



## Review

# Metallurgical process for valuable elements recovery from red mud—A review



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## ABSTRACT

Red mud, namely bauxite residue or red sludge, is a potential valued solid waste produced from the alumina extraction process with substantial reserve of over 2.7 billion tonnes worldwide. Taking into account the rise in iron ore price and scarcity of rare earth supply worldwide, recovering aluminum, iron, sodium and other valuable elements from red mud is significant in the disposal of problems associated with these solid wastes. The current application status and composition characteristics of red mud are first introduced. Metallurgical processes for aluminum, sodium, iron, titanium, vanadium, scandium and other valuable elements recovery from red mud are investigated in detail by subsequent sections. Some mechanisms and performance of solvent extraction involved in the extraction or stripping process are also reviewed in this paper. The result suggests that much work still needs to be done for the improvement of leaching and extraction selectivity as well as efficiency, and also for the development of a green recovery process with environmental benignity, low energy requirements and cost.

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## 1. Introduction

Red mud or red sludge is a solid waste produced in the process of alumina extraction from bauxite ores. It has a rusty red tint, which arises from the existence of ferric oxide. With about 120 million tonnes of this hazardous material produced around the world annually (Klauber et al., 2011), red mud is one of the most important disposal problems in the

mining and metallurgy industry. While in China, approximately 50 million tonnes were generated in 2012, and more than 2.7 billion tonnes has been accumulated up to now in the world. A typical bauxite plant produces one to two times as much red mud as alumina (Ayres et al., 2001; Cao et al., 2013). The amount varies greatly depending on the type of bauxite and technique used in the refining process. Discharge of red mud is damaging to the environment because of its high alkalinity, numerous heavy metals and tiny amount of radioactive elements. Thus, it is an enormous challenge for the alumina industries.

So far bauxite residue has found limited applications in building materials, land reclamation and paving (Piga et al., 1993). Stockpile and dumped at sea are the main disposal methods of processing this solid

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waste. Such a vast tract of land employed by red mud storage not just raises the economic cost but also intensifies the risk of environmental pollution, for instance surface/ground water pollution and haze, for neighboring communities (Dauvin, 2010; Varnavas and Achilleopoulos, 1995). Thus, enterprises and government should pay more attention to reusing and managing the sharp rise and large volume of this solid waste. Development in using red mud as low-cost adsorbents for exhaust gas and wastewater treatment as well as catalysts for catalytic reaction has been widely researched (Crini, 2006; Jones et al., 2006; Pratt and Christoverson, 1982; Sahu et al., 2013). These adsorbent materials can remove heavy metals, inorganic ions, organic compounds or impurities, even viruses and bacteria (Bhatnagar et al., 2011; Liu et al., 2009b). However, the low adsorption capacity and catalyst sintering of raw red mud will bring a negative effect on using. The thermal analysis measurement of bauxite red mud indicates that the decomposition is a complicated and multistep process. It is found that this process in general contains two main decomposition stages and one sub-stage. The whole decomposition process is composed of a range of physiochemical reactions (Janković et al., 2013).

In respect of large scale producing construction material based on red mud, many studies have investigated the preparation of special cements from Bayer red mud (Manfroi et al., 2014; Singh et al., 1997; Tsakiridis et al., 2004). These research results indicate that it is a feasible way to produce cements with the addition of red mud in the raw meal. Compared the quality with ordinary Portland cement, these special cement products can always possess a novel strength. While the amount of additive Bayer red mud is very small and less than 5% can be added (Tsakiridis et al., 2004). It is apparent that this disposal is not an efficient method compared with rapidly expanding red mud. In the field of ceramic production, the addition of red mud ranges from 0 wt.% to 50 wt.% in the dry content of final mixture (Sglavo et al., 2000). Glass-ceramic can also be synthesized by the mixtures prepared with some silicates or minerals and 15–25 wt.% red mud (Pelino et al., 1994). The role of red mud in the ceramic or glass-ceramic is strongly affected by the temperature of thermal treatment (Puskas, 1983; Yang et al., 2008). Besides, the red mud cake is useful as a landfill material for reclaiming land. Generally, the Bayer red mud, after filtering, is compressed and subsequently dewatered into a solid cake or other bodies with a void ratio of <1.5 (Kainuma, 1981).

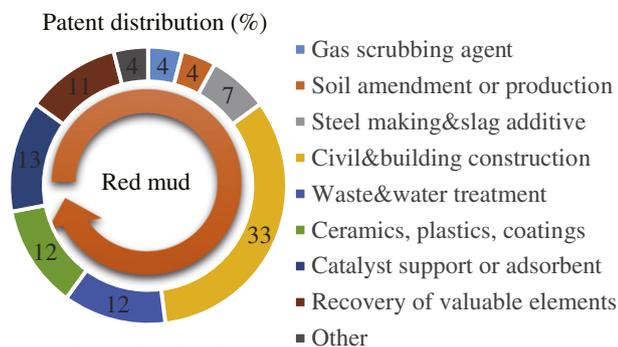
On the other hand, some new reuse methods of red mud are being carried out to utilize this industrial waste and minimize its environmental impact, such as metal recovery including Fe, Al, Ti, Na, V, Sc and Ga (Liu et al., 2009a; Smirnov and Molchanova, 1997; YU et al., 2012; Zhang et al., 2011; Zhong et al., 2009), ceramic/glass-ceramic production using this resulting residue (Liu et al., 2014). And it is a promising and high value added way to use this residue after metal recovery to synthesize

ceramic or glass ceramic. Fig. 1 illustrates the current potential applications of red mud and corresponding patent distribution from 1964 to 2008 in percentage terms (Chandra, 1996; Klauber et al., 2011). Nevertheless, few of them have been economically and commercially applied on an industrial scale.

## 2. Production and characteristics of red mud

Bauxite is a mixture of minerals rich in aluminum hydroxide oxides. Typically, it consists mostly of the minerals gibbsite  $\text{Al}(\text{OH})_3$ , boehmite  $\gamma\text{-AlO}(\text{OH})$  and diaspor  $\alpha\text{-AlO}(\text{OH})$ , mixed with two iron oxides goethite  $\alpha\text{-FeOOH}$  and hematite  $\text{Fe}_2\text{O}_3$ , small amounts of rutile/anatase  $\text{TiO}_2$ , clay mineral kaolinite and other impurities in minor or trace amounts. Red mud is produced during the Bayer process or bauxite calcining method for alumina production. Generally, the primary industrial production of alumina from bauxite is the 'Bayer process' in the world, which accounts for 95% of alumina production (Klauber et al., 2011). Fig. 2 shows a general scheme of alumina production process including the sintering and the well-known Bayer process.

Red mud is an extremely fine particle material with an average particle size less than  $100\ \mu\text{m}$  depending on the grain size of the primary minerals. The specific surface area of bauxite residue ranges from 10 to  $25\ \text{m}^2\cdot\text{g}^{-1}$  (Wang et al., 2008). Fig. 3a presents a red mud waste storage at Agios Nikolaos site in Greece and a certain kind of red mud after water evaporation (Mouchos, 2015). Besides, the scanning electron microscopy images of some kind of red mud are also shown in Fig. 3b (Liu et al., 2007; Zhong et al., 2009). Red mud is mainly composed of numerous residual minerals, for instance, hematite  $\text{Fe}_2\text{O}_3$ , goethite  $\alpha\text{-FeO}(\text{OH})$ , boehmite  $\gamma\text{-AlO}(\text{OH})$ , quartz  $\text{SiO}_2$ , sodalite  $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ , anatase  $\text{TiO}_2$ , and gypsum  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ , with a minor presence of calcite  $\text{CaCO}_3$ , whewellite  $\text{CaC}_2\text{O}_4\cdot\text{H}_2\text{O}$  and gibbsite  $\text{Al}(\text{OH})_3$ . Chemical analysis indicates that red mud are mainly composed of the elements of Si, Al, Fe, Na, Ca, Ti and O, yet with some trace elements, i.e., K, Cr, V, Ni, Ba, Cu, Mn, Pb, Zn, Sc, Ga, Ra, U, Th, etc. Table 1 listed some of the chemical compositions and mineral components of major elements of red mud, which were sampled from different parts of the world (Gräfe et al., 2011; Newson et al., 2006; Paramguru et al., 2005; Snars and Gilkes,



Note: The number of total patents mentioned above is 734 (1964–2008).

Fig. 1. Illustration of the current potential applications of red mud and corresponding patent distribution from 1964 to 2008. Chandra, 1996; Klauber et al., 2011.

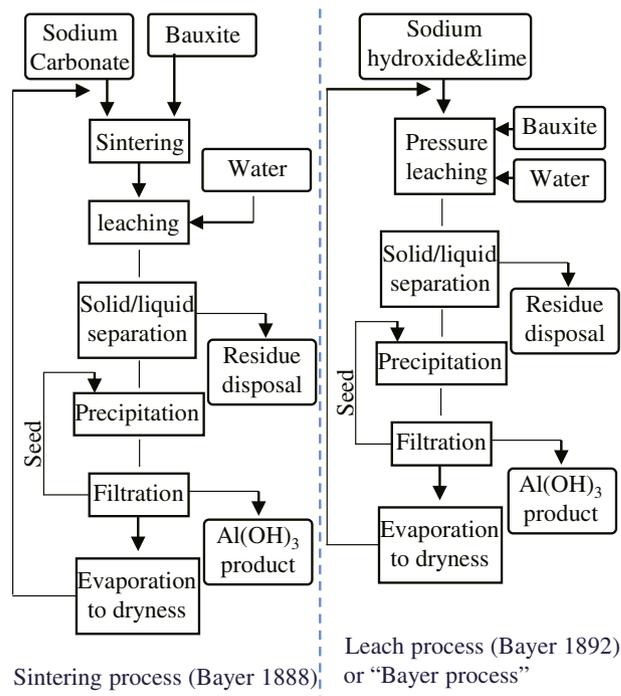


Fig. 2. Flow diagrams for the sintering and leach processes patented by Bayer. Klauber et al., 2011.

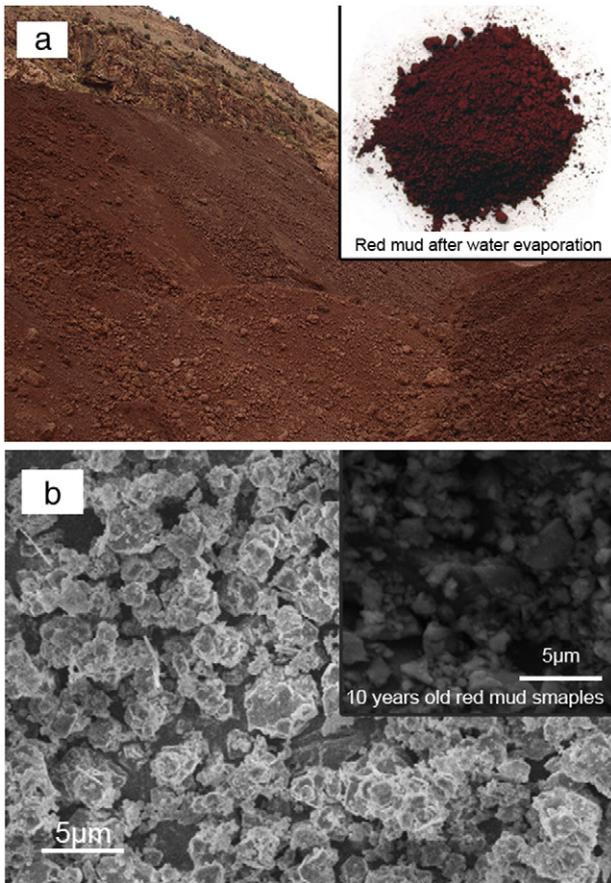
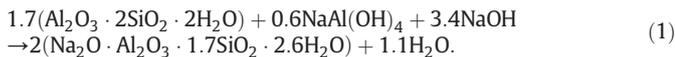


Fig. 3. Images of macrostructure and microstructure of some kind of red mud. Mouchos; Liu et al., 2007; Zhong et al., 2009.

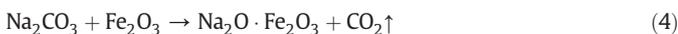
2009). It is worth mentioning that iron oxide is typically the major constituent, then alumina and silica.

