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Review

Hidden values in bauxite residue (red mud): Recovery of metals

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ABSTRACT

Bauxite residue (red mud) is a hazardous waste generated from alumina refining industries. Unless managed properly, red mud poses significant risks to the local environment due to its extreme alkalinity and its potential impacts on surface and ground water quality. The ever-increasing generation of red mud poses significant challenges to the aluminium industries from management perspectives given the low proportion that are currently being utilized beneficially. Red mud, in most cases, contains elevated concentrations of iron in addition to aluminium, titanium, sodium and valuable rare earth elements. Given the scarcity of iron supply globally, the iron content of red mud has attracted increasing research interest. This paper presents a critical overview of the current techniques employed for iron recovery from red mud. Information on the recovery of other valuable metals is also reviewed to provide an insight into the full potential usage of red mud as an economic resource rather than a waste. Traditional hydrometallurgy and pyrometallurgy are being investigated continuously. However, in this review several new techniques are introduced that consider the process of iron recovery from red mud. An integrated process which can achieve multiple additional values from red mud is much preferred over the single process methods. The information provided here should help to improve the future management and utilization of red mud.

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1. Introduction

Red mud is the solid waste generated from the alumina refining of bauxite ore, primarily by the Bayer process which utilizes caustic soda to dissolve the aluminium silicate. The production of 1 tonne of alumina generates between 1 and 1.5 tonnes of red mud (Zhang et al., 2011). With the increasing demand for alumina worldwide, the generation of red mud is estimated to be 4 billion tons by 2015 based upon its current rate of production (Wang et al., 2013), and presently it has already reached well over 2.5 billion tonnes (Boudreault et al., 2013). Red mud is considered a hazardous waste when it has been stockpiled in vast amounts (Wang et al., 2013). The management of red mud continues to be a global concern confronting the alumina industries and regulatory authorities due to the massive volumes generated and the harmful impacts resulting from its disposal. Many strategies have been investigated for improved management of red mud though no cost-effective methods have been implemented. In this review, we propose the development of a technology that could utilize the valuable metals in red mud to provide options for its management after disposal. The disposal of red mud remains a complicated issue because of its high alkalinity (pH 10–13 (Liu et al., 2007)) and the very large quantities generated. Different disposal methods have been practiced around the world including landfill, deep sea dumping and storage in settling ponds. Despite the harmful impact that these methods pose on our environment, the risks of failure of a poorly engineered storage dam can result in even greater social and economic damage (Mayes et al., 2011). Many attempts have been made to find an environmentally friendly and cost-effective method to dispose of or utilize red mud. Several reviews have focused on the utilization options for red mud (Klauber et al., 2011; Liu et al., 2009b, 2011; Paramguru et al., 2004; Snars and Gilkes, 2009; Sushil and Batra, 2008; Wang et al., 2008), including: as adsorbents for pollutant removal, building materials (such as bricks, concrete, cements and road foundation materials), coagulants, catalysts, and as agents for neutralizing acidic waste (Rai et al., 2013). However, all these options can only accommodate a very small fraction of the 90 Mt yr⁻¹ of red mud generated globally (Kumar et al., 2006).

Red mud can be considered as a secondary raw material for the recovery of valuable substances (Erçağ and Apak, 1997). For example, the metals in red mud have recently attracted research interest due to increasing demand and value for iron, titanium, aluminium and the rare earth elements. Red mud contains: 14–45% Fe, 5–14% Al, 1–9% Si, 1–6% Na and 2–12% Ti (Kumar et al., 2006). As a conservative estimate, >12 Mt yr⁻¹ of iron are disposed along in red

mud. Since iron present as oxides/oxyhydroxides is usually the largest component, iron recovery has attracted major attention (Kumar and Premchand, 1998). However, metal recovery from red mud is difficult as the metals are locked up in complex mineral phases. Minerals in red mud include hematite, boehmite, sodalite, aluminosilicate, quartz, perovskite, goethite, cancrinite (Liu et al., 2011; Snars and Gilkes, 2009; Wang et al., 2008). The fine particle size and alkalinity add to the difficulty in recovering metals from these minerals. In spite of these issues, many attempts have been made to extract value from red mud. Liu et al. (2012) developed a feasible zero waste process for the treatment of red mud using soda-lime roasting and chemical extraction. It recovered 75.7% and 80.7% Al and Na, respectively, whilst the recovery of iron depended on the type of reduction products in which weak magnetic or non-magnetic ferrous compounds adhered with impurities (such as spinel aggregates).

This review focuses on studies of the recovery of iron, aluminium, titanium and rare earth elements (REEs) and proposes possible environmentally and economically feasible processes for the beneficial utilization of red mud.

2. Metal content of red mud

As it is derived from the alumina refining process, red mud contains components from bauxite residues (mainly Al and other minor components) and the materials added during refining (such as alkali and Ca). Several publications provide detailed information on the characterization of red muds (Gräfe et al., 2011; Hind et al., 1999; Liu et al., 2013; Zhao et al., 2009) and their treatment and usage (Klauber et al., 2011; Liu and Zhang, 2011; Liu et al., 2011; Wang et al., 2008). A brief summary of the contents of major and minor elements in red mud is presented in Table 1. The iron content can be wide-ranging (4.5–50.6%) depending on the bauxite used and the refining processes employed. Recovery of the iron is possible for red mud containing >51% Fe (Zhu et al., 2012) which is competitive with iron ore in its Fe content. Red mud can also contain elevated concentrations of REEs, such as lanthanides (Ochsenkühn-Petropulu et al., 1996) and scandium (Smirnov and Molchanova, 1997), which may be recoverable using appropriate techniques. Table 2 shows the iron minerals in red mud as well as other minerals containing Al, Ti, Si and REEs. There are more than 300 minerals that contain iron. However, the main minerals used for iron beneficiation include magnetite (Fe₃O₄), hematite (Fe₂O₃), goethite (FeO(OH)), siderite (FeCO₃), pyrite (FeS₂) (U.S. DOI, Geological Survey 1973) (EPA, 1994).

Table 1
Major, minor and trace element contents of red mud.

Major elements	Concentration (%)	Minor elements	Concentration (mg/kg)
Fe	4.52–50.6	U	50–60 Smirnov and Molchanova (1997)
Al	4.42–16.06	Ga	60–80 Smirnov and Molchanova (1997), 89 (Wang et al. (2013)
Si	2.16–14.86	V	730 Wang et al. (2013)
Na	0.98–7.79	Zr	1230 Wang et al. (2013)
Ca	0.39–16.72	Sc	54 Wang et al. (2013), 60–120 Smirnov and Molchanova (1997)
Ti	0.98–5.34	Cr	497 Wang et al. (2013)
Reference	Cengeloglu et al. (2003), Erçağ and Apak (1997), Guo et al. (2013), Jayasankar et al. (2012), Kumar and Premchand (1998), Kumar et al. (2006), Li et al. (2009), (2011), Liu et al. (2012), (2009), Swagat et al. (2013), Vachon et al. (1994), Wang et al. (2013), Yu et al. (2012), Zhang et al. (2011), Zhu et al. (2012)	Mn	85 Wang et al. (2013)
		Y	68 Wang et al. (2013), 60–150 Smirnov and Molchanova (1997)
		Ni	31 Wang et al. (2013)
		Zn	20 Wang et al. (2013)
		Lanthanides	0.1%–1% Ochsenkühn-Petropulu et al. (1996)
		Th	20–30 Smirnov and Molchanova (1997)

Table 2
Mineral forms of major and minor minerals in red mud Samal et al. (2013).

