

RESEARCH HIGHER DEGREE
RESEARCH PROPOSAL

Red Mud Minimisation and Management for the Alumina
Industry by the Carbonation Method

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1. Project title

Red mud minimisation and management for the alumina industry by the carbonation method.

2. Project summary

Bauxite residue (red mud), a by-product of the Bayer process for refining bauxite to alumina, is highly alkaline (pH~13) and its treatment and management pose environmental challenges on alumina industry. Neutralising red mud by carbon dioxide (CO₂) over a range of different operating conditions is necessary in order to optimise the carbonation process and determine the volume of CO₂ captured by red mud.

The objective of this work is to optimise the red mud carbonation in range of different operating conditions with the intent of establishing the optimal ratio of red mud and CO₂ in the carbonation process. The carbonation process will be implemented in a reactor system that is designed to safely operate over the range of relevant parameters (materials of construction, temperature, pressure, residence time, etc.), and that must be controlled under the desired experimental conditions.

Red mud compositions will be examined before and after carbonation by using analyses and titration methods, X-ray diffraction, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM), Atomic Absorption Spectroscopy (AAS) measurement, etc. to investigate the effects of these compositions and physical characteristics on the carbonation process. Finally, an estimate of potential mass of red mud reduced and the volume of CO₂ captured by the mud will be carried out through the alkalinity calculation and analysis methods.

Overall, the project will provide alumina refineries with data on optimisation of the red mud carbonation process under different operating conditions, and with the optimal ratio of red mud and CO₂ in accordance with these conditions. It also contributes a significant part to the red mud minimisation and management strategy via the estimation of CO₂ captured and mass of neutralised red mud.

3. Project details

3.1. Introductory background

Bauxite residue, commonly called red mud, is principal waste by-products generated in the alumina production by the Bayer process. It is composed of hydrous muddy silt combined with very high alkaline solid waste with a pH ranging from 10.5 to over 13 (Borges *et al.* 2011). This cocktail created by physical and chemical treatments of bauxite

in the alumina industry (György & Tran 2010; Zhang *et al.* 2001). The worldwide alumina industry has experienced significant growth over past decades and many producing countries are now struggling with serious problems in managing bauxite residues. The quantity of red mud has been increasing alarmingly due to the rapid increases in the global demand for the aluminium metal in transport, packaging and construction.

The production of 1 tonne of alumina normally results in the generation of 1-1.5 tonnes of red mud (Brunori *et al.* 2005; Kumar *et al.* 2006), however, depending on the bauxite source and alumina extraction efficiency, the quantity of waste generated may vary from 0.3 tonnes for high grade bauxite to 2.5 for very low grade (Borges *et al.* 2011; Kalkan 2006; Nguyen & Boger 1998; Paramguru *et al.* 2005; Sushil & Batra 2008). Consequently, the volume of bauxite residue waste has grown exponentially. In 1940, the inventory of bauxite waste was 22 million tonnes associated with the annual production rate of 1 million tonnes of aluminium metal per year. By 1985, the generation rate of the waste grew to roughly 48.5 million tonnes per annum, and the global inventory of bauxite residue reached 1 billion tonnes (Klauber *et al.* 2011; Power *et al.* 2009, 2011).

In 2007, it was estimated that approximately 120 million tonnes of bauxite residue were produced per year and the inventory of the waste had grown to 2.7 billion tonnes (Figure 1) (Clark *et al.* 2009; Klauber *et al.* 2011; Power *et al.* 2011). Of greater significance was the rapid increase in the rate of waste generation. It took nearly a century to produce the first billion tonnes of red mud, but the second billion tonnes were accumulated approximately 15 years.

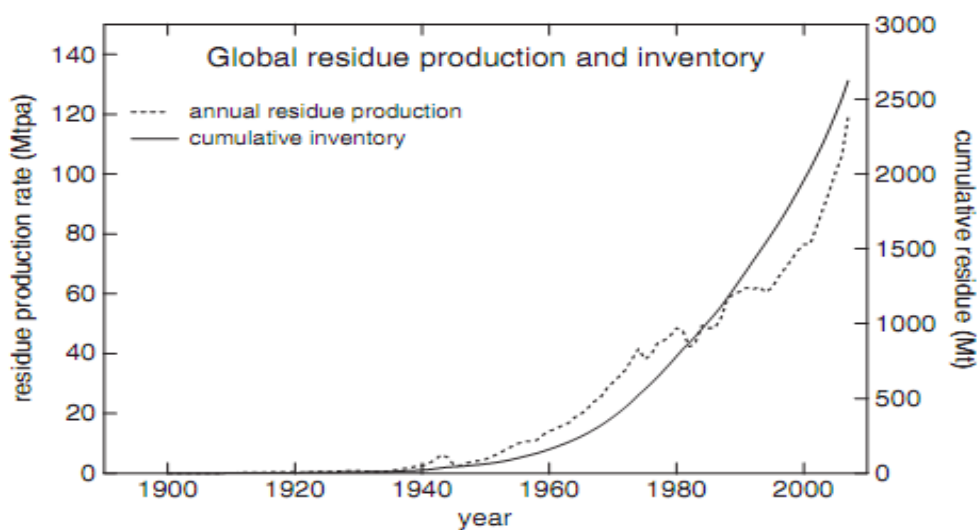


Figure 1. Global production rate and cumulative inventory (Power *et al.* 2011)

Future predictions suggest that approximately 3 billion tonnes will be produced in the period from 2010 to 2015, and this figure could possibly reach 4 billion tonnes by 2015 (Power *et al.* 2009, 2011). This mass of bauxite residue will pose a significant environmental problem as the red mud is highly alkaline (pH>13), fine-grained in nature (over 90% is <10µm), and contains elevated concentrations of sodium (>50g/kg) (Johnston *et al.* 2010). Clearly, appropriate management methods and utilisation practices must be devised to ameliorate this problem. Unfortunately, there are no acceptable solutions for dealing with the red mud in terms of its management and its potential utilisation. Treating the waste would lead to a significant penalty to production cost. As a result, it seems that the red mud disposal problem may be ignored by the industry, the public and governments (Power *et al.* 2009, 2011).

For most alumina plants, the disposal of red mud is a major problem. When the inventory of bauxite residue grew to 1 billion tonnes, its disposal method became an important issue to the future of alumina industry. As noted in the available literature (Power *et al.* 2009), prior to the 1970s, the residual waste was primarily dealt with by two main methods, namely marine discharge and lagooning. Since the 1980s many systematic efforts have been developed to improve the disposal methods of bauxite residue in terms of environmental protection and land conservation (Agrawal *et al.* 2004; Liu *et al.* 2009; Power *et al.* 2009). The major disposal technologies included a wet process, a dry process, and a mixed storage process. Although the above disposal methods have different advantages and disadvantages, currently, dry storage disposal known as “dry stacking” has been widely used for long term storage of bauxite residue in most alumina plants in the world (Liu *et al.* 2009; Power *et al.* 2011).

Researchers have also carried out studies on developing the most effective recycling strategies in order to reuse red mud as a valuable material for different sectors. Clearly, the most important constraints to bauxite residue management, remediation and utilisation are its very high alkalinity and sodicity. It is worth noting that in order to reuse bauxite residue successfully as a valuable by-product for different purposes or for disposal at a lower cost, it is essential to develop more effectively technological approaches (Klauber *et al.* 2011). To date, more than 50 years of research and hundreds of publications and patents on this issue have been developed and recognised worldwide. These studies spanned many areas of using bauxite residue but they mainly considered the five following different fields: construction, chemical, metallurgical, agricultural and environmental applications, (Klauber *et al.* 2009, 2011). There have been significant achievements in using red mud as

an input material for making construction products such as sintered and unsintered bricks, cement, pigments, and road embankments, etc. While, metallurgical applications also contributes a remarkable role in recovering valuable metals from the residual wastes, and most of these utilisation practices in both areas have been patented.

Similarly, agronomic applications have been successfully used and brought about promising results. Many studies on utilising red mud as a fertiliser and soil amendment or production have been conducted in order to improve the quality of soil. Additionally, the use of red mud for absorption of heavy metals, metalloids, inorganics, organics and bacteria in soils and wastewater has been proposed (Klauber *et al.* 2011).

In terms of environmental treatment, the use of industrial wastes as a resource for solving the problems of other wastes sounds very promising. A variety of methods have been employed for neutralising red mud by aqueous carbon dioxides, (Enick *et al.* 2001; Shi *et al.* 2000), SO₂ from flue gases (Fois *et al.* 2007), seawater treatment (Cooling 2007; Hanahan *et al.* 2004), Ca and Mg rich salts, acid treatment (Bonenfant *et al.* 2008a; Khaitan *et al.* 2009). Although these methods have contributed a significant part to the improvement of bauxite residue management, they are often costly, and unlikely to reduce the amount of red mud annually produced in the alumina industry. Therefore, the development of a low-cost solution in terms of processes and materials is very important to the significant reduction of both red mud quantities and greenhouse gases. This research will aim to investigate the red mud neutralisation by carbon dioxide over a range of pressures and to optimise the carbonation process. Then, the calculation of CO₂ volume permanently captured by red mud should also be examined.

3.2. Literature Review

3.2.1. Bauxite residue generation process

Bauxite residue or red mud is produced as an undesirable by-product during the extraction of alumina from bauxite ore in the Bayer process (Figure 2). This process was patented by Karl Josef Bayer between 1887 and 1892 (Power *et al.* 2011; Sparks 2010). This process was so successful that it is now the dominant process for the alumina

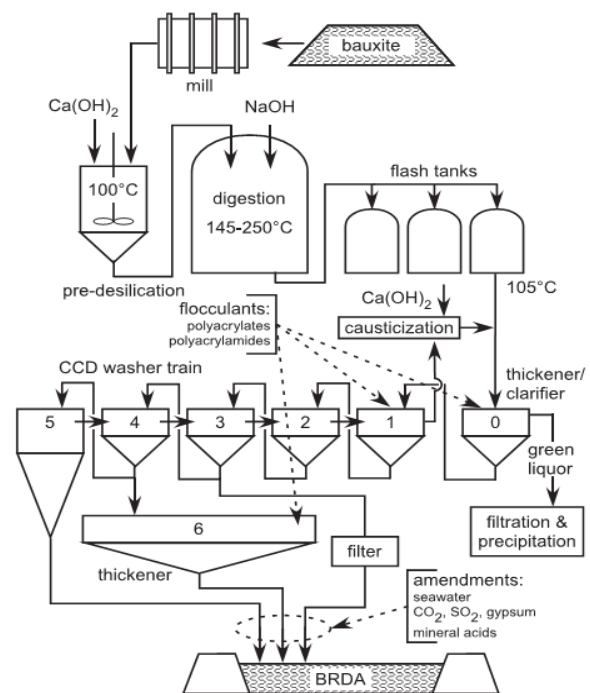


Figure 2. Schematic of a general Bayer process (Power *et al.* 2011)

production. Although its success makes a significant contribution to the mineral processing industry, the process results in an inevitable consequence. The key issue is the generation of the very large amount of difficult to treat residue. It could provide a source of valuable metals if an economic treatment could be devised. The quantities of waste continued to increase exponentially after the Hall-Heroult process for smelting alumina to metal at the end of the nineteenth century (Klauber *et al.* 2009, 2011).