The characteristics of bauxite residue are associated with the process of alumina production. The Bayer process is not a cost-effective way for processing low grade bauxite ores containing the large volume of silica. In Bayer process, the boehmite and gibbsite bauxites are digested by washing with a hot solution of sodium hydroxide. Therefore, the Bayer red mud without calcination consists of fewer pozzolanic active substances. Contrarily, the bauxite calcination red mud can be directly used as the raw materials of construction due to the existence of some reactive substances, for instance  $\beta$ -2CaO·SiO<sub>2</sub> (Liu et al., 2009a). As for high silicon and low grade bauxite ores, the bauxite calcining method is employed (Liu et al., 2007), otherwise Bayer process will lead to the waste of sodium hydroxide and lower the yield of alumina. This phenomenon could be explained by the following reaction.

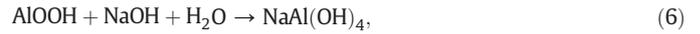


The major reactions in the Bayer process and bauxite calcination red mud are listed as follows.

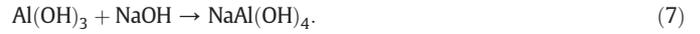
Bauxite calcining method:



Bayer process:  
Boehmite and diasporé,



gibbsite,



Red mud is not a particularly hazardous waste for its caustic. However, the corrosivity owing to the existence of hydroxides is unfavorable for its reuse. As Habashi (1997) pointed out, the pH value of leaching liquor obtained with 1000 times its mass distilled water washing red mud is still high, even more than 10.5. Some neutralization methods like seawater wash treatment, heat treatment and acid neutralization can be taken into account for the change of alkalinity (Wang et al., 2008).

### 3. Recovery of valuable elements from red mud

In the past several decades, the research of reusing solid wastes is brought into sharp focus especially in the field of recovering valuable elements from bauxite residues. Given the mineralogically and texturally diverse in the bauxite ore and red mud, it is difficult to completely separate out the valuable elements from the red mud.

#### 3.1. Recovery of aluminum and sodium from red mud

There is approximately 2.12%–33.1% alumina remaining in common red mud generated from the Bayer process (Gräfe et al., 2011). Generally, hydrometallurgy is employed to extract alumina by using organic or inorganic acids. Zhang et al. (2011) recovered alumina by the formation of andradite–grossular hydrogarnet in hydrothermal process. The hydrochemical method introduced by Ablamoff (Ablamoff and Qian-de, 1988) for recovering Al<sub>2</sub>O<sub>3</sub> is through destroying the structure of sodalite or cancrinite and generating a new crystal phase, for example andradite–grossular hydrogarnet. The results indicate that the hydrothermal process is an effective way as dealing with Fe-rich (20 wt.%) Bayer red mud. A 0.5 wt.% sodium oxide content and 0.3 A/S (mass ratio of Al<sub>2</sub>O<sub>3</sub> to SiO<sub>2</sub>) leached residue can be obtained. Regarding the recovery of alkali, this method also works pretty well. Zhong et al. (2009) used two steps including the transformation of desilication product into NaCaHSiO<sub>4</sub> to recover alumina prior to the hydrolysis of resulting product to recover alkali, and succeeded in recovering 87.8% of Al<sub>2</sub>O<sub>3</sub> and 96.4% of Na<sub>2</sub>O from red mud with the similar method. When the red mud mixed with hydrated lime and subsequently processed including digestion, hydrothermal treatment, calcination and leaching with soda liquor, the recovery of Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>O can go as high as 70% and 90%, respectively (Liu et al., 1997).

Acid leaching of aluminum from red mud was examined by Vachon et al. (1994). The organic and mineral acids, such as sulfuric, citric and oxalic acids, were adopted individually or as mixtures. Optimized recovery of aluminum was obtained (96% alumina solubilization) using a leaching agent with 2:1 of citric to oxalic acids at pH 1.5 adjusting by the addition of sulfuric acid. As compared with the H<sub>2</sub>SO<sub>4</sub> leaching agent at pH 1.0, the mixed leachant showed a higher recovery of aluminum but less economical owing to the high price of organic acids. On the other hand, Bosecker (1986) recovered approximately 47% aluminum from the red mud using oxalic acid as leaching agent.

Bioleaching of Al from red mud was also carried out by Vachon et al. (1994). The microorganisms consisting of sewage sludge bacteria, fungi such as *Aspergillus niger*, *Penicillium notatum*, *Penicillium simplicissimum* and *Trichoderma viride* were tested in the biological leaching experiments. The results revealed that 75% of aluminum can be recovered in a 10% v/v initial red mud concentration using the acids generated by *P. simplicissimum*.

**Table 1**  
Chemical compositions and mineral components of major elements of red mud in different parts of world.  
Paramguru et al., 2005; Newson et al., 2006; Snars and Gilkes, 2009; Gräfe et al., 2011.

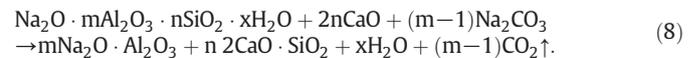
Chemical composition (wt.%) & general composition range	BR Para state	CN Pingguo	DE Baudart	UK	TR Seydisehir	GR Alhellas	AU Eurallumia	IN Damanjodi	JM Kirkvine	US Sherwon
Fe <sub>2</sub> O <sub>3</sub> (6.8–71.9)	45.6	26.9	44.80	36.31	39.84	42.5	35.20	54.80	49.40	50.54
Al <sub>2</sub> O <sub>3</sub> (2.1–33.1)	15.1	26.8	16.20	23.43	20.24	15.6	20.00	14.80	13.20	11.13
TiO <sub>2</sub> (2.5–22.6)	4.29	7.30	12.33	5.97	4.15	5.90	9.20	3.70	7.30	○
Na <sub>2</sub> O (0.1–12.4)	7.50	○	4.00	12.36	9.43	2.40	7.50	4.80	4.00	9.00
SiO <sub>2</sub> (0.6–23.8)	15.6	13.10	5.40	18.25	15.27	9.20	11.60	6.40	3.00	2.56
CaO (0.6–47.2)	1.16	23.50	5.22	4.38	1.80	19.70	6.70	2.50	9.40	7.73
Others	10.75	2.40	12.05	0	9.27	4.70	9.800	13.00	13.70	19.04
Mineral constituent (mol%)	BR Para state	CN Pingguo	DE(GN) Boke	UK	TR Seydisehir	GR Alhellas	AU Eurallumia	IN Renukoot	GN Aughinish	IT(AU) Weipa
Amorphous	×	22	×	38.2	×	×	×	×	×	×
Quartz SiO <sub>2</sub>	●	○	○	1.2	●	○	○	○	●	○
Hematite α-Fe <sub>2</sub> O <sub>3</sub>	●	19	●	13.5	●	●	29	22.2	●	●
Goethite α-FeO(OH)	●	○	●	21.8	●	○	○	10.9	○	●
Magnetite Fe <sub>3</sub> O <sub>4</sub>	○	○	○	○	○	●	○	○	○	○
Ilmenite FeTiO <sub>3</sub>	○	10	○	○	○	○	○	○	○	○
Rutile TiO <sub>2</sub>	○	3	○	4.6	●	○	○	1.8	●	○
Anatase TiO <sub>2</sub>	○	○	●	○	○	○	5	3.8	○	●
Perovskite CaTiO <sub>3</sub>	○	○	○	○	○	●	○	1.1	●	○
Calcite CaCO <sub>3</sub>	●	○	●	0.7	○	○	○	1	○	○
Gibbsite Al(OH) <sub>3</sub>	●	○	●	○	●	○	○	3	●	○
Diaspore α-AlO(OH)	○	○	●	○	○	●	5	0.6	○	●
Boehmite γ-AlO(OH)	○	○	○	○	●	○	6	1	●	●
Calcium silicate CaSiO <sub>4</sub>	○	○	○	○	●	○	○	○	○	○
Imogolite Al <sub>2</sub> SiO <sub>3</sub> (OH) <sub>4</sub>	○	32	○	○	○	○	○	○	○	○
Sodalite Na <sub>4</sub> (Si <sub>3</sub> Al <sub>3</sub> )O <sub>12</sub> Cl	●	○	●	17.5	●	●	16	3.7	●	●
Hydrocalumite Ca <sub>4</sub> Al(OH) <sub>12</sub> ·CO <sub>3</sub>	○	○	○	○	○	○	○	○	○	○
Cancrinite Na <sub>6</sub> (Al <sub>6</sub> Si <sub>6</sub> O <sub>24</sub> )·2CaCO <sub>3</sub>	○	○	○	○	●	○	33	4.7	○	○
Muscovite Al <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH,F) <sub>2</sub>	○	○	○	2.4	○	○	○	○	○	○
Kaolinite Al <sub>2</sub> Si <sub>2</sub> O <sub>5</sub> (OH) <sub>4</sub>	○	○	○	○	○	○	○	○	○	○
Illite	○	○	○	○	○	○	○	○	○	○

Notes: ○: not found; ●: present; ×: not determined.

Illite formula: (K,H<sub>3</sub>O)(Al,Mg,Fe)<sub>2</sub>(Si,Al)<sub>4</sub>O<sub>10</sub>(OH)<sub>2</sub>(H<sub>2</sub>O).

Red mud first mixed with a certain amount of calcium carbonate and then smelted at 1400 °C, a high recovery of aluminum and sodium can be easily achieved due to the phase transformation of red mud into (Na,Ca)<sub>2</sub> - x(Al,Fe<sup>3+</sup>)<sub>2</sub> - xSi<sub>x</sub>O<sub>4</sub> (0.2 ≤ x ≤ 0.5) (Bruckard et al., 2010). The solubility and dissolution rate of Al<sub>2</sub>O<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> increased in water leaching system with augmenting CaO/SiO<sub>2</sub> ratio from 0.1 to 2 in the slag by the addition of CaCO<sub>3</sub> to the red mud. 55% Al and 90% Na can be extracted at 60 °C with water leaching of the resulting slag at 20 wt.% solids. 50% Al and 75% Na can be recovered at 50 wt.% solids. After leaching the 50 wt.% solids twice with the first leachate, levels of 130 g·L<sup>-1</sup> Al and 125 g·L<sup>-1</sup> Na in liquor can be obtained. Alumina can also be recovered from iron rich red mud by sintering process (Qiusheng et al., 2008). In this method, the addition of sodium ferrite (Na<sub>2</sub>O·Fe<sub>2</sub>O<sub>3</sub>) to 10%–12% and the increase of sintering duration time to 30–40 min were beneficial to addressing the generation of indissoluble compound salts, for example 3CaO·Al<sub>2</sub>O<sub>3</sub>, Na<sub>2</sub>O·Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub> and 4CaO·Al<sub>2</sub>O<sub>3</sub>·Fe<sub>2</sub>O<sub>3</sub>, which could improve the leaching of alumina. The effects of sintering temperature, relevant chemical reactions and formulation on the alumina recovery were also researched based on the thermodynamic analyses (Qiusheng et al., 2008). In addition to the method of mentioning in front, reduction sintering process can also be used to recover alumina and ferric oxide from iron rich Bayer red mud (Li et al., 2009). Adjusting the atmosphere during the sintering process of iron rich red mud, the ferric oxide could undergo reduction (800–1075 °C) to magnetite with carbon as the reductant, or to metallic iron when the ferric oxide reduction synchronize with the emergence of sodium aluminate and calcium silicate. Given favorable sintering conditions, the alumina and iron oxide recovery can respectively reach 89.71% and 60.67% by subsequent process of leaching and magnetic beneficiation (48 kA·m<sup>-1</sup>). A high recovery of 75.7% Al and 80.7% Na can also be achieved through soda-lime roasting followed by water

leaching of the roasted products (Liu et al., 2012). The soda-lime roasting process made the dissolution of aluminum and sodium easier owing to the formation of sodium aluminosilicate phase. This phenomenon can be explained by the following relevant chemical reaction.



The SiO<sub>2</sub> thermodynamic activity would be reduced as the increase of CaO concentration in the roasting process. Meanwhile, the addition of CaO would improve the dissolubility of aluminum and sodium in the water leaching process, and SiO<sub>2</sub> became less able to support the generation of sodium aluminosilicate phase at high temperature. The reductive roasting atmosphere could also influence the ferrous phase in equilibrium system and be in favor of the aluminum and sodium recovery.

A combined pyro- and hydrometallurgical process can also be employed to recover aluminum, iron and titanium elements (Piga et al., 1993). Well mixed starting materials of red mud, coal, lime and sodium carbonate were first subjected to reducing sintering at 800–1000 °C. The resulting fine sintered products underwent water-leaching at 65 °C for 1 h and 89% aluminum involved in the products were leached out. The filtrate obtained can be recycled in the Bayer process. After magnetic separation process, 73–79% titanium in the non-magnetic fraction was also extracted by following steps of sulfuric acid leaching, hydrolyzing, filtering and roasting. On the other hand, a pig iron consisting of 93–94% ferrum content was obtained by smelting of the magnetic fraction at 1480 °C. The pyro- and hydrometallurgical process are given in Fig. 4.