Element	Mineral	Chemical formula
Fe	Hematite	$\alpha\text{-Fe}_2\text{O}_3$
	Goethite	$\alpha\text{-FeOOH}$
	Magnetite	Fe_3O_4
	Ilmenite	$\text{FeO}\cdot\text{TiO}_2$
	Ferryhydrite	$\text{Fe}_2\text{O}_3\cdot 0.5\text{H}_2\text{O}$
	Maghemite	$\gamma\text{-Fe}_2\text{O}_3$
Al	Gibbsite	$\alpha\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$
	Boehmite	$\alpha\text{-Al}_2\text{O}_3\cdot \text{H}_2\text{O}$
	Diaspore	$\beta\text{-Al}_2\text{O}_3\cdot \text{H}_2\text{O}$
Ti	Anatase	TiO_2
	Rutile	TiO_2
	Perovskite	CaTiO_3
	Ilmenite	$\text{FeO}\cdot\text{TiO}_2$
Si	Quartz	SiO_2
	Kaolinite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
	Sillimanite	Al_2SiO_5
	Halloysite	$\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$
	Sodalite	$\text{Na}_8(\text{Al}_6\text{Si}_6\text{O}_{24})\text{Cl}_2$
	Cancrinite	$\text{Na}_6\text{Ca}_2[(\text{CO}_3)_2[\text{Al}_6\text{Si}_6\text{O}_{24}]\cdot 2\text{H}_2\text{O}]$
	REEs	Monazite
Xenotime	YPO ₄	
Synchysite-(Ce)	$\text{CaCe}(\text{CO}_3)_2\text{F}$	

3. Techniques investigated for iron recovery from red mud

Since the initiation of iron extraction from red mud, there are many techniques that have been intensively investigated for practical implementation, such as solid-state carbothermic reduction, acid leaching, smelting in a blast furnace and magnetic separation. A new concept of using red mud directly for iron making/smelting gives further promise. However, the impurities existing in red mud, such as Al, S, P, Na, Ca, Mg, Si, hinder its realization in practice as the alumina content can cause problems for slag fluidity and the high alkalinity is not compatible with the refractory and alkali accumulation (Hammond et al., 2013). Researchers, industry and government institutes are still struggling to implement any technique in the field. Transportation costs for delivering red mud to a processing plant and other technical difficulties normally diminish the possibility of implementing these techniques. A more complete utilization of red mud has emerged as a feasible solution to achieve zero waste and fully utilize the resources hidden in red mud wastes. This would add value to the iron recovery process and make it both economically and environmentally acceptable. Several attempts at this approach have been made recently. A review of advanced techniques is required in order to develop any complete utilization process. In the following section we summarize the main processes used for iron and other metals recovery from red mud.

Because of the inherent economic incentives for iron recovery from red mud, research activities may result in filing a patent for a new process. A Google patent search for patents filed between 2009 and 2014 using the key words 'iron recovery from red mud' showed that most of the patents (around 47%) were from China. Selected patents with the main techniques reported are summarized in Table 3. Detailed information is presented in the following sections. We can generally classify the main techniques used as direct magnetic separation, pyrometallurgical recovery and hydrometallurgical recovery. Some schemes are illustrated in Fig. 1.

3.1. Direct magnetic separation

A list of metals being recovered with the techniques investigated is summarized in Table 4. Iron recovery has been explored by direct magnetic separation from red mud for reduced energy

costs compared to pyrometallurgical recovery, whilst maintaining Ti and other metals in a more leachable form (Xiang et al., 2001). Red mud (in slurry form) is subjected to high intensity magnetic separation. The resulting magnetic product can then be used as an ingredient for iron production or as a pigment for pottery making. The non-magnetic portion can be used in building materials or added back into the Bayer process (Hammond et al., 2013). The recovery of iron, is however, low (Fursman, 1970). The scheme for the separation is illustrated in Fig. 1(I).

A magnetic separation process was used to produce value from the byproduct (>90 μm fraction) from alumina refineries in Western Australia (Jamieson et al., 2006). The raw materials (red sand) were directly trained through a standard mineralogical process (low intensity magnetic separator, LIMS and wet high intensity magnetic separator, WHIMS) to produce various fractions including a high iron oxides (40% Fe) fraction, silica and a mixture of iron and silica. Different usages for the three fractions included iron, concrete material and general fillings. Li et al. (2011) used a high gradient superconducting magnetic separation (HGSM) system to separate the extremely fine red mud particles (<100 μm) into the high and low iron content fractions. The HGSM system is reported to be more efficient in separating fine magnetic particles as it generates an order-of-magnitude stronger field than ordinary ferromagnetic-core electromagnets and the cost for superconducting magnets for industrial application is considerable (Li et al., 2011). Two red mud samples differing in iron content were used (41.08% and 20.84% Fe). The Fe content increased to 45.46% and 35.47%, respectively, after being fed into the HGSM for separation of the high iron portion. The mass recovery of iron concentrates was about 10% after separation regardless of red mud types. Recycling of the low iron portion did not increase the iron concentration in high iron fraction. However, the residues still contained 31.47% and 9.86% Fe after eight cycles of the two red mud samples. The inter-growth of Fe and Al, Si, Na, Ti evidenced in elemental mapping in red mud is a disadvantage for iron mineral separation by HGSM. Slon[®] vertical ring and pulsating high gradient magnetic separators have been used (Peng and Huang, 2011); 53–58% iron grade was achieved for this case study but a low overall recovery rate (28–35%) was reported.

3.2. Pyrometallurgical recovery of iron

Pyrometallurgical recovery of iron from red mud is one of the most popularly investigated methods. Red mud is either reduced in the solid state followed by magnetic separation to recover iron, or reduced by smelting in a blast/electric/low shaft furnace (with or without preparation) to produce pig iron (Kumar and Premchand, 1998). The iron content in red mud is not as competitive a source as in high iron content ores (~60%). Given the presence of other components as drawbacks for iron recovery from red mud (Kumar and Premchand, 1998), processes have been developed for the simultaneous recovery of the other major constituents Al, Ti and other metals.

There have been many investigations of the direct reduction of Fe in red mud to a magnetic fraction or to metallic iron. The overall scheme of the process is shown in Fig. 1(II). A reductant, in either the gaseous or solid phase, and energy are required for the process. The reductants used have included carbon powder (Liu et al., 2009a), coal (Zhu et al., 2012), low ash coal char (Liu et al., 2012), carbon (Li et al., 2009; Raspopov et al., 2013), coke (Swagat et al., 2013) or a waste carbon source such as sawdust and bagasse (Xiang et al., 2001). The selection of reductants originated from the DRI (direct reduced iron) process; they include lignite, anthracite, coke and activated carbon. The reactivity and ash content of coal used is reported to have significant influence on the extent and rate of metal reduction (Liu and Mei, 1995). With

Table 3
Summary information on iron recovery techniques from red mud from selected international patents.