As can be seen from the figure 2, red mud and its management start at the process of separation of the green liquor from solids remaining after digestion (Power *et al.* 2011). The residue after separating from the green liquor in a thickener will be transferred to a series of the counter-current decantation (CCD) washing units in order to wash the residue and to recover NaOH and NaAl(OH)₄ for recycling back to the process. The collected residue after washing in the CCD usually passes to a further filtration or thickening process to increase its solids content before discharge into the disposal area (Power *et al.* 2011).

Basically, red mud consists of essentially in-soluble compounds of bauxite, such as iron, titania and some un-digested soluble alumina minerals and other compounds that were formed in the processing (György & Tran 2010). Red mud also contains an amount of coarse particles called “sand”. The volume of sand varies from less than 1% to nearly 50% depending on bauxite source, but the normal amount is around 5% (György & Tran 2010). As mentioned above, the Bayer process generated the large amount of red mud. However, this waste was not treated further for recovering mineral values with appropriate methods or reusing as a resource for other purposes. It was directly discharged into the environment as cheaply and conveniently as possible without environmental concerns. This will pose an adverse impact on the ecosystem because of its high alkalinity.

3.2.2. Physico-chemical and mineralogical properties of red mud

Red mud contains a mixture of metal oxides that were originally present in bauxite ore and could be formed in the Bayer process (Agrawal *et al.* 2004; Singh *et al.* 1997; Sushil & Batra 2008). The chemical and mineralogical properties of red mud vary significantly depending on different bauxite sources and digestion process parameters (Altundogan *et al.* 2000; Bertocchi *et al.* 2006; Cengeloglu *et al.* 2003; Collazo *et al.* 2005; Gong & Yang 2000; György & Tran 2010; Koumanova *et al.* 1997; Park & Jun 2005; Pontikes *et al.* 2007; Tsakiridis *et al.* 2004; Yalcin & Sevinc 2000). The major compositions of red mud encompass a significant quantities of metal oxides such as Fe₂O₃, Al₂O₃, SiO₂, TiO₂, Na₂O, CaO, MgO and a numerous other minor elements like K, Cr, V,

Ni, Cu, Zn, Mn, etc. (Singh *et al.* 1997; Sushil & Batra 2008). Table 1 shows the chemical compositions of red mud in different plants.

Table 1. Chemical constituents of red mud in various locations (wt.%)
(adapted from György & Tran (2010))

	Weipa (Australia)	Trombetas (Brasil)	South Manchester (Jamaica)	Darling Range (Australia)	Iszka (Hungary)	Parnasse (Greece)
Digestion temperature	240 ⁰ C	143 ⁰ C	245 ⁰ C	143 ⁰ C	240 ⁰ C	260 ⁰ C
Al ₂ O ₃	17.2	13.0	10.7	14.9	14.4	13.0
SiO ₂	15.0	12.9	3.0	42.6	12.5	12.0
Fe ₂ O ₃	36.0	52.1	61.9	28.0	38.0	41.0
TiO ₂	12.0	4.2	8.1	2.0	5.5	6.2
Na ₂ O	9.0	9.0	2.3	1.2	7.5	7.5
CaO	-	1.4	2.8	2.4	7.6	10.9
L.O.I	7.3	6.4	8.4	6.5	9.6	7.1
Others	3.5	1.0	2.8	2.4	4.9	2.3

Red mud is a very fine material with a particle size distribution, typically ranging from 1-150µm, with over 90% by volume below 10µm (Clark *et al.* 2009; Johnston *et al.* 2010). It has a very low settling rate (0.014-35.9 cm/ks), a range of density of 2.6-3.5 t/m³ (György & Tran 2010), and a high surface area (Sushil & Batra 2008). The pH of red mud varies from 10 to 13.5, so it has a highly caustic nature that can harm the environment (György & Tran 2010; Johnston *et al.* 2010; Sushil & Batra 2008). According to the X-ray diffraction analysis, the major mineral compositions of red mud are shown in Table 2 (Brunori *et al.* 2005; György & Tran 2010; Lopez *et al.* 1998; Sushil & Batra 2008; Wang *et al.* 2005).

Table 2. Major mineralogical compositions of red mud

No.	Name	Chemical formula	No.	Name	Chemical formula
1	Gibbsite	Al(OH) ₃	11	Quartz	SiO ₂
2	Boethmite	AlO(OH)	12	Calcite	CaCO ₃
3	Goethite	FeOOH	13	Rutile	TiO ₂
4	Hematite	α-Fe ₂ O ₃	14	Halloysite	Al ₂ Si ₂ O ₅ (OH) ₄
5	Iron hydroxide	Fe(OH) ₃	15	Sodalite	Na ₂ OAl ₂ O ₃ 1.68SiO ₂ 1.73H ₂ O
6	Magnetite	Fe ₃ O ₄	16	Cancrinite	3NaAlSiO ₄ .NaOH
7	Anatase	TiO ₂	17	Whewellite	CaC ₂ O ₄ .H ₂ O
8	Bayerite	Al(OH) ₃	18	Katoite	Ca ₃ Al ₂ SiO ₂ (OH) ₁₂
9	Diaspora	AlO(OH)	19	Gypsum	CaSO ₄ .2H ₂ O
10	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	20	Etc.	

3.2.3. Methods used for disposal of red mud

Before the 1970s, there were two main conventional wet disposal methods used in alumina refineries, namely marine discharge and lagooning (Klauber *et al.* 2011). Generally, the former practice looks simpler than the latter in terms of economic and technological sites. However, these methods contributed a significant role to the management of red mud at that time.

3.2.3.1. Marine disposal method

Marine disposal was employed in France, Greece, the USA, Australia and Japan for several years given seawater's neutralisation capacity to the causticity of red mud (György & Tran 2010). During marine disposal, the residue slurry generated from the Bayer process is directly pumped into the deep ocean through the pipeline system. Although environmental impact assessment reports revealed that, there were no adverse impacts on the water quality and coastal organisms at the sedimentation areas in Japan, this disposal practice has been discouraged by the UNIDO (United Nations Industrial Development Organisation 1985). As a result, there has been a trend to shift from ocean or river disposal into lagooning or other methods, and as noted in the available literature no refineries established after 1970 employed the marine disposal. Currently, 2-3% of global alumina production use marine disposal for the treatment of red mud (Power *et al.* 2011).

The Gramercy plant in Louisiana in the USA discharged its red mud into the Mississippi river until 1974, when it adopted lagooning for waste storage and subsequent treatment. Interestingly, this transition, which removes residue from the river and relocate it to land-based impoundments, was initiated voluntarily by the Kaiser Company (Kirkpatrick 1996). Several refineries in Japan consider marine disposal of the residue as a main method because of limited land area available for disposal. However, in 2005 these plants made a commitment to International Marine Organisation to stop discharging the waste in the sea by 2015, and will employ other alternative practices for residue disposal (International Marine Organisation 2005). Similarly, refineries at Gardanne in France, which still employ marine disposal, are also scheduled to cease their waste disposal into the ocean by 2015 (Martinet-Catalot *et al.* 2002).

3.2.3.2. Lagooning method

The use of lagoon is now normally practised for dumping red mud (György & Tran 2010). The red mud slurry is directly disposed of into the land-based impoundments (Power *et al.* 2011) called a red mud pond (Figure 3). The practice requires increased engineering input considering topography, linings and material's issues, and construction

complexity, etc. when compared to the marine option, but it is now widely applied in many refineries in the world. These requirements aim to mitigate potential leakage of caustic and alkaline water into the soil and ground water. Unfortunately, in many plants built prior to 1960, there was often no special sealing applied at the bottom of the pond. This resulted in the contamination of the surrounding soils and ground water, with consequent adverse impacts on human's health (György & Tran 2010).



Figure 3. Lagooning red mud disposal (György & Tran 2010)

It is suggested that, the best practice of lagooning is to line the pond with a single compacted clay bed or multiple ones of up to 300-400mm thick in order to isolate the red mud from the original soil or rock of the pond (György & Tran 2010; Liu *et al.* 2009). Furthermore, an alternative security can be employed by using multiple layers of plastic or geo-membrane materials to create a seal between the red mud and the supporting clay bed (Cooling 1989).

However, many studies have reported that the caustic soda content of the red mud reacts with the clays over several decades to form amorphous sodium aluminium hydro silicates and ultimately zeolite via a series of complex reactions (Gerrise & Thomas 2008). These reactions increase the hydraulic conductivity of the clay bed, leading to potential pollution of the aquatic system after over decades. These problems could be mitigated by neutralising the slurry before disposing, for instance, by adding mineral acids like sulphuric acid, or by mixing the slurry with seawater (Power *et al.* 2009, 2011).

Generally, lagoon disposal is the simplest land-based disposal, which is widely used in the world, but it is still reliant on good engineering practice for residue storage, so it may result in high cost of operation. Furthermore, the wet method is often problematic because of its high risk of leakage, instability and liquefaction. According to the statistics, about 35 major tailings dam failures have been recorded worldwide since 1970, leading to at least 471 human deaths and environmental depletion (Sofrá & Boger 2002). The newest problem that tragically demonstrated in Hungary in October 2010 was the impoundment wall breakdown at the Ajka Timföldgyár alumina plant, causing red mud flood and long-term environmental damage (Enserink 2010).

3.2.3.3. Dry stacking method

An alternative disposal method for the storage of bauxite residue called dry stacking has been introduced. This process was employed the first time at the Burntisland Alumina plant in Scotland in 1941 (György & Tran 2010). Unlike lagooning, dry mud stacking is termed thickened tailings disposal and implies that the washed red slurry from the Bayer process is

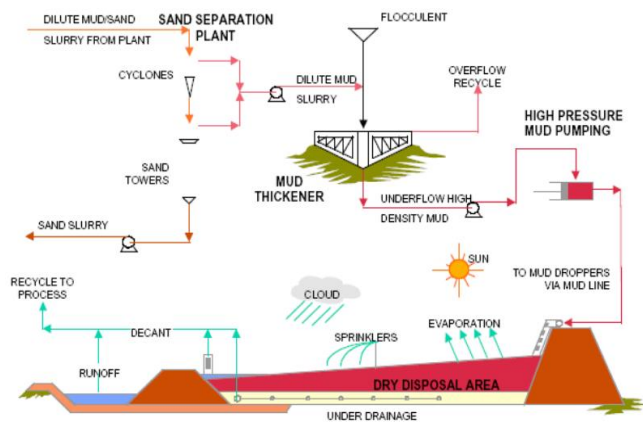


Figure 4. Schematic of dry stacking system (Alcoa 2011)

consolidated or dewatered to a paste with an initial content of approximately 48-55% solids before discharging (Figure 4). Therefore, it was considered to be cost-effective and inconsiderable environmental problems (Purnell 1986).