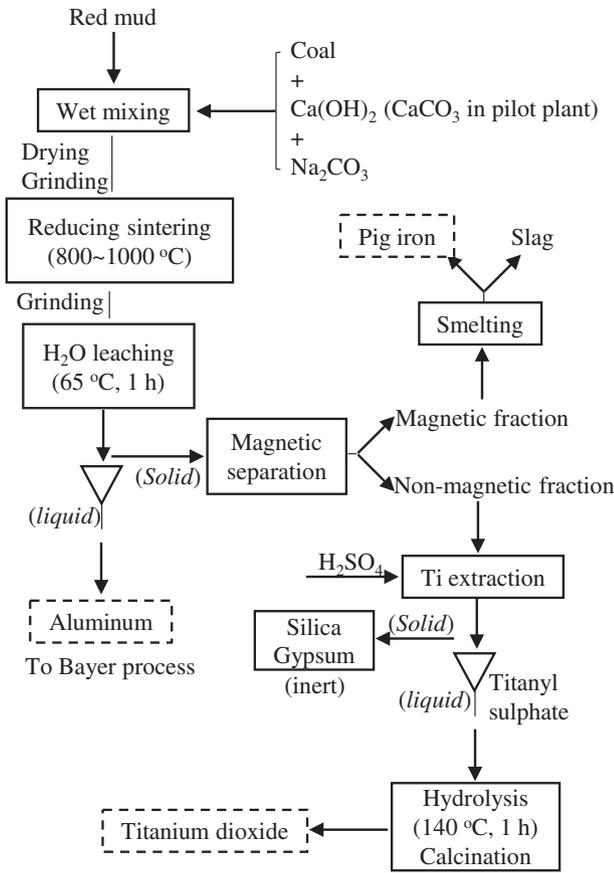


Fig. 4. A flow diagram for complete beneficiation of red mud by reducing sintering and magnetic separation. Piga et al., 1993.

3.2. Recovery of iron from red mud

As mentioned above, iron oxide in red mud is typically the major constituent and the concentration of TFe in ferric oxide varies between 6.8 wt.% and 71.9 wt.% depending on the iron grade of bauxite (Gräfe et al., 2011; Jayasankar et al., 2012). Recovery of iron from solid waste can be directly carried out using a physical process, i.e. magnetic separation. The magnetic products obtained can be applied as a sintering material for ironmaking or as a pigment for pottery or ceramic making (Hammond et al., 2013; Jamieson et al., 2006). In brief, the magnetic separation process would appreciate the total value of red mud. This method had been employed to recover iron oxides from the red mud as early as 1970. However, the performance of extracting was poor at that time (Stickney et al., 1970). The pulsating high-gradient magnetic dressing would provide a better separation result than common magnetic separation, especially for red mud after the process of pre-treatment and grinding (Li, 2005). The high gradient superconducting magnetic separation (HGSMS) system was believed to be a high efficient way in separating fine magnetic particles in liquid suspensions. This is due to the fact that HGSMS system will set up a stronger magnetic field than ordinary ferromagnetic-core electromagnets. On the other hand, the cost of superconducting magnets is economically feasible for industrial application (Ohara et al., 2001). Various iron oxide contents of raw red mud would also affect the separation result when the extremely fine red mud particles with particle size less than 100 μm was carried out on a HGSMS system (Li et al., 2011). The experimental result indicates that the efficiency of HGSMS on red mud containing 29.79% Fe<sub>2</sub>O<sub>3</sub> is higher than that containing 58.74% Fe<sub>2</sub>O<sub>3</sub>. The iron oxide concentrations in iron rich and poor red mud residues were 52.0% and 14.1%, respectively. The stronger magnetic intensity was

applied, the higher recovery of iron oxides in the separation process. Nevertheless, the more intergrowth of Fe, weak magnetic and non-metallic materials would also be easily captured and extracted to the magnetite concentrates regardless of red mud types and that would lead to the decrease of concentrate grade. If red mud was first subjected to recovery of strong magnetic iron concentrates using a cylindrical medium intensity magnetic separator, and then the tailing obtained was processed through the open circuit roughing and concentration to recover weak magnetic iron concentrate by a Slon® vertical ring and pulsating high gradient magnetic separator, an iron concentrate containing TFe ≥ 54% can be obtained and the recovery of iron is 28%–35% (Peng and Huang, 2011). Fig. 5 illustrates the flow chart of iron recovery from red mud slurry.

Roasting and reduction smelting processes of pyrometallurgy are other methods to recover iron from bauxite residue (Kumar and Srivastava, 1998). The typically simplified roasting and reduction smelting of red mud treatment are shown in Fig. 6 (Kumar and Srivastava, 1998) and Fig. 7 (Zhu et al., 2012), respectively. Though these processes are common high cost procedure compared to magnetic separation, many attempts have been made to find an economically feasible way for the practical industrial applications. Various reductants appear mainly in the form of solid phase including carbon powder (Li et al., 2009; Liu et al., 2009a; Raspopov et al., 2013), graphite (Jayasankar et al., 2012), soft coal (Zhu et al., 2012), coal char (Liu et al., 2012), coke (Rath et al., 2013) etc. Besides the influence of different kinds of reducing agents on the extent and rate of iron reduction or recovery, it is reported that the reactivity and volatile matter content of reductant have also a remarkable effect (Xiangong et al., 1996). In terms of coal quality, the theoretically needed coal is characterized as the

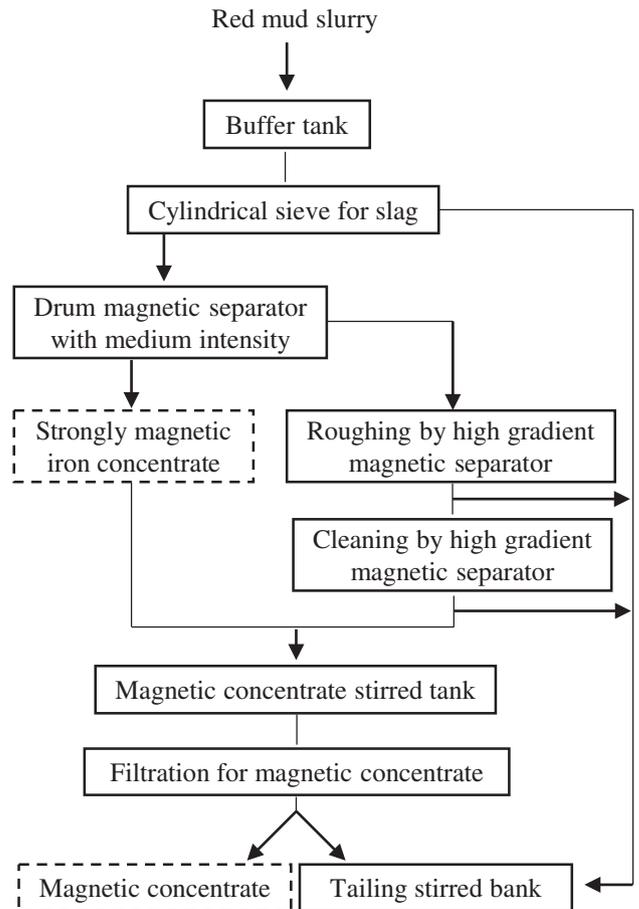


Fig. 5. A flow diagram of iron recovery from red mud slurry. Peng and Huang, 2011.

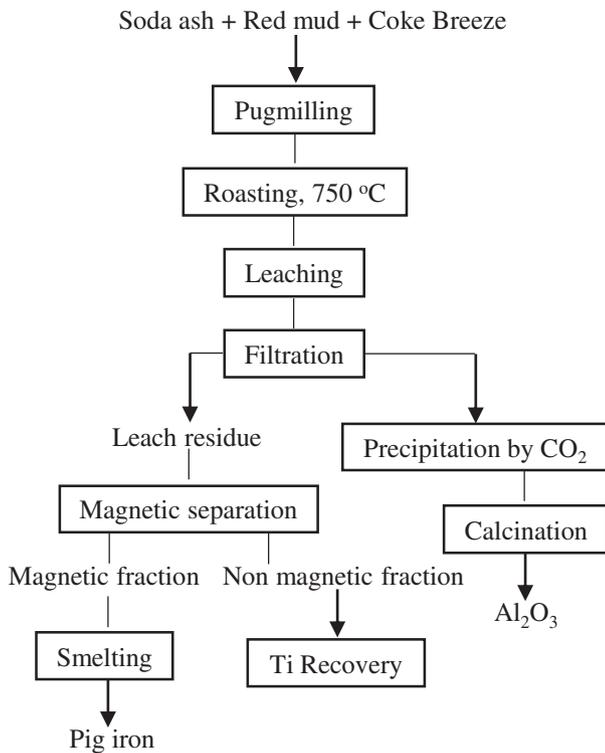


Fig. 6. A flow diagram for the recovery of Al, Fe, Ti from red mud. Kumar and Srivastava, 1998.

following condition, namely, large ratio of  $[(F_c + V_m):(A + W)]$  ( $F_c$ : fixed carbon content;  $V_m$ : volatile content;  $A$ : ash content;  $W$ : other incombustible content), high ash composition ratio of  $[(SiO_2 + TFe):(Al_2O_3 + other)]$ , low ash content and high reactivity (Yongkang and Xiangong, 1995). Furthermore, a certain amount of additives, such as magnesium salt, calcium salt, sodium salt and compound salt, can also

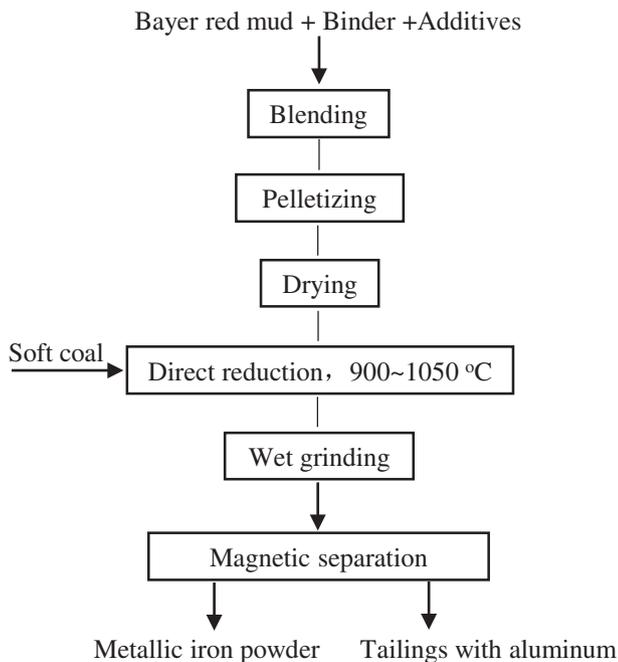


Fig. 7. A flow diagram of upgrading iron from red mud. Zhu et al., 2012.

improve efficiency of coal based direct reduction of iron rich red mud. Due to the addition of strong basic additives during the reducing process, the structure of complex iron oxides can be destroyed by alkaline and alkaline earth ions first and then displaced by these oxides. This phenomenon will also lead to the decrease of apparent activation energy and the increase of reducing rate (Qiu et al., 1996). Take dolomite, for example, Jayasankar et al. had investigated the influence of 10%–16% of dolomite on iron recovery and suggested that the iron recovery would reach the maximum value of ~71% as the addition of dolomite was 12% (Jayasankar et al., 2012). Besides, the influences of sodium sulfate and sodium carbonate on the metallization degree of iron and the extent of magnetic concentrate recovery were also conducted. In order to obtain a high recovery of 94.5%, the optimized condition should be adopted with roasting temperature of 1050 °C, time of 60 min, 6%  $Na_2SO_4$  and 6%  $Na_2CO_3$  (Rao et al., 2013). Iron nuggets containing 96.52 wt.% Fe can be achieved when the carbon-bearing pellets with 1.6  $X_c:X_o$  and 1.0 basicity were maintained at 1400 °C roasting for 30 min (Guo et al., 2013). It is worthwhile to note that the molten mixture after reduction process was quenched in liquid nitrogen. Nugget obtained is mainly composed of 96.52 wt.% TFe, 3.09 wt.% C, and traces of 0.051 wt.% Si, 0.013 wt.% Mn, 0.076 wt.% P and 0.091 wt.% S. The result indicates that the major factors affecting metallization ratio are reduction temperature, time and ratio of  $X_c:X_o$ . However, another study has shown that cast iron is completely separate from slag phase in a temperature range of 1200–1500 °C, which is inconsistent with the former result. Perhaps the reason lies in the fact that the reactivity of the carbon-containing mixture is improved by the fine-grained structure of hematite particles (Raspopov et al., 2013). During the roasting-magnetic process of iron recovery, the red mud with other additives is commonly roasted in the form of separate pellets. While a high iron recovery of 81.40% and metallization ratio of 96.98% result can be achieved with roasting the consolidated cylinder green bodies at 1300 °C for 30 min prior to quenching and magnetic separation (1 A magnetic field intensity) (Liu et al., 2009a). In the preparation of consolidated samples, the slaked lime was applied as an activator. In addition to the study of recovering iron, these authors also made great subjects for extracting the other metallic recovery from red mud, for instance Al and Na (Liu et al., 2012). The process is similar to Fig. 6. After the soda-lime roasting and leaching process, the leached residue consisted of magnetite  $Fe_3O_4$ , hercynite  $Fe(Fe,Al)_2O_4$  and ulvospinel  $TiFe_2O_4$ . However, 51.2% Fe recovered was lower than the former result of 81.40%. This could be assigned to the fact that the magnetic ferrous phases usually agglomerate together with other impurities, such as larnite, calcium aluminoferrite and sodium aluminosilicate phase, thus resulting in the decrease of iron percentage (wt.%) in the magnetic concentrate and recovery ratio.