Patent number	Procedures/aims	Comment
CN101648159 B (2009) Peng and Huang (2011) Method for recovering iron concentrates from alumina red mud	The ferromagnetic portion firstly separated using a medium magnetic separator, followed by separation of the weakly ferromagnetic portion using SLon Vertical Ring and Pulsating High Gradient Magnetic Separators. Mixing the two portions for further dehydration to obtain iron ore	Direct magnetic separation
CN103074456 A (2013) Liu et al. (2013) Method for recycling iron from waste red mud in alumina production	Red mud dried (water content 1–10%), crushed (<0.15 mm) and pelletized. Mixing red mud pellets(30–80%) with coke (20–30%), limestone (0–10%), and dolomite (0–10%) in a specific ratio, following smelting (1500–1650 °C) and separation, metal iron (~94%) can be obtained	Pyrometallurgy, similar to WO2009056863A2 (2009) Perry, (2009), US 20090175782 A1 (2009) Krause and Rohm (2009), WO 2012100004 A1(2012) Amiran, (2012)
CN102559979 B (2013) Zhang et al. (2013) A process for the production of direct reduced iron from red mud	The procedure involves: the graphane (accelerant) is mixed with red mud according specific ratio (red mud 85–99.5%, accelerant 0.5–15%), the Fe content in red mud >30%, the mixture is used for preparation of green compact. After a reducing agent (the fixed carbon content (C _{fix}) > 60%) and the green compact together into a reducing tank layer by layer, the reducing tank is placed in a kiln car, and sealed with a sealing cover. The kiln car is fired with a tunnel kiln at 1000–1300 °C for 20–50 h. Surface cleaning the fired product	Different preparation method for iron reduction.
CN103031443 A (2012) Wang and Zhao (2013) Method of dealkalizing red mud and recovering aluminum and iron	Red mud mixed with H ₂ SO ₄ (20–30 g/L) at 30–110 °C with solid:liquid ratio of 3–6 and mixed at 200–500 r/min for 20–80 min. The mixture was then roasted (100–800 °C, 20–80 min) and washed (3–8 times). Recovery of iron was conducted using precipitation or resin adsorption from the leaching solution. The Na ₂ O content in the residue was significantly reduced while iron was recovered. By-product Na ₂ SO ₄ was also obtained	Hydrometallurgy to recovery Fe and Al.
WO2013104059 A1 (2013) Boudreault et al. (2013) Processes for treating red mud	Red mud leached using HCl to obtain a leachate comprising aluminium ions and a solid. Other metals such as Fe, Ni, Co, Mg, and rare earth elements can be obtained from the leachate while TiO ₂ and SiO ₂ can be extracted from the solid	Hydrometallurgy, related to: US 61/584,993, US 61/706,074, and US 61/713,719
CN102976374 A (2012) Li et al. (2013b) Conversion method of iron minerals in production process of alumina	Red mud or bauxite ore with additives (iron or ferrous compounds) were added into NaOH (60–520 g/L) or sodium aluminate solution (solid:liquid ratio of 2–20) for preparation of original slurry. The slurry was incubated at 100–350 °C for 0.2–12 h. Iron in the slurry was transformed to magnetite which can be separated	Incorporated iron recovery into the alumina refining process.
CN102851425 A (2012) Li et al. (2013a) Method for high-efficiency separation and comprehensive utilization of iron, aluminum and sodium in high-iron red mud	High iron content red mud mixed with iron ore and coke for pelletizing. Direct reduction of iron using rotary hearth furnace after drying and preheating. The product generated was used for further smelting until iron metal obtained. The residue was used for recovery of alumina while the waste gas was used for sodium recovery	Recovery of iron from red mud was incorporated into the iron ore smelting process.
CN102071315 B (2012) Cui et al. (2012) Method for separating iron from raffinate in process of extracting scandium from red mud	Iron was recovered from the raffinate after Sc concentration from red mud using TBP. The procedure involved pre-treatment of TBP, preparation of extraction agent using sulfonated kerosene and TBP and the extraction agent was treated using 30% H ₂ O ₂ , reverse extraction at 50 °C with 0.01 M HCl; precipitation using 0.5–1.5 M ammonium hydroxide to obtain iron hydroxide. Iron oxide can be obtained after calcination at 500–550 °C for 40–60 min	Recovery of iron from red mud was incorporated into extraction of Sc.
CN102500596 B (2011) Jiao et al. (2013) Red mud harmless comprehensive recycling technology suitable for Bayer process	Red mud firstly neutralized to pH 7.5–9 followed by gravity separation to obtain high specific gravity (3.6–5.5) portion and a low specific gravity portion (2–5). The latter was used for recovery of alumina by flotation whilst the former was calcined at 850–1350 °C to obtain magnetite after drying	Complex usage of red mud
WO 2010079369 A1 (2010) Papadopoulos et al. (2010) Valuable products obtained from red mud	In this procedure reported, ultra-pure products of silicon dioxide, calcium sulphate, titanium dioxide, alums and ferrites (magnetite) were obtained and their feasibility for industrial usage was evaluated. A solution containing only sodium and aluminium cations obtained was appropriate for being recycled back into the Bayer method. The chemicals used, including hydrochloric acid, sulfuric acid, sodium hydroxide or ammonia, can be almost completely recycled. Even energy is gained at certain stages, reducing the energy consumption of an industrial plant	A complex process for the usage of red mud to achieve zero waste.
CA 2529249 C (2012) Jha et al. (2012) Extraction process for reactive metal oxides	The procedure involved extraction of alumina from different types of bauxite ores and red mud residues and of titanium dioxide from ilmenite. Iron oxide is first reduced to metallic iron to yield a high-C iron alloy and an Al and Ti metal oxide-rich slag. The slag was then treated with alkali carbonate to form alkali aluminates and titanates. Separation of the alkali aluminates was achieved by water leaching following which hydroxide of alumina is precipitated by bubbling CO ₂ . The residue from water leaching was treated with sulphuric acid and TiO ₂ is precipitated via a hydrolysis route	A complex process for the usage of red mud.

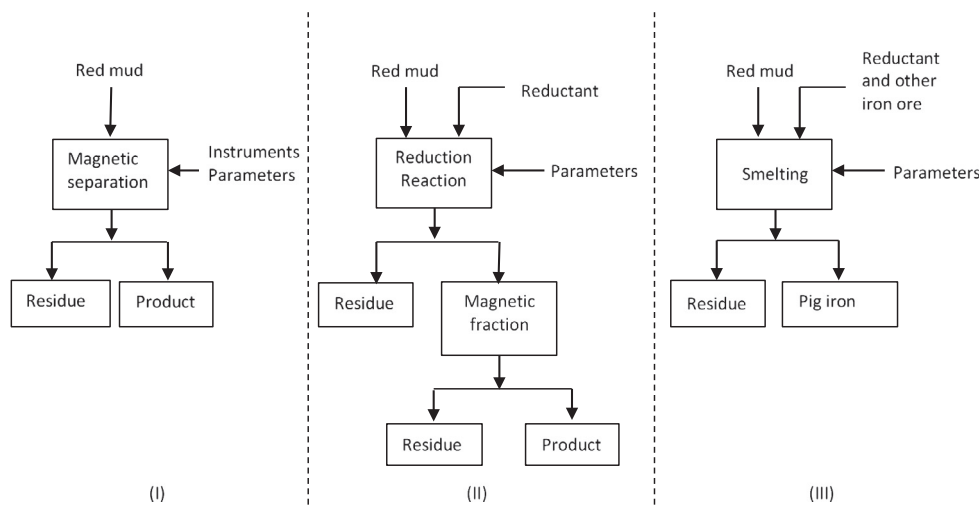


Fig. 1. Simplified schemes illustrating iron recovery from red mud investigated by (I) direct magnetic separation; (II) pyrometallurgical recovery by reduction and separation and (III) red mud used directly in iron ore smelting.

an increase in ash content the rate will decrease. The ideal quality of coal employed is reported as follows: low ash content, high reactivity, large ratio of $(F_c + V_m):(A + W)$ (where F_c is fixed carbon content, V_m is volatile content, A is the ash content, W is the other incombustible content) and high ash composition ratio $(\text{SiO}_2 + \text{TFe}):(\text{Al}_2\text{O}_3 + \text{other})$ and is able to form the moderate porosity (Liu and Mei, 1995). However, for consideration of any lowering of the cost of iron recovery from red mud, the selection should also depend on availability and cost apart from separation efficiency. Screening of appropriate waste materials may be an effective option for cost reduction.

