

Review of Bauxite Residue “Re-use” Options

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EXECUTIVE SUMMARY

This report addresses Item 4 in the schedule of Contract for the Provision of Services number 2490 for the ATF-06-3 project *Management of Bauxite Residues* for the Department of Resources, Energy and Tourism (DRET), Commonwealth Government of Australia. Note that this review is confined to published literature and patents. It does not specifically include those items of industry research except where they appear in the public domain.

The question of what to do with bauxite residue arose with the development of the Bayer process for alumina refining and the recognition that it generated a large amount of waste material. In the subsequent 120 years residues were disposed of with the aim of long-term storage, with a wide range of industry practice depending on local circumstances. Despite over 50 years of research and hundreds of publications and patents on the subject, little evidence exists of any significant utilization of bauxite residue at any time. In this review the reasons are examined, future opportunities are identified, and a way forward is proposed. This review considers all avenues of residue “re-use”, or more appropriately use¹, but concentrates on the *few highest volume uses of lowest risk*. Utilization is considered as taking the residue in some non-hazardous form (as a by-product) from the alumina refinery site and using it as feedstock for another distinct application. Although residues from different bauxites have generic similarities, their specific make-up and residue location can influence their suitability for a given type of use. There are four primary reasons for this inaction: *volume, performance, cost and risk*, with the last two probably being overriding. In terms of cost there are better options for raw material input from virgin sources (lower cost for better grades) that do not come with the same perceived risks as bauxite residue. The risks are composition based, both technical and community perception and relate to: soda, alkalinity, heavy metals and low levels of naturally occurring radioactive material (NORM). Amongst the outcomes of this review are a set of *Research Priority* recommendations to address the *Knowledge Gaps* identified that, amongst other factors, are impeding the implementation of residue use.

The global inventory of bauxite residue stored on land currently is estimated to be over 2.7 billion tonnes, with an annual growth rate of over 120 million tonnes. Although this is one of the largest masses of mineral processing residue globally, it does not mean that bauxite residue storage is a global problem in the same manner as are, for example, greenhouse gases, CFCs, or plastic bags. Bauxite residue is not randomly distributed about the globe in an uncontrolled manner, but predominantly exists in discrete locations at which it is generally well contained, closely controlled and subject to strict regulatory requirements. The residue is necessarily managed on a local basis, in terms of geography, jurisdiction, and operating company. Despite a long-standing recognition of the disadvantages associated with such residue storage, it

¹ Re-use of waste product is the appropriate term for material used and then disposed. Bauxite residue is a waste by product that has not been used so “use” and “utilization” are the more appropriate terms.

has nevertheless continued to be the preferred solution on balance of economic, environmental and social considerations.

To successfully transition bauxite residue from a by-product to be disposed at a cost, to a product of value, will require more than the development of technological solutions. Arguably a choice of technologies already exists to fully utilise bauxite residue. The barriers that will need to be overcome may be summarised as follows:

Volume

- Reuse options must be high volume

Performance

- Substituting for low cost virgin raw materials – performance must equal
- Effective removal/treatment of soda for some applications

Cost

- Evaluating the economics of current BRDA management
- Economics of additional downstream processing
- Co-use of other by-product waste streams

Risk

- Removal of soda, alkalinity and removal or immobilization of heavy metals and NORM
- Lifetime of the secondary product
- Liability issues covering heavy metals and NORM components

Volume: To make a significant impact on the amount of residue stored, uses that will consume large quantities of residue on an ongoing basis are required. Even for relatively low-technology applications (e.g. road base) this would require a large commitment of resources. For high technology applications (e.g. integrated production of metals towards zero waste) the establishment of major industrial plant would be required, which significantly increases the difficulty of implementation.

Performance: The performance of residue in any particular application must be competitive with the alternatives in relation to quality, cost and risk. For example, residue sand as a building material must be competitive with existing resources of mined virgin sand; extraction of iron from residue must compete with established iron ore resources, etc.

Cost: The economic viability for any use option must be demonstrated on a case-by-case basis. The overall lack of progress on use suggests that no strong economic case has been established to date.

Risk: For any given application, it must be *demonstrated that the risk associated with it is less than the risk associated with continued storage*. These risks include health, safety and environmental issues associated with transport, processing and application, and business risk associated with economic costs, product quality and various liabilities. This is not only an issue of alkalinity, heavy metals and NORMs, but also one of product performance. Critically also, the new utilization product must not compromise the production of alumina, which is the primary objective of the alumina refinery.

Factors surrounding risk are the most difficult to quantify, yet risk minimisation is an imperative of current residue management and underpins the strategies of storage and disposal. Implementation of value-adding utilization options is the alternative to continuous improvement of storage practices. As is the case with the value

dimension, risk is a function of local and regional conditions as well as of the technology in question. The perception of bauxite residue as a waste has been established by historical and current practices. The barrier that this presents should not be under-estimated, and stakeholder involvement will be essential for any successful deployment of new products. Whilst the public concern is understandable, the fact remains that very large tonnages of equally (or arguably *more*) hazardous industrial by products such as fly ash are routinely used on a massive scale (31.6 million tons per year in the US as an example). The same outcome should be possible for bauxite residue.

As well as overcoming these intrinsic barriers, implementation of utilization will likely also require incentives to initiate change on a case-by-case basis. These could be provided through direct government support and/or regulation, collaborative arrangements between industry, community and government, industrial synergy projects, or any combination of former.

To provide a framework to move forward, residue utilization has been organized into three Value Opportunities and these are each further divided into three Key Priority Areas (KPAs).

Value Opportunity 1: Construction and Chemical Applications

KPA1: Civil and building construction

KPA2: Catalysts and adsorbents

KPA3: Ceramics, plastics, coatings and pigments

Value Opportunity 2: Environmental and Agronomic Applications

KPA4: Waste water and effluent treatment

KPA5: Waste gas treatment

KPA6: Agronomic applications

Value Opportunity 3: Metallurgical Applications

KPA7: Recovery of major metals

KPA8: Steel making and slag additive

KPA9: Recovery of minor metals

The Research Priority recommendations and associated Knowledge Gaps are tabulated below along with a list of suggested Implementation Support Priorities. The latter recognises that technology is only one dimension of a successful utilization industry.

Research Priorities

Knowledge Gap	Research Project
The development of environmental and agronomic applications of bauxite residues depends on a detailed knowledge of the speciation and physicochemical behaviour of metal ions and complexes as a function of composition and environment. Such knowledge is lacking and it is a critical adjunct to conventional environmental/agronomic research.	Detailed speciation studies on a range of bauxite residues across a variety of conditions and applications. Entails metal ions and complexes, with particular attention to leaching and general physicochemical behaviour of toxic species and naturally occurring radioactive materials (NORMs).
The actual cost (ongoing and future) of current residue storage practices is unknown. This critically impacts on the economics of utilization.	A detailed cost analysis of current residue storage practice including future liabilities. This should be undertaken for several generic refinery locations.
The manufacture of geopolymers based on bauxite residue has been identified as an area of major potential, but the technology has not been developed.	Develop processes for the manufacture of geopolymers based on bauxite residue. This should also include the option of controlled low strength materials. A parallel cost/benefit analysis should also be undertaken.
The potential for high volume use exists in civil construction areas for residue and/or residue components. Local industrial synergies are the key driver but technical gaps exist.	The area of use for civil engineering and construction should be reviewed in more detail. Both in terms of technical requirements for product substitution and opportunities for regional synergies.
A number of processes have been proposed, but never implemented, for the simultaneous recovery of the major metals from bauxite residue (towards “zero waste” objective).	A detailed cost/benefit analysis, of one or more specific process proposals, is needed to establish economic viability. This could range from true zero waste to regional opportunities such as the production of titania from high Ti residues in India.
Accurate information on historical and current storage utilization (types and rates of deposition) on a site-by-site basis is not available.	Establish and maintain a database of the amounts of bauxite residue produced, stored and utilised on an individual refinery basis.

Implementation Support Priorities

Implementation Opportunity	Support Requirement
<p>A number of opportunities have been identified for the application of bauxite residue in construction and materials applications. Implementation of specific opportunities in the APP region could have a significant impact on the rate of residue utilization and conservation of virgin resources. Specific applications include:</p> <ul style="list-style-type: none"> • Additive to Portland cement • Component in light-weight aggregates • Development of sand fraction as a construction material • Component of bricks and blocks • Generic filler & pigment for various materials 	<p>Support may include some or all of the following:</p> <ul style="list-style-type: none"> • Research to refine the technology • Evaluation of product substitution opportunities to create regional synergies • Techno-economic, environmental impact and risk analysis • Product and market development • Development of standards and regulations • Specific incentives to progress
<p>There are many references, particularly patent literature, to applications of bauxite residue as a fluxing agent in steel making. There is however no information on the amount to which this has been implemented or what potential it may have for the future.</p>	<p>A detailed review on the application of bauxite residues as an additive in steel making. Evaluate current usage, technical issues and future potential.</p>

1. INTRODUCTION

This Review is part of the ATF-06-3 project on the Management of Bauxite Residues for the Department of Resources, Energy and Tourism (DRET), Commonwealth Government of Australia, and represents completion of Item 4 in the schedule of Contract for the Provision of Services number 2490. As such it also represents part of the overall commitment of the Australian Government toward the Asia-Pacific Partnership on Clean Development and Climate (<http://www.app.gov.au/>). China and India are also involved in research components of the ATF-06-3 project. Please also refer to the three parallel review documents that relate to Items 3, 5 and 7 in the aforesaid Contract:

DMR-3608 Review of bauxite residue storage practices (Item 3)

DMR-3610 Review of bauxite residue alkalinity and associated chemistry (Item 5)

DMR-3611 Priority research areas for bauxite residue (Item 7)

1.1 Purpose of the Asia-Pacific Partnership (clause 6.2)

The Asia-Pacific Partnership on Clean Development and Climate (APP) brings together Australia, Canada, China, India, Japan, Korea, and the United States to address the challenges of climate change, energy security and air pollution in a way that encourages economic development and reduces poverty. The APP represent around half the world's emissions, energy use, GDP and population, and is an important initiative that engages, for the first time, the key greenhouse gas emitting countries in the Asia Pacific region. With its focus on the development, deployment and transfer of cleaner more efficient technologies, the APP is also unprecedented in the way business, government and researchers have agreed to work together. The APP is also the first time that industry has been afforded an opportunity as equal partners in global climate change discussions.

The objectives for the APP include to:

- *Meet the growing energy needs, reduce poverty and achieve the development goals of partner countries and reduce greenhouse emissions and intensity of partner economies;*
- *Strengthen cooperative efforts to effectively build human and institutional capacity in partner countries;*
- *Actively engage the private sector with considerable marshalling of financial, human and other resources from both public and private sectors;*
- *Demonstrate substantial practical action in the near term as an approach to addressing climate change;*
- *Develop and deploy clean fossil and renewable energy technologies and practice including longer-term transformational energy technology; and*
- *Develop and disseminate best management practice and technology in:*
 - *Aluminium, steel, cement and coal mining industry sectors*
 - *Energy efficiency in building appliances, and*
 - *Power generation and transmission.*

INTRODUCTION

The Project aims to address the high volume of bauxite residue (red mud) produced during the processing of alumina from bauxite. It will identify, develop and deploy technologies and practices for the alternative use of bauxite residues or improved storage practices. Thus the project will enable the development of best practice residue management options to reduce the reliance on stockpiling and storage, or to make stockpiling and storage more environmentally acceptable. [1-3].

1.2 Scope of the review of bauxite residue “re-use” options

The question of what to do with bauxite residue initially arose with the development of the Bayer process for alumina refining in 1887 [4] and the recognition that it generated a large amount of waste material. In the subsequent 120 years the approach has changed from one of unconstrained disposal to that of containment in engineered storages, with a wide range of industry practice. This aspect is outlined in detail in DMR-3608, and as noted therein the current global inventory of residue now exceeds some 2.7 billion tonnes. A number of reviews of what to do with bauxite residue have been previously published [1-3, 5-22] covering various aspects, broad and narrow. This review is one of a coherent series and intended to be considered in conjunction with the on-line residue database BRaDD². The primary aim of this review is to suggest residue use options of most promise, the barriers that exist, and an identification of the knowledge gaps (see also the summary document DMR-3611) so that effective use on a large industrial scale can be most effectively enabled. It is not the aim of this review to identify the utilization option or options that will work.

In the context of this review we define “re-use” or use as taking the residue in some form (as a by-product rather than a waste) from the alumina refinery site and using it for another distinct application, preferably long-term. This is deliberately separated from the case of a well-engineered BRDA being rehabilitated to another use at the end of its storage life, e.g. return to natural habitat or use for agriculture or light industry. This review does not cover utilization options involving BRDA rehabilitation. Although rehabilitation is an option (and is a likely outcome under current planning) use of the residue in large volumes may turn out to be the preferred environmental option, e.g. if it took advantage of the large amount of energy already invested in creating the material and saved the consumption of a traditional virgin resource. Transient “one-off” applications, e.g. for sand mixture used for metal casting moulds [23] or for catalyst applications [8] have little justification for support as they have the same mass of residue at the end of the process that then requires disposal or further utilization.

² BRaDD – Bauxite Residue and Disposal Database is an electronic database covering the widest possible range of information regarding bauxite residue. It is a key part of the ATF-06-3 project. Designed for on-line access by APP countries it is expected to be launched in 2009. As it is a database capable of interrogation to get a wide variety of pertinent information it only requires a regular update of new entries to maintain its usefulness. The intent is that as additional information becomes available, from industry through the APP process, and from China and India, it will be incorporated into the tables as part of the updated on-line BRaDD database.