The Giulini GmbH refinery in Germany was the next pioneer in using dry stacking method of rotary vacuum filter cake in the early 1970s with the consideration of reducing the land area needed for disposal and maximising the return of soda and alumina to the process (Haerter & Shefer 1975). Next, this practice was introduced at the Alcan refinery followed by the achievement of Alcoa in 1985 (Paradis 1992). Compared to the lagooning, two layers of sealing are concurrently needed at the bottom of the disposal site. The first is an at least 600mm thickness compacted clay liner, which is placed at the bottom. Then, the upper layer is a plastic membrane, which is often used high-density polyethylene (HDPE), and offers a good resistance to high soda and pH environment (György & Tran 2010).

Dry stacking is in relation to the progressive deposition of dewatered red mud onto sloped and under-drained drying bed (Sofrá & Boger 2002) to facilitate the consolidation process. It represents an engineering paradigm shift. In addition, it is necessary for the tailings to be engineered in order to suit the disposal requirements. It means that it is crucial to understand how the process of transport of residue and deposition characteristics can be affected by material properties and operational parameters (Sofrá & Boger 2002). In other words, a successful dry stacking method requires a good understanding of the rheology of bauxite residue (Power *et al.* 2011). Clearly, rheology plays an important role in determining essential parameters for dry stacking method operation.

The understanding of the system's rheology will help to design a prudent dry disposal system by forecasting the angle of repose, or slope created by the deposited

tailings. A good prediction of the slope allows improving the efficiency and stability of residue storage. As a result, there is an erudite understanding of the relationship between the rheological properties of red mud, operating conditions and depositional behaviour; it will be possible to obtain the desired slope of the disposal system by manipulating the operating or rheological parameters (Sofrá & Boger 2002). Regarding the rheological properties of bauxite residue, yield stress and viscosity are the most important parameters that are considered a function of solids content and the shear and compression history of the red mud for thickening slurry, designing transport, spreading behaviour and predicting the slope formation (Green & Boger 1997; Sofrá & Boger 2002). Successful manipulation of these parameters may improve handling and transport of slurry by pipeline to the disposal site at very high solids loadings and in large volume with least energy requirement, and enhance the process of compaction and drying (Nguyen & Boger 1998).

Furthermore, improved understanding of rheology may help to determine:

- (i) the required concentration of bauxite residue for optimal process of spreading and drying of the red mud when it was deposited;
- (ii) the optimal conditions for the tailings to be handled and transported via the pipeline; and
- (iii) the feasibility of dewatering of the red mud to fulfil the required concentration for disposal (Sofrá & Boger 2002).

This means that a thorough knowledge of rheology of concentrated tailings in shear and under compression may be employed to not only deal with red mud disposal problem, but also improve and optimise the discharging process, according to Nguyen & Boger (1998).

To summarise, the dry stacking method appears to possess significant advantages in comparison with other methods. It has been successfully employed at Alcoa in Western Australia and most other refineries in the world as the new disposal strategy (Nguyen & Boger 1998) given its advantages. Firstly, the high dam wall is eradicated and the stability of the deposit is improved as the concentrated and consolidated tailings can create a residues stack of conical geometry (Sofrá & Boger 2002). In addition, the land footprint required for the storage is reduced and improved because higher tailings densities are achieved. More importantly, solids loadings pumped to disposal site are very high with nearly 70wt.% of solids densities as achieved by Alcoa refinery (Cooling & Glenister 1992). Finally, potentially environmental risks of leakage and hazardous contaminations are significantly lowered, and the area management and ability of rehabilitation is fully

assisted due to rapid de-liquoring process. As a result, in the 1970s in Australia, the USA and Europe, the amount of red mud handled by the conventional wet disposal method (lagooning) accounted for 70-80%, the remaining of 10% was disposed of by marine method. However, this figure was considerably different with the lagooning disposal reducing to 25%, whereas, ocean discharge made up 15% and the dry stacking method occupied about 60% by 2008 (Gräfe *et al.* 2009).

3.2.3.4. Dry cake disposal method

Dry cake disposal is also a dry disposal practice, where the slurry is mechanically dewatered as much as possible in order to create a dry cake with more than 65% of solid content before disposing of (Power *et al.* 2011). The most significant feature that differs from dry stacking practice is that there is no further dewatering once the residue has been dumped at the storage site. Similar to the other practices, this method also offers an advantage feature that risk of alkalinity and caustics can be further diminished by neutralising or washing in the filtration on vacuum drum filters (Shah & Gararia 1995).

However, it is impossible to obtain a dry cake by using only means of thickening; therefore, it does require a filtration phase (Power *et al.* 2011). This combination is essential to overcome the capillary resistance inside the residue's pores in order to dewater the cake thoroughly. This practice has been successfully deployed in a pilot scale, for example at the Hindalco plant at Renukoot (Shah & Gararia 1995) and the Aluminiumoxid Stade (Germany) plant with the solids content of over 75% achieved (Bott *et al.* 2002). However, this practice seems to be unlikely specified for utilisation in alumina refineries as such in available information because the dry stacking is often used as its advantages and preferred disposal strategy.

3.2.4. The red mud utilisation options

It is clear that the rate of red mud production and its alkaline and caustic properties will pose seriously adverse impacts on the environment and human health if there are no proper minimisation and management solutions. Currently, many alumina plants in the world are still discharging the red mud into the ocean, or land-based impoundments, or dry stacking ponds. These practices are just conventional solutions for storing red mud in different ways. They will not actually help to minimise and reuse this waste as a valuable material in terms of economic, environmental and social considerations. Confronted with the problem, many different technologies have been developed in the efforts of long-term remediation and utilisation applications of red mud in order to minimise to the environmentally acceptable level.

3.2.4.1. The utilisations of red mud in construction

Building materials seem to be one of the most successful applications that could consume a significant red mud quantity. The study conducted in early 1936 (Thakur & Sant 1983a) showed that the contents of iron and alumina in red mud can contribute a crucial part to the setting and strength properties of the cement, but the soda is detrimental. The use of calcium replacing soda in the study can foster the ability of red mud as an additive; however, the process of residue calcinations has to be done in a very high temperature of 1000⁰C. Similarly, Liu *et al.* (2009) also advocated that the production of cement from the mix of 50% red mud and other solid wastes and modifiers has reached the standard of Portland 42.5 cement, but the limited content of sodium in cement according to the newest standard could lead to the prohibition of using red mud in cement production.

Additionally, research on using a mixture of gypsum, bauxite and red mud for preparing special cements was performed by Singh *et al.* (1996, 1997). The authors concluded that with the red mud content of 20-50% by dry weight added in the composition of the material mix, it is possible to produce cements with superior setting strengths when compared to normal Portland cement. Nonetheless, it is assumed that if all of the red mud could be used in cement production, this amount would consume less than 1.6% of the annual residue production not mention to the cost of residue processing and transportation (Klauber *et al.* 2011). Therefore, it was recommended that this application should be employed locally in order to meet the minimum cost of residue processing.

Many studies on using red mud for manufacturing bricks and blocks have been conducted. Although the production of brick from red mud has been studied and patented, and looked technically sound, there are no significant large-scale implementations in this practice recorded in the literature. There were two key reasons related to this problem. The first is the competition from materials and the processes. The second is that there are no certainties about the technical, environmental and health problems in relation to these new products (Klauber *et al.* 2011). A case study conducted in Jamaica by McCarthy *et al.* (1992) has revealed these issues in detail. It indicated that the manufacturing of bricks from residue has illustrated the technical feasibility, and the alumina producers were willing to support the development of the process. However, the main properties bricks such as long-term stability, leaching and ionising radiation were not almost mentioned. A case study showed that the radon levels from bauxite residue bricks recorded were approximately 2-3 times higher than that of the conventional concrete (Pinnock 1991; 1999). This will pose a potential impact on human health.

A recent investigation on developing unsintered bricks from red mud generated by Shandong Aluminium Plant in China has been conducted (Yang & Xiao 2008). In this study, researchers considered five key experimental plans in order to identify the optimal ratio of red mud to other materials such as fly ash, the percentage of sand, the effect of lime, gypsum and Portland cement. It is noteworthy that the manufacturing process of unfired bricks was implemented at the ambient temperature. The results concluded that the optimal percentages (in weight) of red mud bricks consist of red mud (25-40%), fly ash (18-28%), sand (30-35%), lime (8-10%), gypsum (1-3%) and Portland cement (just 1%). The products have met the first class brick standard of China with good durability in severe climate conditions and high strength. Furthermore, such products could be competition in materials and the process of production as they consume lower energy and cost.

3.2.4.2. The utilisations of red mud in chemical applications

In the context of using bauxite residue as catalysts, many applications have been widely published thanks to the contents of Fe_2O_3 and TiO_2 of red mud and its high surface area and low cost material sources (Klauber *et al.* 2009, 2011). Recent studies conducted by Sushil & Batra (2008, 2012) have demonstrated the use of red mud as a catalyst in hydrogenation, hydro-dechlorination, exhausted gas clean-up and other areas. These authors concluded that unmodified red mud had a poor performance as a catalyst compared with pure iron oxide or commercial catalysts.

In addition, it was found that red mud-based catalysts need some pre-treatments or activation such as drying, screening, size reduction, heat treatment (about 400°C), acid treatment in order to ameliorate their activity and efficiencies. These pre-treatments will lead to the increase in the cost of production. On the other hand, the applications in this area are considered unfeasibly technical performance not mention to the cost competition (Klauber *et al.* 2011). Therefore, they could not be the target of reducing global bauxite residue inventory.

In the production of ceramics, red mud is considered a beneficial material that creates a barrier for radiation shielding (Amritphale *et al.* 2007). This is because the formation of a dense ceramic matrix produced from liquid phase sintering. This matrix demonstrated the shielding thickness and compressive and impact strength better compared to normal Portland cement-based shielding materials. Although the applications in this area are really in wide range, they consume a low volume of bauxite residue and require some pre-treatments. Therefore, it should be recommended that they are only potential for the local development of products (Klauber *et al.* 2011).