The microwave radiation as a source of heat had been applied successfully in reduction roasting process for recovering iron from red mud (Samouhos et al., 2013). Compared with the conventional heating method, microwave heating is a cleaner and more manageable method and will not generate temperature gradient theoretically as heating the dielectric specimens. While the limited microwave source lifetime and maximum power are principal disadvantages. The experimental results indicate that a magnetic concentrate containing 35.1% TFe and 69.3% metallization degree can be obtained after wet magnetic separation process (feed: 10 wt.% solids, 0.3 A magnetic field intensity). The duration time of microwave heating shows a huge decrease (almost 40%) over the conventional method. Notwithstanding, the magnetic concentrate appears a higher metallization degree than the conventional reduction roasting process. Besides, all the radionuclides involved in the red mud residue are considerably lower than the clearance levels ( $1000 \text{ Bq} \cdot \text{kg}^{-1}$ ) after microwave radiation treatment (Samouhos et al., 2013).

Apart from the process of pyrometallurgical iron recovery from red mud, acid leaching for recovering iron had also been investigated. A high iron recovery of 97.46% can be obtained with the process of

calcination at 600 °C and subsequent leaching using 6 M H<sub>2</sub>SO<sub>4</sub> (Uzun and Gulfen, 2007). Furthermore, the recovery of aluminum (64.40%) was also investigated and the dissolution of aluminum was slower than that of iron. The iron and aluminum dissolution rates were well consonant with the first order reaction mechanism, i.e.  $[-\ln(1 - \alpha)] = kt$ , where  $\alpha$  is the fraction of iron or aluminum dissolved at time,  $t$  is time in minute and  $k$  is the reaction rate constant in min<sup>-1</sup>. Oxalic acid can also be applied as a leachant to extract the iron from red mud (YU et al., 2012). The extraction rate of iron was about 96% after leaching process using 1 mol·L<sup>-1</sup> oxalic acid leachant at 75 °C for 2 h. And then in the precipitation process, the application of photocatalysis caused by UV irradiation was helpful to rapidly transform most of ferric oxalate into ferrous oxalate ( $\beta$ -FeC<sub>2</sub>O<sub>4</sub>·2H<sub>2</sub>O). Besides, the recovery and concentration of Al<sup>3+</sup>, Fe<sup>3+</sup>, Ti<sup>4+</sup> and Na<sup>+</sup> ions from red mud had been carried out on charged cation exchange membranes as a function of H<sup>+</sup> ion concentration in stripping phase (Çengelöglu et al., 2001; Cengelöglu et al., 2003). It was found that H<sup>+</sup> played the role of pumping ions and balanced the transport fluxes; the increase in the concentration of hydrogen ions would improve the transport efficiency generally. In case of SA<sub>3</sub>T membrane, the 'recovery factor' of sodium ions can reach as high as 31.90 when red mud solution is diluted two times (Cengelöglu et al., 2003). Although hydrometallurgical recovery will produce secondary wastes, this preferential adsorption method exhibits a novel recovery method and is worth perfecting further.

The bioleaching technology for the treatment of iron oxide ores is getting more and more attention since it is an ecological and low energy consumption metal extracting method (Eisele and Gabby, 2014; Laguna et al., 2011; Qu and Lian, 2013), which dominates biohydrometallurgy as compared with other metals. In general, microorganisms of mechanisms in promoting the iron minerals dissolution can be classified into two types. One is produced various organic acids complex with Fe<sup>2+</sup> and Fe<sup>3+</sup> to increase the solubility of corresponding iron minerals; the other is facilitating the transformation of Fe<sup>3+</sup> into Fe<sup>2+</sup> state, as ferrous form has a higher solubility than ferric compounds (Eisele and Gabby, 2014). *Desulfuromonas palmitatis* was believed to be able to dissolve part of iron minerals from bauxite. Specially, 95% of amorphous ferrihydrite can be dissolved, while 'more-crystalline goethite' does not exceed 9% and crystalline hematite is less than 1.2%. The high pH value of red mud would restrict the extracting process of iron oxides of bioleaching, and therefore there is hardly any work focusing on that field (Papassiopi et al., 2010).

Overall, the industrial applications ask for any cutting the cost of iron recovery to be taken into account. The options of recovery technique should be made on the basis of economic feasibility and practicability other than the recovery efficiency.

### 3.3. Recovery of titanium and vanadium from red mud

Titanium is mainly present as titanium dioxide (TiO<sub>2</sub>). It is a popular photocatalyst and applied in the manufacture of white pigments. The concentration of anatase or rutile titanium in the red mud varies between 2.5 wt.% and 22.6 wt.% (Gräfe et al., 2011), as shown in Table 1. Through the hydrometallurgy of sulfuric acid leaching process, titanium can be easily extracted and recovery can reach 64.5% when leaching at 60 °C with 6 N acid concentration and 1:20 ratio of solid to liquid (Agatzini-Leonardou et al., 2008; Tsakiridis et al., 2011). 46% of iron recovery and ~37% of aluminum recovery can be obtained simultaneously. Erçağ and Apak (1997) developed a technique to recover TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and pig iron by furnace smelting and extractive metallurgy from red mud. First pelletized mixture consisting of red mud, dolomite and coke was sintered at 1100 °C for 1 h, then molten pig iron was separated from the slag owing to the higher specific gravity and surface tension of iron when smelting at 1550 °C for 0.5 h. The resulting slag was leached with 30% H<sub>2</sub>SO<sub>4</sub> at 90 °C. The 84.7% of TiO<sub>2</sub> recovery can be achieved based on the slag weight with 5% D2EHPA (di-(2-ethylhexyl)

phosphoric acid) kerosene extracting the diluted leachate. Kasliwal and Sai (1999) described a new method for enrichment of titanium dioxide in red mud. The content of TiO<sub>2</sub> in the red mud was concentrated and can reach 36% after the simple process of hydrochloric acid leaching. While the enrichment of titanium dioxide will be enhanced by facilitating the dissolution of alumina and silica after sodium carbonate roasting leached residue prior to water leaching process. The maximum enrichment of TiO<sub>2</sub> is approximately 76% under the optimum roasting temperature of 1150 °C for 115 min.

Apart from pyrometallurgical process, many efforts have been carried out on different types of acids to extract titanium dioxide from red mud. In case of sulfuric acid leaching process (Mehta and Patel, 1951; Şayan and Bayramo lu, 2000), the recovery of the titania can be achieved by taking advantage of formation of RSO<sub>4</sub>·Ti(SO<sub>4</sub>)<sub>2</sub>, where R represents Zn, Cu, Mn, Co and Mg (Mehta and Patel, 1951). Şayan and Bayramo lu (2000) investigated the effects of temperature, leaching time, acid normality and solid to liquid ratio on sulfuric acid leaching of Ti from red mud by statistical modeling method. TiO<sub>2</sub> in red mud can also be recovered by the process of digestion with concentrated H<sub>2</sub>SO<sub>4</sub> or SO<sub>3</sub> gas. Red mud was first digested with sulfuric acid or with sulfur trioxide gas at a temperature in the range between 250 °C and 350 °C to prepare sulfates which could be leached out with water from the resulting mass (Zimmer et al., 1978). Subsequently the titanium hydroxide precipitation can be obtained from hydrating solution by filtering off or by decantation or both after the hydrolysis process at a temperature of ≥90 °C. Vaporizing the remaining solution or mixing with the acetone, the sulfates of sodium, aluminum and iron were crystallized and separated out. In order to decompose the sulfates, the solid sulfates obtained were then heated at 900–1000 °C to generate the corresponding oxides with the giving off of a gas mixture consisting of SO<sub>3</sub> and SO<sub>2</sub>. While the sodium sulfate is unaffected and can be leached out with water. After completely washing out of Na<sub>2</sub>SO<sub>4</sub>, the Al<sub>2</sub>O<sub>3</sub> and iron oxide remaining in the solid state were then separated from each other by the known Bayer process. Fig. 8 illustrates the whole process of reclamation treatment of red mud (Zimmer et al., 1978). Besides, the titanium and zirconium can be enriched through the process of sulfuric acid leaching and alkali-fusing (Kasai et al., 1994). The red mud of sodalite was decomposed and removed with diluted sulfuric acid leaching at 25 °C for 10 min. The remaining residue was subjected to further leaching with 0.5–2 mol·L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> at 120 °C to dissolve hematite. The alkali-fusing process would make the silicon dioxide more easily be leached out with water. After these treatments, the concentrations of Ti and Zr in the red mud residue can reach 84% and 3%, respectively. The whole enriching process is shown in Fig. 9. However, as for direct extracting the titanium dioxide from the red mud by hydrochloric acid, there are almost no literatures published. The reason could be attributed to the low dissolubility of TiO<sub>2</sub> in the hydrochloric acid solution (Kasliwal and Sai, 1999; Piga et al., 1993).

Solvent including Cyanex 301 and Cyanex 302, namely bis-(2,4,4-trimethylpentyl)dithiophosphinic acid and bis-(2,4,4-trimethylpentyl)monothiophosphinic acid can be employed to extract Ti<sup>4+</sup> from some commonly associated metal ions, such as Mg<sup>2+</sup>, Mn<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, Ce<sup>4+</sup> and V<sup>5+</sup>, found in red mud (Deep et al., 2007). The result suggests that extraction of Ti<sup>4+</sup> can be easily achieved in a wide pH range of 1.0–1.6. The separation from coextracted Fe<sup>3+</sup> can be accomplished by selective stripping with 0.1 M oxalic acid, i.e. 3% H<sub>2</sub>O<sub>2</sub> in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Through the stripped organic phase can be regenerated by washing them with 0.1 M oxalic acid and 0.1 M tartaric acid to remove Fe<sup>3+</sup> and Al<sup>3+</sup> respectively, large volume of acids were consumed in those procedures, especially with regard to dissolving red mud. Di-2-ethylhexyl phosphoric acid (D2EHPA, H<sub>2</sub>A<sub>2</sub>) is an effective extractant for extracting tetravalent titanium from sulfate medium (Islam and Biswas, 1981) or chloride solution (Biswas and Begum, 1998; Islam and Biswas, 1981). In the chloride solution extraction system, the following reaction will occur during the course of loading and the

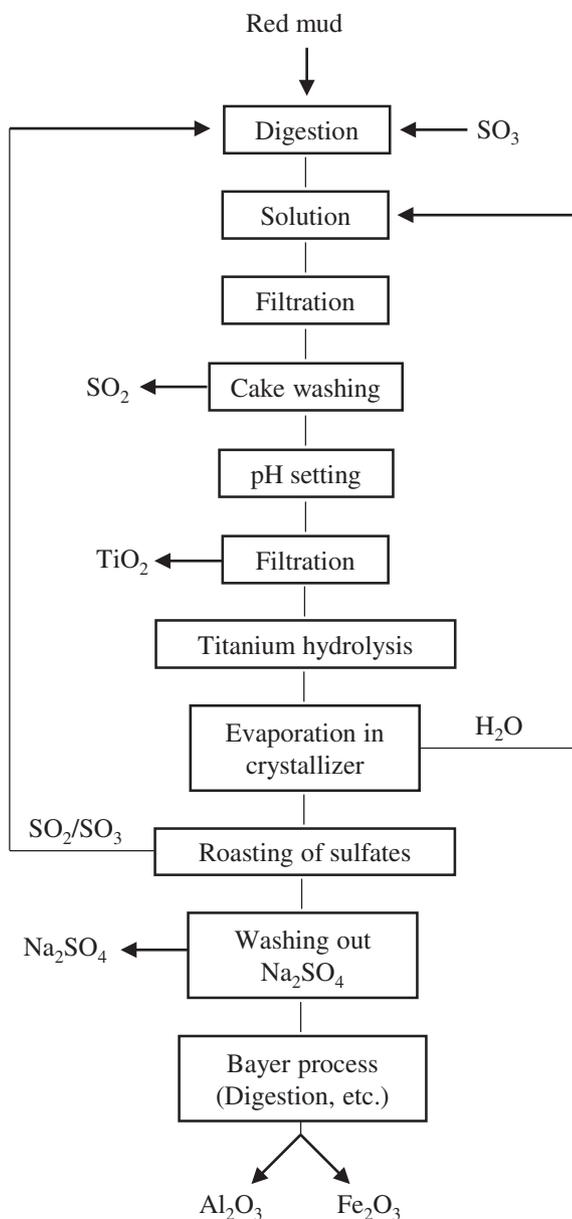
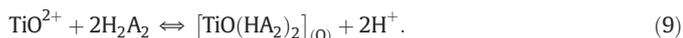


Fig. 8. A flow diagram of Ti, Na, Al and Fe recovery with sulfuric acid or  $\text{SO}_3$  digestion. Zimmer et al., 1978.

extraction efficiency is not influenced by the concentration of chloridion.