Direct reduction of red mud is possible for obtaining pig iron after magnetic separation. Guo et al. (2013) produced iron nuggets by directly reducing the carbon-bearing pellets of red mud and coal at 1400 °C for 30 min. The nuggets so obtained have 96.52% Fe and are low in Si and Mn but have a high content of S and P. However, there remained Fe minerals in the slag (reduced Fe and unreduced Fe_2SiO_4). Jayasankar et al. (2012) used thermal plasma technology (a 35 kW DC extended arc thermal plasma reactor) to reduce red mud to produce pig iron. The red mud was mixed with fluxes (10% dolomite and lime) and graphite (fixed carbon, 99%) as a reductant and smelting proceeded for 15 min. An optimal recovery of Fe was around 71%. Raspopov et al. (2013) studied the morphology of the iron oxides in red mud samples taken from the Ural Aluminum Plant (UAZ, Kamensk-Ural'skii) and the Alyum Plant (Tul'chiya) storage by Mössbauer spectroscopy which showed that their red mud contained hematite, lepidocrocite, goethite and mineral iron-aluminosilicate. However, after reduction and smelting with excess carbon charge in the temperature range 1200–1500 °C, the metallic (cast iron) and slag phases generated could easily be separated while the C content in the cast iron ranged from 2.0% to 2.3% (Raspopov et al., 2013).

Parameters involved in the roasting process have also been studied extensively, including the carbon source, carbon:red mud ratio, temperature, and magnetic conditions. Liu et al. (2009a) reported on the parameters influencing direct reduction roasting of red mud by carbon materials. They thoroughly mixed red mud with carbon (18:100 carbon:red mud) and additives (6:100 additives: red mud) prior to pressing the mixture with a cylinder mould. The shaped columnar samples (briquettes) were then roasted at 1300 °C for 110 min before being immediately quenched with water. A magnetic separator was then used (1 A [ampere]) after milling the products. The residues generated were proposed

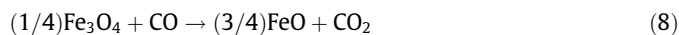
as being suitable for building materials. The total content of iron in the concentrated materials was 88.77%, with a metallization of 97.69% and a recovery of 81.40% (Liu et al., 2009a). Apart from recovering iron, Liu et al. (2012) employed a soda-lime roasting process prior to leaching and magnetic separation of the fine red mud (<75 μm) aiming to develop an economically-feasible zero waste utilization process. The soda-lime roasting facilitates the formation of sodium aluminosilicate which can then be recovered by leaching. These authors found that the optimum roasting conditions are as follows: a molar ratio of Ca:Si about 2, Na:Al about 1, with 0.5 g coal char per 100 g red mud, and roasting at 1000 °C for 3 h in N_2 . The roasted samples were then added into a water leaching reactor (50 g, <125 μm into 100 mL water) controlled at 60 °C for 15 min. A recovery of 75.7% and 80.7% for Al and Na were achieved after leaching, respectively. Magnetic separation (1.0 A, field intensity 110 mT) was applied on the leaching residue for recovery of iron. Magnetite (Fe_3O_4), hercynite ($\text{Fe}(\text{Fe}, \text{Al})_2\text{O}_4$), and ulvospinel (TiFe_2O_4) were detected in the residue and 51.2% of Fe was recovered in a magnetic concentrate (Liu et al., 2012). Instead of adding soda and lime, Zhu et al. (2012) mixed red mud with 1% binder and 8% sodium carbonate and pelleted the mixture prior to direct reduction with addition of soft coal at 1050 °C for 80 min. A recovery of 95.7% of Fe was achieved after grinding the sintering product (90%, <74 μm) and magnetic separation at a magnetic field intensity of 0.08 T. Another study (Rao et al., 2013) has also shown that the addition of sodium sulphate and sodium carbonate assisted in the reduction roasting process. A magnetic concentrate containing 90.12% iron (recovery 94.95%) was obtained from a red mud containing 48.23% total iron in the presence of 6% Na_2SO_4 , 6% Na_2CO_3 and optimal conditions: a roasting temperature of 1050 °C, roasting time of 60 min, magnetic separation feed fineness of 90% passing 74 μm , and a magnetic field intensity of 0.1 T (Rao et al., 2013). Li et al. (2009) conducted a thermodynamic analysis of the reduction process of red mud components (Al_2O_3 , Fe_2O_3 , Na_2O , CaO, etc.) by carbon materials. Their results suggested that the reduction of ferrite can be realized by controlling the atmosphere during the sintering process, and the temperature favourable for the formation of sodium aluminium and calcium silicate. The procedure involved reduction-sintering (800–1075 °C), leaching and magnetic beneficiation (48–240 kA/m) which resulted in a recovery rate for alumina reaching 89.71% and 60.67% whilst the grade of Fe in magnetite concentrate was 61.78% under the optimized sintering conditions (Li et al., 2009).

Table 4
Recovery of valuable metals from red mud.

Source	Metals recovered	Procedure description	Ref.
Red mud (China, Australia)	Fe	<i>Direct magnetic separation</i> : red mud was directly separated through high gradient superconducting magnetic separation system (Li et al., 2011), low intensity magnetic separator and a wet high intensity magnetic separator (Jamieson et al., 2006) to recover Fe	Li et al. (2011), Jamieson et al. (2006)
Red mud (China, Turkey)	Fe, Al, Na, Ti	<i>Pyrometallurgical process</i> : the process involved adding additives, reduction roasting and magnetic separation. Additions included sodium carbonate, anthracite and limestone, and carbon. The mixture were dried and roasted at high temperature followed by milling and separation by a magnetic separator. Leaching at different conditions can be involved in the procedure to recovery of Al, Na and Ti	Zhu et al. (2012), Li et al. (2009), Guo et al. (2013), Liu et al. (2009), (2012), Erçağ and Apak (1997)
Red mud (Indian)	Fe	<i>Pyrometallurgical process</i> : direct reducing of Fe in red mud using thermal plasma technology by smelting in a 35 kW DC extended arc thermal plasma reactor with addition of fluxes and graphite	Jayasankar et al. (2012)
Red mud (Indian)	Fe	<i>Pyrometallurgical process</i> : 'Elgai' process was used involving mixing red mud, charcoal, and soda in a rod mill and pelletizing, roasting the pellets at 700–925 °C, leaching the roasted materials with water, magnetic separating of residue for iron recovery	Kumar and Premchand (1998)
Red mud (Turkey)	Al, Fe, Ti, Na	<i>Donnan dialysis</i> : polysulfonated membrane separation from red mud solution (HCl 1.0 M)	Çengelöglu et al. (2001), Cengelöglu et al. (2003)
Red mud (Indian)	Fe, Al	<i>Hydrothermal process</i> : Red mud was calcined at different temperature (200–1000 °C) followed by leaching using sulfuric acid solution (2, 4, 6, 8, 10 mol/L). The dissolution of iron was faster than that of aluminium and 97.46% iron and 64.40% aluminium were recycled for red mud calcined at 600 °C while using 6 mol/L H ₂ SO ₄ for the dissolution	Uzun and Gulfen (2007)
Bayer red mud (China)	Al, Na	<i>Hydrothermal process</i> : an autoclave reactor mounted with temperature meter and rotation speed controlled incubator was used in the experiments, temperature: 200–280 °C, 196–433 g/L Na ₂ O was added, CaO was added to maintain CaO-to-SiO ₂ mole ratio in RM: 1.5 (including the CaO in RM), liquid:solid mass ratio at 8. After reaction, the slurry was filtered and then washed with deionized water at 80 °C for 10 min before being dried for 10 h at 80 °C	Zhang et al. (2011)
Red mud (Canada)	Al	<i>Hydrometallurgical and bioleaching process</i> : leaching recovery of Al in red mud was conducted using sulfuric and organic acid (citric, oxalic acids) with a maximum 96% recovery of Al whereas bioleaching of red mud using organic acid producing sewage sludge bacteria and pure strains of fungi demonstrated 75% recovery of Al under the conditions described	Vachon et al. (1994)
Red mud (Greece)	Ti	<i>Hydrometallurgical process</i> : the leaching of Ti of red mud by sulfuric acid (6 N) was conducted in a 500 mL five-necked round bottomed split reactor, which was fitted with a glass stirrer, a vapour condenser and a thermometer, at solid:liquid ratio of 1:20 and 60 °C. 64.5% of Ti was recovered whereas 46% and 37% of Fe and Al were recovered	Agatzini-Leonardou et al. (2008)
Red mud (Indian)	Ti	<i>Hydrometallurgical process</i> : Solvent extraction of Ti using hydrochloric acid containing Cyanex 302 and Cyanex 301	Deep et al. (2001)
Red mud (Indian)	Ti	<i>Pyrometallurgical process</i> : acid leaching of red mud with HCl followed by roasting the leached residue with sodium carbonate	Kasliwal and Sai (1999)
Red mud (China)	Heavy metals, REEs, radioactive elements	<i>Bioleaching process</i> : Bench leaching process using <i>Aspergillus niger</i> (remediation of toxicity of red mud) or <i>Penicillium tricolor</i> which was isolated from red mud for removal of REEs and radioactive elements	Qu and Lian (2013), Qu et al. (2013)
Red mud (Russian, Australia, Greece)	Sc, U, Y, Ce, La and other Lanthanides	<i>Hydrometallurgical process</i> : The procedure involved separation of metals following by acid leaching. The leaching process involved sulphuric acid, nitric acid, hydrochloric acid, and other selective reagents. Separation of metals by resin, filtration, liquid-liquid extraction by various extractants (such as di(2-ethylhexyl) phosphoric acid (DEHPA, (RO), POOH, where R = CsH) in hexane, 0.05 M D2EHPA and 0.05 M TBP in Shellsol D70, Cyanex 301, and Cyanex 272) were investigated to obtain high recovery of the valuable metals. Parameters in the procedure, such as the leaching agent, contact time, temperature, pressure and solid to liquid ration, were optimized. A maximum recovery of La (99.9%) was obtained by Abhilash et al. (2014) at conditions: 3 M H ₂ SO ₄ at ambient (35 °C) temperature, S/L ratio of 10 g/L and agitation rate of 200 rpm for 1 h; 99.9% Ce recovery at conditions: 75 °C and solid/liquid ratio of 10 g/L in 3 M H ₂ SO ₄	Abhilash et al. (2014), Ochsenkühn-Petropoulou et al. (2002), (1996), (1995), Smirnov and Molchanova (1997), Wang et al. (2013)