3.2.4.3. The utilisations of red mud in metallurgy

There were about 135 patents granted between 1964 and 2008 related to metallurgical applications, 17% out of which are subject to bauxite residue (Klauber *et al.* 2011). The major metals recovered from bauxite residue are often iron, aluminium, titanium and sodium. The process of iron, aluminium and titanium recovery exclusively and in combination has been reviewed in previous studies (Paramguru *et al.* 2005; Thakur & Sant 1983b). However, the available literature showed that proposed process of

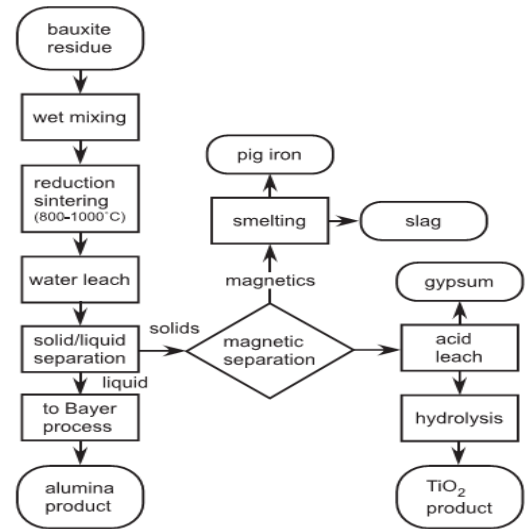


Figure 5. A flowsheet for recovery of Fe, Al and Ti from bauxite residue (Piga *et al.* 1993)

these metals seem to be technically complex, and it requires a big investment in establishing large, capital and energy intensive plants (Figure 5). Therefore, there are no the large scale extraction of metals from bauxite residue being employed to date. This is because of lacking of detailed techno-economic, market and environmental evaluation for the process that is suitable for the specific regional conditions.

Apart from that, according to Klauber *et al.* (2011) there were also 16 patents regarding minor metals extraction from bauxite residue. These focused on recovering minor metals such as scandium, rare earth elements, zinc, cadmium, lead, vanadium and silicon. A research conducted by Russian scientists demonstrated the feasibility of recovering minor metals like titanium, scandium, uranium and thorium from the residue in Nikolaev alumina plant, where processes bauxites from a number of sources in Brazil, Guyana, Australia, Guinea and India (Pawlek 2008). The results showed that the extraction of minor metals did not reduce the amount of residue to be stored. On the other hand, depending on the processing method, the extraction may make the residue more or less difficult to use or store. This means that the residue after minor metals extraction was normally used as construction material, but it would be acidic and may have different properties relating to leaching of metals, flocculation and consolidation behaviour (Klauber *et al.* 2011).

3.2.4.4. The utilisations of red mud in agriculture

A number of investigators have studied potential use of untreated red mud to improve soil given its ability for fixation of heavy metals (Liu *et al.* 2011). The study on

the biological and chemical assessments of in situ fixation of metals in soil using red mud conducted by Lombi *et al.* (2002; 2002) is a typical example. This study reported a remarked decrease in the concentration of heavy metals in the soil pore water following treatment using 2% red mud and 5% beringite (an alkaline alumino silicate). The research also confirmed that red mud treatment could significantly accelerate the production of soil microbial biomass.

Similarly, research has been conducted using batch, pot and field experiments involving gravel sludge and red mud to deal with contaminated agricultural soils near a former Pb/Zn smelter in Austria (Friesl *et al.* 2006). The field experiment results showed that heavy metals such as Cd, Pb and Zn could be minimised by up to 96%, 99% and 99%, respectively in treated soils. As well, red mud can retain the content of phosphorus significantly and reduce soil acidity effectively (Liu *et al.* 2011; Snar *et al.* 2004; Summers *et al.* 2001). Furthermore, in a pot experiment, Friesl *et al.* (2003) found that compared to unamended soil, red mud could considerably decrease Cd, Zn, and Ni uptake in fescue and amaranthus (*Amaranthus hybridus L.*) by up to 87%, 81% and 87%, respectively.

It is evident that bauxite residue can improve the cycle of phosphorus in agricultural areas having sandy soils with low phosphate and other nutrient holding capacities (Klauber *et al.* 2011). This occurs because the mud has two useful properties with respect to phosphate cycling, namely reducing phosphate leaching into ground and surface water, and creating a phosphate pool which is subsequently available to plants for improved growth. A number of studies employed by the Western Australian Department of Agriculture reported that bauxite residue is useful for improving P retention, reducing run-off into the Peel Inlet and the Harvey Estuary by up to 75%. Concurrently, pasture yields were increased by 25% on average and in well-controlled areas by up to 200%. This retention of P in the soil reduces the damaging effects of eutrophication caused by phosphate leaching into the Peel-Harvey ecosystems (Klauber *et al.* 2011).

3.2.4.5. The utilisations of red mud in environmental treatment

Bauxite residue has become important in environmental services given its capacity to remove metals and metalloids due to its high alkalinity and oxidising potential. The mud's alkalinity makes metals able to be hydrolysed and precipitated in sequestration, and the presence of high concentrations of iron, aluminium and titanium oxides assists sorption reactions of metals and metalloids to occur quickly. As well, red mud contains a considerable amount of TiO₂, which facilitates oxidation reactions thereby lowering the toxicity of metals like As⁺³ to As⁺⁵, Cr⁺⁶ to Cr⁺³ in their salted compounds.

Wastewater treatment applications by using red mud, such as the removal of contaminants both metals and metalloids from water streams, have been widely touted (Genc-Fuhrman *et al.* 2005; Genc-Fuhrman *et al.* 2007; Genc-Fuhrman *et al.* 2004a, 2004b; Genç *et al.* 2003; Gupta *et al.* 2004; Gupta & Sharma 2002; Li *et al.* 2006; Liu *et al.* 2007; Liu *et al.* 2011; Palmer *et al.* 2010; Wang *et al.* 2009; Zhang *et al.* 2008). These studies confirmed that red mud demonstrates a promising ability to remove toxic heavy metals, inorganics and organics, metalloids, phenolic compounds and bacteria alike in wastewater. Improving wastewater is a consequence of the basic advantage of red mud, which is a versatile mixture of adsorbents and flocculants that can sequester or adsorb pollutants from the wastewater (Liu *et al.* 2011).

The result from the study of removing phosphate from wastewater by using red mud reported that red mud (following treatment by sulphuric acid) could potentially remove up to 70% of phosphate in the pH range of 6.5-7.5 (Couillard 1982). Similarly, at pH = 7, pH removal reached 99% if red mud was treated with HCl (concentration = 0.25 mol/L) at 700⁰C for 2 hours (Li *et al.* 2006; Liu *et al.* 2007), and its performance was better than treated fly ash. However, Klauber *et al.* (2011) observed that there was little evidence to support postulated removal efficiencies of 70% and 99% as the original level of phosphate and application rate were not reported.

Apart from phosphate removal, researchers have also investigated nitrate, fluorides and boron adsorption by red mud. An experiment on comparison of nitrate adsorption between activated red mud with 20% HCl and raw red mud was conducted by Cengeloglu *et al.* (Cengeloglu *et al.* 2006). The authors observed that the adsorption capacity of the activated mud was fivefold higher than that of the raw mud, and the rate of nitrate removal reduced at pH values exceeding 7. The effect of pH on the rate of adsorption was explained by ligand exchange reactions occurring between metal oxides and the nitrate ion in the red mud and the activated red mud. Unfortunately, the author did not quantify the cost for activation process in order to determine if the activation step is economically justified.

Numerous studies using red mud as an adsorbent for removal of heavy metals in wastewater have been successfully conducted (Altundogan *et al.* 2002; Altundoğan & Tümen 2003; Genc-Fuhrman *et al.* 2004a; Gupta *et al.* 2001; Gupta & Sharma 2002; Li *et al.* 2010; Soner Altundogan *et al.* 2000; Zhu *et al.* 2007). These studies concluded that red mud has an effective capacity for adsorbing and precipitating heavy metals due to its high pH. Furthermore, after physical and chemical treatments such as heating, or the addition of seawater, HCl, or H₂O₂, a very finely grained red mud with high surface and charge ratios

is produced. This mud strongly combines with heavy metals (Altundogan *et al.* 2002; Brunori *et al.* 2005; Lin *et al.* 2004; Liu *et al.* 2011). As well, the results confirmed that pH, contacting time, adsorbent dosage, initial pollutant concentrations and presence of other ions are the key factors for successful adsorption. The efficiency of adsorption may increase if the solution pH is retained above 5 (Gupta & Sharma 2002). Oxide components such as Fe₂O₃, Al₂O₃ and TiO₂ play an important role in removal of heavy metals due to their high adsorption affinity. Unfortunately, the studies did not identify which oxide possessed has the highest affinity for a given heavy metal ion (Liu *et al.* 2011).

Apart from the inorganic removal, substantial efforts have been also made in eliminating organics such as phenol and its derivatives, dye and bacteria from wastewater by using red mud (Liu *et al.* 2011). Many methods of dye removal, such as sedimentation, filtration, chemical treatment, oxidation, biological treatment, and adsorption and ion exchange, have been widely introduced by using low cost adsorbents, including red mud, as its cost efficiency compared to commercial adsorbents (Gupta & Suhas 2009; Liu *et al.* 2011). A study on using red mud as an adsorbent for removing congo red and acid violet from aqueous solution has been conducted (Namasivayam & Arasi 1997; Namasivayam *et al.* 2001). The result showed that the removal capacity of red mud for the dye was recorded to be 4.05mg/g and the mechanism of adsorption is mostly ion exchange.

It is recorded that an experiment on using red mud mixed with sand for removing bacteria and virus has been employed (Wang *et al.* 2008). The study was implemented by column technique and using red mud neutralised by 5% gypsum and incorporated to form 30% of amended sand. The result showed that the removal rate of *Escherichia coli*, *Salmonella adelaide* and poliovirus-1 in secondary effluent from wastewater treatment plant was significantly improved. The order of removal was Poliovirus>*E. coli*>*S. adelaide* (Wang *et al.* 2008).

In the field of waste gas treatment, a process developed and patented by the Sumitomo Aluminium Company (Japan) in the mid-1970s, reported that SO₂ could be removed from the emission using bauxite residue slurry (Klauber *et al.* 2011). SO₂ gas scrubbing will lower the pH in the slurry and to demolish the structure of desilication products – an alkaline buffering material in bauxite residues (Gräfe *et al.* 2011; Klauber *et al.* 2011). Today, this process, often called the Sumitomo process, is still employed in industry but it is only applied in limited number of refineries for reducing SO₂ emission, for instance in power generation plants using coal (Fois *et al.* 2007). Clearly, the use of red mud for trapping SO₂ has been ongoing, and is the successfully implemented

environmental application at the Eurallumina (Italy) (Gräfe *et al.* 2011; Klauber *et al.* 2011). However, the use of red mud for the removal of SO₂ seems to be unlikely to consume a large amount of the waste compared to the total mass of red mud produced. Therefore, it can be seen that this application does not appear to be potentially significant (Power *et al.* 2011).