Vanadium is an important chemical element with atomic number 23. Because of the novel physical properties of vanadium such as high tensile strength, hardness and fatigue resistance, ubiquitous vanadium is employed in a wide range of ferrous and non-ferrous alloys for various commercial applications including train rails, tool steels, catalysts and aerospace (Moskalyk and Alfantazi, 2003).  $\text{V}_2\text{O}_5$  can be recovered from red mud through a carbon adsorption and desorption route (Mukherjee et al., 1990). In this process, the red mud consisting of 20 wt.%  $\text{V}_2\text{O}_5$  was first leached out with hot water for 30 min, then adsorbed with activated charcoal at a pH of  $\sim 2.5$  and a temperature of  $\sim 80^\circ\text{C}$ . Subsequently the loaded charcoal was desorbed with a suitable

eluent of 10% ammonia solution at  $\sim 85^\circ\text{C}$ . After that, the vanadium bearing cake was precipitated out from the stripping solution. Finally, pure vanadium pentoxide (99.9%) was obtained by the calcination of the cake. The schematic flow chart for the recovery of  $\text{V}_2\text{O}_5$  from the Bayer red mud is presented in Fig. 10.

These techniques involved here are mainly carried out on laboratory-sized equipment for titanium and vanadium recovery. However, so far, there are no indications that the laboratory-based study has been applied on a commercial scale. On the other hand, extension of lab trials to bulk trial and commercial application would require significant resources. To make a profit, the extraction plant should be located close to the alumina works, otherwise the recovery of titanium and vanadium is not competitive with extraction from natural sources due to the extra transportation cost.

#### 3.4. Recovery of scandium and gallium from red mud

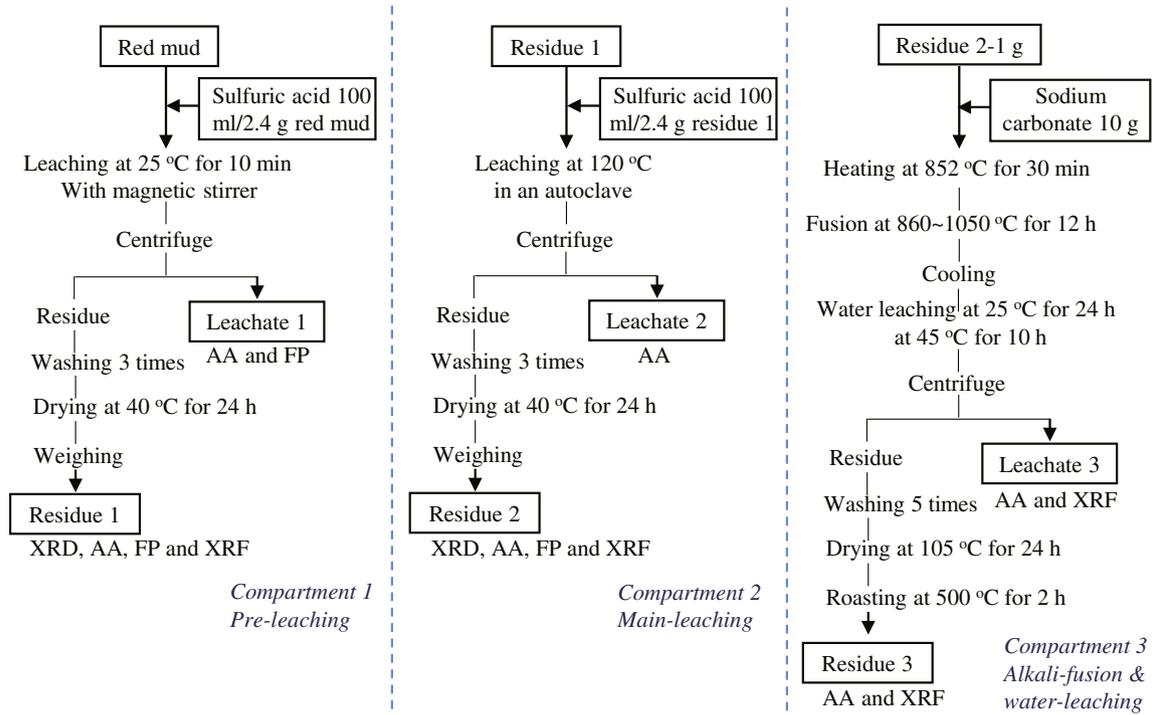
Bauxite ore more or less contains trace amount of scandium oxide in nature. While the concentration of scandium is enriched to almost two times in red mud (Ochsenkühn-Petropulu et al., 1994). Most scandium exists as associated minerals in bauxite or red mud coupled with the occurrence of isomorphism (Chi, 1993; Xiao, 1996). And the general composition range is 60–120 ppm, as shown in Table 2 (Abhilash et al., 2014; Ochsenkühn-Petropoulou et al., 2002; Samouhos et al., 2013; Smirnov and Molchanova, 1997; Wang et al., 2013; Xiao, 1996). Part of other trace elements of red mud obtained from different countries is also listed in this table. If a certain kind of mineral of scandium content is larger than 0.002% (20 ppm), it can be generally accepted as important scandium resources and worth exploiting (Shaoquan and Suqing, 1996). Take for instance Jamaican bauxite, the bauxite of scandium in the form of  $\text{Sc}_2\text{O}_3$  ranges between 87 ppm and 113 ppm. While the level of scandium in the red mud is accumulated up to 200–390 ppm (Wagh and Pinnock, 1987). In Greece, the dry red mud of scandium abundance is generally 130 ppm or  $\sim 0.02\%$  of  $\text{Sc}_2\text{O}_3$  (Ochsenkühn-Petropulu et al., 1994), which demonstrates that red mud is a significant and potential scandium resource. Because of the high levels of impurities such as alumina, silica, iron and titanium oxides, recovering scandium directly from the red mud is difficult to implement.

Scandium can be selectively extracted by the activated carbon modified by tributyl phosphate (TBP) in case of dissolving red mud in a 6 M HCl solution with a 0.25 volume ratio at  $60^\circ\text{C}$  for 4 h (Zhou et al., 2008). After conducting adsorption process based on observable variables, the adsorbent and adsorbate were separated by filtration and the recovery efficiency was carried out by testing the filtrate on an inductively coupled plasma-optical emission spectrometer. The result suggests that the chemical reaction, rate-controlling step, plays a major role in the adsorption of the scandium ions using modified activated carbon. Mechanism of adsorption may be explained by following chemical reaction (Chen, 2005; Zhou et al., 2008).



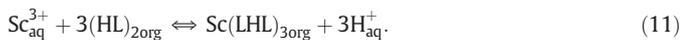
Where PO means the active sites on the surface of modified activated carbon. Abovementioned equation exhibits the fact that each of scandium ions may consume two active sites in the adsorption process. The optimum adsorption capacity can be achieved with  $\sim 6.25 \text{ g} \cdot \text{L}^{-1}$  adsorbent at temperature of  $35^\circ\text{C}$  for 40 min. Hubicki (1990) had also succeeded in separating  $\text{Sc}^{3+}$  from rare earth elements using selective ion-exchangers. And the concentration of  $\text{Sc}^{3+}$  can be enriched to  $500 \text{ g} \cdot \text{L}^{-1}$  with 6 M HCl. Besides the conventional adsorbent, it is worthwhile to note that the functional porous hybrid materials exhibit an enhanced selectivity for the heavier rare earth elements (Florek et al., 2014).

A combined ion exchange-solvent extraction method was identified by Ochsenkühn-Petropulu et al. (1995), Fig. 11 depicts the flow sheet of whole process. The sufficiently mixing of materials of red mud and



**Fig. 9.** Flow diagrams of Ti and Zr enrichment with pre-, main-leaching and alkali-fusion & water-leaching. XRD: X-ray powder diffraction analysis; XRF: X-ray fluorescence analysis; AA: Atomic absorption analysis; FP: Flame photometric analysis. Kasai et al., 1994.

$\text{Na}_2\text{CO}_3/\text{Na}_2\text{B}_4\text{O}_7$  (1:1) with a mass ratio of two to one sintered at 1100 °C for 20 min prior to dissolving with 1.5 M HCl to 50 ml solution. Half volume of leachate was then subjected to a column experiment using 15 ml of Dowex 50W-X8 resins. After the process of ion exchange separation, the major elements of Fe, Al, Ti, Na, Si and Ca and minor ones of Ni, Cr, Mn and V were washing out by 150 ml of 1.75 M HCl. The scandium and other impurities, such as yttrium and lanthanides, were eluted with 100 ml of 6 M HCl. Subsequently, the eluate of scandium was selectively extracted by 0.05 M di(2-ethylhexyl)phosphoric acid (DEHPA,  $(\text{RO})_2\text{POOH}$ , where R is  $\text{C}_8\text{H}_{17}$ ) in a nonpolar solvent of hexane after adjusting the pH of elute solution to ~0 with  $\text{NH}_4\text{OH}$ . During this extraction process, DEHPA presented in dimeric form of  $(\text{HL})_2$  and the extraction system of mechanism could be inferred from following reaction (Forsberg et al., 1983; Ochsenkühn-Petropulu et al., 1995).



To ensure the occurrence of cation exchange reaction was available, the acidity of less than 1 M and ratio of extracted scandium complex to extractant less than  $10^{-3}$  are required. After that,  $93 \pm 5\%$  scandium was quantitatively stripped out as  $\text{Sc}(\text{OH})_3^{3-}$  in aqueous phase by 2 M NaOH after at least 5 minute duration time.