Several chemical reactions may be involved in the reduction of iron in red mud (Swagat et al., 2013). These are listed below:





Whereas most research has focused on reduction roasting of the iron in red mud, Samouhos et al. (2013) used a process which involved microwaves for the roasting step. Microwave heating can generate heat instantaneously inside the moderately absorptive materials (dielectrics) instead of heat from the outside surface and it is believed to be a clean, practical and achievable heating source (Metaxas and Meredith, 1983) but the cost of equipment may be of concern. The process developed by Samouhos et al. (2013) included the reduction of red mud using lignite (30.15 wt.% C_{fix}), followed by wet magnetic separation to produce a raw material which was suitable for sponge or cast iron production. The content of the reductive agent and the microwave heating time both influence the degree of reduction of iron. Iron transformation follows the $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}$ sequence, as confirmed by XRD (X-ray diffraction) and TGA/DTA (Thermogravimetric analysis/Differential thermal analysis). Under optimized conditions, a magnetic concentrate of iron (35.2%) with a metallization of 69.3% was obtained which required less time (a 40% decrease) for roasting, with a higher degree of metallization compared to the conventional reduction roasting process.

The conventional reductive roasting of iron in red mud deserves further investigation with regard to the mechanisms and the optimization conditions in addition to introducing other emerging techniques to facilitate the recovery rate and the iron content. In this way, it should be possible to realize the goal of minimization of red mud waste whilst generating economic value; this is the challenge.

3.3. Hydrometallurgical recovery of iron

Besides pyrometallurgical recovery, extraction of iron from red mud by hydrometallurgical processes has also been investigated by several workers. Sulphuric acid has been investigated for dissolution of iron from red mud (Debadatta and Pramanik, 2013; Uzun and Gulfen, 2007). Optimized recovery of iron (47%) was achieved at leaching conditions of 100 °C, 24 h, using 8 N sulphuric acid and at a solid:liquid ratio of 5:100 (Debadatta and Pramanik, 2013). Calcination at 873 K prior to leaching using 6 M sulphuric acid achieved 97% recovery of iron from red mud (Uzun and Gulfen, 2007). Yu et al. (2012) treated red mud using oxalic acid, facilitated by UV irradiation for iron recovery. The iron content of the red mud (12.31%) was reduced to <0.7%. It was solubilized as Fe(III) oxalate. The solution obtained was then irradiated with UV light to produce Fe(II) oxalate precipitation with >90% transformation. The residue was used to produce refractory materials. Cengenoglu et al. investigated the recovery and concentration of Al, Fe, Ti, Na by Donnan dialysis (Çengeloglu et al., 2001, 2003). Their red mud samples were firstly dissolved in HCl prior to recovering the metals using a polysulphonated ion-exchange membrane of the solution. The recovery rates for Fe, Al, Na, Ti ranged from 0.03–15.13%, 0.02–16.45%, 0.96–31.90%, 0.01–14.23%, respectively. Although various efforts have been made for improved iron recovery, the general iron recovery ranged from 0.03% to 97% for hydrometallurgical methods which have potential issues including low reaction rate and the introduction of secondary waste.

3.4. Potential usage of other techniques

Biotechnologies that can solubilize and so recover metals have been increasingly developed as they are 'clean' and economically-viable alternatives to traditional metal recovery techniques (Laguna et al., 2011). Bioleaching processes that can dissolve iron have been investigated extensively. They are mainly applied for the removal of iron impurities from materials, recovering iron from

ores that are resistant to more conventional concentration methods and the liberation of iron from other metals (Eisele and Gabby, 2012). The solubility of iron compounds can be increased through organic acid complexation by carboxylic acids such as oxalic, citric, pyruvic, malic, and humic and tannic acids generated by bacteria, or by the reduction of iron (III) to iron (II) by bacteria (Eisele and Gabby, 2012) in bioleaching processes. A wide range of bacteria that can produce organic acids for extracting iron from an insoluble phase are used for this purpose, with many of them being aerobic. Anaerobic organisms can also produce organic acids through fermentation of organic matter and so provide further dissolution opportunities for iron. Two types of iron mechanisms have been identified: assimilation (iron uptake into the cells) and dissimilation (solubilization of iron) (Laguna et al., 2011). Although bioleaching processes have been investigated and applied in several fields for iron removal from kaolin (Aghaie et al., 2012; He et al., 2011), from silica (Štyriaková et al., 2012), and from bauxite (Anand et al., 1996; Deo et al., 1999; Papassiopi et al., 2010; Vasan et al., 2001) or iron recovery (Eisele, 2005; Laguna et al., 2011), no such efforts have been made for the recovery of iron from red mud. This is primarily due to its high pH which is not favourable for bacterial growth. However, Laguna et al. (2011) investigated iron dissolution carried out at pHs > 7 using mixed bacterial cultures. This study advanced the possibility of using a multiple step process to recover enriched iron involving bioleaching of iron following acid leaching and the reduction of pH with other acidic wastes. The advantage here is that costs can be reduced through the recovery of other metals and also waste reduction. However, neither this process nor other investigations using bioleaching have been demonstrated at commercial scale. Much work still needs to be done using bioleaching as a cost-effective and efficient technology for the recovery of Fe from red mud.

4. Recovery of other metals

Other metals have also been investigated for concentration from red mud as listed in Table 4, either by single recovery processes or by incorporating into the iron recovery process. These metals include aluminium, titanium, REEs and others, which are discussed in the following sections.