2. GENERAL REVIEW OF BAUXITE RESIDUE REUSE

2.1 Historical perspective

The process patented by Bayer in 1892 was a breakthrough in mineral processing that enabled alumina to be extracted from bauxite ore economically on a large scale. This process, which is now generally known as “the Bayer process”, was so successful that it became the basis of a major new industry which has since grown exponentially. Bayer himself noted that an inevitable consequence of his process was the production of significant quantities of residue that he recognised as a possible source of iron:

“The red, iron-containing residue that occurs after digestion settles well and, with sufficient practice, can be filtered and washed. Due its high iron and low aluminium oxide content, it can be, in an appropriate manner, treated or with other iron ores be smelted to iron”. (Bayer patent [24])

The concept of bauxite residue as an iron resource has been tested by a number of workers over the intervening 120 years, however an “appropriate manner” of treatment remains elusive. Following the twin breakthroughs of the Bayer process for extracting alumina from bauxite and the Hall-Heroult process for smelting it to metal at the end of the nineteenth century, the production of aluminium, and therefore of bauxite residue, grew rapidly. Dealing with the residue in ways that minimised cost and complexity contributed to the favourable economics of the process and hence to its rapid expansion. As a result, residues were not further treated for the extraction of iron or other metals, but were disposed as cheaply and conveniently as possible for the site concerned. For the first half of the 20th century industry disposal was mostly by the creation of land-based ponds, generally called “red mud lakes”, with a minor proportion being disposed of by direct marine discharge. The inventory of residue on land therefore grew with the industry, reaching a cumulative amount of an estimated 200 million tonnes by 1960 (Figure 1).

During World War II bauxite residues were used as a source of alumina in the USA due to import constraints. The sinter processes used were however expensive, and were abandoned post-war. In the 1960’s attempts to find practical, economic ways of utilising bauxite residue were initiated in the USA. In 1966 the US Bureau of Mines (USBM) initiated a program of research “to determine feasible uses of red mud” [25]. The focus of the work was “to develop methods for directly utilizing or for recovering mineral values from red mud”. The primary motivation for the research was to find a solution to an environmental issue, as indicated by the statement that the residue “presents a storage problem where accumulated in mud ponds and a pollution problem where discharged into rivers” [25]; the creation of value from the residue itself therefore appeared as an enabler to the solution of the environmental issue rather than as an end in itself. The USBM report further identified a variety of ways in which residue could be used, either as a source of metals or for use in building materials of agriculture.

GENERAL REVIEW OF BAUXITE RESIDUE REUSE

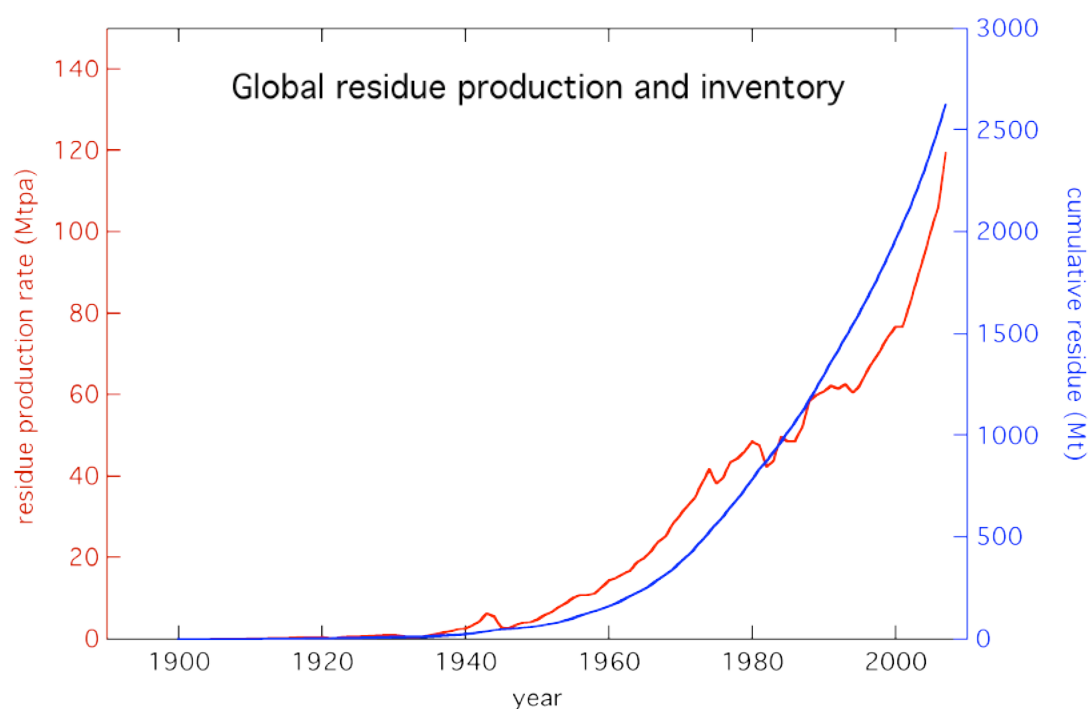


Figure 1: Global production rate and cumulative inventory of bauxite residue³

In the decades since this early USBM work, a considerable body of knowledge has been created in relation to the application of bauxite residue over a broad spectrum of possible uses. However, despite a considerable body of patent and academic literature on the subject, we could find no evidence of residue actually being utilised in any significant quantities to date. The global inventory of bauxite residue has therefore continued to rise in direct proportion to the production of alumina, so that the total amount of bauxite residue stored on land in 2008 is estimated to be over 2.7 billion tonnes (Figure 1).

In the context of the potential to utilise bauxite residue for the extraction of metals other than aluminium, it revealing to note that Bayer patented two processes for extracting alumina from bauxite (Figure 2). The first of these survives today as a minor contributor to the overall industry. The second, patented in 1892, became known as “the Bayer process” and was largely responsible for the major expansion of the industry in the 20th century, currently underpinning the technology of over 95% of alumina production globally. The reason for the limited application of the first process is that it relies on high temperature sintering of the bauxite as a first step. This is effective in breaking down the alumina-containing minerals and rendering them into a soluble form as sodium aluminate, but is highly energy and capital intensive. To this day it is reserved for the more refractory ores such as those

³ Where alumina production data is not directly available, the annual production values have been inferred by applying a factor of 2.1 to the production values for aluminium metal. This factor is calculated from the stoichiometric ratio of 1.9 plus an additional 0.2 to allow for alumina being produced for non-metallurgical uses (8.4% in 2007) [26], and for dust and other losses in the conversion of the oxide to the metal. Bauxite residue tonnage has then been estimated by applying a factor of 1.5 to the alumina production [27].

GENERAL REVIEW OF BAUXITE RESIDUE REUSE

containing diaspore as the main alumina mineral. Such ores are found in northern latitudes and are processed in Russia and China for example. The major expansion of the industry in the latter part of the 20th century was based on the processing of gibbsitic and boehmitic bauxites which are amenable to direct pressure leaching as specified in Bayer's 1892 patent. The large deposits of gibbsitic bauxite that are available in the tropical and sub-tropical regions of Jamaica, Australia, South America and Africa have been a key to the growth of the industry. The focus on gibbsitic bauxites continues.

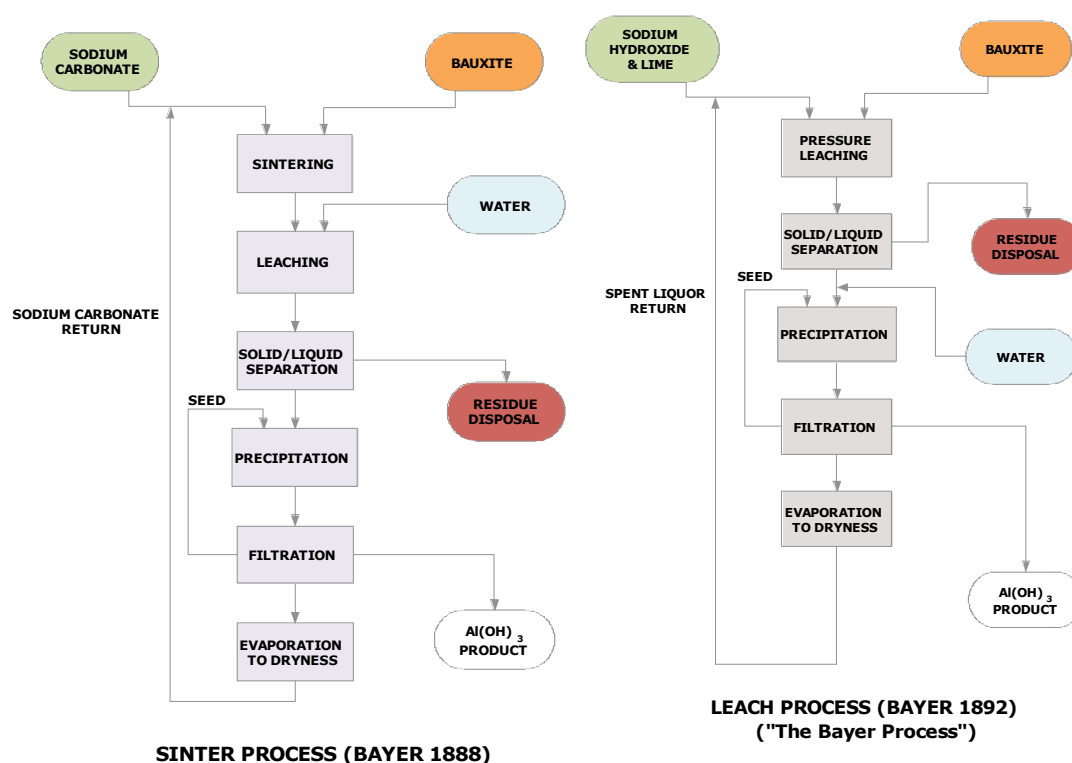


Figure 2: Flow diagrams for the two processes patented by Bayer

The historical success of the leach process over the sinter process is important in the context of bauxite residue utilization as many of the ways that have been proposed for creating value from residue are based on the extraction of metals (iron, titanium, aluminium, vanadium etc.) which in most cases involves high temperature residue sintering as a first step. Note the contrast to the Bayer process whose viability is based on avoidance of sintering. How could such a metal extraction process compete with established methods of smelting high purity hematite (which, like gibbsitic bauxite, are available in abundance) for the production of iron? This perspective reveals one of the reasons for the lack of progress in the utilization of bauxite residue, and highlights the need for overall techno-economic analysis as a starting point for any proposed utilization technology.

Although a “generic” by-product, the actual composition of residue can impact on possible utilization options. Bauxite residues vary in composition and associated properties, both because of differences in bauxite feed and the nature of the Bayer refinery circuit. The residue can also be impacted upon if the bauxite is pre-treated, e.g. calcination [28]. The additional costs involved in materials handling means that

mining old BRDA locations is unlikely compared to the option of using fresh residue streams. In the event of re-mining though, chemical reactions over time within the residue body would alter the utilization approach. The more likely fresh stream residue use has important implications in the nature of final processing, in particular dewatering. For example, the technical advantages of high pressure steam filtration [15, 29] outweigh even the latest conventional thickener technology, increasing solids from some 50-55% to over 75% and with a much lower residual soda content. Any increased capital cost will be partially off-set by producing a more readily usable material.

2.2 Liability – waste, residue or industrial by-product?

Depending upon jurisdiction, untreated bauxite residue may be classified as a hazardous material for transport off-site. Primarily due to its alkalinity [30] rather than heavy metal or naturally occurring radionuclide content (NORM). In the US for example, generally only caustic removal or neutralization would be required prior to transport, this is covered by Subtitle C of the Resource Conservation and Recovery Act (RCRA). Interestingly, the MSDS for Bauxaline® (revision date 24/7/2008) clearly states it to be a non-hazardous product with no transport or regulatory controls (Canada, USA, EU). The substantive processing of residue to produce Bauxaline® is only dewatering. However, from a statutory viewpoint, the NORM content can place residue at the classification boundary between non-radioactive and radioactive. This will vary with bauxite composition and so also between refineries (it can also “change” with time with different bauxite feeds). It is important to realize that the levels of radioactivity are very small. The average refinery yield of 1.75 tonnes of bauxite residue per tonne of alumina, and the 80% extraction of 40% w/w Al_2O_3 graded bauxites (DMR-3610) means that, compared to the original bauxite, the average residue activity level is only ~ 80% higher. In the context of worldwide variations in actual background radiation and subsequent exposure (as opposed to man made exposures through X-rays etc) this is a negligible increase. At present, annual average human exposure from background sources is 2.0 mSv (central value in the asymmetric distribution is 2.4 mSv). However, depending on actual geographic location exposure can be from 1 to 10 mSv [31] i.e. up to 500% larger than the average.

From a viewpoint of residue utilization and public perception, terms such as “waste” and “hazardous material” have negative connotations. Ensuring sufficient soda removal and/or neutralization prior to down stream processing would enable residue to be transported and handled as a non-hazardous material and to be properly designated as a by-product. Exceptions are likely to be location specific cases relating to heavy metal or NORM levels; which illustrates the importance of further research into elemental associations, liberation and chemistry with the various residues. Such scientific knowledge would considerably clarify the liability related issues and aid risk assessments.

It is of some interest to compare the virtually zero utilization of bauxite residue with other industrial wastes or by-products, e.g. coal and fly ash (or more generically coal and combustion products CCP). In the US, the 2007 fly ash production was 71.7 mt of which 44% was used [32]. The concentration of U and Th in fly ash is typically 10-30 and 10-40 ppm [33] so the radionuclide level is similar to bauxite residue. In

GENERAL REVIEW OF BAUXITE RESIDUE REUSE

terms of ^{226}Ra , ^{232}Th and ^{40}K activities comparisons of Hungarian fly ash with Hungarian bauxite residue clearly show the fly ash to be significantly higher for the ^{226}Ra and ^{40}K [9].

Further confusion arises from the promotion and application of proprietary products made from bauxite residue. Registered trade marks and associated technologies can become confusing to potential users if the composition (and hence characteristics) change without notice, or if a given product is re-marketed under a different name. For example BauxsolTM had been promoted extensively [34-49] from the mid-1990's, but BauxsolTM appears to have been renamed or reformulated as the current class of products are termed ViroMineTM and Terra BTM. Whilst it is important to preserve intellectual property rights, the overall success of high volume bauxite residue utilization may well be best promoted through reference to generic technologies. This would also be consistent with a high volume, low margin approach as the most likely to succeed.

One theme that sometimes arises in the “re-use” category is that of accepting the present practice of bauxite residue management and then asking the question of whether the large tonnage of caustic material might not be a suitable material for co-adsorption or sequestration of another pollutant. Examples range from CO_2 [43, 50-52] through to $\text{Hg}(0)$ [53-55]. If the sequestration (such as with CO_2) produces a more benign residue, the process makes sense, but a heavy metal loaded material would be a worse case scenario than untreated bauxite residue. Co-disposal of industrial wastes for an improved waste stability outcome e.g. temporary control of redox potential to meet TCLP [56]; much like deliberate dilution to meet a statutory target, is poor practice. Companies managing BRDA sites would be unlikely to accept co-disposal scenarios. Some recent effort has also gone into leach test design and subsequent formulation of preliminary standards [57, 58]. This is relevant not only to BRDA management but also to testing of down stream products based on residue. Some of the concern has arisen out of the inadequacy of the US EPA Toxicity Characteristic Leaching Procedure (TCLP) test that has been routinely applied to industrial wastes, although it was originally designed only for municipal waste disposal sites [56].