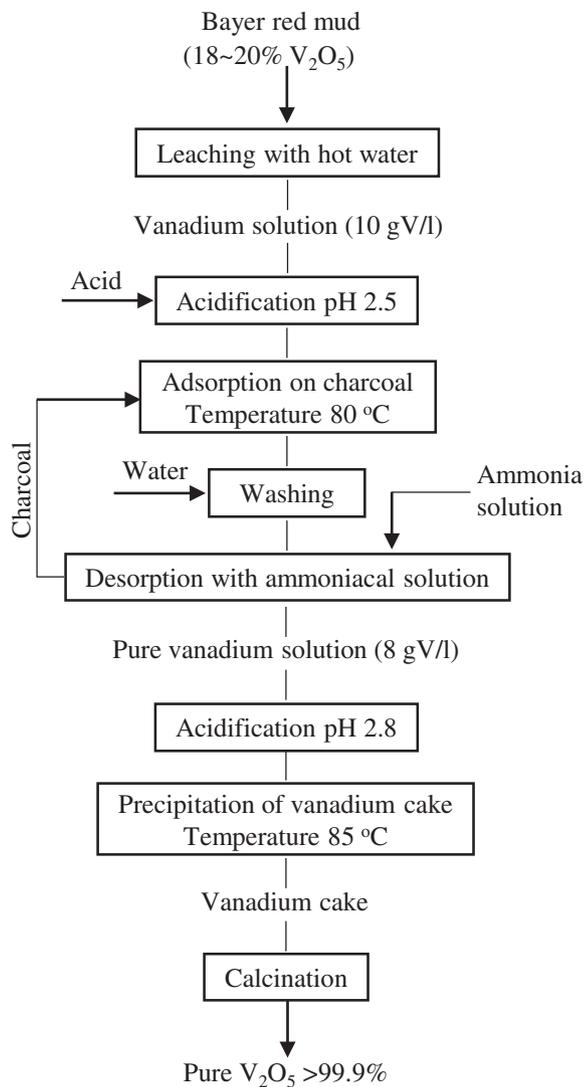
Fig. 12 illustrates a pilot-plant process based on the former laboratory-scale for the extraction of scandium from red mud that contained economically interesting concentration of scandium element (Ochsenkühn-Petropoulou et al., 2002). First, a batch of red mud was directly dissolved in 0.6 N diluted nitric acid at normal atmospheric temperature and pressure conditions. This procedure in this innovative method is different from the fusion process of laboratory scale. It is beneficial to the selectively leaching of scandium and the minimization of dissolving efficiency of iron from solid to liquid (<4%). It should be noted that iron is a hardly separable element from scandium since the similar ionic radii (Ochsenkühn-Petropulu et al., 1996). Furthermore, a predictive correlation for the scandium leaching efficiency  $\eta_{\text{Sc}}$

based on the unreacted-core model was pointed out and listed as the following.

$$\eta_{\text{Sc}} = \frac{15.03}{\frac{M_d}{V} C_{\text{Sc, RM}}} \left[ 1 - 0.00635 \left( \frac{M_d}{V} \right)^w \right] \quad (12)$$

where  $\frac{M_d}{V}$  is the ratio of dry red mud weight to leachate solution volume,  $\text{kg} \cdot \text{L}^{-1}$ ;  $C_{\text{Sc, RM}}$  is the concentration (w/w) of scandium in the dry red mud,  $\text{mg} \cdot \text{kg}^{-1}$ ;  $w$  is the unary operator for dimension correction,  $\text{L} \cdot \text{kg}^{-1}$ . The influences of agitation mode, solid to liquid ratio  $\frac{M_d}{V}$ , leachate acidity and number of stages on scandium recovery efficiency were studied. The most favorable scandium recovery of conditions is that  $\frac{M_d}{V}$  ratio is more than 0.1, meanwhile agitation period in one stage is sufficient and a pH value ranges between 0 and 0.2 to obtain the highest ratio of  $C_{\text{Sc}}$  to  $C_{\text{Fe}}$ . Notwithstanding the feasibility of ion-exchange, it is unwise to extract scandium from low concentration leachate of red mud by conventional methods of ion exchange. Since the high concentration of other metal elements, such as Fe, Ti, and Al, plays a role of impurities or contaminants and will produce a negative influence on the efficiency of resin (Wang and Cheng, 2011). This behavior will be further explained by the following paragraph.

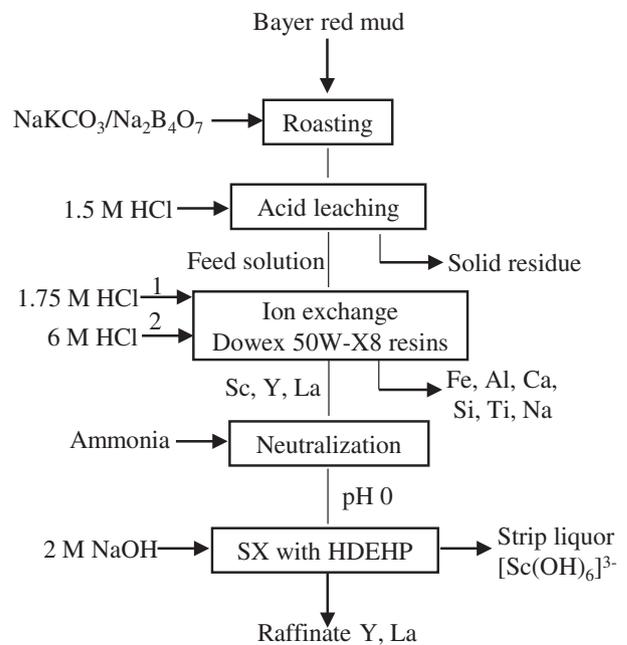
Selective acid leaching and solvent extraction of scandium (~99% recovery) from an Australian red mud was explored by Wang et al. (2013). Leaching tests on this kind of red mud showed that diluted  $\text{H}_2\text{SO}_4$  (0.5 M) displayed a better performance as compared with the same concentration of  $\text{HNO}_3$  and HCl at a 0.05 ratio value of solid to liquid and 23 °C for 120 min. The loading capacity of 0.05 M di-(2-ethylhexyl) phosphoric acid (D2EHPA)/0.05 M tributyl phosphate (TBP) extraction system worked best among a series of extractants. Larger than 99% Zr and 40% Ti can be removed from the leachate with 0.025 M Primene JMT (1,1,3,3,5,5,7,7,9,9-decamethyl decyl amine) in Shellsol D70 (100% aliphatic diluent) with A/O ratio of 5 and pH value



**Fig. 10.** A flow diagram for the recovery of high purified  $V_2O_5$  from red mud through carbon adsorption and desorption route. Mukherjee et al., 1990.

of 0.2–0.5 at 40 °C prior to extraction process (Wang et al., 2013). Fig. 13 displays the conceptual flow sheet for the scandium recovery from red mud.

Carbon dioxide being introduced to red mud pulp can provide for the partial recovery of scandium (Yatsenko and Pyagai, 2010). Significantly, the carbonization of red mud pulp to extract scandium is of



**Fig. 11.** A flow diagram of Sc recovery from red mud. Ochsenkühn-Petropulu et al., 1995.

great importance to weaken the negative impacts of solid waste stockpiles by transforming the strong alkaline phase into a carbonate–hydrocarbonate one and also bring down the greenhouse effect to some extent. On the other hand, scandium is concentrated in the finely dispersed fraction of red mud after the separation process by a cyclone battery. Besides the leaching agent mentioned above, the leaching test had also been carried out on sodium carbonate solution, 50% sulfuric acid and 3 M hydrochloric. The result suggests that scandium recovery of over 75% at least can be achieved after the process of further leaching, solvent extraction, stripping and precipitation (Xiufen et al., 2003).

Gallium is a kind of widely distributed trace element with  $\sim 10 \text{ g} \cdot \text{t}^{-1}$  in the lithosphere, namely rare metal (Poedniok, 2008). It commonly appears as the intergrowth of Al in bauxites due to the geochemical affinity between aluminum and gallium. The cost of gallium extraction individually is far higher than the gallium value. Typically, gallium is a by-product of the production of alumina or zinc. During alumina production, Bayer liquor obtained from bauxite digestion process is the primary feed of gallium. Generally, Bayer liquor of gallium contained accounts for  $\sim 70\%$  of the total amount, and the other of 30% gallium cannot be completely dissolved out from bauxite and left in the red mud. Statistically, about 90% of world gallium is produced from Bayer liquor (Lu et al., 2008). Fractional precipitation, electrochemical deposition, solvent extraction and ion exchange are the primary methods of

**Table 2**

Composition and occurrence mode of part of trace elements in the red mud (ppm).

Xiao, 1996; Smirnov and Molchanova, 1997; Ochsenkühn-Petropoulou et al., 2002; Samouhos et al., 2013; Wang et al., 2013; Abhilash et al., 2014.

Elements	Sc	Y	Ga	V	Cr	U	Th	REEs
AU	54	68	89	730	497	○	○	○
Guizhou, CN	158	266	570	4220	848	59	201	2600
Pechiney, GR	60.6	60.1	○	○	○	○	○	○
GR	○	○	○	1600 <sup>a</sup>	2800 <sup>a</sup>	○	○	○
IN	50	10	○	6800	○	○	○	○
Alcan, IN	130–162 <sup>a</sup>	○	○	○	○	○	○	○
USSR	60–250 <sup>a</sup>	○	○	○	○	○	○	○
General composition	60–120	60–150	60–80	○	○	50–60	20–30	355–1400 <sup>a</sup>
Occurrence mode	Associated minerals <sup>b</sup>							

Notes: ○: not found.

<sup>a</sup> Including the weight of oxygen of corresponding oxides.

<sup>b</sup> This phenomenon typically occurs in the phase of monazite ( $Ce, La, Pr, Nd, Th, Y$ ) $PO_4$ , xenotime  $YPO_4$  and other minerals of red mud.

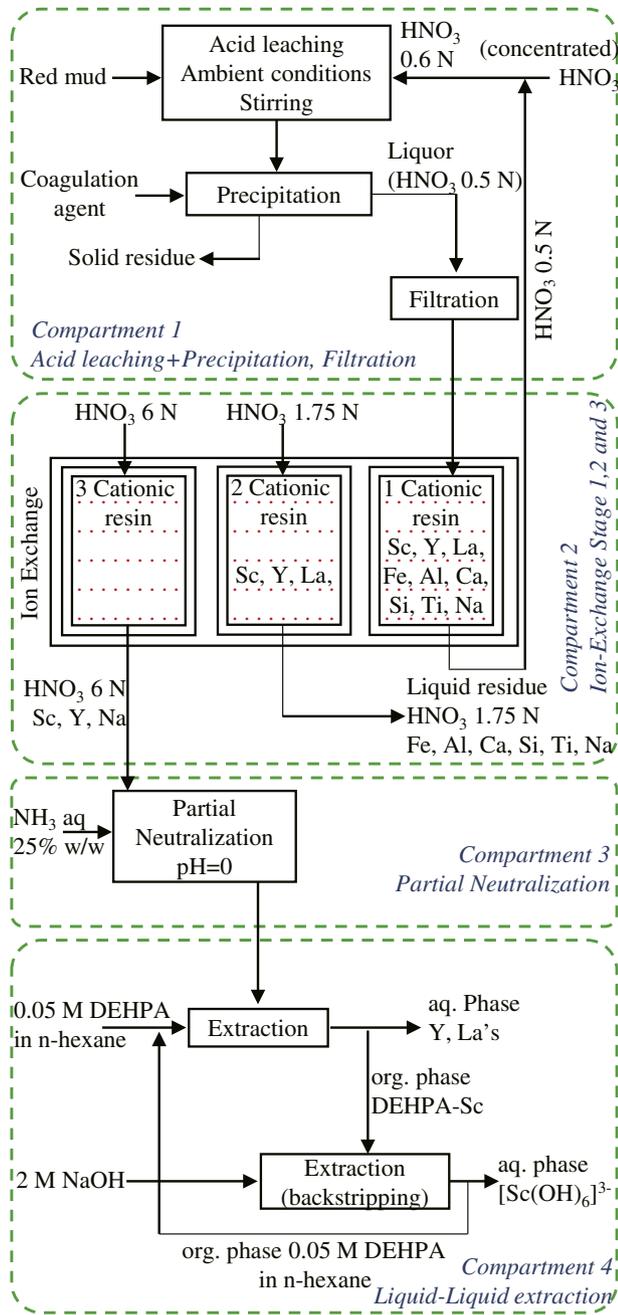


Fig. 12. Schematic flow diagram of pilot Sc recovery. Ochsenkühn-Petropoulou et al., 2002.

recovering gallium from Bayer solutions, furthermore, solvent extraction and ion exchange demonstrate a better extractive performance compared with others in the recent studies (Zhao et al., 2012). Nevertheless, research work regarding extracting gallium from red mud has not been reported up to the present.

It is obvious that the extraction of either scandium or gallium is not an economical feasible way owing to the low content of rare valuable elements and the massive impurities such as Fe, Ca, Al, Ti, and Na in the red mud. During the leaching process, the most of impurities were dissolved with acids and subsequently co-absorbed by the column experiment of resin, leading to the deterioration of resin loading capacity. After the absorption process, the impurities adsorbed on the surface of resin need to be eluted with extra quantities of acids. The consumption of alkali liquor for neutralizing eluate will also rise. Operation costs will therefore be improved by this fact.