4.1. Aluminium

The aluminium remaining in red mud residue varies from 4% to 16% (Table 1). This additional aluminium source has also attracted intensive research interest. The alumina is either extracted using organic or inorganic acids, or by using bacteria. For example, a hydrothermal process was employed to recover alumina and alkali from both iron-rich and low-iron red mud samples to obtain the andradite-grossular hydrogarnet phase (Zhang et al., 2011). The results showed that a leached residue containing 0.5 wt% Na_2O and 0.3 A/S (mass ratio of $\text{Al}_2\text{O}_3:\text{SiO}_2$) could be achieved with iron-rich red mud under optimal conditions. Sulphuric, citric and oxalic acids have all been used to extract Al from red mud either individually or as mixtures by Vachon et al. (1994). A mixture of 2:1 citric and oxalic acids (pH = 1.5, adjusted by H_2SO_4) dissolved 96% Al in their red mud. Consequently, due to the high price of organic acids, biological leaching was also conducted by these authors. The acid-producing bacteria and fungi include the sewage sludge microorganisms, *Aspergillus niger*, *Penicillium notatum*, *P. simplicissimum* and *Trichoderma viride*. A high recovery of 75% of Al was observed using acids generated by *P. simplicissimum* (10% v/v initial red mud concentration). Another report focused on flotation recovery of alumina (Fan et al., 1992). Characterization of red mud showed that the distribution of Al_2O_3 was not homogenous

as more existed in the coarser fractions than in the finer fractions. Diaspore (70–80%) was trapped by hydromica, hydrating Ca aluminosilicate and oxide iron minerals. A classification followed by a re-grinding process was used to obtain cleaner surfaces of aluminium minerals prior to flotation. The resulting concentrate contained 52.75% Al_2O_3 (recovery 77.85%) and 7.01% SiO_2 (Fan et al., 1992). The recovery of aluminium can also be achieved using soda by fluxing, smelting and leaching practices on red mud (Bruckard et al., 2010). These investigators found that the addition of calcium carbonate into the dried red mud to obtain a $\text{CaO}:\text{SiO}_2$ ratio of 2 increased the rate and extent of dissolution of alumina and soda. Leaching of this material at 60 °C achieved dissolution of 55% Al and 90% Na at 20 wt% solids and dissolution of 50% Al and 75% Na respectively, at 50 wt% solids. The leach liquor was proposed to be recycled in the Bayer process (Bruckard et al., 2010).

4.2. Titanium

Titanium dioxide is one of the most important materials in our daily life as it has a wide range of applications (such as in pigments, paints, sunscreen, catalysts). Red mud can contain high concentrations of Ti in the form of anatase, rutile or it can coexist with other minerals. It has therefore been investigated for the recovery of Ti to produce further value from bauxite waste. There are two main methods for the utilization of Ti in red mud: pyrometallurgical and hydrometallurgical recovery (Agatzini-Leonardou et al., 2008). The pyrometallurgical methods usually involve extraction of pig iron, as discussed in previous sections. Red mud is calcined at a temperature between 800 and 1350 °C and smelted with a carbonaceous reducing agent in an electric furnace to obtain molten iron and a slag that contains mainly titanium dioxide, alumina and silica (Agatzini-Leonardou et al., 2008). Metallic iron is separated and the slag digested for recovery of aluminium and Ti from solution (Erçağ and Apak, 1997; Kasliwal and Sai, 1999). Kasliwal and Sai (1999) introduced leaching red mud with hydrochloric acid followed by roasting the leached residue with sodium carbonate. TiO_2 recovery increased from 36% to 76% after introducing roasting at 1423 K for 115 min for leaching at 363 K. Pyrometallurgical processes are often criticized due to their high energy consumption and so hydrometallurgical methods have also been extensively investigated. Various acids have been examined for the extractability of titanium from red mud, such as dilute sulphuric acid (Mehta and Patel, 1951; Şayan and Bayramoğlu, 2000), concentrated sulphuric acid (Zimmer et al., 1978) and hydrochloric acid (Damodaran and Gupta, 1955). Solvent extraction of titanium from red mud has also been conducted using hydrochloric acid containing mono- and disulphur analogues of bis-(2,4,4-trimethylpentyl) phosphonic acid, namely bis-(2,4,4-trimethylpentyl) monothiophosphonic acid (Cyanex 302) and bis-(2,4,4-trimethylpentyl) dithiophosphonic acid (Cyanex 301) (Deep et al., 2001). A hydrolysis and calcination process followed the acid leaching stage for the recovery of TiO_2 from leachate. 3% H_2O_2 in 0.5 M H_2SO_4 and 4 M $\text{HCl}/\text{H}_2\text{SO}_4$ were used for stripping the TiO_2 (Deep et al., 2001). A recovery of c. 60–70% titanium was generally achieved. Parameters including temperature, leaching time, acid concentration, solid:liquid ratio and stirring rate have all been optimized to maximize the yield of TiO_2 (Şayan and Bayramoğlu, 2000). The techniques reported here focused on laboratory scale for recovery of titanium but no evidence was found for the implementation of laboratory-based study at commercial scale. Extension of laboratory-based studies to field-scale would require significant resources from industry.

4.3. Rare earth elements (REEs) and other elements

Red mud can contain a significant quantity of other metals, rare earth elements and radioactive elements, such as scandium

(60–120 g/t), gallium (60–80 g/t), yttrium (60–150 g/t), uranium (50–60 g/t) and thorium (20–30 g/t) (Smirnov and Molchanova, 1997). Given the rapid increase in the price of rare earth elements (REEs) and rare earth oxides (REOs) which, in 2010, was \$300/kg and had increased to \$3600/kg in 2011 (EPA, 2012), red mud has been avidly investigated for recovery of these valuable elements. Not only has the recovery of REEs been focused on a single process, but incorporation of REEs recovery into the complex utilization of red mud is also being considered for the economical beneficial and waste-free goal.

Recovery of vanadium, zirconium and gallium from red mud is of increasing economic interest (Ochsenkühn-Petropulu et al., 1995). Mukherjee et al. (1990) investigated the recovery of pure vanadium oxide from Bayer sludge (a by-product during the production of alumina from some bauxite ores by the Bayer process) by adsorption from solution onto activated carbon. The process developed can achieve high recovery of 99.9% pure V_2O_5 . The process involves the solubilization of vanadium, adsorption on to activated charcoal, desorption and precipitation and then calcination to yield pure V_2O_5 . Parameters influencing the recovery and purity of V_2O_5 have been investigated. A schematic flow chart for the recovery process was presented by the authors. Recovery of gallium from Bayer liquor (the liquor after precipitation in refining process) was recently reviewed by Zhao et al. (2012). Currently, four methods have been investigated (Zhao et al., 2012) to recover gallium from Bayer solutions, including fractional precipitation, electrochemical deposition, solvent extraction and ion exchange (Selvi et al., 2004). All these methods recover gallium before it concentrates in the red mud solid. Recovery of ZrO_2 has also been conducted whilst recovering TiO_2 (Toshihiro Kasai et al., 1994). The procedure involved decomposing and removing sodalite from red mud using sulphuric acid at room temperature, followed by leaching at 120 °C to dissolve hematite, so leaving anatase, zircon, quartz and other insoluble elements enriched in the residue. After alkali-fusing red mud to remove SiO_2 and successively leaching with water, the TiO_2 was enriched to 84% and >4.5% ZrO_2 was obtained.