2.3 The nature of bauxite residue

In order to see how bauxite residue may be transformed from a disposal liability to a valuable product, it is useful to consider bauxite residue from two different perspectives. The first is as a mixture of metal oxides and other compounds which exist or would be created upon heating above 1000°C , and which could be separated for the production of the corresponding metals (the “metallurgical” view shown in Figure 3). This quantifies the major components of a “typical” residue (see Table 4 in DMR-3610 for an “average” bauxite residue) as oxides of iron and aluminium, followed by silicon, calcium, titanium and sodium. LOI (Loss on Ignition) represents organic and inorganic carbon and water that is chemically bound in the minerals. This is a typical type of analysis as reported by X-ray fluorescence (XRF). Virtually all sodium and most of the calcium are present as a result of the treatment of the bauxite with caustic soda and lime in the Bayer process. The remainder of the elements originate from the bauxite. This paradigm channels thinking to a limited range of pyro- and hydro-metallurgical processes for the separation of metals from residue [3, 6].

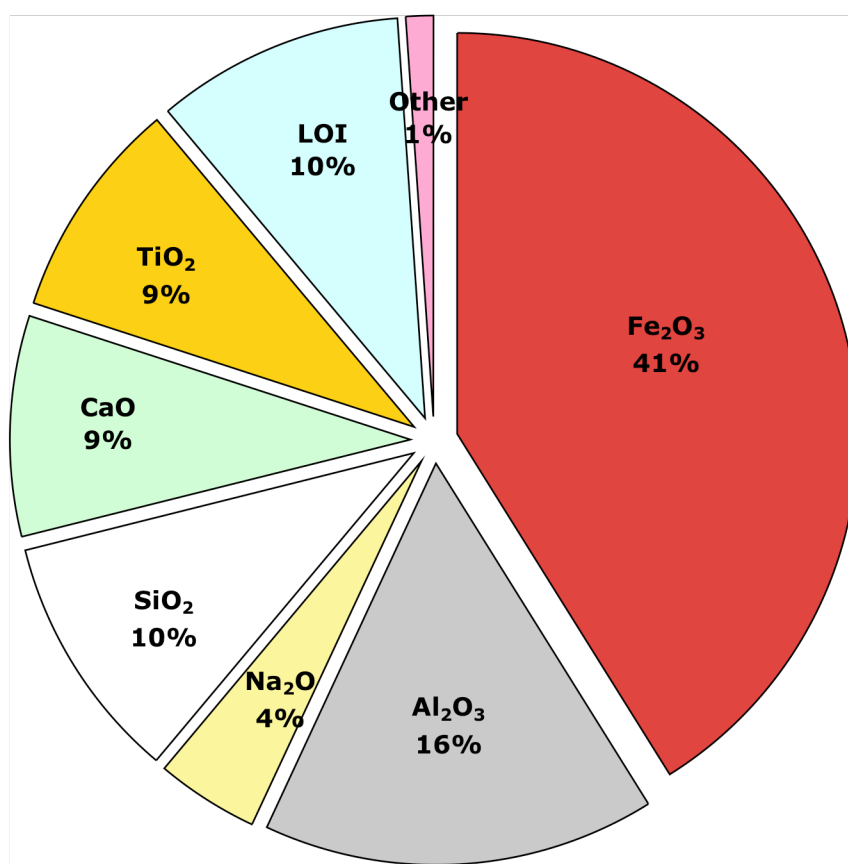


Figure 3: Composition of bauxite residue: metallurgical view (data from DMR-3610)

The second way to view bauxite residue is as a mixture of minerals in various classes, (as shown in Figure 4) that would typically be determined by methods such as powder X-ray diffraction (powder-XRD) for the crystalline components and inferred by other methods for the amorphous fraction. This could be termed the “mineralogical” view, in which the residue is seen instead as a mixture of chemical, physical and mineralogical entities that could be modified to suit specific purposes that take advantage of its specific properties rather than as a source of metals. Such purposes could be to create or enhance soils, as a catalyst or catalyst support, as a filler for plastics or cement, or as a construction material in its own right [2]. Some of the minerals come from the bauxite, but many are either modified or created during the treatment of the bauxite in the Bayer process. The quartz and the titanium minerals are largely unaltered by the Bayer process, but the iron minerals may be altered in composition and proportions from what was in the parent ore. For example a proportion of the original goethite ($\alpha\text{-FeOOH}$) may be converted to hematite ($\alpha\text{-Fe}_2\text{O}_3$), depending on the specific process conditions. The gibbsite ($\text{Al}(\text{OH})_3$) and boehmite ($\gamma\text{-AlOOH}$) in the residue will be a mixture of undigested material from the bauxite and material that has been re-precipitated in the process. Sodalite, cancrinite, dawsonite, and most of the calcium-containing phases are present as a result of the Bayer process.

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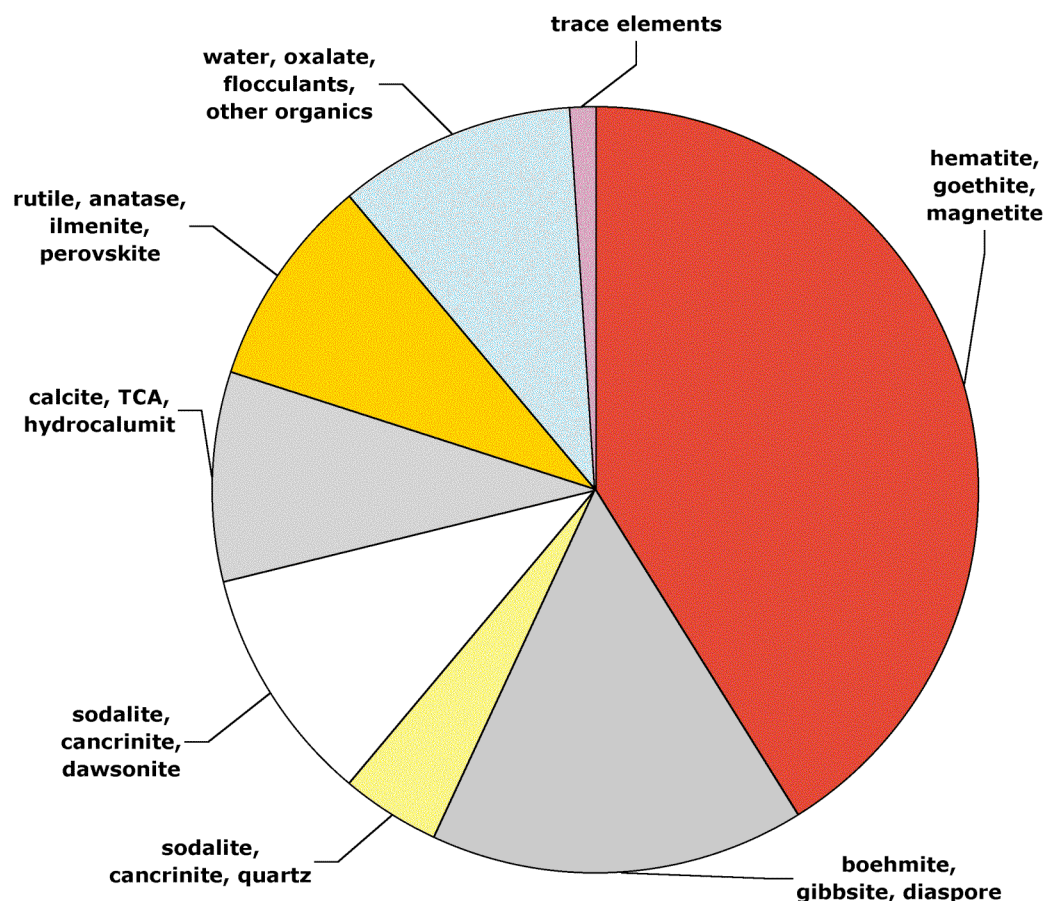


Figure 4: Composition of bauxite residue: mineralogical view (data from DMR-3610)

2.4 General survey of patent activity

A review of the numbers of patents filed as a function of time and area of application provides an indication of the degree of interest in value creation from bauxite residue, and also gives an insight into the areas of most interest. Whilst a useful starting point for analysis, it does not provide information on the plausible implementation of any technology, nor necessarily the volume of residue involved. The patent search was based on the ISI Derwent Innovations Index (Patents) that covers 1960 onwards. Patents prior to 1960 may exist but based on the general literature there appears to have been little interest in uses for bauxite residue in that period and the first patents in this review are from 1964.

Figure 5 illustrates the numbers of patents per decade from 1964 to 2008, sorted across 11 application areas in descending order of total patents. The overall numbers of patents peaked in the 1970's and then declined. By contrast soil related applications have steadily increased. The relative distribution is shown in Figure 6. Noteworthy is that construction applications outnumber each of the nearest three categories by ~2.5 times. Also the top four categories in patent activity all refer to mineralogical applications or the "mineralogical" view of residue.

GENERAL REVIEW OF BAUXITE RESIDUE REUSE

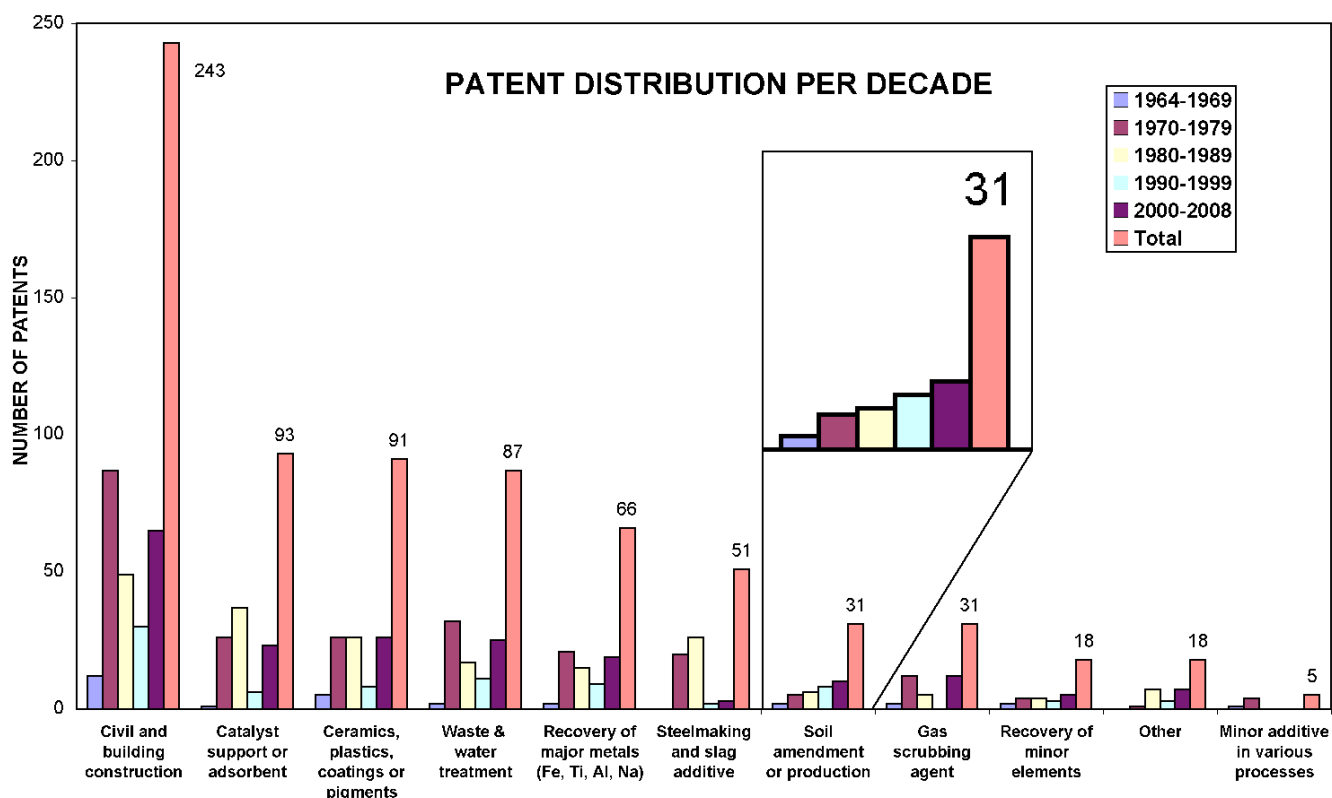


Figure 5: Numbers of patents per decade from 1964 to 2008 as a function of usage classification.

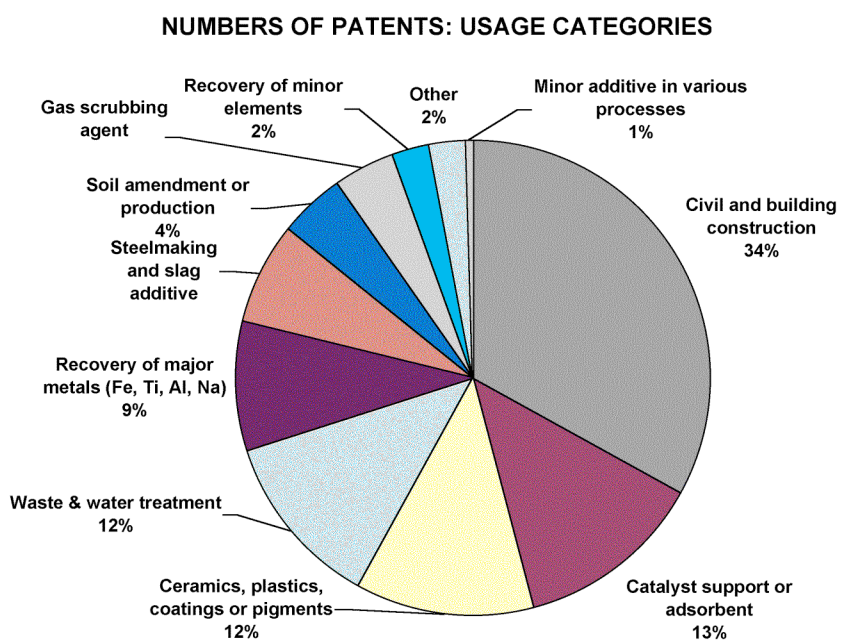


Figure 6: Percentage patents in each usage category for the total of 734 patents discovered in the period 1964 to 2008.