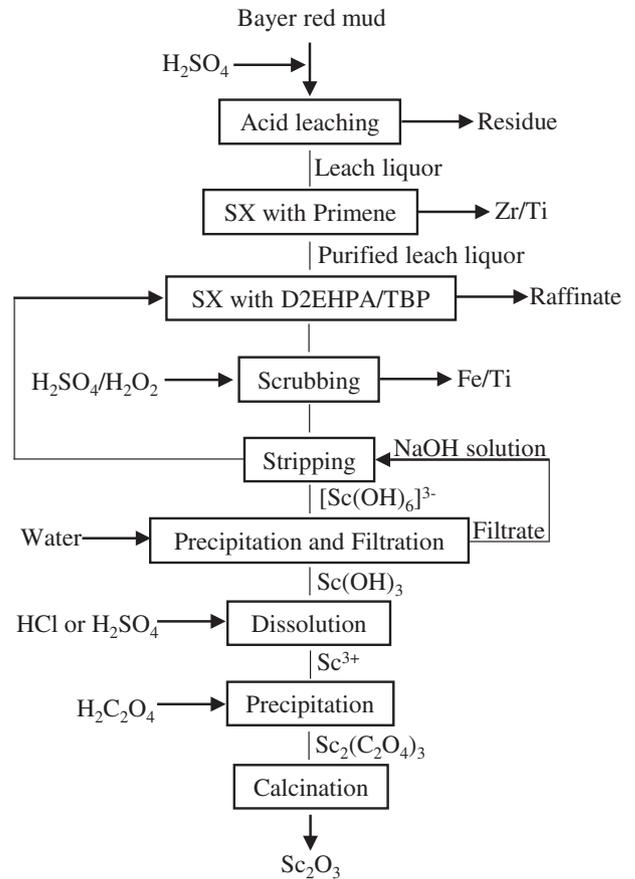


Fig. 13. A conceptual flow diagram of Sc recovery from red mud. Wang et al., 2013.

### 3.5. Recovery of other metals from red mud

In addition to the occurrence of scandium and gallium in the red mud, it still contains tiny amounts but valuable of other rare earths and radioactive elements, for instance, yttrium ( $60\text{--}150\text{ g}\cdot\text{t}^{-1}$ ), uranium ( $50\text{--}60\text{ g}\cdot\text{t}^{-1}$ ), thorium ( $20\text{--}30\text{ g}\cdot\text{t}^{-1}$ ), etc. (Borra et al., 2014; Smirnov and Molchanova, 1997). The data is also shown in Table 2. When rare earth elements are incorporated in some products such as wind turbines, hybrid electric vehicles, and defense applications, the performance of final products will be improved greatly so that it cannot be irreplaceable by alternative materials. Moreover, thanks to the further development of industries and limited mineral resources as well as the demand of rare earths increases rapidly in the past 15 years, the recovery them from red mud has received increasing attention (Du and Graedel, 2011).

Sulfuric acid sorption process provided an alternative method of recovering scandium and uranium from red mud (Smirnov and Molchanova, 1997). Nitrogen–phosphorus-containing amphoteric resins of AFI-21 and AFI-22 were used to adsorb ions of scandium and uranium. The adsorption capacity of ion-exchangers was significantly influenced by pH value, which of 0.9–1.5 was selected for this investigation in consideration of minimizing aluminum loading capacity and reducing acid consumption. Besides, scandium presented as hydrolyzed cation, i.e.  $\text{Sc}(\text{H}_2\text{O})_6^{3+}$ , in the solution with a pH range of 0.5–4.0. The increase of pH will lead to the transition of scandium to a pseudo-colloidal state. As a result, except for 50% scandium recovery, part of radioactive uranium and thorium were also recovered from the  $\text{H}_2\text{SO}_4$  pulp of red mud. The titanium was precipitated out from preliminary eluate by thermo-hydrolysis and enriched to 35–40% in the precipitated

cake. The resulting crude scandium cake consists of 5–7% Sc, 4.5% U, and 0.9% Th.

Fulford et al. developed a sulfur dioxide introduced leaching process for selectively recovering rare earth elements with atomic numbers of 57–71, as well as scandium and yttrium, from Bayer red mud without the concurrent dissolution of iron and titanium compounds to the leachate (Fulford et al., 1991). The red mud slurry was first digested with a dilute sulfurous acid solution. Adjusting the pH values among the range of 1.8–3.2, a final digestion solution of rare earth elements coupled with few of impurities was obtained. In a two stage digestion, most of sodalite-type products containing soda, alumina and silica were dissolved into solution with a pH range of 2.6–3.2. As pH lower to approximately 1.8–2.5, rare earth elements and further of sodalite-type products were leached out. Splitting the second leach into two pH stages of 2.0–2.4 and 1.5–2.0, leachate containing part of rare earths with especially few impurities got through three leaching stages. While in the single stage process (slurry pH ~2.0), the impurities of soda, alumina and silica were dissolved along with the rare earth elements. Subsequently, the resulting leachate went through solvent extraction and the objective rare earth elements were stripped out with various pH values and organic phase. In this research, the solvent extractants, such as DEHPA, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHEHPA), esters of phosphonic acid (Cyanex 272), esters of thiophosphonic acid (Cyanex 301) and mixtures of abovementioned organic phase with tributyl phosphate (TBP) or trioctylphosphine oxide (TOPO) or organic diluent of kerosene, are investigated. Generally, TOPO will decrease the extraction degree of light and middle rare earth elements except yttrium and heavy rare earths. The extraction and purification performance of referring to solvent are summarized in Table 3 (Fulford et al., 1991; Wang and Cheng, 2011). In the present invention, nevertheless rare earth elements can be easily leached out from many red muds, the same elements in the parent bauxite are not readily leachable in dilute mineral acids. Besides, a further advantageous feature resides in the fact that a large part of SO<sub>2</sub> or SO<sub>3</sub> used in leaching procedure can be recovered and reused.

On the other hand, lanthanides including ~60% heavy elements (Dy, Er, Yb), ~50% middle ones (Nd, Sm, Eu, Gd) and ~30% light ones (La, Ce, Pr) as well as 96% yttrium and 80% scandium can be selectively leached out from Bayer red mud with dilute nitric acid (0.5 M) under moderate leaching conditions (temperature of 25 °C, leaching time of 24 h, solid to liquid of 1:50) and without using any preliminary treatment (Ochsenkühn-Petropulu et al., 1996). Meanwhile, the leaching system has poor dissolution ability for the major compositions of red mud matrix, especially with regard to iron oxides (only 3% dissolved). Without the interferences of impurities of iron oxides, the determination of lanthanides and yttrium in the leachate by inductively coupled plasma-atomic emission spectroscopy will thus be much more accurate. The leaching experiment was also carried out on 0.5 M HCl, however the distribution coefficients of scandium and yttrium compared to the corresponding result of 0.5 M HNO<sub>3</sub> were much lower.

Recovering lanthanum and cerium from Indian red mud was carried on the process of sulfuric acid leaching and solvent extraction in bench scale (Abhilash et al., 2014). The results suggest that maximum recovery of La (99.9%) is obtained by leaching with 3 M H<sub>2</sub>SO<sub>4</sub>, solid to liquid ratio of 10 g·L<sup>-1</sup> and agitation of 200 rpm at 35 °C for 1 h and following extraction with one of the three solvents, namely, DEHPA, Cyanex 272 and Cyanex 301. Further increase in temperature up to 75 °C, the leach recovery of La decreased to 37%. 99.9% of Ce recovery was achieved by leaching with the same conditions mentioned above except extraction with Cyanex 301; 44% of Ce recovery at 35 °C with Cyanex 301. Besides, no matter what solvent extraction was employed, the scandium was almost completely co-extracted out from leachate.

*Penicillium tricolor* of fungi was successful in the application of biological leaching of rare earths and radioactive elements from red mud (Qu and Lian, 2013). The oxalic and citric acids of fungi metabolic products played an important role in bioleaching process through chelation or complexation. The highest extraction yields ranging from 20% to 75% can be obtained with a two-step process—pre-culturing the fungus in sucrose medium for 72 h to get a marked increase in biomass prior to the addition of sterilized red mud—at 10% (w/v) pulp

**Table 3**  
Performance or selectivity of solvent extraction and mineral acids under various conditions.  
Fulford et al., 1991; Wang and Cheng, 2011.

Performance	Liquor pH/acid concentration	Extractant concentration/methods	Elements extracted/selectivity
Extraction	pH 1.5–2.0	0.05–0.1 M organophosphorus extractant	Atomic number: 65–71, Y, part of Gd, Nd, Ca
Extraction	pH 2.0–2.5	0.1–0.2 M organophosphorus extractant	Atomic number: 57–63, some further Ca, Al
Extraction	pH 1.5–2.0	0.2–0.3 M organophosphorus extractant	Atomic number: 57–71, Sc, Y, some Ca and Al
Extraction	1–11 M HCl, HClO <sub>4</sub> or HNO <sub>3</sub>	0.75 M HDEHP in n-heptane or cyclohexane	Sc <sup>3+</sup> ~ Ti <sup>4+</sup> , Zr <sup>4+</sup> , Hf <sup>4+</sup> > Y <sup>3+</sup> > La <sup>3+</sup> > Mn <sup>2+</sup>
Extraction	3–10 M HCl	Purified HDEHP in n-octane	Sc <sup>3+</sup> >> Fe <sup>3+</sup> > Lu <sup>3+</sup> > Yb <sup>3+</sup> > Er <sup>3+</sup> > Y <sup>3+</sup> > Ho <sup>3+</sup>
Extraction	0.5 M HCl	20% HDEHP, 15% TBP and in kerosene	Sc <sup>3+</sup> > Fe <sup>3+</sup> > Al <sup>3+</sup> > Mg <sup>2+</sup>
Extraction	pH 1.5–3.5 H <sub>2</sub> SO <sub>4</sub>	0.2 M D2EHPA and 1% TBP in Escaid 110	Sc <sup>3+</sup> ~ Zn <sup>2+</sup> > Ca <sup>2+</sup> ~ Al <sup>3+</sup> > Mn <sup>2+</sup> > Cr <sup>3+</sup> ~ Mg <sup>2+</sup> ~ Ni <sup>2+</sup> ~ Si
Extraction	0.5–11 M HClO <sub>4</sub>	0.1 M HDEHP in toluene	Sc <sup>3+</sup> > Fe <sup>3+</sup> > Al <sup>3+</sup> > Mg <sup>2+</sup>
Extraction	0.5–1.5 M H <sub>2</sub> SO <sub>4</sub>	Purified HEHEHP in n-heptane	Sc <sup>3+</sup> ~ Th <sup>4+</sup> > Ce <sup>4+</sup> > Fe <sup>3+</sup>
Extraction	1.5–5 M H <sub>2</sub> SO <sub>4</sub>	Purified HEHEHP in n-heptane	Sc <sup>3+</sup> > Ce <sup>4+</sup> > Th <sup>4+</sup> > Fe <sup>3+</sup>
Extraction	pH 1–5.5 H <sub>2</sub> SO <sub>4</sub>	HEHEHP 0.2 M Ionquest 801 and 1% TBP	Sc <sup>3+</sup> > Zn <sup>2+</sup> > Al <sup>3+</sup> > Mn <sup>2+</sup> ~ Cr <sup>3+</sup> ~ Ca <sup>2+</sup> ~ Mg <sup>2+</sup> ~ Ni <sup>2+</sup> ~ Si
Extraction	0.01–1 M HClO <sub>4</sub>	0.1 M HEHEHP in toluene	Sc <sup>3+</sup> > Fe <sup>3+</sup> > Al <sup>3+</sup> > Mg <sup>2+</sup>
Extraction	3–10 M H <sub>2</sub> SO <sub>4</sub>	0.048 M Cyanex 272 in n-hexane	Sc <sup>3+</sup> ~ Th <sup>4+</sup> > Fe <sup>3+</sup> > Lu <sup>3+</sup>
Extraction	pH ~1 H <sub>2</sub> SO <sub>4</sub>	0.1 M Cyanex 272 and 5% TBP	Sc <sup>3+</sup> >> Al <sup>3+</sup> > Ni <sup>2+</sup> ~ Si > Mn <sup>2+</sup> ~ Mg <sup>2+</sup> ~ Ca <sup>2+</sup> > Cr <sup>3+</sup>
Extraction	3–10 M H <sub>2</sub> SO <sub>4</sub>	0.048 M Cyanex 302 in n-hexane	Zr <sup>4+</sup> > Sc <sup>3+</sup> > Th <sup>4+</sup> > Fe <sup>3+</sup> > Lu <sup>3+</sup>
Extraction	3–10 M H <sub>2</sub> SO <sub>4</sub>	0.048 M Cyanex 301 in n-hexane	Zr <sup>4+</sup> > Sc <sup>3+</sup> ~ Fe <sup>3+</sup> > Th <sup>4+</sup> > Lu <sup>3+</sup>
Extraction	7–8 M HCl	100% TBP	Sc <sup>3+</sup> ~ Zr <sup>4+</sup> > Th <sup>4+</sup>
Extraction	4–6 M HClO <sub>4</sub>	100% TBP	Sc <sup>3+</sup> > Zr <sup>4+</sup>
Extraction	5.8 M HCl	40% P350 in kerosene	Sc <sup>3+</sup> > Ti <sup>4+</sup> , Y <sup>3+</sup> , Al <sup>3+</sup> , Ca <sup>2+</sup> , Mg <sup>2+</sup>
Extraction	2.0–7.0 M H <sub>2</sub> SO <sub>4</sub>	5% Cyanex 923 in kerosene	Zr <sup>4+</sup> > Sc <sup>3+</sup> > Ti <sup>4+</sup> ~ Lu <sup>3+</sup> > Fe <sup>3+</sup>
Extraction	1–5 M HCl	5% Cyanex 923 in kerosene	Sc <sup>3+</sup> > Th <sup>4+</sup> > Lu <sup>3+</sup>
Extraction	2.0–7.0 M H <sub>2</sub> SO <sub>4</sub>	5% Cyanex 925 in kerosene	Zr <sup>4+</sup> > Sc <sup>3+</sup> > Lu <sup>3+</sup> > Ti <sup>4+</sup> > Fe <sup>3+</sup>
Extraction	0.5–2.5 M HCl	5% Cyanex 925 in kerosene	Th <sup>4+</sup> > Sc <sup>3+</sup> > Lu <sup>3+</sup>
Extraction	1–5 M HCl	5% Cyanex 925 in kerosene	Sc <sup>3+</sup> > Th <sup>4+</sup> > Lu <sup>3+</sup>
Extraction	–	DEHPA → EHEHPA → Cyanex 272	Light rare earths → heavy rare earths
Purification	0.1–0.2 M H <sub>2</sub> SO <sub>3</sub> or mineral acids	–	Ca, La and lightest rare earths
Purification	1–3 M HNO <sub>3</sub>	–	Atomic number: 51–71
Purification	1–6 M HCl or H <sub>2</sub> SO <sub>4</sub>	–	Atomic number: 51–71
SO <sub>2</sub> recovery	pH 2.4–3.0	H <sub>2</sub> SO <sub>3</sub> /heating	SiO <sub>2</sub>
SO <sub>2</sub> recovery	pH 3.2–4.0	H <sub>2</sub> SO <sub>3</sub> /heating	Al <sub>2</sub> O <sub>3</sub>