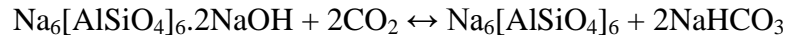
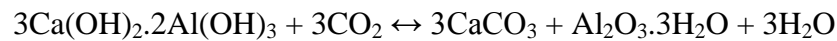
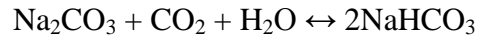
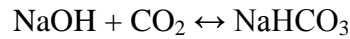
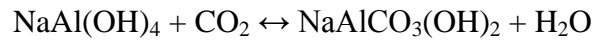
3.2.4.6. Carbonation of red mud by using carbon dioxide (CO₂)

The application of industrial wastes as agents to deal with environmental problem has grown in popularity. This is because these solutions not only resolve the significant amount of pollutants, but also enhance the importance of reusing the wastes as a valuable resource in an economic aspect.

In the environmental context, the volume of CO₂ in the atmosphere is rapidly increasing and reaching the level of approximately 375ppm in 2005, and it is projected that atmospheric CO₂ concentration will be at around 560ppm by the end of the century (IPCC 2001). This will lead to the climate change and severe global warming affecting human health, industries and agricultural activities. Therefore, using industrial wastes, such as metal oxide bearing materials, for capturing CO₂ may potentially make a significant contribution to global warming mitigation. Possible materials could be alkaline and alkaline earth oxides (MgO, CaO) naturally present in silicate rocks or alkaline industrial residues such as slags from aluminium industry (IPCC 2005).

Alumina production using the Bayer process annually generates a large amount of waste red mud. The disposal of this residue is often expensive and may cause additional environmental problems given its highly caustic nature. The reuse of red mud for other purposes such as wastewater treatment, soil improvement, construction material production, removal of volatile organic compounds, etc. as discussed in section 3.2.4 has been widely studied. Additionally, red mud wastes could potentially be used as an important material for the capture of CO₂ due to the presence of adsorbing oxides and its high alkalinity using the carbonation process (Bonenfant *et al.* 2008a).

Carbonation of red mud is the process of adding gaseous or liquid carbon dioxide (CO₂) to the red mud slurry before discharging into the disposal areas (Cooling *et al.* 2002). The carbon dioxide reacts with alkaline compounds in the slurry to form carbonate species leading to a reduction in pH of the red mud. The carbonation process involves the following reactions:



The first pilot study considering the use of this waste red mud for contacting with CO₂ was implemented by Alcan at their Saramenha Ouro Preto refinery in Brazil in 1983 (Power *et al.* 2011). Subsequently, the process was employed by Alcoa with the aim of lowering the pH of the slurry before disposing of as a dry stacking waste. Many trials were conducted between 1991 and 1996 and these studies confirmed the potential of the red mud as an effective CO₂ adsorbent, for example it was employed at the Kwinana refinery in 2000 (Cooling *et al.* 2002). The carbonation plant established in the Kwinana has operated at the range of CO₂ dose rate varying from 16 to 25.5 kg of CO₂ per kL of red mud slurry (48% wt/wt). It was observed that the lowest pH was 8.5 at the CO₂ dose rate of 25.3 kg/kL under the current operating conditions at the Kwinana (Cooling *et al.* 2002).

Simultaneously, researchers have investigated the use of high pressure of liquid CO₂ in carbonating red mud (Shi *et al.* 2000). In these experiments, red mud slurries were contacted with CO₂ liquid at 297⁰K and high pressure of 6.7-10MPa. The results showed that liquid CO₂ was more effective in pH reduction than vapour phase CO₂, and the initial pH value decreased rapidly to 7-8, and then slowly rose to 9-9.5. The amount of CO₂ sequestered was approximately 2.3g per 100g of red mud. Similarly, bauxite residue was neutralised by CO₂, yielding lower pH and faster kinetics of neutralisation with higher pressures of CO₂. The amount of carbon sequestration potential of annual red mud production (30 million metric tonnes/year) was estimated in the order of 0.029-0.057 million metric tonnes/year (Khaitan 2007). This quantity is small in comparison with annual residues production.

The mineral carbonation process involves in the dissolution kinetics of metallic values in the slurry (Uzun & Gulfen 2007) and is often influenced by temperature, particle size, pH and pressure of CO₂ (Bobicki *et al.* 2012; Prigiobbe *et al.* 2009). The kinetics of red mud carbonation involves in the dissolution of tricalcium aluminate (C3A) and calcite precipitation in solid phase reactions (Khaitan *et al.* 2009). Based on the experiments and data on field (Khaitan *et al.* 2010), it can be concluded that the kinetics of C3A dissolution occurs slowly as the red mud is carbonated, and the dissolved Ca precipitates as calcite, lowering the equilibrium pH of carbonated slurry. Therefore, the dissolution of C3A seems

to be kinetically limited, and it may be accelerated by changing carbonation conditions such as increasing temperature or the pressure of CO₂.

Similarly, researchers (Bonenfant *et al.* 2008b; Huijgen *et al.* 2005) have successfully accomplished the direct aqueous carbonation of steelmaking slags both at ambient conditions and at elevated temperature (100⁰C) and pressure (19bar). The results confirmed that although the extent of carbonation achieved seems to depend primarily on the elemental and mineral composition of the slag, the carbonation kinetics are significantly faster at increased temperature and pressure. Particle size is also important factor affecting the carbonation kinetics, with smaller particles (38-106µm) carbonating significantly better than larger ones (Huijgen *et al.* 2005; Baciocchi *et al.* 2009; Lekakh *et al.* 2008).

Contrarily, a study conducted by Bartzas *et al.* (2010) concluded that the pressure did not appear to largely influence carbonation kinetics, particularly for low ratio values of 0.01 and 0.1 atm. This is probably related to the fact that under the tested partial pressure of CO₂, the carbonation process was kinetically controlled by Ca dissolution rather than by CO₂ diffusion. However, the final carbon content was directly proportional to the partial pressure of CO₂. In other words, when the CO₂ partial pressure increased from 0.2 to 1 atm, the carbon content increased from 0.86% to 1.16%. This is elucidated that it is likely because an increase in pressure of CO₂ raises the dissolved CO₂ concentration lowering pH, and raises the concentration of CO₃⁻ that finally precipitated as calcite. Therefore, further studies on red mud carbonation kinetics should be conducted to develop models for kinetics of the process.

A preliminary study on carbonation of raw red mud to determine the capacity of waste in capturing CO₂ showed that the removal process is rapid and the added carbon dioxide produced a large increase in bicarbonate alkalinity (Jones *et al.* 2006). The raw red mud slurry contacted with gaseous CO₂ at a constant pressure of 68.9kPa, and flow rate of 200mL/minute in a range of different times. Although this is a preliminary study, the capacity of red mud to capture CO₂ has been proven. Based on the amount of CO₂ (4L) captured by red mud and its density (1.87 kg/m³), it is estimated that there are about 7.48g of CO₂ taken up by 10g of wet red mud (Jones *et al.* 2006). In other words, the volume of 748kg of CO₂ (wet weight) was captured by per tonne of red mud.

A research group, led by Yadav *et al.* (2009), studied the sequestration of carbon dioxide by using red mud. Their work set out to determine the main mineral phases in red mud responsible for the carbonation process, and to evaluate the capacity of CO₂ uptake in

different size red mud fractions at the ambient pressure and temperature. The conclusion was that red mud has an effective potential for sequestration of CO₂, and the principal minerals responsible for the carbonation were chantalite (CaAl₂SiO₄(OH)₄) and cancrinite (Na₆Ca₂Al₆Si₆O₂₄(CO₃)₂). In addition, the red mud fraction with the size of 30µm, a pH of 7 and a density of 1.8 g/cm³ was found more effective for CO₂ capture, whilst the carbonation capacity was 5.3g of CO₂/100g of red mud.

Carbonation of red mud could provide an important tool for managing red mud wastes at refineries. It can modify both the physical and chemical properties of the red mud (Power *et al.* 2011). Carbonated red mud dries more rapidly because the surface crust of the red mud is removed; leading to the faster cracking behaviour thereby speeding up the process of evaporation. Furthermore, the carbonation process also improves the mechanical strength of the red mud. These impacts contribute significantly to the long-term utilisation of the residue drying area.

Carbonation of mineral processing wastes is considered to be an inexpensive and safe treatment process that results in the formation of thermodynamically stable products (Huijgen *et al.* 2005). This process could prove to be an effective approach to overcome problems in storing and managing red mud. As well, carbonation of red mud may provide other significant benefits (Cooling *et al.* 2002). It could decrease the risk of seal material failure (clay or HDPE) in the storage pond, thereby reducing the risk of underground water pollution. Further, it could lower the risk of future classification of red mud as a hazardous waste, therefore could improve its usefulness for other purposes such as soil amendment and construction materials. Finally, it could develop the quality of drainage water and reduce the impact of greenhouse gases as well.

From the literature on red mud carbonation, it can be seen that the carbonation process is influenced by a range of parameters, such as pressure of CO₂, chemical and physical properties of red mud. Many studies showed that red mud with different compositions has different capacity of capturing CO₂. Moreover, red mud fraction of different sizes also has different effectiveness of CO₂ capture, as shown for example by Yadav *et al.* (2009). Therefore, mineralogical and chemical constituents of red mud in the carbonation should be also examined in the project.

The literature also showed that the liquid CO₂ seems to be more effective in neutralising red mud than vapour CO₂ phase. This is because the carbonic acid formed in the water with pH values less than 3 neutralises the basic compounds of the red mud leading to the rapid reduction of pH (Shi *et al.* 2000). Additionally, the rate and extent of

red mud neutralisation is directly proportional to the pressure of CO₂. In other words, the higher the CO₂ pressure, the higher the carbon can be captured in aqueous phase, therefore leading to the higher values of carbon sequestration. Hence, it is possible to sequester more carbon if further studies in carbonation in different ranges of CO₂ pressure to be conducted so as to optimise the carbonation process and determine the volume of CO₂ captured by red mud in the efforts of global warming reduction.

3.3. Aims/Objectives of the project

3.3.1. Aims

The principal aim of the project is to develop an effective engineering solution by using red mud to contact with an industrial waste gas – CO₂ in range of different operating conditions in order to optimise the carbonation process and determine the volume of CO₂ captured by red mud. This will lead to the minimisation of the solid waste disposal problem in the alumina industry and the further reduction of greenhouse gas discharging into the environment.

3.3.2. Objectives

The research will focus on the following objectives:

- To study range of operating conditions in red mud carbonation.
- To determine effect of red mud composition and physical characteristics on the carbonation process.
- To evaluate the capacity of raw red mud and seawater neutralised red mud in removing CO₂ in a range of pressures of CO₂.
- To determine the optimal ratio of red mud and CO₂ in the carbonation process and its carbonation conditions.
- To develop models for kinetics of red mud carbonation process.
- To calculate the potential amount of red mud reduced for the alumina industry and the volume of greenhouse gas captured by the red mud.