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To fully assess the potential volume of residue that could be viably (both technical and economic) consumed by any of these processes is outside the scope of this review. Nevertheless, the applications related to civil and building construction, soil amendment and production, and extraction of the main metals are all aimed at utilising or treating the residue in bulk, and so can be assumed to have the potential to consume significant quantities of residue if fully implemented. For specific applications (e.g. virgin aggregate) the total consumption is well known and easily exceeds residue production. The other categories relate to the application of bauxite residue as an additive or minor component in a number of materials, and so are unlikely to be high volume. In many cases (particularly in catalyst applications) the residue is listed as a possible but non-essential component. The recovery of high value minor elements could create economic value, but is not able to reduce the overall bulk of residue to disposal.

2.5 Implementation: drivers and barriers

The absence to date of any large-scale utilization of residue does not mean that the alumina industry has been inactive in researching residue utilization, simply that an impasse exists that has not been addressed. As outlined in this and other reviews, there are numerous application possibilities that have been researched and developed over the last five decades, covering a very wide range of possible end uses. These range from low volume boutique applications such as industrial catalysts, through to larger scale uses in building and construction. The reasons for the lack of implementation of residue utilization do not appear to be primarily related to a lack of possible technologies. Although there is little analysis in the literature of drivers, enablers and barriers to progress, logically utilization will have barriers of *volume*, *cost* and *risk* that vary with each application. To analyse the subsequent life-cycle and associated risks of a single end-use is non-trivial, so multiple use applications are unlikely. Chance of success is enhanced with just one or two of the best possible options. Whilst it is useful to review the technology of residue utilization in all areas (especially as it adds to base knowledge of residue chemistry and behaviour) greater consideration is necessarily given herein to the *few highest volume uses of lowest risk*.

The primary barrier of *risk* has three main techno-environmental components; soda, alkalinity, heavy metals and naturally occurring radioactive material (NORM). Something as “simple” as the soda content has enormous technical ramifications in everything from construction applications through to agronomy. By comparison, NORM levels are very low (they represent a negligible hazard) and are technically of little consequence but are significant for public perception. Sodium and alkali content (OH^- , CO_3^{2-}) may or may not require removal or modification (depending upon utilization application). The heavy metal and NORM contents necessitate either removal or immobilization. Removal generates a further waste problem so effective “immobilization” would be preferred. It is reasonable to assume that sodium and alkali levels would most likely be addressed at the refinery and the heavy metal and NORM content would be transferred down-stream with the bulk of the residue. The potential environmental impact highlights the substantial social risk component; that is community acceptance of the utilization option. This should not be underestimated and stakeholder consultation and involvement remain an essential ingredient of any successful utilization. The perceived social risk (eco-systems, human health) could easily restrict use in the developed industrialized world if not conducted properly

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[59]. For example, immobilization in a structural element could be considered acceptable in highway construction but not if incorporated into a domestic dwelling. Notwithstanding engineering or technical advances, only a few applications are ever likely to be acceptable.

Given regulatory permission, residue use requires a seller and buyer such that both parties benefit. The alumina refiner sees *volume*, *cost* and *risk*; the secondary processor sees *volume*, *performance*, *cost* and *risk*; the buyer sees *performance*, *cost* and *risk*. As large volumes of residue are available and assuming technical performance can be met, we are left with the key barriers of *cost* and *risk* in order to progress large scale residue utilization. Consequently, two things are required. Firstly, a sound knowledge of the *total* cost of the current practice of bauxite residue storage. One way of understanding that is to ask the question “what would a given alumina producer pay, at the refinery gate, to have the residue taken away and have no or limited future liability?” Quantifying storage economics and associated liability is the first step that would allow market forces to facilitate utilization options as that cost would mitigate down stream processing costs. A clarification of residue use liability, both in terms of the original alumina refinery as well as the secondary processors would also be useful. This would be irrespective of the role the alumina producers play in the production of residue feed-stock. It is noteworthy that partway through the Peel-Harvey trials of Alkaloam[®], the State of Western Australia and Alcoa World Alumina entered into a deed of indemnity “under which the State agreed to indemnify Alcoa against all actions, proceedings, claims, damages, costs and expenses that Alcoa might be liable for or incur” [60]. As noted in Section 2.2, the extensive use of fly ash may provide some insight into how to deal with liabilities and hazardous materials, not only technically, but in a policy sense. This liability issue is outside the scope of this review, but it is very clear (from known residue characteristics and experiences such as Alkaloam[®]) that it is a real barrier to use and needs to be negotiated. As Harris [61] has noted in the Western Australian context (as an example) “the regulatory process of approval for by-product re-use is at present an arduous process...”.

An important secondary incentive factor is whether a down-stream utilization product could also incorporate other industrial waste streams. The idea of industrial area synergies and complementary chemistries has gained support and is increasingly being applied [61, 62]. This synergy can impact positively on both *cost* and *risk*. Depending upon locality, these waste material volumes can be comparable to that of bauxite residue. Solid waste generation in India [12] has bauxite residue as only 15th in ranking amongst its vast waste array.

In brief summary the key residue utilization issues are *volume*, *performance*, *cost* and *risk*:

Volume

- Reuse options must be high volume

Performance

- Substituting for low cost virgin raw materials – performance must equal
- Effective removal/treatment of soda for some applications

Cost

- Evaluating the economics of current BRDA management
- Economics of additional downstream processing

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- Co-use of other by-product waste streams

Risk

- Removal of soda, alkalinity and removal or immobilization of heavy metals and NORM
- Lifetime of the secondary product
- Liability issues covering heavy metals and NORM components

Volume: To make a significant impact on the amount of residue stored, uses that will consume large quantities of residue on an ongoing basis are required as the production rate of 120M tpa illustrates. Even for relatively low-technology applications (e.g. road base) this will require a large commitment of resources. For high technology applications (e.g. integrated production of metals towards zero waste) the establishment of major industrial plant would be required, which significantly increases the difficulty of implementation.

Performance: The performance of residue in any particular application must be competitive with the alternatives in relation to quality, cost and risk. For example, residue sand as a building material must be competitive with existing resources of mined virgin sand; extraction of iron from residue must compete with established iron ore resources, etc. Specifications for new products must be developed and controlled to meet customer requirements and to ensure customer confidence, even if those products are provided free of charge (i.e. on the basis that the saving in storage costs and other benefits offset the cost of production). For example, the performance of a fertiliser or soil additive would need to be quantified and product quality controlled so that its application could be assessed in relation to other possible fertilisers, and to enable the customer to have confidence in the product.

Cost: The economic viability for any use option must be demonstrated on a case-by-case basis. The overall lack of progress on utilization suggests that no strong economic case has been established to date. Certainly there are no examples that we could locate in the literature of a comprehensive economic analysis that demonstrates economic viability for any utilization option. There are no specific properties of residue that are so unique that would cause the material to displace a virgin raw material in the market place as a feed stock, either now or in the foreseeable future, for existing industrial processes. There are simply better options for raw material input (lower cost for better grades).

Risk: For any given application, it must be *demonstrated that the risk associated with it is less than the risk associated with continued storage*. These risks include health, safety and environmental issues associated with transport, processing and application, and business risk associated with economic costs, product quality and various liabilities. For the fertiliser example, risks related to leaching to groundwater, take-up of heavy metals and NORMs in crops, and uncontrolled dissemination as dust would need to be assessed. This is not only an issue of alkalinity, heavy metals and NORMs, but also one of product performance. Critically also, the new product must not compromise the production of alumina, which is the primary objective of the alumina refinery. Such analysis is an essential precursor to progress.

Given this framework the review is structured in two ways. Firstly, all known possible utilization options have been considered within the scope. Whilst most will not fulfil the key utilization requirements, particularly *volume* and *cost*, much of the applied technical research is generic in the sense that knowledge from research into areas such as adhesives and binders might well have application in soil modifiers etc.

Moreover the technical work can also feed into an understanding of the residue chemistry (DMR-3610). Secondly, the review sets out to identify the best use options going forward, which naturally leads in part to priority research areas (DMR-3611). The review is confined to published literature and patents. It does not specifically include those items of industry research except where they appear in the public domain. It would be expected that any residue utilization work undertaken by industry that was commercially viable would be in the public domain in some form, even if some proprietary aspects were withheld.

According to the literature, the primary drivers for utilization strategies for bauxite residue appear to be related to minimisation of environmental impact and liability, e.g. Fursman [25], from which it is clear that the research was undertaken in order to find possible solutions to a storage and pollution problem, and to do so in such a way for economic benefit in the process. Similar sentiments were expressed in a 1974 review by Thakur and Sant [1] in the context of India becoming a major alumina producer: “the question is: should we continue to throw away red mud at increasing cost in the context of stricter anti-pollution laws? Or, should we find out a technology at least to recover some of the important though minor constituents like vanadium, alkali, etc.?” [1] The authors go on to describe how the whole of the mud could be utilised to produce useful products, including a wide range of major and minor metals (V, Na, Al, Fe, Ti, Ga, Zr, Mo, and even Be), cements and building materials, fillers and pigments, and adsorbents. Their review quotes 108 references related to the utilization of red mud and concludes with the statement that: “The task is by no means easy and both the research laboratories and the alumina manufacturing units will have to make sustained and coordinated efforts to arrive at an economic proposition”. The same authors produced two more detailed reviews on the subject in 1983 [2, 3]. A paper entitled “Recovery of value-added products from red mud” by Mishra et al [17] proposes a “zero waste” method for the production of metals, in particular iron, titanium and aluminium, from red mud.

From these various studies related to the utilization of bauxite residue, it is clear that there are many technologies that exist or could be developed for transforming bauxite residue into useful products. In spite of this, the statements by Thakur et al in their 1974 paper that “Despite prolonged research and a number of patents available, no major industry has come up based on the utilization of red mud”, and “except for minor use in cement and roads, red mud is hardly being utilized ... as a major raw material” [1] remain as true today as 35 years ago.

2.6 Perspective: global versus local

Discussions on the need to reduce the amount of bauxite residue being stored are generally framed in a global context, as we have done in the introduction to this review by drawing attention to the 2.7 Bt of residue currently existing and the increasing rate of production globally. A similar approach was taken in the formulation of the Alumina Technology Roadmap (AMIRA) [63] by the industry, and is common in the introductions to studies, patents and reviews on the subject [5].

While there is a large and ever increasing amount of bauxite residue being stored globally, and that this is an issue that needs to be addressed, it does not mean that residue storage is a global problem in the same way as many pollutants (greenhouse

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gases, CFCs, or plastic bags, for example). The *key distinction* is that bauxite residue is not randomly distributed in an uncontrolled manner, but exists in discrete locations that are generally well contained, closely controlled and subject to strict regulatory requirements. Bauxite residue is necessarily managed on a local basis, in terms of geography, jurisdiction, and operating company. This has a number of implications for the transition of bauxite residue from a waste to be disposed at a cost to a product with value to be gained. These may be summarised as follows:

- Bauxite residue is managed by the operators of the associated Bayer process plants as an essential part of the overall operation. Such operations are conducted within the laws, regulations and practices that apply at the specific location, and according to the operating practices and engineering requirements of the operating company as they apply to the individual plant.
- Apart from general guidance discouraging maritime disposal [64], there appear to be no globally binding laws or standards that apply to bauxite residue.
- Management of bauxite residue is carried out in such a way as to optimise the requirements of the economic, environmental and social factors and legal requirements which apply at the location.
- Any departure from established management practices will inevitably be seen by operators, governments and communities as potentially leading to increased risk. Any such departure, such as establishing a new product stream from a previous waste stream, must therefore meet stringent requirements in relation to the applicable economic, environmental and social factors and legal requirements in order to be even considered, let alone to succeed.

In combination the above factors act as a powerful deterrent to change. Thus, while the environmental disadvantages associated with residue storage are an important consideration, a sole focus on that is unlikely to stimulate a major shift from storage to utilization. In order for such change to occur:

- The nett value created by the change must be significantly and demonstrably greater than the cost of the current practice.
- The risk profile (environmental, economic, social and legal) associated with the change must be less than for the current practice.
- There must be specific incentives to trigger the change on a case-by-case basis.

2.7 The way forward: value opportunities and risk

2.7.1 Value opportunities

As discussed above, there are two broad utilization classes for bauxite residue that have the potential to create value. These we have referred to as the “mineralogical” and “metallurgical” applications. Of necessity the demonstration of net value is a case-by-case issue, but for the discussion of value creation we will designate three broad Value Opportunities:

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Value Opportunity 1: Construction and Chemical Applications

Value Opportunity 2: Environmental and Agronomic Applications

Value Opportunity 3: Metallurgical Applications

The categories identified in the patent review can be used to as a starting point for separating the Value Opportunity (VO) sub-categories (Key Priority Areas, or KPAs). We have added Agronomic Applications as an additional KPA because, although not highlighted in the patent literature, is an area prominent in the academic literature and clearly has high potential for large-scale beneficial applications. The resulting VO/KPA relationships are shown schematically in Figure 7. Furthermore, it is the only application area in which the number of patents filed has steadily increased over the last four decades.

The challenge (for the industry, governments and other stakeholders) is to work together to identify specific projects within particular KPAs for development on a priority basis. This would most likely be a site by site or regional basis before any implementation of utilization projects globally.

2.7.2 Risk management

Risk minimisation is the current imperative of bauxite residue management and underpins the current strategies of storage and disposal. The main response to increasing environmental awareness and the corresponding increase in environmental regulation has been to improve the technology and practices of residue storage to meet evolving expectations and continuously improve risk management. This has led, for example, to moves away from marine disposal, development of dry stacking, improved lining systems for impoundments, better dust management, and increasingly sophisticated methods for the management of ground and surface waters (for more detail on management practices see DMR 3608). Utilization is the alternative to continuous improvement of storage practices. The risk profile associated with change to utilization has the elements as outlined in section 2.5.