Scandium, the most extensively researched REE, is in some cases almost doubly-enriched in red mud compared to the original ore (Ochsenkühn-Petropulu et al., 1994). Ores with a scandium content range of 0.002–0.005% (20–50 mg/kg) can be considered as important resources for scandium and deserve full exploitation (Shaoquan and Suqing, 1996). The Sc concentration expressed as Sc_2O_3 is accumulated to as high as 200–390 mg/kg in one Jamaican red mud compared to 87–113 mg/kg in the original bauxite (Wagh and Pinnock, 1987). Furthermore, the Sc concentration in one red mud from China was enriched from 41 mg/kg in bauxite ore to 105 mg/kg, as Sc determined by XRF (X-ray fluorescence) by our research group. Considering the vast amount of red mud generated each year (90 Mt (Kumar et al., 2006)), there is a very significant potential amount of scandium with hidden value. Different methods can be used for the extraction of REEs from suitable materials including hydrometallurgical, electrometallurgical and pyrometallurgical processes (EPA, 2012). Some information on the concentration of scandium from red mud is available in the existing literature (Wang and Cheng, 2011; Wang et al., 2011). The recovery of REEs from red mud mainly focuses on hydrometallurgical methods. Wang et al. (Wang et al., 2013) recovered scandium from a synthetic red mud leaching solution by solvent extraction using D2EHPA (Di-(2-ethylhexyl) phosphoric acid). These authors firstly leached scandium from their Australian red mud by dilute sulphuric acid. The leach solution was then further extracted using a solvent including organophosphorus acids (Cyanex 272 – bis/2,4,4-trimethylpentyl/ phosphonic acid, Ionquest 801-2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester and DE2HPA), a carboxylic acid (Versatic 10 – Neodecanoic acid), a primary amine

(Primene JMT – a primary aliphatic amine in which the amino nitrogen atom is linked to a tertiary carbon) and two chelating reagents (LIX 984N – un-modified 50:50 blend of aldoxime LIX 860 and ketoxime LIX 84N, and LIX54-100 – b-diketones). The recovery of scandium reached 99% using the process described with 0.05 mol/L D2EHPA and 0.05 mol/L TBP (tri-butyl phosphate) in Shellsol D70 (100% aliphatic diluent) as the extractant. Direct leaching using sulphuric acid (50%) or hydrochloric acid (3 mol/L) was investigated in a study with another Chinese red mud (Si et al., 2003), followed by solvent extraction and precipitation. Recovery was >80% for Sc. Different amphoteric resins have been used for the separation of scandium and uranium from other radioactive and valuable components in red mud following direct acid leaching with sulphuric acid (Smirnov and Molchanova, 1997). Zhou et al. (2008) reported almost complete recovery of Sc by adsorption with active carbon modified by tri-butyl phosphate (TBP), after leaching red mud with 6 mol/L HCl at a volume ratio of 1:4 at 60 °C for 4 h.

In most cases, the recovery of multiple metals have been investigated. A Greek red mud containing 0.1% lanthanides and yttrium was assessed for the recovery of lanthanides and yttrium by selective leaching with diluted nitric acid (Ochsenkühn-Petropulu et al., 1996). The recovery percentages achieved 90% for Y, up to 70% for heavy lanthanides (Dy, Er, Yb), 50% for middle lanthanides (Nd, Sm, Eu, Gd) and 30% for light lanthanides (La, Ce, Pr). In the light of these laboratory-scale results, the authors (Ochsenkühn-Petropoulou et al., 2002) conducted a pilot-plant operation with HNO₃ leaching at ambient temperature and pressure.

Recovery of valuable metals is incorporated into the process for recovering iron or alumina from red mud. For example, a combined pyro- and hydrometallurgical process was used for recovering pig iron and leaching of Sc and Ti (Piga et al., 1993; Rayzman and Filipovich, 1999). The iron in red mud was reduced and sintered with coal, lime and sodium carbonate at 800–1000 °C, after which alumina was re-leached with hot water at 65 °C (Piga et al., 1993). The slag after sintering contained Sc (420 mg/kg), TiO₂ (19.4%), lanthanide oxides (1470 mg/kg) and Y (180 mg/kg). It was then leached with H₂SO₄ followed by hydrolysis at 140 °C to recover Ti. The residue solution can be used for further recovery of Sc by precipitation or solvent extraction (Piga et al., 1993). Abhilash et al. (2014) investigated different solvents (DEHPA, Cyanex 272 and Cyanex 301) for the extraction of La and Ce from Indian red mud. The procedure involved acid leaching and subsequent liquid-liquid extraction of the leached metals. Parameters affecting the maximum recovery were also studied, including temperature, solid:liquid (S:L) ratio, agitation rate and time. They found

that 99.9% La was recovered with 3 mol/L H₂SO₄ at 35 °C, S:L ratio of 1:100 and an agitation rate of 200 rpm for 1 h and using the three solvent whilst 99.9% Ce recovery was achieved at 75 °C and S:L ratio of 1:100 and using Cyanex 301. This reagent can achieve complete extraction of La, Ce and Sc as compared to DEHPA and Cyanex 272 (Abhilash et al., 2014). Most recently, Qu et al. (2013) used a bioleaching method to extract the rare earth and radioactive elements. They found 10% pulp density can achieve the highest removal of REEs and radioactive elements with the leachability ranging from 20% to 80%.

Though various methods have been investigated for rare metals recovery, a lack of information on cost-effective estimation at field level hinders real application of these promising techniques.

5. Integrated processes for complete utilization of red mud

Our review of past and current efforts to utilize the valuable materials in red mud highlights certain limitations that must be overcome before the techniques being implemented. For example, red mud is generated and currently stored where processing for alumina recovery from bauxite ore (Bayer's process) is performed. However the recovery processes normally require transportation of red mud to the recovery plants, e.g. for iron making operations, which is likely to increase costs. Therefore, utilization processes that can be adopted locally near the bauxite processing facility are preferable. Furthermore, the recovery of metal values using pyrometallurgical processes normally requires high energy inputs. For iron recovery by pyrometallurgical methods, the quality of pig iron and composition of the slag is critical for optimum temperature requirements and refractory stability. The hydrometallurgical method is likely to introduce secondary pollutants and raises issues related to the disposal of leach residues. Some 'green', environmentally-friendly and cost-effective processes are needed to realize these values in red mud. Table 5 provides a short summary of the advantages and disadvantages of these recovery methods.

Alternatively, complete utilization strategies can be developed for minimizing red mud waste whilst concentrating iron and other valuable materials. Fig. 2 illustrates the procedure for development of such a complete utilization of red mud. A full characterization and selection of utilization processes are integrated in the procedure based on which complete utilization strategy is developed. In such a complex usage of red mud, valuable metals are recovered as well as gaining major materials such as iron, aluminium and alkali all in the same process in order to reduce the costs and waste. Utilization strategies for the residues can also be incorporated into

Table 5

Summary of techniques used for metal recovery from red mud.

Metals	Methods	Advantages	Disadvantages	Ref.
Fe	Magnetic separation	Low energy input	Low efficiency due to fine particle size and coexistence of iron minerals with other minerals	Hammond et al. (2013)
	Hydrometallurgy Pyrometallurgy	Improved efficiency (1) A product with reduced metallic Fe or pig iron amenable to steelmaking is possible. (2) Additional values can be added, such as recovery of alumina, titanium, alkali, etc.	Introducing secondary pollutants (1) High energy input. (2) Needs pre-removal of alumina and alkali oxides if red mud is mixed into a blast furnace. (3) Pure solid iron-rich product is difficult to obtain due to the association between iron minerals and other oxides	
Al	Hydrometallurgy	(1) High efficiency (2) Green process to use bacterial leaching	(1) Usage of organic acids involves high cost. (2) Bioleaching process usually take a longer time	Vachon et al. (1994)
Ti	Incorporated with iron recovery by pyrometallurgy Hydrometallurgy	Can be additional value to iron recovery	High energy input	
REEs	Various techniques	High efficiency (1) Additional value to the existing process (2) Recovery to generate economic income	Introduces acid and solvent wastes (1) Generally complex process. (2) Other chemicals needed	

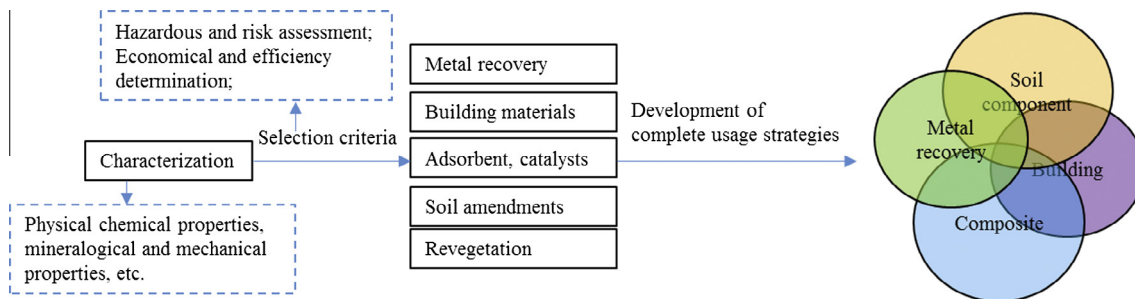


Fig. 2. Illustration of complete usage of red mud procedure.