3.4. Methods

In order to achieve the objectives mentioned above, the following methods will be employed in this research.

3.4.1. Determination of red mud composition

Red mud composition plays an important role in the red mud carbonation; therefore, it will be examined before and after the process. Chemical properties will be determined by analyses and titration. Mineralogical constituents of red mud will be quantified using X-ray diffraction, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy

(TEM) and Atomic Absorption Spectroscopy (AAS) methods. Physical characteristics of red mud, such as specific density and particle size distributions will be determined by measurement using the standard methods.

3.4.2. Carbonation of red mud

Carbonation of red mud will be studied in a carbonation reactor system. Construction of this reactor system will be a vital part of the project.

- The reactor system will be designed to safely operate over the likely range of relevant parameters for the red mud carbonation process (e.g. materials of construction, temperature, pressure, residence time, etc.). The reactor must be controlled to maintain the desired experimental conditions.
- Initial and final pH of the samples will be measured.
- Red mud composition after carbonation will be also determined by analyses and titration. Mineralogical constituents of carbonated red mud will be quantified using X-ray diffraction, Scanning Electron Microscopy (SEM), and Transmission Electron Microscopy (TEM) methods.
- Then, the titration method will determine the degree of carbonation and concentration of CO₂ via changes of alkalinity, carbonate and bicarbonate concentration, and to examine the volume of CO₂ consumed by the red mud
- The carbonation experiments will be repeated in a change of different conditions.

3.4.3. Reaction kinetics

Carbonation reaction kinetics involve in the dissolution of tricalcium aluminate (C3A) and the precipitated of calcite. Thus, all red mud samples will be analysed in order to determine the concentration of Ca²⁺ before and after carbonation process. The Thermogravimetric Analysis (TGA) method will be used for kinetic analyses.

A plot of Ca²⁺ concentration as function of time will be experimentally determined. Then a lead squares kinetic model will be developed.

3.4.4. Methods for alkalinity calculation

After carbonation experiments, data calculation and analyses will be used to quantify the effects on the carbonation process.

Alkalinity calculation and analysis will be based on methods issued by the USGS (2007). In these methods, the following sub-methods will be used: Theoretical Carbonate Titration Curve Methods; Calculation of Alkalinity, Hydroxide, Carbonate, Bicarbonate; and Advanced Speciation Method. The results obtained will be compared with theoretical predictions.

3.5. Significance/Contribution to the Discipline

The expected research outcomes from the project will be:

- Optimisation of the red mud carbonation process under different operating conditions
- Determination of the optimal ratio of red mud and CO₂ in accordance with these conditions
- Calculation of the potential amount of CO₂ captured and mass of neutralised red mud

These outcomes will provide alumina refineries with solutions to the problems involving red mud storage and utilisation. In addition, the project will provide data and information about optimal carbonation process that can be implemented for practical scale up and design of red mud carbonation plant. Finally, the project will support other industries that can use waste from red mud as valuable materials in other purposes.

4. Budget

The list of anticipated costs for the research project are summarised in the following sections:

4.1. Equipment and Materials

The reactor required for red mud carbonation will be constructed in house as a 0.5L stainless steel pressure vessel with a maximum design pressure of 100bar and temperature of 300K. The cost of the pressure vessel with the associated instrumentation is estimated to be \$AUD2,000.

Other equipment items required for carrying out experiments e.g. glassware, pipette, beaker, pH meter, stirrers are available in the lab.

Materials include red mud, CO₂, chemicals, and other consumables required for the project will be purchased when needed.

The costs for materials and consumables are estimated to be about \$AUD1,000 per annum and would be obtained from the School of Chemical Engineering.

4.2. Attendance at Conferences

It is projected that the researcher will attend the conferences related to the research, and may contribute papers to the conferences. The cost for this activity consists of travel and accommodation and so on, is estimated about \$AUD 2,000, and would be funded by the School of Chemical Engineering and other travel support funds.

5. Research Plan, Timeline and Thesis Contents

5.1. Research plan and tentative timetable

Based on the regular timeframe of PhD. research, the research will be conducted within 4 years full time including 6 months of refining research proposal. The tentative time division will be illustrated as follows:

Table 3. Tentative timetables for the research project

Activities	2010		2013		2014		2015	
	Feb-Aug	Sep-Dec	Jan-Jun	Jul-Dec	Jan-Jun	Jul-Dec	Jan-Jul	Jul-Dec
Literature review and proposal writing	Green	Green						
Determination of red mud composition		Blue	Blue	Blue				
Design of carbonation reactor system			Purple	Purple				
Carbonation of red mud			Red	Red	Red	Red	Red	
Study of range of operating conditions in the carbonation			Olive	Olive	Olive	Olive	Olive	
Effect of red mud compositions on the carbonation process				Yellow	Yellow	Yellow	Yellow	
Modelling reaction kinetics for the carbonation process				Green	Green	Green	Green	
Determining efficiency of CO ₂ uptake						Cyan	Cyan	
Publications					Magenta	Magenta	Magenta	Magenta
Thesis writing								Blue

5.2. Proposed contents of thesis

Chapter 1. Introduction to the Study

Chapter 2. Literature Review and Definitions

2.1. Overview of bauxite residue management

2.1.1. *Definition of bauxite residue*

2.1.2. *History perceptive of bauxite residue*

2.1.3. *The nature of bauxite residue*

2.1.4. *The physical and chemical properties of bauxite residue*

2.2. General review of bauxite utilisation

2.2.1. Construction and chemical applications

2.2.2. Environmental and agronomic applications

2.2.3. Metallurgical applications

2.3. Carbonation of red mud

Chapter 3. Experiments and Methodology

Chapter 4. Results and Discussion

Chapter 5. Summary and Conclusion

5.1. Summary of Key Findings

5.2. Further Research

References

6. Other requirements

In order to meet the requirements of School of Chemical Engineering to fulfil the Completion of the Core Component, the project is normally presented at the School seminar. Additionally, the researcher must attend seminar program held by the School for Higher Degree by Research students as a part of the Core Component of the Structured Program (CCSP).

7. References

Agrawal, A., Sahu, K.K. & Pandey, B.D. 2004, 'Solid waste management in non-ferrous industries in India', *Resour. Conserv. Recy.*, 42 (2), 99-120.

Alcoa 2011, *Long term residue management strategy*, Alcoa, Australia, viewed 02 June 2012, <www.alcoa.com/australia/en/pdf/2011_ltrms_pinjarra_refinery.pdf>.

Altundogan, H.S., Altundogan, S., Tumen, F. & Bildik, M. 2000, 'Arsenic removal from aqueous solutions by adsorption on red mud', *Waste Manag.*, 20 (8), 761-767.

Altundogan, H.S., Altundogan, S., Tumen, F. & Bildik, M. 2002, 'Arsenic adsorption from aqueous solutions by activated red mud', *Waste Manag.*, 22 (3), 357-363.

Altundoğan, H.S. & Tümen, F. 2003, 'As(V) removal from aqueous solutions by coagulation with liquid phase of red mud', *J. Environ. Sci. Health A: Tox. Hazard. Subst. Environ. Eng.*, 38 (7), 1247-1258.

Amritphale, S.S., Anshul, A., Chandra, N. & Ramakrishnan, N. 2007, 'A novel process for making radiopaque materials using bauxite-Red mud', *J. Eur. Ceram. Soc.*, 27 (4), 1945-1951.

Bacocchi, R., Costa, G., Poletti, A. & Pomi, R. 2009, 'Influence of particle size on the carbonation of stainless steel slag for CO₂ storage', *Energy Procedia*, 1 (1), 4859-4866.

- Bartzas, G., Xenidis, A. & Papassiopi, N. 2010, 'Carbon dioxide sequestration using bauxite residue slurry: Experimental and modelling studies', *Proceedings of Protection and Restoration of the Environment X*, Corfu, Greece.
- Bertocchi, A.F., Ghiani, M., Peretti, R. & Zucca, A. 2006, 'Red mud and fly ash for remediation of mine sites contaminated with As, Cd, Cu, Pb and Zn', *J. Hazard. Mater. B*, 134 (1-3), 112-119.
- Bobicki, E.R., Liu, Q., Xu, Z. & Zeng, H. 2012, 'Carbon capture and storage using alkaline industrial wastes', *Progress in Energy and Combustion Science*, 38 (2), 302-320.
- Bonenfant, D., Kharoune, L., Sauves, S., Hausler, R., Niquette, P., Mimeault, M. & Kharoune, M. 2008a, 'CO₂ sequestration by aqueous red mud carbonation at ambient pressure and temperature', *Ind. Eng. Chem. Res.*, 47 (20), 7617-7622.
- Bonenfant, D., Kharoune, L., Sauves, S., Hausler, R., Niquette, P., Mimeault, M. & Kharoune, M. 2008b, 'CO₂ sequestration potential of steel slags at ambient pressure and temperature', *Ind. Eng. Chem. Res.*, 47 (20), 7610-7616.
- Borges, A.J.P., Hauser-Davis, R.A. & Ferreira de Oliveira, T. 2011, 'Cleaner red mud residue production at an alumina plant by applying experimental design techniques in the filtration stage', *Journal of Cleaner Production*, 19 (15), 1763-1769.
- Bott, R., Langeloh, T. & Hahn, J. 2002, 'Dry bauxite residue by hi-barR steam pressure filtration', in Chadrashkar, S. (ed.), *Proc. 6th Int. Alumina Quality Workshop*, AQW Incorporation, Brisbane, pp. 24-32.
- Brunori, C., Cremisini, C., D'Annibale, L., Massanisso, P. & Pinto, V. 2005, 'A kinetic study of trace element leachability from abandoned-mine-polluted soil treated with SS-MSW compost and red mud. Comparison with results from sequential extraction', *Analytical and Bioanalytical Chemistry*, 381 (7), 1347-1354.
- Brunori, C., Cremisini, C., Massanisso, P., Pinto, V. & Torricelli, L. 2005, 'Reuse of a treated red mud bauxite waste: studies on environmental compatibility', *J. Hazard. Mater.*, 117 (1), 55-63.
- Cengeloglu, Y., Kir, E., Ersoz, M., Buyukerkek, T. & Gezgin, S. 2003, 'Recovery and concentration of metals from red mud by Donnan dialysis', *Colloids and Surfaces A: Physico-chemical Engineering Aspects*, 223 (1-3), 95-101.
- Cengeloglu, Y., Tor, A., Ersoz, M. & Arslan, G. 2006, 'Removal of nitrate from aqueous solution by using red mud', *Separation and Purification Technology*, 51 (3), 374-378.
- Clark, M.W., McConchie, D.M. & Johnston, M. 2009, 'Bauxite refinery residues, potential for waste utilisation', in J.R. Lavelle (ed.), *Waste management: Research, Technology and Developments*, Nova Science Publishers, Inc., New York, pp. 289-310.
- Collazo, A., Fernandez, D., Izquierdo, M., Novoa, X.R. & Perez, C. 2005, 'Evaluation of red mud as surface treatment for carbon steel prior painting', *Progress in Organic Coatings*, 52 (4), 351-358.