GENERAL REVIEW OF BAUXITE RESIDUE REUSE

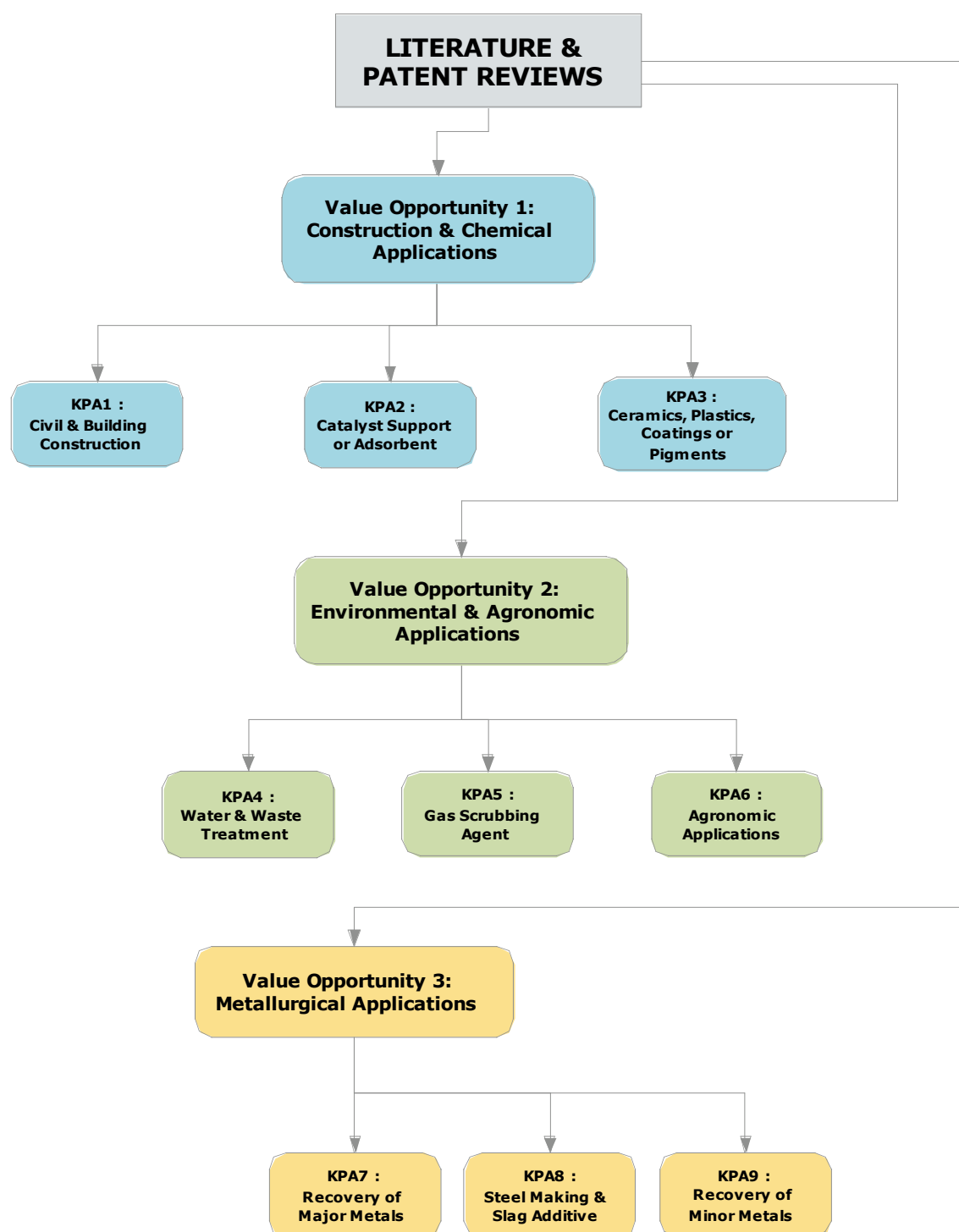


Figure 7: Organisation of Value Opportunities into Key Priority Areas.

3. DETAILED LITERATURE AND PATENT REVIEW OF RESIDUE REUSE

The literature on bauxite residue utilization is concerned primarily with the technical aspects. Environmental aspects are generally discussed only to provide justification for pursuing utilization options; with the exception of agronomy, environmental issues related to utilization options are seldom mentioned. Similarly, economic aspects are seldom discussed; couched in terms of the potential value of the proposed product, ignoring the costs of production, the volatility of price and other matters essential to a sound economic evaluation. Issues related to stakeholders, legal liabilities, government regulation and product quality assurance are also rarely mentioned. It is noted that *consideration of these non-technical aspects is an essential adjunct to the technology in the development of residue use*. This review of utilization options has been arranged according to the Value Opportunity structure described above in section 2.7. Some sense of where the applications of most interest are can be gained by analysing the Chemical Patents Index Manual Codes or CPI Manual Codes. Also sometimes referred to as “Derwent classification codes”. This is a proprietary alpha-numeric patent classification code within the Derwent World Patents Index (DWPI). The results of CPI codes analyses are presented in this section for each sub-category of application, i.e. on a KPA basis and provides a basis for initial ranking of applications, which are then further discussed in relation to the results of the review of the published literature.

3.1 Construction and chemical applications

Value Opportunity 1, Construction and Chemical Applications, includes the following three Key Priority Areas: Civil and Building Construction, Catalyst and Catalyst Support or Adsorbent, and Ceramics, Plastics, Coatings or Pigments. 463 patents were filed in this category between 1964 and 2008, which is 59% of the total number of patents relating to bauxite residue in that period. This relatively large number of patents is indicative of the potential for use of large amounts of residue in this category of applications.

3.1.1 KPA 1: Civil and building construction

The results of CPI codes analysis of the patent search in this category (Figure 8) show that 10 of 61 codes accounted for 81% of all the code allocations in this grouping. The most frequently used code was L02: “Refractories, ceramics, cement”, which was associated with 218 (90%) of the 242 patents in this group. Two other codes, P43: “Working cement, clay, stone” and Q41: “Road, rail, bridge construction” also refer specifically to structural applications.

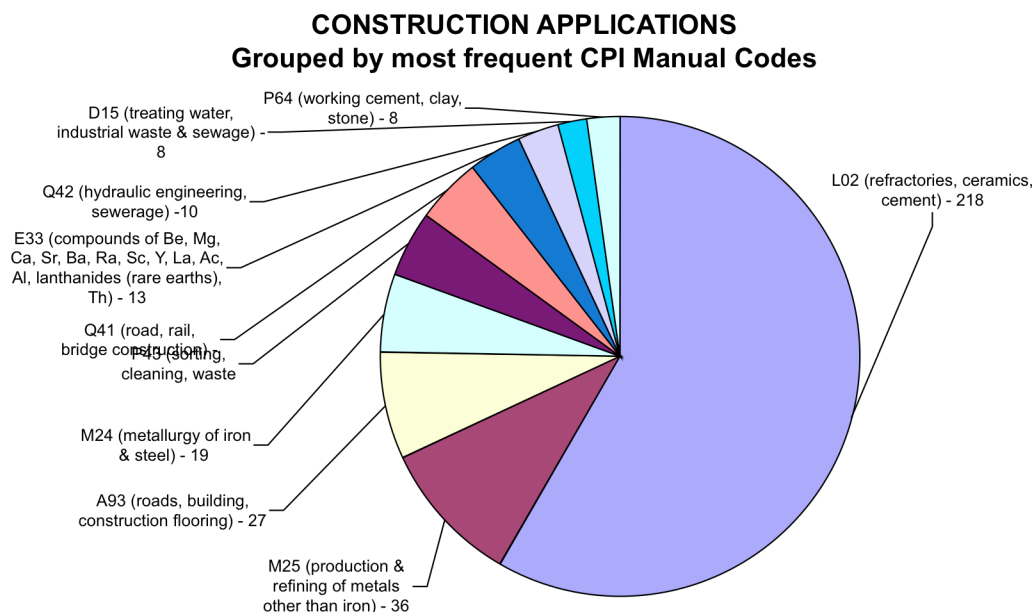


Figure 8: Chemical Patents Index (CPI) Manual Codes analysis for construction applications. These 10 codes account for 81% of all code allocations in this category. The number of times each code allocated across the 242 patents is also shown.

Building materials stand out as an application which could consume significant residue volume. Concrete is the dominant construction material in the world today, so the addition of residue to cement and/or concrete in any significant amounts, or as a geopolymer replacement, presents a value opportunity. For example annual crushed stone aggregate consumption in the US amounts to 1.63 billion tonnes per annum (5-year average, 2004-2008) [65] with worldwide consumption in the order of 20 billion metric tonnes, compared to some 120M tpa bauxite residue estimate. A re-processed residue product that emulates an aggregate would only need to meet specification/cost parameters for <0.5% of applications to consume the entire world-wide residue production. Aggregates generally either become foundation bases or encapsulated in concretes, leading to long cycle lives, minimum human contact and minimization of toxicity and NORM issues. The use in concretes is particularly attractive as the process of aggregate synthesis would be expected to effectively inert the residue, moreover the encapsulation would further improve safety. Engineering requirements for aggregate are primarily compressive strength. The same possible usage figure arises from cement volumes. The annual global production of cement in 2008 was 2.9 Bt [66] and as cement accounts for only about 10-15% of concrete volume (and hence approximately the same % w/w) the global annual concrete production is up to ~29 Bt. Hence, the incorporation of bauxite residue into concrete via cement at just 0.4% would be sufficient to consume all annual bauxite residue production.

A number of partial reviews of building materials applications (aggregates, bricks, cement, concrete and road materials) have been published, e.g. [2] and references therein. As a generalization the primary liability is the sodium content, especially for structural elements requiring strength. Substitution of monovalent Na^+ with divalent cations such as Ca^{2+} can significantly improve the properties of residue and their

applicability in construction applications. Residues naturally high in 2CaO-SiO_2 have been used untreated for road base [2].

3.1.1.1 Cement

The use of bauxite residue as an additive to Portland cement has been the subject of a number of studies from as early as 1936 [2]. The iron and alumina contents of the residue can be beneficial to the setting and strength properties of the cement, but the soda is detrimental. Replacement of the soda with calcia improves the performance of the residue as an additive. It should be noted that in this application the residue has to be calcined to temperatures in the order of 1000°C , either as a pre-treatment or in combination with the production of quicklime.

Singh et al [67, 68] investigated using of mixtures of gypsum, bauxite and bauxite residue in the preparation of special cements. Residue was chosen as a source of alumina and iron in preference to other industrial by-products because of its low silica content, and it was found to perform better than fly-ash. By optimising the firing temperature and the composition of the mix it was possible to prepare cements with superior setting strengths to ordinary Portland cement, with red mud additions in the range 20 to 50% by dry weight. The bauxite and residue used were sourced from the HINDALCO Renukoot plant and used as received, without causticization or washing. The titanium content of the mud was found to be beneficial to concrete strength [67, 68].

Bauxite is commonly used directly in cement-making as a source of alumina and iron for the production of both Portland and calcium aluminate cements. The global usage of bauxite in this application in 1999 was estimated at 1.0-1.2M tpa, making its use as a cement additive the largest non-metallurgical use of bauxite [69]. However, this is less than 1% of the total production of bauxite [70] in the same year, so even if all of the bauxite additive to cement could be substituted by residue it would account for less than 1.6% of the annual production of residue. Nonetheless, raw material cost is a factor limiting increased usage of bauxite in cement applications, so there is the possibility that if suitable bauxite residue could be supplied at lower cost (assuming the technical feasibility of the application) then usage rates could be increased. The key components of delivered cost are processing and transport costs. Hence, applications that require minimal processing of the residue and are implemented locally should be favoured, especially if other incentives apply. An example is the potential application of bauxite residue to cement manufacture in Greece. Recent studies by Tsakiridis et al [71] and Vangelatos et al [72] have examined the feasibility of using residue as a minor additive to Portland cement in the local cement industry. The work was carried out under a government-sponsored project aimed at utilising red mud in construction materials as part of a program to mitigate seawater disposal of residue from the Aluminium Hellas plant. A pilot-scale study has demonstrated that Portland cement with acceptable properties can be prepared containing up to 5% residue, which if incorporated into the cement production in Greece would consume all of the residue produced by the Hellas plant. The cost of processing the residue for incorporation into the cement was estimated at €10/tonne of dry residue, most of which is due to the need to pressure filter the residue prior to addition to the raw cement mix [72].

3.1.1.2 Aggregate

The major component of concrete is the inert aggregate that is bound together by the cement. Aggregates may consist of a wide variety of materials, but are classified as either coarse or fine. In its most basic form, the coarse aggregate is natural gravel or a coarse fraction of crushed rock and similarly, fine aggregate is native or synthetic sand. There have been many studies and a number of patents on the production of coarse aggregates from bauxite residues, in particular from the finer “mud” fraction.

The preparation of aggregates from red mud requires a number of processing steps, including drying, pelletizing and calcining. Although it seems unlikely that an aggregate based on residue could be competitive with other alternatives (e.g. crushed stone), because of the cost of calcination [73], the published work on this as a residue utilization option appears contradictory. For example Sagoe-Crentsil and Brown [74] imply that residue could replace the aluminosilicate fractions for geopolymers, but base this on work combining a synthetic alkali waste stream (8.9 % w/w Na₂O, 28.7 % w/w SiO₂ and 62.5 % w/w H₂O) with fly-ash. Whilst the test materials only required mixing and curing at 85°C for 2 hours and could exhibit (depending on sodium, silicate and aluminate ratios) compressive strengths of almost 50 MPa; this is not the same as actually testing residue. Moreover, a fairly typical lake water from a BRDA might have S of 35 g/L Na₂CO₃, an A/C of 0.4 and C/S of 0.65 (see glossary); which equates to about 2 % w/w Na₂O, 2.1 % w/w Al₂O₃, and so is a substantially weaker alkali stream. Evaporatively increasing concentration would be of limited use as the alkali would completely carbonate. As noted earlier compressive strength is one of the key attributes for aggregate substitution. For comparison the compressive strength of a natural marble might range over 100-180 MPa, so a geopolymer of up to 50 MPa would have limited applications. Composites based on lime, silica and limestone to Jamaican residue [75] only managed compressive strengths of 22 MPa. Compressive strengths of gravels used in concrete manufacture vary widely [76] depending upon source, typically ranging 165-235 MPa, with >94% of aggregate used for gravels having over 70 MPa compressive strength. Direct drying and firing of residues may produce acceptable synthetic aggregates. Showa Denko et al. filed a series of patents [2], [77-80] with firing conditions such as 220°C for 40 min, then 1200°C for 2.5 hours which produced a product with compressive strength comparable to or better than gravel. Firing or sintering to produce a low value material such as aggregate obviously has problems and the preferable route would remain some type of geo-polymer reaction. Nonetheless it would be worthwhile to at least consider the approximate economics of sintering. Knowing green density, sintered density, loss on ignition and heat capacity characteristics enables at least the energy requirements to be determined.