density. On the other hand, the same authors, Y Qu et al., had also investigated the bioleaching of heavy metals such as As, Ba, Cr, Cu, Ni, and Pb from red mud by using *A. niger* of another fungi (Qu et al., 2013). Compared with one step and two step bioleaching methods, the spent medium one would provide a better performance for leaching heavy metals when employed *A. niger* as the leaching fungus. And the highest leaching ratios can be accomplished with 1% (w/v) pulp density via spent medium bioleaching.

In the acid leaching process, large volumes of acid solution were produced by the application of mineral acids like H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl, which required to be further recycled or neutralized. Furthermore, in most cases the leaching equipment also needs to be pressure- and acid-proof.

#### 4. Conclusions and outlook

The optimum recovery results of metallurgical process for the mainly valuable elements were summarized in Table 4 (Zhong et al., 2009; Vachon et al., 1994; Li et al., 2009; Liu et al., 1997, 2009a, 2012; Peng and Huang, 2011; Uzun and Gulfen, 2007; Eisele and Gabby, 2014; Erçağ and Apak, 1997; Deep et al., 2007; Mukherjee et al., 1990; Ochsenschüh-Petropulu et al., 1995, 1996; Ochsenschüh-Petropoulou et al., 2002; Abhilash et al., 2014). The routes for extraction of valuable elements from red mud could be generally classified into three types, i.e. hydrometallurgy, pyrometallurgy and biometallurgy. In most extraction cases, the predominantly adopted method of which is hydrometallurgy. While it is not an economical beneficial and zero-emission method for the researchers to take full advantage of red mud residues. In comparison to this mineral acid leaching process, the combined bio-hydrometallurgical one is typically taken as a green process for recovery of valuable metals from red mud. The advantages of environmental benignity, low energy requirements and costs, as well as flexibility

in operations are attributed to the so-called green process. Not only has the recovery of valuable metal elements been concentrated on single extraction efficiency, but the cost of roasting, mineral acids and organic solvent, if need be, and also the equipment of resistance of acid and alkali should be taken into account.

Nearly all the researches have employed inorganic acids as leachant to extract valuable elements, especially for rare earth elements. The primary shortcomings of the chemical leaching process come from massive acid consumption and environmental pollution. These plants must thus be responsible for the potential environmental problems originated from the usage of hazardous materials during the extraction. In view of the introduced secondary pollutants or by-products from hydrometallurgical recovery, it is the major restriction on the application of this extraction. In addition, due to the low exchange reaction rate and small quantity of elution yields, it is almost unfeasible to directly extract scandium from red mud through ion exchange separation method. And the ion exchangers cannot be reused multiple times since the effect of impurities. On the other hand, pyrometallurgical method for the extraction of valuable elements from red mud consumes large energy in sintering or roasting the starting materials. Take, for instance, the iron extraction on this process from red mud. The optimum roasting or sintering temperature is critical to the quality of pig iron and composition of slag. The stability of refractory is yet associated with the composition and temperature of slag and molten iron. As for the future techniques of recovering valuable metals from red mud, it must be more environmentally-friendly and cost effective, as well as more efficient to make the red mud be considered as a mineral resource or building material rather than a solid waste.

In the recovery process, it is not be profitable to recover valuable metals from red mud solely or one by one. As a result of this fact, multiple recovery or incorporation of the extraction of Al, Na, Ti, Sc, rare earth elements into iron recovery process should be designed and developed

**Table 4**

Summary of metallurgical process for valuable elements recovery from red mud.

Zhong et al., 2009; Vachon et al., 1994; Li et al., 2009; Liu et al., 1997, 2009a, 2012; Peng and Huang, 2011; Uzun and Gulfen, 2007; Eisele and Gabby, 2014; Erçağ and Apak, 1997; Deep et al., 2007; Mukherjee et al., 1990; Ochsenschüh-Petropulu et al., 1995, 1996; Ochsenschüh-Petropoulou et al., 2002; Abhilash et al., 2014.

	Metallurgical process	Optimum results	Specific method parameters & weaknesses	Application scale
Al	Hydrochemical	87.8% Al 96.4% Na	Al <sub>2</sub> O <sub>3</sub> extraction: 45% NaOH solution, CaO/red mud = 0.25, L/S = 0.9, 0.8 MPa, 200 °C, 3.5 h; Na <sub>2</sub> O extraction: 7% NaOH solution, L/S = 3.8, 0.9 MPa, 170 °C, 2 h & not found	Laboratory
	Bioleaching	75%	Acid exudate of <i>P. simplicissimum</i> (acid leaching), 3 h & poor efficiency for the recycling process, high cost	Laboratory
Na	Pyro- and hydrometallurgy	89.71%	Reduction sintering: 1050 °C, 20 wt.% carbon, 1.5 h; leaching & high energy consumption	Laboratory
	Hydrothermal treatment	90% Na 70% Al	Hydrothermal treatment: mixed with CaO prior to steam curing (100 °C, 1 MPa); low temperature calcination (750–950 °C); leaching: 3–6% Na <sub>2</sub> CO <sub>3</sub> , L/S = 5, 60 °C, 15 min & high energy consumption	Laboratory
Fe	Pyro- and hydrometallurgy	80.7% Na 75.7% Al	Soda-lime roasting: Ca/Si ≈ 2.0 (molar ratio), Na/Al ≈ 1.0 (molar ratio), ~0.5 wt.% coal, 1000 °C, 3 h; water leaching L/S = 2; 60 °C, 15 min & high energy consumption	Laboratory
	HGSMS Pyrometallurgy	28–35% 81.4%	As shown in Fig. 5 & poor performance for the Fe rich red mud, less integrowth required Roasting: 15.3 wt.% Carbon, CaCO <sub>3</sub> (MgCO <sub>3</sub> )/red mud = 0.06, 1300 °C, 110 min; quenching, magnetic separation. & high energy consumption	Pilot Pilot
Ti	Pyro- and hydrometallurgy	97.46% Fe 64.4% Al	Calcination: 600 °C, acid leaching: 6 M H <sub>2</sub> SO <sub>4</sub> & secondary waste (waste acid), energy consumption	Laboratory
	Bioleaching	95%	<i>D. palmitatis</i> & amorphous ferrihydrite required, low pH required	Laboratory
V Sc	Pyro- and hydrometallurgy	84.7%	Smelting: 1/1/0.165/19.5 = red mud/lime stone/coke/bentonite, 1100 °C, 1 h; 1550 °C, 0.5 h; acid leaching 30% H <sub>2</sub> SO <sub>4</sub> , 90 °C; extracting 5% D2EHPA & high energy consumption, secondary waste (waste acid)	Laboratory Laboratory
	Hydrometallurgy	97 ± 2%	1 g red mud leaching with H <sub>2</sub> SO <sub>4</sub> : HF = 1:5 and a few drops of concentrated HNO <sub>3</sub> , Cyanex 301 and 302 & secondary waste (waste acid), large volumes of acid consumption	Laboratory
V Sc	Hydrometallurgy	~50%	As shown in Fig. 10 & high concentration of V <sub>2</sub> O <sub>5</sub> needed	Laboratory
	Pyro- and hydrometallurgy	93 ± 5%	As shown in Fig. 11 & high energy consumption; large volume of acid consumption, secondary waste (waste acid); complicated	Laboratory
Other metals	Hydrometallurgy	50–75%	As shown in Fig. 12 & large volume of acid consumption, secondary waste (waste acid), complicated	Pilot
	Hydrometallurgy	30–90% La, Ce, etc. 99.9% La; 44% Ce 99.9% Ce; 37% La	0.5 M HNO <sub>3</sub> , 25 °C, 24 h, L/S = 50 & acid consumption and secondary waste (waste acid), blind selection Acid leaching 3 M H <sub>2</sub> SO <sub>4</sub> , solid to liquid ratio of 10 g·L <sup>-1</sup> , 35 °C, 1 h, 200 rpm; extraction with DEHPA or Cyanex 272/301 & acid consumption and secondary waste (waste acid) Acid leaching 3 M H <sub>2</sub> SO <sub>4</sub> , solid to liquid ratio of 10 g·L <sup>-1</sup> , 75 °C, 1 h, 200 rpm; extraction with Cyanex 301 & acid consumption and secondary waste (waste acid)	Laboratory Laboratory Laboratory

Notes: L/S: mass ratio of liquid to solid.

to make the recovery become more economically feasible. The resulting residues after metal recovery can be used as raw materials for the preparation of building decorations, catalytic supporting materials, adsorbents, etc., which is beneficial to minimizing the effects on environment. Besides, it is not a wise move to incorporate red mud into blast furnace with iron ore owing to the fact that the appearance of large volumes of alkali metals and alkaline earth metals in the red mud will produce the erosion effect on the lining. The characteristics of mineral components and composition are critical to the choosing of mineral acids and the recovery of valuable elements. On the other hand, the detailed information on the red mud is of help to the development of a practical complex utilization technique and therefore need to be clarified.

Red mud is the most promising scandium resources owing to the concentration and availability of scandium, but it is not suitable for the extraction of valuable elements in trace amounts from red mud with pyrometallurgical method because of substantial energy requirement. Hydrometallurgical method typically comprising of pre-treating likely grinding and roasting, acid leaching, solvent extraction, precipitation and calcination for the recovery of Al, Na, Ti, Sc and rare earth elements is practiced widely. While in the separation of objective materials like scandium from other purities, the co-dissolution and co-extraction of valuable elements could interfere the performance of extraction and stripping. Much work still needs to be done for the improvement of leaching and extraction selectivity, as well as efficiency. Besides the research on selectivity, it is also necessary for us to develop new extraction system with high selectivity and low acid consumption.

In the future, the occurrence mode of trace elements should be focused and researched. It is also interesting to note that the pretreatment performance of new processing routs like microwave heating, quenching in liquid nitrogen for red mud. Besides, researchers should pay more attention to the feasibility of alkaline leaching of trace elements. If this behavior follows the recovery of Al and Na by hydrothermal or hydrochemical method and Fe by HGSMS, the whole metallurgical process will be much 'greener'. In summary, the recovery of Fe, Al, Na, Ti and additional rare earth elements from red mud is valuable and significant in the disposal of problems associated with these solid wastes and the rise in iron ore price and the scarcity of rare earth supply worldwide. In order to elaborate an environmentally friendly and high value added technique for the comprehensive utilization of red mud, much fundamental research work is worth perfecting further.

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