- Cooling, D.J. 1989, 'Developments in the disposal of residue from the alumina refining industry', in Campbell, P.R. (ed.), *Light Metals*, TMS, Halifax, pp. 49-54.
- Cooling, D.J. 2007, 'Improving the sustainability of residue management practices-Alcoa world Alumina', in A.B. Fourie & R.J. Jewell (eds.), *Past and thickened tailings: A guide*, Australian Centre for Geomechanics, Perth, pp. 3-16.
- Cooling, D.J. & Glenister, D.J. 1992, 'Practical aspects of dry residue disposal', *Light Metals*, TMS, pp. 25-31.
- Cooling, D.J., Hay, P.S. & Guilfoyle, L. 2002, 'Carbonation of bauxite residue', in Chadrashekar, S. (ed.), *Proc. 6th Int. Alumina Quality Workshop*, AQW Incorporation, Brisbane, pp. 185-190.
- Couillard, D. 1982, 'Use of red mud, a residue of alumina production by the Bayer process, in water treatment', *Sci. Total Environ.*, 25 (2), 181-191.
- Enick, R.M., Beckman, E.J., Shi, C. & Xu, J. 2001, 'Remediation of metal-bearing aqueous waste streams via direct carbonation', *Energy & Fuels*, 15 (2), 256-262.
- Enserink, M. 2010, 'After red mud flood, scientists try to halt wave of fear and rumors', *Science*, 330 (6003), 432-433.
- Fois, E., Lallai, A. & Mura, G. 2007, 'Sulfur dioxide absorption in a bubbling reactor with suspensions of Bayer red mud', *Ind. Eng. Chem. Res.*, 46 (21), 6770-6776.
- Friesl, W., Friedl, J., Platzer, K., Horak, O. & Gerzabek, M.H. 2006, 'Remediation of contaminated agricultural soils near the former Pb/Zn smelter in Austria: batch, pot and field experiments', *Environ. Pollut.*, 144 (1), 40-50.
- Friesl, W., Lombi, E., Horak, O. & Wenzel, W.W. 2003, 'Immobilisation of heavy metals in soils using inorganic amendments in a greenhouse study', *Journal of Plant Nutrition and Soil Science*, 166 (2), 191-196.
- Genc-Fuhrman, H., Bregnhøj, H. & McConchie, D. 2005, 'Arsenate removal from water using sand-red mud columns', *Water Res.*, 39 (13), 2944-2954.
- Genc-Fuhrman, H., Mikkelsen, P.S. & Ledin, A. 2007, 'Simultaneous removal of As, Cd, Cr, Cu, Ni and Zn from stormwater- Experimental comparison of 11 different sorbents', *Water Res.*, 41 (3), 591-602.
- Genc-Fuhrman, H., Tjell, J.C. & McConchie, D. 2004a, 'Adsorption of Arsenic from water using activated neutralized red mud', *Environ. Sci. Technol.*, 38 (8), 2428-2434.
- Genc-Fuhrman, H., Tjell, J.C. & McConchie, D. 2004b, 'Increasing the arsenate adsorption capacity of neutralized red mud (Bauxsol)', *J. Colloid Interface Sci.*, 271 (2), 313-320.
- Genc, H., Tjell, J.C., McConchie, D. & Schuiling, O. 2003, 'Adsorption of arsenate from water using neutralized red mud', *J. Colloid Interface Sci.*, 264 (2), 327-334.

- Gerrise, B. & Thomas, G. 2008, 'Transport of bauxite residue leachate through clay liners of storage impoundments: A synthesis of experimental and simulated data', *Proc. 8th Int. Alumina Quality Workshop*, Darwin, Australia, pp. 154-161.
- Gong, C. & Yang, N. 2000, 'Effect of phosphate on the hydration of alkali-activated red mud-slag cementitious material', *Cement Concrete Res.*, 30 (7), 1013-1016.
- Gräfe, M., Power, G. & Klauber, C. 2009, 'The Asia-Pacific partnership: An important new initiative for a sustainable alumina industry', *Light Metals*, 5-9.
- Gräfe, M., Power, G. & Klauber, C. 2011, 'Bauxite residue issues: III. Alkalinity and associated chemistry', *Hydrometallurgy*, 108 (1-2), 60-79.
- Green, M. & Boger, D.V. 1997, 'Yielding of suspensions in compression', *Ind. Eng. Chem. Res.*, 36 (11), 4984-4992.
- Gupta, V.K., Ali, I. & Saini, V.K. 2004, 'Removal of chlorophenols from wastewater using red mud: an aluminum industry waste', *Environ. Sci. Technol.*, 38 (14), 4012-4018.
- Gupta, V.K., Gupta, M. & Sharma, S. 2001, 'Process development for the removal of lead and chromium from aqueous solutions using red mud-an aluminium industry waste', *Water Resources*, 35 (5), 1125-1134.
- Gupta, V.K. & Sharma, S. 2002, 'Removal of Cadmium and Zinc from Aqueous Solutions Using Red Mud', *Environ. Sci. Technol.*, 36 (16), 3612-3617.
- Gupta, V.K. & Suhas 2009, 'Application of low-cost adsorbents for dye removal-A review', *J. Environ. Manag.*, 90 (8), 2313-2342.
- György, B. & Tran, M.H. 2008, *Dewatering, disposal and utilisation of red mud*, viewed on 25 February 2012, <www.redmud.org/files/banvolgyi040110.pdf>.
- Haerter, M. & Shefer, B. 1975, 'A new red mud disposal system', *Proc. 9th Int. Manifestation of ICSOBA*, Dubrovnik, Yugoslavia.
- Hanahan, C., McConchie, D., John, P., Creeiman, R., Clark, M. & Stocksiek, M. 2004, 'Chemistry of seawater neutralisation of bauxite refinery residues (red mud)', *Environ. Eng. Sci.*, 21 (2), 125-138.
- Huijgen, W.J., Witkamp, G. & Comans, R.N.J. 2005, 'Mineral CO₂ sequestration by steel slag carbonation', *Environ. Sci. Technol.*, 39 (24), 9676-9682.
- International Marine Organisation 2005, *Report of the twenty-eighth meeting of the scientific group*, Scientific Group Meeting-28th Meeting, IMO, London, UK.
- IPCC 2001, *Climate change 2001: The Scientific Basis. Contributions of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change*, Houghton, J.T., Ding, Y., Griggs, D.J., Nuguer, M., van der Linden, P.J., Dai, X., Maskell, K. & Johnson, C.A. (eds.), Cambridge University Press, United Kingdom and New York.

- IPCC 2005, *IPCC Special Report on Carbon Dioxide Capture and Storage*. Prepared by Working Group III of the Intergovernmental Panel on Climate Change, Metz, B., Davidson, O., de Coninck, H.C., Loos, M. & Meyer, L.A. (eds.), Cambridge University Press, United Kingdom and New York.
- Johnston, M., Clark, M.W., McMahon, P. & Ward, N. 2010, 'Alkalinity conversion of bauxite refinery residues by neutralization', *J. Hazard. Mater.*, 182 (1-3), 710-715.
- Jones, G., Joshi, G., Clark, M. & McConchie, D. 2006, 'Carbon capture and the Aluminium Industry: Preliminary studies', *Environ. Chem.*, 3 (4), 297-303.
- Kalkan, E. 2006, 'Utilisation of red mud as a stabilisation material for the preparation of clay liners', *Eng. Geol.*, 87 (3-4), 220-229.
- Khaitan, S. 2007, 'In-situ neutralisation of stored bauxite residue', PhD. thesis, Carnegie Mellon University, Pittsburgh, Pa.
- Khaitan, S., Dzombak, D.A. & Lowry, G.V. 2009, 'Mechanisms of neutralisation of bauxite residue by Carbon dioxide', *J. Environ. Eng.*, 135 (6), 433-438.
- Khaitan, S., Dzombak, D.A., Swallow, P., Schmidt, K., Fu, J. & Lowry, G.V. 2010, 'Field evaluation of bauxite residue neutralization by Carbon dioxide, vegetation, and organic amendments', *J. Environ. Eng.*, 136 (10), 1045-1053.
- Kirkpatrick, D.B. 1996, 'Red mud production development', in Hale, W. (ed.), *Light Metals*, TMS, Anaheim, pp. 75-80.
- Klauber, C., Gräfe, M. & Power, G. 2009, *Review of Bauxite Residue "Re-use" options*, Asia-Pacific Partnership Project ATF-06-3: "Management of Bauxite Residues", National Research Flagships Light Metals-CSIROs.
- Klauber, C., Gräfe, M. & Power, G. 2011, 'Bauxite residue issues: II. Options for residue utilization', *Hydrometallurgy*, 108 (1-2), 11-32.
- Koumanova, B., Drame, M. & Popangelova, M. 1997, 'Phosphate removal from aqueous solutions using red mud wasted in bauxite Bayer's process', *Resour. Conserv. Recy.*, 19 (1), 11-20.
- Kumar, S., Kumar, R. & Bandopadhyay, A. 2006, 'Innovative methodologies for the utilisation of wastes from metallurgical and allied industries', *Resour. Conserv. Recy.*, 48 (4), 301-314.
- Lekakh, S.N., Rawlins, C.H., Robertson, D.G.C., Richards, V.L. & Peaslee, K.D. 2008, 'Kinetics of aqueous leaching and carbonisation of steelmaking slag', *Metallurgical and Materials Transactions B*, 39 (1), 125-134.
- Li, Y., Liu, C., Luan, Z., Peng, X., Zhu, C., Chen, Z., Zhang, Z., Fan, J. & Jia, Z. 2006, 'Phosphate removal from aqueous solutions using raw and activated red mud and fly ash', *J. Hazard. Mater.*, 137 (1), 374-383.