The issue of calcination cost may also not be as negative as initially perceived. In the Australian context, aggregates for construction are typically crushed basalts with a feldspar-olivine composition (blue metal). A cost of ~A\$50 m⁻³ relates to ~ A\$30 per tonne (depending upon aggregate). Prices in the US are much lower, about US\$9 per tonne [65]. This price range does not allow for expensive processing. As a guide, ordinary Portland cement is a world traded bulk commodity, with a generally stable price; average price for US cement 1999-2003 was US\$77.07 per tonne [81] and leading up to the world boom of 2004-2007, some US\$93.50 per tonne [82]. At an exchange rate of US\$0.70 this would reasonably reflect a long-term average of some A\$110-134 per tonne. One of the key aspects of cement production is that because

calcining to high temperatures (1400-1500°C for long periods) is a major part of the process it can provide a very good guide to the likely costs of heating a material on a large scale with no fuel value and low input costs for raw materials (as opposed to roasting a sulphide ore which has fuel value). For cement production, fuel costs are the main cost for calcining to clinker and power costs for grinding the clinker to cement. In Australia total energy costs (calcine and grind) are around 20% of production costs [83], with fuel and power about equal contributors. It would therefore be reasonable to assume that a high temperature residue treatment could be undertaken at approximately A\$22-27 per tonne, less than the cost of aggregate.

Light-weight aggregates

The preparation of special light-weight aggregates (LWAs) is another area of possible application for bauxite residues. LWAs are in increasing demand for the production of light-weight concretes for applications such as high-rise buildings, particularly in areas of high earthquake risk. They are good insulators (heat and sound) and are fire-resistant [84]. LWAs are prepared by calcination of raw materials that contain chemically bound water or carbonate, which can be calcined to form porous granules with low specific gravity and impervious outer surfaces. Bauxite residues can be used as a raw material in LWA production because they contain a number of suitable hydroxide minerals (e.g. gibbsite, boehmite, goethite) and carbonates. The percentage of bauxite residue in the mix could be as high as around 30% w/w in combination with a range of other materials, and the mixture is calcined at temperatures in the range 1000-1300°C (JP720158391B, JP10011524-A, JP790114603B, JP51026923-A, JP54003831-A, JP56096768-A, DE3339575-C2, KR2003011756-A, JP2004299950-A, KR812670-B1). While the use of bauxite residue in the preparation of LWAs is technically feasible, we could find no examples of comparisons with competing materials, of implementation or of economic analysis in this area.

Low-Strength Aggregates

In the utilization industrial by-products, an alternative to the manufacture of high-strength construction materials is the production of controlled low strength materials (CLSM) for certain applications. CLSM is mainly used for filling cavities in civil engineering works, particularly if future excavation may be required. The key characteristics required of these materials are therefore low mechanical strength and good flowability. Katz and Kolver [85] have described techniques for producing CLSM from fly ash, cement kiln dust, asphalt dust, bottom ash, quarry waste and crushed sand, using ordinary Portland cement as a binder and encapsulating agent. It was found that materials with satisfactory mechanical properties could be produced with minimal amounts of added cement, and that the leaching rates of most trace metals was significantly less for the CLSM than for the untreated material.

The production of CLSM from bauxite residues can be expected to be problematic because alkali levels in the pore water and the presence of sodalites (desilication products) in the solids, but the high moisture may be an advantage in reducing the requirement for added water. For those residues with a high sand fraction the separation of the sand further treatment and use as CLSM may be feasible. In any case, careful testing would be required to ensure that compliance with environmental requirements were met, particularly in relation to leachability and radiation standards.

Sand substitution

The preparation of fine aggregate, or sand, is a significant opportunity for some bauxite residues. In particular, the residues produced from the bauxites of the granitic areas of the Darling Range contain a high sand fraction, typically around 50% w/w. This has led to the development of coarse red sand a potential product for use in cement mix [86] or as a construction aggregate in its own right [87].

Coarse red sand has also been evaluated as a component of road base. The sand was mixed with fly ash, lime kiln dust and cement to produce a stabilised pozzolanic mixture suitable for the production of an improved base material for road construction in Western Australia [88]. Road making alone could consume very large quantities of residue sand. For example, the construction of the recently completed Perth to Bunbury Highway (70.5 km of dual carriageway construction) alone required 12 million tonnes of sand [89]. The rate of total residue production of the Alcoa's three refineries in Western Australia in 2007 was approximately 17M tpa, so the amount of sand produced was about 8.5M tpa (BRaDD). Allowing for about 25% of the sand to be retained for use in the construction of residue storage areas themselves, diversion of the remaining 6.4M tpa of sand production to the construction of the highway would have potentially consumed 2 years worth of coarse red sand production, with the added benefit of reducing the need for extraction of natural sand, a finite resource, for construction purposes [87]. From a global perspective, 6.4M tpa is approximately 5% of world residue production, so successful implementation of coarse red sand as a construction material on an ongoing basis would make a significant impression on the residue storage where sand fractions are high.

Of all the possible applications of bauxite residue, the use of coarse red sand in construction applications is technically simple. Size separation and washing followed by neutralisation (e.g. with CO₂), then further washing and drying. Even so, there are a number of significant technical and non-technical barriers to implementation. For example, the elements that would need to be addressed for any successful utilization would include:

- Completion of all necessary testing and technical studies required for certification of the product in the proposed applications.
- Confirmation of the sustainability of the venture, in particular its long term economic viability, environmental soundness, and community acceptance.
- Ensuring that the residue utilization operation did not compromise the core refinery business.
- Raising the necessary capital to fund the project.
- Establishment of suitable processing plant and integrated distribution systems.
- Stakeholder acceptance of the new product and its development within an existing raw materials extraction and supply business network.
- A favourable commercial and regulatory environment.

Investigations of local synergistic opportunities in cement, aggregate and sand applications could result in medium to high volume use for bauxite residue.

3.1.1.3 Bricks and blocks

There are two distinct approaches to brick and block manufacture from the fine fraction of bauxite residue depending on whether the material is kiln fired or not. Conventional clay bricks are fired at around 1000 °C to achieve the required strength. Unfired bricks are made by including cement or other inorganic or organic binders.

According to the review by Thakur and Sant [3], residue can be added to the mix as either a major or minor component. It has been shown that bricks of comparable quality to commercial clay bricks can be prepared from bauxite residue mixed with natural materials such as clay or shale. Other waste products such as fly ash and coke dust may also be added. Lightweight bricks can be manufactured by including other additives such as ferrosilicon and foaming agents. Unfired bricks can be prepared with bauxite residue as either a major or minor component by including setting agents, which may be inorganic (gypsum, lime, cement) or organic (polymethyl methacrylate, polyvinyl acetate, etc) [3].

Our patent search revealed 14 patents in the period 1972-2008 relating to the manufacture of bricks with red mud. Of these, 3 referred to fired and 11 to non-fired bricks, as summarised in Table 1. Fired bricks can be made with up to 92% red mud at relatively low temperatures (around 1000 °C). Clay and various other materials can be incorporated including fly ash and various other industrial by-products, according to the availability of the ingredients and the desired properties of the product. The manufacture of non-fired bricks requires the incorporation of one or more binding agents. The most popular binding agents are calcium-containing compounds, most often quicklime, limestone or gypsum. One patent (NL1035134-C6) uses rice chaff as the binder, which it is claimed acts by forming silicates by reaction with the alkali in the mud. Organic polymers have also been used.

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Table 1. Summary of patents relating to bricks containing red mud.

Fired Bricks				
Patent No.	Year	% Mud	Firing Temp. (°C)	Other Components
DE2063028-B	1972	50-92	900-1000	Clay
CN14200097-A	2003	?	?	Fly ash, ore tailings, phosphorous dregs, slag, sand, sulphuric acid residue
CN101269948-A	2008	70-90	900-1200	Clay
Non-Fired Bricks				
Patent No.	Year	% Mud	Setting Agent	Other Components
JP54039436-A	1979	?	Cement Lime Gypsum	Borax
CN107942-A	1995	?	Lime Gypsum	Coal ash Sand
DE4430446-A	1995	>50	Ca compounds	
KR2006079292-A	2007	12-22	Unspecified	Lime waste
CN101020603-A	2008	15-50	Lime	Fly ash Silica sand
CN101205126-A	2008	22-40	Lime Gypsum	Fly ash Aggregate
CN101215142-A	2008	20-35	Cement Plaster	Fly ash Acetylene sludge Slag
CN101219883-A	2008	22-42	BaSO ₄ Gypsum Lime	Sandstone Fly ash
CN1844029-A	2008	25-40	Phospho-gypsum	Coal ash Aggregate Carbide slag
NL1035134-C6	2008	>50	Rice chaff	-
CN101289310-A	2009	?	Cement Plaster	Sand Concrete Slag

Despite the existence of these studies and patents establishing the technical feasibility of using of bauxite residue in brick manufacture, we were not able to find reference to any significant implementation in this area. The main reasons for this seem to be competition from materials and processes already in place, and uncertainties about the technical, environmental and health risks associated with the proposed new products. These issues are well explained by a case study in Jamaica [90]. The situation in Jamaica in the 1980's appeared to be ideal for the establishment of bauxite residue as a standard brick-making material. The residue was readily available from the local alumina industry, one of the largest concentrations of alumina production capacity in the world at the time and a dominant component of the national economy. At the same time, there was a severe shortage of housing and of building supplies, so a new, low cost source of bricks was desirable. Bricks made from residue had been shown to be technically sound, and the alumina producers were willing to participate in the

supply of residue and development of the brick manufacturing process. Nevertheless, issues such as the perception that bauxite residue bricks would be deployed in poor areas only, and uncertainties about their long-term stability, leaching and ionising radiation properties meant that widespread use of red mud bricks did not eventuate. A key issue that arises in the context of building materials (particularly house-bricks) containing red mud is that of ionising radiation. Somlai et al [9] demonstrated that the amount of residue from Hungarian bauxite that could be used in brick manufacture would be limited to 15% to comply with the recommended minimum of 0.3 mSv y^{-1} specified by the EU Radiation Protection 112 guidelines [91], based on ^{226}Ra and ^{232}Th activity in the residue.

A synergistic process for brick-making using bauxite residue has recently been tested in Turkey, where the world's largest deposits of boron ores are located. The processing of the boron ores leads to the production of large amounts of boron-contaminated clay slimes. The processing company also operates an alumina refinery in the same region. It has been found that the boron residue slimes are an excellent fluxing agent for the production of fired bricks from the bauxite residue from the alumina refinery. The researchers have proposed this as a synergistic opportunity to ameliorate two industrial residues by combining them in the manufacture of a useful product [92].

A recent study by Yang and Xiao [73] describes a process for making unfired material suitable for making bricks and blocks using bauxite residue produced from the sinter process (see Figure 2) that is in use in China for processing diasporic ores. In this process the bauxite is first sintered with lime at a temperature of about 1200°C before leaching with caustic soda. This results in a residue with $\beta\text{-2CaO.SiO}_2$ as the major crystalline phase, in contrast to Bayer process residues, in which the major phases are haematite, goethite, boehmite, gibbsite, sodalite, quartz and various calcium compounds. The presence of $\beta\text{-2CaO.SiO}_2$, which is also a major component of ordinary Portland cement, enables the formulation of high-strength products without the need for further sintering. It was found that bricks which meet the Chinese criteria for 1st-class brick can be made by mixing red mud with fillers and bonding agents. The optimal ranges of composition are given in Table 2. The manufacturing process is carried out at ambient temperature (Figure 9) and the product meets Chinese national standards for bricks. It appears that the process could readily be adapted to produce construction materials in other forms, such as large blocks for building walls and retaining structures for example.

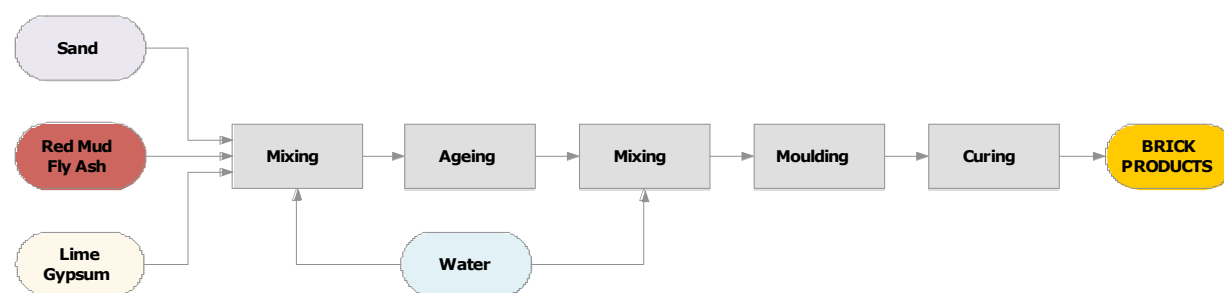


Figure 9: Schematic of brick-making process using red mud from sinter process
Optimal composition (% w/w) red mud (25-40%), fly ash (18-28%), sand (30-35%), lime (8-10%), gypsum (1-3%) and Portland cement (1%). (After Yang and Xiao [73]).

A qualitative sense of the barriers to implementation may be gained by designating strengths and weaknesses as “1” and “-1” respectively, with a zero designation for a property judged as neutral, as shown in Table 2. Noteworthy is that unfired bricks appear more promising than fired bricks.