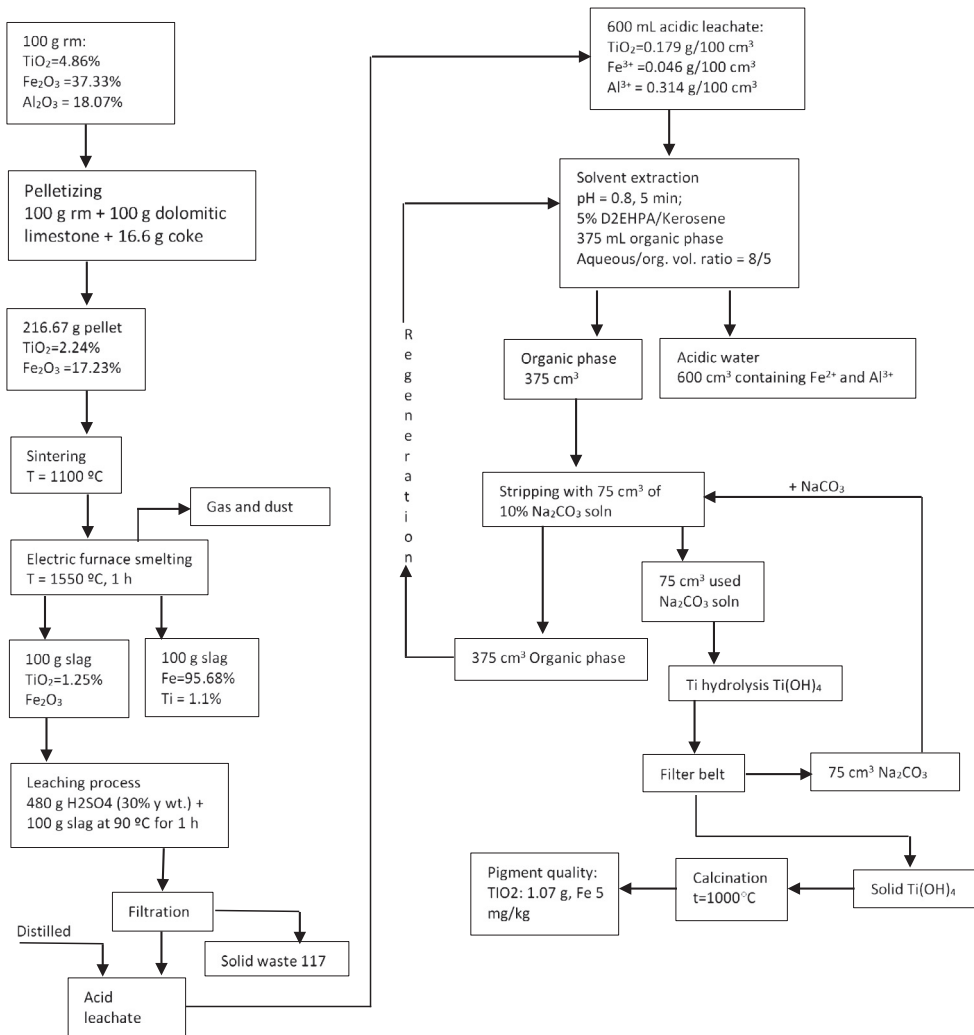


Fig. 3. Overall flow sheet for complex usage of red mud Erçağ and Apak (1997).

the process. Several attempts have been made to achieve these goals. For example, Erçağ and Apak (1997) developed a two-stage procedure for the recovery of TiO_2 , Al_2O_3 and pig iron from red mud. As shown in Fig. 3, in the first instance red mud was mixed with dolomite and coke and then sintered ($1100\text{ }^\circ\text{C}$) and smelted ($1550\text{ }^\circ\text{C}$) to produce pig iron and a slag. These workers then used 30% H_2SO_4 to extract Fe, Ti and Al in the slag at $90\text{ }^\circ\text{C}$. Solvent extraction was used to separate Fe, Ti and Al, Si using 5% D2EHPA in the leachate. Ferric iron was reduced and recovered whilst silica and alumina were recovered from the acidic waters. The organic phase containing Ti was stripped with 10% Na_2CO_4 solution,

hydrolyzed and calcined to produce pigment-grade TiO_2 . A stoichiometric flow sheet for the whole process is illustrated in Fig. 3 (Erçağ and Apak, 1997). Although the integrated process developed by these workers is novel and is promising, its application at field scale has never been trialed. Given the large volume of red mud that continues to be generated by the alumina industries, it may be worth extending the technology at field scale through a multi-scale collaboration involving all stakeholders that generate red mud – an approach that is yet to be tested.

Liu et al. (2009a) investigated the feasibility of using the roasting process on the residue generated after iron recovery to

generate building materials. The aluminosilicate residues after magnetic separation were mixed with slaked lime and pressed with a cylinder mould II ($\Phi 30 \text{ mm} \times 50 \text{ mm}$) at 20 MPa. The samples were then cured in a braising-boiler with the steam of 80 °C at 1 atmosphere pressure for 11 h. Liu et al. found that the brick specimens prepared achieved maximum compressive strength of 24.10 MPa after addition of 13% hydrated lime when roasting. Rao et al. (1997) studied the refractory applications of the residue after magnetic separation of red mud for recovery of Fe and Al and showed that the reduction of iron can significantly decrease the magnetic intensity required for separation (from 14000 to 2000 Gauss). The final non-magnetic product contained 77% Al_2O_3 with a recovery of 69%.

6. Conclusions and future perspectives

This review presents the techniques developed and investigated for recovery of iron, aluminium, titanium and REEs from red mud. There are basically two methodologies: pyrometallurgy and hydrometallurgy. Attempts at incorporating red mud into the blast furnace with iron ore and feeding red mud back into the alumina refining processes have been made but have shown low efficiency. Incorporation of the recovery of aluminium, titanium and REEs into iron recovery from red mud helps to reduce the operational cost. There is clearly a great need for further research for the following reasons:

- (1) In view of the scarcity of iron supply worldwide and the concerns associated with red mud disposal, it is important to utilize the source of additional iron in red mud which is both economically and environmentally desirable.
- (2) More detailed information on minerals characterization in red mud is critical to the recovery of iron and the development of a practical complex utilization technique.
- (3) Since single recovery is not always economical, multiple recovery of valuable metals should be developed, so making the process economically feasible.
- (4) Development of novel uses for the residues after metal recovery such as for building materials, catalytic supporting materials, adsorbents, which will all assist in environmentally friendly waste minimization.
- (5) Zero waste and complex utilization of red mud requires novel techniques that are safer, cleaner and efficient. Introducing new techniques from other research fields should promote the future utilization of red mud as a resource rather than a waste.

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