- Li, Y., Wang, J., Luan, Z. & Liang, Z. 2010, 'Arsenic removal from aqueous solution using ferrous based red mud sludge', *J. Hazard. Mater.*, 177 (1-3), 131-137.
- Lin, C., Maddocks, G., Lin, J., Lancaster, G. & Chu, C. 2004, 'Acid neutralising capacity of two different bauxite residues (red mud) and their potential applications for treating acid sulfate water and soils', *Aust. J. Soil Res.*, 42 (6), 649-657.
- Liu, C., Li, Y., Luan, Z., Chen, Z., Zhang, Z. & Jia, Z. 2007, 'Adsorption removal of phosphate from aqueous solution by active red mud', *J. Environ. Sci.*, 19 (10), 1166-1170.
- Liu, W., Yang, J. & Xiao, B. 2009, 'Review on treatment and utilization of bauxite residues in China', *Int. J. Miner. Process.*, 93 (3-4), 220-231.
- Liu, Y., Naidu, R. & Ming, H. 2011, 'Red mud as an amendment for pollutants in solid and liquid phases', *Geoderma*, 163 (1-2), 1-12.
- Lombi, E., Zhao, F.J., Wieshammer, G., Zhang, G. & McGrath, S.P. 2002, 'In-situ fixation of metals in soils using bauxite residue: biological effects', *Environ. Pollut.*, 118 (3), 445-452.
- Lombi, E., Zhao, F.J., Zhang, G., Sun, B., Fitz, W., Zhang, H. & McGrath, S.P. 2002, 'In-situ fixation of metals in soils using bauxite residue: chemical assessment', *Environ. Pollut.*, 118 (3), 435-443.
- Lopez, E., Soto, B., Arias, M., Nunez, A., Rubinos, D. & Barral, M.T. 1998, 'Adsorbent properties of red mud and its use for wastewater treatment', *Water Res.*, 32 (4), 1314-1322.
- Martinet-Catalot, V., Lamerant, J.M., Tilmant, G., Bacou, M.S. & Ambrost, J.P. 2002, 'Bauxaline: a new product for various applications of Bayer process red mud', in Schneider, W. (ed.), *Light Metals*, TMS, Columbus, pp. 125-131.
- McCarthy, S., Armour-Brown, V.S., Iyer, V.S., Desu, S.B., Kander, R.G. & Vaseashta, A. 1992, 'Utilisation of Jamaica bauxite tailings as a building material and its socio-economic considerations', in Glenister, D.J. (ed.), *International Bauxite Tailings Workshop*, Australian Bauxite and Alumina Producers, Perth, Western Australia.
- Namasivayam, C. & Arasi, D.J.S.E. 1997, 'Removal of congo red from wastewater by adsorption onto waste red mud', *Chemosphere*, 34 (2), 401-417.
- Namasivayam, C., Yamuna, R.T. & Arasi, D.J.S.E. 2001, 'Removal of acid violet from wastewater by adsorption on waste red mud', *Environ. Geol.*, 41 (3-4), 269-273.
- Nguyen, Q.D. & Boger, D.V. 1998, 'Application of rheology to solving tailings disposal problems', *Int. J. Miner. Process.*, 54 (1-4), 217-233.
- Palmer, S.J., Nothling, M., Bakon, K.H. & Frost, R.L. 2010, 'Thermally activated seawater neutralised red mud used for the removal of arsenate, vanadate and molybdate from aqueous solutions', *J. Colloid Interface Sci.*, 342 (1), 147-154.

- Paradis, R.D. 1992, 'Disposal of red mud using wet stacking technology', *Proc. Int. Bauxite Tailings Workshop*, Perth, Western Australia, pp. 179-186.
- Paramguru, R.K., Rath, P.C. & Misra, V.N. 2005, 'Trends in red mud utilisation - A review', *Mineral Processing & Extractive Metallurgy Review*, 26 (1), 1-29.
- Park, S.J. & Jun, B.R. 2005, 'Improvement of red mud polymer-matrix nanocomposites by red mud surface treatment', *J. Colloid Interface Sci.*, 284 (1), 204-209.
- Pawlek, R.P. 2008, *Alumina refineries and producers of the world*, Aluminum, Verlag.
- Piga, L., Pochetti, F. & Stoppa, L. 1993, 'Recovering metals from red mud generated during alumina production', *J. Miner. Metals Mater. Soc.*, 45 (11), 54-59.
- Pinnock, W.R. 1991, 'Measurements of radioactivity in Jamaican building materials and gamma dose equivalents in a prototype red mud house', *Health physics*, 61 (5), 647-651.
- Pinnock, W.R. 1999, 'Radon levels and related doses in a prototype Jamaican house constructed with bauxite waste blocks', *Radiation Protection Dosimetry*, 81 (4), 291-299.
- Pontikes, Y., Nikolopoulos, P. & Angelopoulos, G.N. 2007, 'Thermal behaviour of clay mixtures with bauxite residue for the production of heavy-clay ceramics', *J. Eur. Ceram. Soc.*, 27 (2-3), 1645-1649.
- Power, G., Gräfe, M. & Klauber, C. 2009, *Review of Current Bauxite Residue Management, Disposal and Storage: Practices, Engineering and Science*, Asia-Pacific Partnership Project ATF-06-3: "Management of Bauxite Residues", National Research Flagships Light Metal-CSIROs.
- Power, G., Gräfe, M. & Klauber, C. 2011, 'Bauxite residue issues: I. Current management, disposal and storage practices', *Hydrometallurgy*, 108 (1-2), 33-45.
- Prigiobbe, V., Hanchen, M., Werner, M., Baciocchi, R. & Mazzotti, M. 2009, 'Mineral carbonation process for CO₂ sequestration', *Energy Procedia*, 1 (1), 4885-4890.
- Purnell, B.G. 1986, 'Mud disposal at the Burntisland alumina plant', *Light Metals*, pp. 157-159.
- Shah, R.P. & Gararia, S.N. 1995, 'Upgradation of alumina refinery at Hindalco, Renukoot (India)', in Ivan, J. (ed.), *Light Metals*, TMS, Las Vegas, pp. 25-29.
- Shi, C., Xu, J., Beckman, E.J. & Enick, R.M. 2000, 'Carbon dioxide sequestration via pH reduction of red mud using liquid CO₂', *ACS Division of Fuel Chemistry*, 45 (4), 703-705.
- Singh, M., Upadhyay, S.N. & Prasad, P.M. 1996, 'Preparation of special cements from red mud', *Waste Manag.*, 16 (8), 665-670.
- Singh, M., Upadhyay, S.N. & Prasad, P.M. 1997, 'Preparation of iron rich cements using red mud', *Cement Concrete Res.*, 27 (7), 1037-1046.

- Snar, K.E., Gilkes, R.J. & Wong, M.T.F. 2004, 'The liming effects of bauxite processing residue (red mud) on sandy soils', *Aust. J. Soil Res.*, 42 (3), 321-328.
- Sofrá, F. & Boger, D.V. 2002, 'Environmental rheology for waste minimisation in the minerals industry', *Chem. Eng. J.*, 86 (3), 319-330.
- Soner Altundogan, H., Altundogan, S., Tumen, F. & Bildik, M. 2000, 'Arsenic removal from aqueous by adsorption on red mud', *Waste Manag.*, 20 (8), 761-767.
- Sparks, T. 2010, 'Alumina-Filtration in the alumina production process', *Filtration and Separation*, 47 (3), 20-23.
- Summers, R.N., Bolland, M.D.A. & Clarke, M.F. 2001, 'Effect of application of bauxite residue (red mud) to very sandy soils on subterranean clover yield and P response', *Aust. J. Soil Res.*, 39 (5), 979-990.
- Sushil, S. & Batra, V.S. 2008, 'Catalytic applications of red mud, an aluminium industry waste: A review', *Applied Catalysis B: Environmental*, 81 (1-2), 64-77.
- Sushil, S. & Batra, V.S. 2012, 'Modification of red mud by acid treatment and its application for CO removal', *J. Hazard. Mater.*, 203-204, 264-273.
- Thakur, R.S. & Sant, B.R. 1983a, 'Utilisation of red mud. 1-Analysis and utilisation as raw material for absorbents, building-materials, catalysts, filler, paints and pigments', *J. Sci. Ind. Res.*, 42 (2), 87-108.
- Thakur, R.S. & Sant, B.R. 1983b, 'Utilisation of red mud. 2-Recovery of alkali, iron, aluminum, titanium, and other constituents and the pollution problems', *J. Sci. Ind. Res.*, 42 (8), 456-469.
- Tsakiridis, P.E., Agatzini-Leonardou, S. & Oustadakis, P. 2004, 'Red mud addition in the raw meal for the production of Portland cement clinker', *J. Hazard. Mater. B*, 116 (1-2), 103-110.
- United Nations Industrial Development Organisation 1985, *Environmental Aspects of Alumina Production*, UNEP, Nairobi.
- USGS 2007, *Alkalinity Calculation Methods*, Oregon Water Science Centre, viewed 5 June 2012, <<http://or.water.usgs.gov/alk/methods.html>>.
- Uzun, D. & Gulfen, M. 2007, 'Dissolution kinetics of iron and aluminium from red mud in sulphuric acid solution', *Ind. J. Chem. Technol.*, 14 (3), 263-268.
- Wang, Q., Luan, Z., Wei, N., Li, J. & Liu, C. 2009, 'The color removal of dye wastewater by magnesium chloride/red mud (MRM) from aqueous solution', *J. Hazard. Mater.*, 170 (2-3), 690-698.
- Wang, S., Ang, H.M. & Tade, M.O. 2008, 'Novel applications of red mud as coagulant, adsorbent and catalyst for environmentally benign processes', *Chemosphere*, 72 (11), 1621-1635.

- Wang, S., Boyjoo, Y., Choueib, A. & Zhu, Z.H. 2005, 'Removal of dyes from aqueous solution using fly ash and red mud', *Water Res.*, 39 (1), 129-138.
- Yadav, V.S., Prasad, M., Khan, J., Amritphale, S.S., Singh, M. & Raju, C.B. 2009, 'Sequestration of carbon dioxide (CO₂) using red mud', *J. Hazard. Mater.*, 176 (1-3), 1044-1050.
- Yalcin, N. & Sevinc, V. 2000, 'Utilization of bauxite waste in ceramic glazes', *Ceram. Int.*, 26 (5), 485-493.
- Yang, J. & Xiao, B. 2008, 'Development of unsintered construction materials from red mud wastes produced in the sintering alumina process', *Constr. Buil. Mater.*, 22 (12), 2299-2307.
- Zhang, S., Liu, C., Luan, Z., Peng, X., Ren, H. & Wang, J. 2008, 'Arsenate removal from aqueous solutions using modified red mud', *J. Hazard. Mater.*, 152 (2), 486-492.
- Zhang, Y., Qu, Y. & Wu, S. 2001, 'Engineering geological properties and Comprehensive utilisation of solid waste in aluminium industry', *Environ. Geol.*, 41 (3-4), 249-256.
- Zhu, C., Luan, Z., Wang, Y. & Shan, X. 2007, 'Removal of cadmium from aqueous solutions by adsorption on granular red mud (GRM)', *Separation and Purification Technology*, 57 (1), 161-169.