Table 2. Conceptual ranking of strengths and weaknesses of the types of bricks that can be made from red muds (1=strength, 0=neutral, -1=weakness)⁴

Barriers	Bayer Residue		Sinter Residue	
	Fired	Non-Fired	Fired	Non-Fired
Energy Requirement	-1	1	-1	1
Manufacturing Cost	-1	1	-1	1
Radiation	-1	-1	0	0
Leachability	0	-1	0	-1
Competing Materials	-1	-1	-1	-1
Perception of “Waste”	-1	-1	-1	-1
Overall “Score”	-5	-2	-4	-1

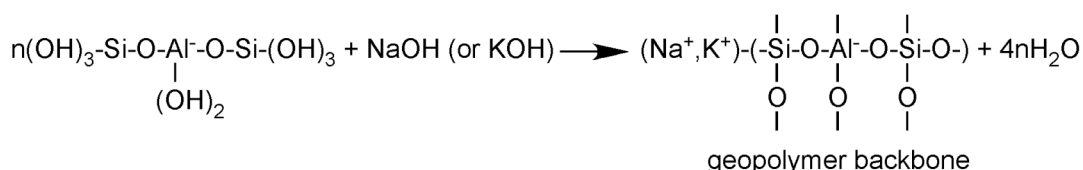
Investigations of local synergistic opportunities is warranted for the development of manufacturing processes for bricks and blocks using low energy, non-fired techniques.

3.1.1.4 Geopolymers

Geopolymerisation is an emerging technology being developed for the utilization of industrial by-products including fly-ash, slags and kiln dusts [93]. Geopolymers have a number of advantages over the established ordinary Portland cement-based (OPC) concrete technology, in particular an 80% reduction in overall CO₂ emissions intensity. They can be prepared with excellent mechanical properties and are superior

⁴ The assessment of Sinter Mud as “0” (neutral) in relation to radiation is based on the predominantly silicate composition described by Yang and Xiao [73], it may be different for diasporic bauxites containing higher levels of iron minerals for example.

to OPC for immobilising toxic metals. In contrast to OPC, which relies on the formation of hydrated calcium silicates, geopolymers are formed by the polycondensation of silica and alumina precursors which are reacted with alkali to form the polymers. The key to geopolymer formation is the dissolution of silica and alumina in an alkaline environment, followed by re-precipitation to form an amorphous solid polymer. The overall reactions are represented in Figure 10 [94].



Bauxite residue contains a number of aluminium- and silicon-containing minerals and some soda that could be used for geopolymer formation. Additional sodium hydroxide may be needed to achieve the necessary dissolution (over the temperature range of ambient to 160°C), depending on the initial concentration, dissolution time, and other parameters required to optimise the overall process [93, 94]. Other sources of alumina, silica or both may also be needed to achieve the required final composition and properties. Fly ash or steel-making slags may be useful in this respect, or it may be necessary to add clay or sodium silicate. While there is a substantial and growing literature on the formation of geopolymers from fly ash and various slags, we could find no published work to date relating to the use of bauxite residue in this connection. However, the Centre for Sustainable Resource Processing (CSRP) has established a “Geopolymer Alliance”⁵ to carry out research in collaboration with industry partners aimed at developing the fundamental understanding required to manufacture geopolymers for use in concretes on a regional basis. Their related website includes the claim that “geopolymers with impressive physical properties have been successfully manufactured from bauxite residue. This new material opens up opportunities for utilization of significant amounts of industry by-product”.

In principle, it appears that bauxite residue may have a role in the future development of geopolymers into mainstream construction materials, and that this could be the basis of a significant application of bauxite residue as a raw material. To achieve this will require research on the applicability of bauxite residue in geopolymer materials, and developing mixtures and production methods to optimise the resulting products on a local and regional basis, taking into account the availability of other resources

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such as fly ash, clay and caustic soda, the existing industries and supply chains, and the needs of local communities and businesses.

Support is warranted for research towards the development of manufacturing processes for geopolymer materials using bauxite residue. This has the potential to become a major use for the residue, and to have significant benefits in the supply of low cost, low energy materials to the construction industry.

3.1.1.5 Construction and radioactivity

Problems are likely to arise with some domestic construction materials. Somlai et al [9], based on ^{226}Ra and ^{232}Th activity in residue from Hungarian bauxite, demonstrate that the possible use of residue in (for example) brick manufacture is very limited. The NORM content of residue typically significantly exceeds the world average for building materials, and, within the EU Radiation Protection 112 guidelines [91] (recommended dose of $<0.3\text{--}1\text{ mSv y}^{-1}$) it would not be possible to exceed a residue content of 15% in bricks without the dose exceeding 0.3 mSv y^{-1} . The content in cements could be higher simply because less cement is used in masonry construction. China probably has one of the highest residue utilization patterns, mainly into building products, with claims of up to 10% [95] but this maybe a reflection of less stringent environmental regulation. Kovler discusses a range of issue around the use of industrial by products in construction [96]. In dealing with NORM there are two approaches that can be taken for the radioactivity assessment. The first involves a chemical analysis of the elements present that have radioactive isotopes; as the lifetime and product-daughter relationships are well understood, both the activity and exposure consequences can be calculated. For bauxite residue, this would require an assessment of U, Th, Ra, Ac, Po, Pb, At, Bi, Po, Tl and Pa content. Here secular equilibrium is assumed, i.e. the daughter half-life is much shorter than the parent half-life. Also implicit is, that the alumina refining process does not selectively distort the relative concentrations of the daughters due to their differing chemistry. As the refined output is high purity alumina, this is a reasonable assumption for the residue. The second approach for radionuclides is a direct measure of actual activity. For example Akinci and Artir [97] point out from direct gamma ray spectroscopy that the radioactivity for Seydisehir (Turkey) residue is within safe limits for use as filler in products such as roof tiles. Both approaches have advantages, e.g. the elemental analysis is easier for a routine analytical service to provide and the activity estimate comes from a calculation.

3.1.2 KPA 2: Catalysts or adsorbents

The results of CPI codes analysis of the patent search in this category (Figure 11) are show that 11 most frequently used of 44 codes accounted for 72% of all the code allocations in this grouping. The frequently used codes were H09: “Fuel products not of petroleum origin, e.g. coal gasification”, which applied to 31 (23%) of the 137 patents in this group, and H04: “Petroleum processing, treating, cracking, reforming”, which applies to 24 (17.5%). The remaining codes indicate a wide range of other potential applications, mainly related to pollution control and organic synthesis.

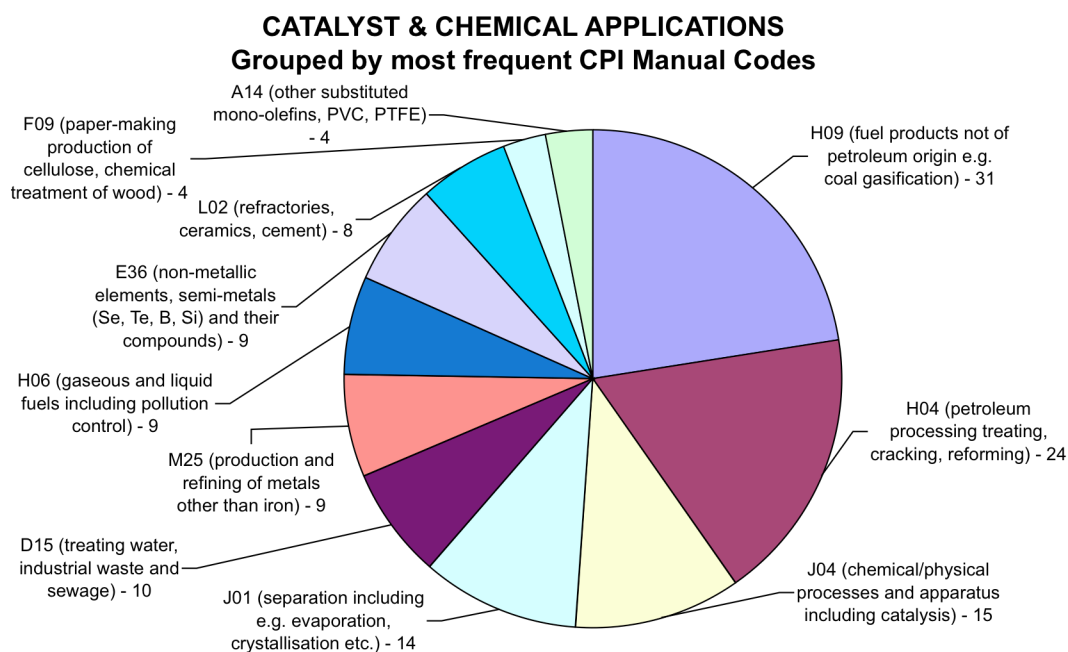


Figure 11: Chemical Patents Index (CPI) Manual Codes analysis for catalyst and chemical applications. These 10 codes account for 72% of all code allocations in this category. The number of times each code was allocated across the 137 patents is also shown.

Catalytic applications have been widely touted [98-105], mainly because of its Fe_2O_3 and also TiO_2 content and high surface area, but also because it is viewed a cheap and disposable source of fine sized raw material. Sushil and Batra [8] have reviewed the catalytic applications for hydrogenation, hydro-dechlorination, exhaust gas clean-up and other areas. However they concluded that the performance of unmodified residue was poor compared to straight iron oxides or commercial catalysts. Most applications require some prior treatment, or “activation”, of the residue to improve catalytic efficiencies. Such activation procedures include size reduction, heat treatment (usually to 400°C to convert hematite to magnetite), sulphidization, and even acid addition to dissolve the iron and other minerals that are then believed to precipitate in a more active form. Removal of Ca and Na is also desirable, because Na in particular promotes sintering and corresponding loss of specific surface area at elevated temperatures. Other researchers also agree with the generally poor performance of residue [106]. The hydrogenation of coal may be an exception, found to be effective in this application without special prior treatment other than presumably drying and pulverising. A summary of some of the potential applications of red mud as a catalyst is shown in Table 3.

DETAILED LITERATURE AND PATENT REVIEW OF RESIDUE REUSE

Table 3. Performance of red mud-based catalysts in hydrogenation, liquefaction and gas treatment applications (adapted from [8], and references therein)).

Application	Catalyst	Temp (°C)	Press (MPa)	Conversion Efficiency (%)
Hydro-dechlorination of organochlorine compounds	Calcined red mud	300		39
Coal hydrogenation	Untreated red mud	400	10	>90
Coal liquefaction	Sulphur-treated red mud	450		7.2**
Straw hydrogenation	Untreated red mud	400		99
Biomass liquefaction	Sulphur-treated red mud	400		99
Naphthalene hydrogenation	Activated red mud	350	3.45	49
Naphthalene hydrogenation	Activated red mud	405	6	80
Methane combustion	Activated red mud	650		30
SO ₂ reduction	Untreated red mud	640		30
Nitric oxide oxidation	Cu-impregnated red mud	350		50

* Weight %

** Mol %

Development of bauxite residue as a catalyst will depend on finding applications in which it can be cost-competitive with other alternatives. It will not generally be able to compete on technical performance, so implementation would depend on low unit cost outweighing the disadvantage in unit performance for each particular application. This would seem to rule out any but the most basic of pre-treatments, but would have to be evaluated on a case-by-case basis. Even if suitable applications are found and implemented, it is unlikely that this area could ever consume sufficient residue to have even a measurable impact on the amount of residue produced. Additionally the spent catalyst itself has to be disposed of and it could well be more toxic than the original residue. This area is therefore not a priority in relation to the goal of reducing the amount of residue stored globally.

3.1.3 KPA 3: Ceramics, coatings, plastics and pigments

The results of CPI codes analysis of the patent search in this category (Figure 12) show that 13 of 59 codes accounted for 65% of all the code allocations in this grouping. The most frequently used codes were L02: “Refractories, ceramics, cement” which applied to 47 (51%) of the 92 patents in this classification, M25: “Production and refining of metals other than iron” (16%), G01: “Inorganic pigments and non-fibrous fillers” (12%), and G02: “Inks, paints, polishes” (10%).

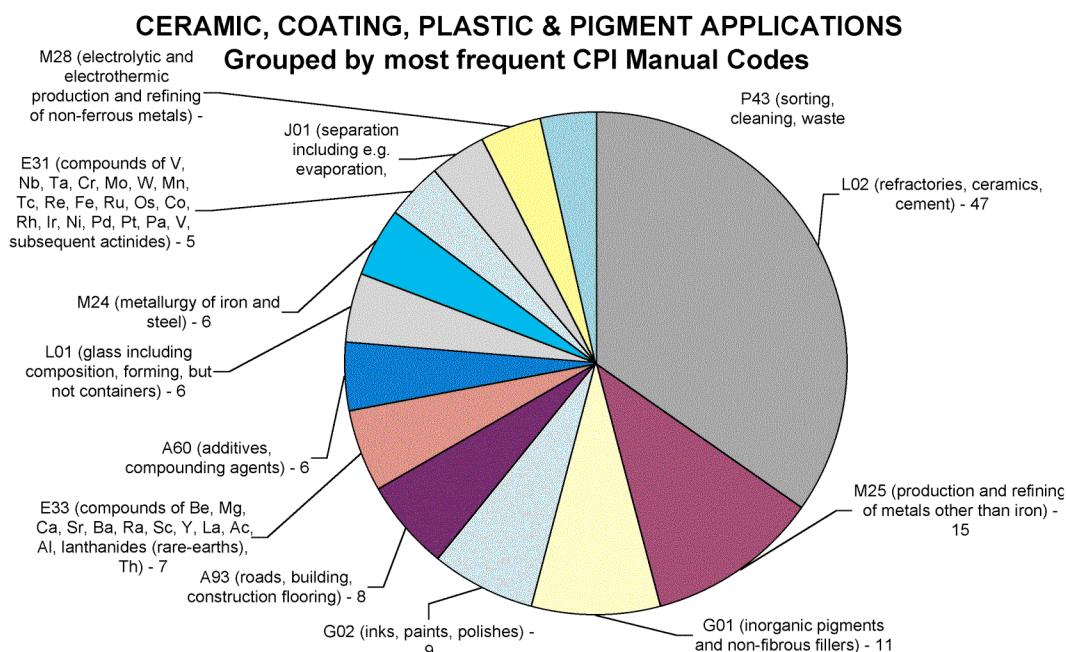


Figure 12: Chemical Patents Index (CPI) Manual Codes analysis for ceramic, coating, plastic and pigment applications. These 13 codes account for 65% of all code allocations in this category. The number of times each code was allocated across the 92 patents is also shown.

