondary resources such as iron, aluminium, copper, zinc and other metals from these residues is gaining increasing interest (Brunner and Rechberger, 2015). Phosphorus extraction from municipal solid waste incinerator fly ash by acid and base leaching, and precipitation had a recovery rate of 70% (Kalmykova and Karlfeldt Fedje, 2013).

7.3. Biological resource

Numerous studies on the spontaneous revegetation of alkaline residues have highlighted the presence of internationally rare orchid-rich calcareous grassland (Ash et al., 1994; Kiehl et al., 2010; Shaw, 1998; Tischew et al., 2014). Calcium rich, nutrient-poor substrates often lend themselves to floral diversity and, in many cases, alkaline residue disposal sites can obtain formal conservation designations (Raper et al., 2014). These properties also raise the possibility of directing surface restoration at disposal sites towards these communities, offering a significant opportunity for high economic value environmental enhancement, beyond simple remediation.

8. Summary of research needs

Future research needs range from fundamental science questions to issues of waste policy and governance (Table 4). These can be summarised into:

1. Research into the mechanisms controlling oxyanionic metal(-loid) leaching, both to understand the polluting potential of the residues, and to better engineer leaching schemes for waste stabilisation and for resource recovery.
2. Research into environmental mobility and fate of oxyanionic metal(-loid)s as the pH is gradually neutralised. Full, mechanistic understanding of the fate and biological impacts of these often

overlooked pollutants (Anton et al., 2014) will assist regulators in designing and implementing effective monitoring regimes.

3. Upscaling of proposed new environmental technologies to field conditions so that their efficacy can be properly evaluated, and a proper Life Cycle Assessment made. A promising array of studies on metal recovery and residue after-use have been conducted, however these are largely confined to the laboratory scale.
4. Better understanding of the governance, policy and social issues that affect waste management decisions. These could include volatility of commodity markets (especially in the case of developing new recovery technologies) and the complexities of waste policy at national and international level (Bian et al., 2012; Deutz, 2014; Gregory et al., 2013; Lombardi et al., 2012).

This will underpin more sustainable management and increased valorisation of these increasingly abundant global by-product streams to both minimise the environmental risks and maximise mineral resource use efficiency.

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Appendix A. Supplementary data

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