In technology terms this group represents the simplest area in which to implement utilization for many of the typical products. For example, pigment fillers into fired clay products is established technology. Although the simpler technical route means that these areas are potentially attractive in developing economies, it does not mean that energy efficiency, product performance and product safety necessarily follow. Pigment application is limited in tonnage; for example India and Spain lead the world in natural minerals pigment production (over 80% of world production, mainly iron oxides), but annual production for 2007 was 375,000 tonnes [107] for India and 141,500 tonnes for Spain [108]; small compared to residue production. Ceramics applications of residue are as pigment or filler, and the possible tonnages across a variety of applications are difficult to determine. Moreover, with both pigments and ceramics, the end-use item can be in a variety of forms, this makes controlling the release of the material into “completely” safe applications problematic. The use of residue in this area has been covered in the reviews by Thakur and Sant [1] and Paramguru [5]. The application of residue to ceramics ranges from as a major component of the ceramic mix, to a minor component added as a pigment or glazing agent. A wide range of recipes have been developed for various applications, including pots, household fittings, domestic and refractory tiles, and building blocks, in which the bauxite residue may be used in combination with other by-products such as fly ash and slags. Until recently the approach to formulating such materials has been largely empirical, but in 2000 Sglavo et al [109, 110] reported on systematic studies of the influence of bauxite residue in the production of fired ceramics from clay-residue mixtures as a function of residue concentration and firing temperature. It was found that dried residue is an inert component of the mix for firing temperatures up to 900°C, which makes it useful as a filler and red colouring agent in the

production of traditional clay-based ceramics (tiles, bricks, pots) fired below 1000°C. Because it is an inert filler under these conditions, the strength of the product decreases with increasing residue content, which limits the amount that can be added. At higher temperatures the presence of soda and silica in the residue promotes the formation of sodium silicates which improves the flowability of the material and increases the final strength of the product. Iron and titanium react above 1000°C to form iron titanates which further increase the strength and impart a brown colour to the product [109, 111].

The presence of silica, soda and calcia in bauxite residue are beneficial in the formation of vitreous glazes. Yalçun et al have shown that up to 37% of bauxite residue addition was possible in the production of glazes in the manufacture of a range of domestic and industrial porcelain products, due to the formation of a range of sodium and calcium silicates and alumino-silicates [112].

Bauxite residue has also found application as an inert filler in a range of plastics and rubber, and as a pigment in paint [1, 2, 5]. Most such applications require some sort of pre-treatment before use, from simple drying and screening or particle size reduction, to neutralisation with acids or acidic gases or heat treatment. All such pre-treatments inevitably add to the overall cost of the product, and so must be minimised if the residue is to find application.

Residue has been tested as a component of protective coatings, for example in plasma-spray coatings on aluminium and copper structures as a wear-resistant coating [5]. Amritphale et al [113] have demonstrated that bauxite residue can be beneficial in the preparation of ceramic barriers for radiation shielding because of the formation of a very dense ceramic matrix due to liquid-phase sintering. The barriers showed superior properties to conventional Portland cement-based shielding materials in terms of shielding thickness requirement and compressive and impact strengths.

In summary, there is a wide range of possible low technology uses of bauxite residue in this classification, but they are generally low-volume uses. Some of these applications require only minimal preparation of the residue prior to application, which may then only involve mixing and moderate heat treatment and/or moulding to create the final product. It seems that few such applications have been developed to any significant extent to date, but there appears potential for local and regional development of products both for local use and for export. Encouragement of specific projects at the individual refinery or regional level could therefore be beneficial.

3.2 Environmental and agronomic applications

Many water treatment applications have been suggested and developed using modified bauxite residues, from improving conventional waste water streams [13, 37-42, 114-119] through to treatment of acid mine drainage (AMD) [62, 120-125]. Similarly the removal of acidic gases from waste streams, in particular SO₂, by passing it through a bauxite residue slurry [126, 127]. Substantial efforts have also been made in agronomic applications for soil amendment from issues of acidity to phosphorus retention [128-138].

3.2.1 KPA 4: Waste water and effluent treatment

Water treatment is a consistent theme for modified bauxite residues, from improving conventional waste water streams [13, 37-42, 114-119] through to treatment of acid mine drainage (AMD) [62, 120-125]. The former relies on its ability to sequester or adsorb through a variety of mechanisms undesirable constituents of water such as arsenic and phosphate, whereas the AMD treatment is primarily one of neutralisation of the acid by excess hydroxide (OH^-), carbonate (CO_3^{2-}), aluminate ($\text{Al}(\text{OH})_4^-$) and other buffers, both in soluble and solid states present in the bauxite residue. In the course of neutralisation, heavy metals present in AMD and bauxite residues may precipitate and/or adsorb on the surfaces of insoluble metal oxide surfaces already present [139].

Lopez and coworkers tested gypsum amended bauxite residues from the Spanish alumina refinery in San Ciprian as a possible aggregate to be introduced into wastewater streams [140]. Gypsum amended bauxite residues formed stable aggregates with good stability in aqueous solution. The maximum adsorption capacities at near neutral pH was in order of copper > zinc > nickel ~ cadmium which reflects the approximate hydrolysis behavior of these metals. The retention behavior of the same four metals in a continuous column leaching experiment with urban sewage sludge (pH 7.5-8.0) showed 100% retention for nickel, 68% for copper and 56% for zinc.

Genç-Fuhrman et al. [40] tested activated⁶ and passive BauxsolTM⁷-coated sands in a competitive adsorption scenario to remove As, Cd, Cr, Cu, Ni and Zn from stormwater. The acid activated BauxsolTM-coated sand performed better for the removal of As and Cr, which were present as oxy-anions in solution, while the passive BauxsolTM-coated sand performed better for the metal removal of metals such as Cu and Cd, which were present as metal cations. Although both experiments started at pH 6.5, the individual solids buffered their solution pH, with passive BauxsolTM-coated sand having a pH of 8.6 and activated BauxsolTM-coated sand having a pH of 6.8. A similar study [38] for arsenate sorption on BauxsolTM showed the ability of the seawater neutralized sorbent to remove circa 0.3 and 0.4 $\mu\text{mol m}^{-2}$ of arsenate at pH 7.5 and 6.3 respectively, which is small in comparison to arsenate adsorption on pure goethite, which achieves 2-3 $\mu\text{mol m}^{-2}$ of surface coverage at similar pH [141, 142].

Couillard [143] for example found that residue activated by (an unspecified) sulphuric acid treatment could remove some 70% of phosphate from water in the pH range of 6.5 to 7.5, but gave no data on the adverse consequences of using it as a “coagulant”. With hydrochloric acid and subsequent heat treatment residue has been found to remove up to 99% of phosphate at pH 7 and generally performed much better than treated fly ash [114]. Studies have concluded that there may be no toxicological problems in the use of suitably treated residue products for water treatment [14, 144, 145] but further investigations are required. One of the problems with the environmental impact is that the various studies have been conducted on residues of different origins, with different pre-treatments, differing leaching and toxicological tests and differing environmental jurisdictions. Standardisation of methodologies and

⁶ Acid treated

⁷ BauxsolTM is seawater neutralized bauxite residue. Passive refers to not-acid treated.

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reference samples is necessary to enable meaningful comparisons to be made. For example, figures of “70%” or “99%” have little relevance if the context of original phosphate levels and application rates are unknown.

The application of raw and amended bauxite residues to environmental remediation and clean-up has mostly focused on their high potential for sequestration of metals and metalloids. Two characteristics of bauxite residues contribute to this high sequestration potential: 1) the high alkalinity, which favours hydrolysis and precipitation of metals as hydroxides and carbonates, and 2) the large concentration of iron, aluminium and titanium oxides (including hydroxides and oxyhydroxides), which provide surface sites for sorption reactions by metals and metalloids. In addition, the presence of TiO_2 can facilitate oxidation reactions such as $\text{As(III)} \rightarrow \text{As(V)}$. Consequently, sources of and areas affected by metal and metalloid contamination are potential application areas for bauxite residues. These are:

- Waste waters and effluents from industrial and municipal facilities.
- Acid mine drainage (AMD) and acid sulphate soils.
- Soils contaminated with organic (PAHs/ VOHs) and inorganic (metals/ metalloids) toxins.

In order to understand the fate of metals and metalloids in a geochemical environment such as bauxite residues or bauxite residue amended soils, it is necessary to understand the term “sorption” and the associated concepts of surface complexation and the stability of surface complexes. For a brief discussion of sorption and its importance in this context please refer to the Appendix. In the last 20 years, significant advances have been made to distinguish between metal and metalloid sorption mechanisms and resulting surface complexes, and likewise, in identifying which surface complexes have greater and lesser stability. Sorption and surface complex stability are concepts of paramount importance when evaluating bauxite residues for their suitability to sequester metals and metalloids. Equally important are solid phase speciation of the metals and metalloids. However, to date, studies of such critical information have not been conducted. As a consequence, the nature of the surface species is unclear and desorption and sequential extraction reactions only provide indirect, operationally defined speciation definitions. Consequently, it is warranted that the speciation of the most environmentally critical metals and metalloids is investigated spectroscopically under varying environmental conditions. This should entail initially the investigation of Pb, Cd, Cu, chromate and arsenate, and would be expandable to additional metals/metalloids such as Hg, U, Ag and Se.

Aside from the alumina refining industry and government agencies the most active promoter of residue derived products has been the Australian based company Virotec Global Solutions Pty. Ltd (formally Virotec International Ltd.) [34-49]. Good claims have been made and in some cases independent tests have been carried out [146]. These products are manufactured entirely from overseas sourced residue [147].

Conceptually the chemistry that allows a residue product to successfully treat waste water streams also means that it may be very suitable to bind the components (such as arsenic and phosphate) in an *in situ* barrier context [148] such as a permeable reactive barrier (PRB). It should be noted although the residue chemistry is critical, it is only one of the relevant technical issues for utilization. There will usually be additional engineering requirements for implementation. For example two of the

issues with the use of residue within a PRB system (as with any adsorbent system) is that of permeability (initial and time dependent) and limited capacity. This can be particularly important if the sequestering chemistry is pH dependent and highly acidic plumes eventually consume the contained alkali content and change the effectiveness of the material (or even cause a subsequent release event).

It is necessary that the speciation of the most environmentally critical metals and metalloids is investigated spectroscopically under varying environmental conditions.

3.2.1.1 Acid mine drainage and acid sulphate soils

A number of research studies have looked into the possibility of utilizing raw bauxite residues and amended bauxite residues as neutralisation agents for acid sulphate and acid mine tailings [120, 121, 123]. Doye and Duchesne [123] observed that acid mine tailings originally at pH 3 reached a pH of 6 when reacted with 10 wt. % bauxite residues, before the pH began to decline slowly again. When the same mine tailings were reacted with 50 % w/w bauxite residues, the pH was stable near pH 9. In contrast, Paradis et al. [120] observed that a 10 % w/w bauxite residue amendment to acid mine drainage maintained the pH between 7 and 9.5 for 125 days. In order to prolong the neutralisation effect of bauxite residues, Paradis et al. [121] treated bauxite residues with brine and observed that the equivalent alkalinity of the brine treated solids was greater than 3000 mg CaCO₃ kg⁻¹.

Recently, Tuazon and Corder [62] published a lifecycle assessment of seawater neutralized bauxite residues (SNBRs) to compare the CO₂ emissions and electricity requirements against the performance of CaCO₃ to neutralize acid mine drainage at a site in Queensland. The results showed SNBRs would emit only 20% of the CO₂ and consume only 44% of the electricity when compared to CaCO₃. However, SNBRs have a significantly lower acid neutralizing capacity and commensurate transport costs are much higher (estimated fuel penalty to be 12 times larger than that for CaCO₃).

These results highlight the need for a full cost/benefit and environmental impact analyses in assessing the viability of each specific application proposed for bauxite residue on a situational basis. In Australia, AMD causes approximately \$60 million per annum in damages and since 1997 has cost the Australian Industry about \$900 million (1997 dollars). By comparison, costs to the Canadian industry is about C\$2-C\$5 billion [149].

This indicates that there is significant market for AMD neutralisation technology.

3.2.1.2 Contaminated soils

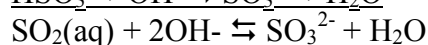
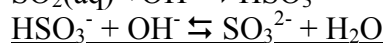
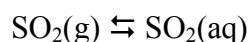
Lombi et al. [150, 151] tested the efficiency of bauxite residues from Hungary to lower metal concentrations (Cd, Cu, Ni, Pb, Zn) in soil pore waters and metal uptake into oilseed, pea, wheat and lettuce. Two soils, one metal contaminated soil from France and a sewage sludge contaminated soil from the UK were investigated. A 2 % w/w bauxite residue treatment was as effective in lowering metal concentrations in soil pore waters in both soils and across the plant species as 5% of beringite (modified alumino-silicate coal-ash component). The sequential extraction of the metals from the soil solids showed that the metals were partitioning preferentially onto the iron

oxide fraction in both bauxite residue treated soils, whereas in the control soils, the majority were sequestered as exchangeable, outer-sphere complexes. These results show a reduction in plant-available metal ions by the presence of bauxite residue, and the corresponding reduction in metal uptake by the plants in this study.

3.2.2 KPA 5: Waste gas treatment

3.2.2.1 *SO₂ dissolution in residue*

In the mid 1970's, the Sumitomo Aluminium Company patented a process by which SO₂ could be removed from waste gases by passing it through a bauxite residue slurry [126]. In the alkaline slurry, SO₂ rapidly consumes 2OH⁻ to release SO₃²⁻ and H₂O [152]:



In the presence of air, SO₃²⁻ oxidizes to SO₄²⁻. This process is known today in the as the Sumitomo process and is used in a limited number of refineries to reduce their SO₂ emissions from use of coal for power generation [127]. One of the beneficial side effects of using SO₂ gas scrubbing is the concomitant pH reduction in the residue slurry and the destruction of desilication products (one of the alkaline buffering minerals in bauxite residues). To date, SO₂ scrubbing by residue is the only ongoing and successfully implemented environmental application of bauxite residues. Scrubbing SO₂ has also successfully implemented at Eurallumina (Sardinia, Italy). Related is the use by Alcoa (Kwinana) of sequestering CO₂ as part of residue neutralization, although this improves residue storage the long term sequestering performance, compared to naturally occurring carbonation, is not clear. However, these applications do not reduce the mass of residue that requires disposal.

3.2.3 KPA 6: Agronomic applications

3.2.3.1 *General soil amendment*

The beneficial attributes of bauxite residues for decontaminating effluents, acid mine drainage or contaminated soils can also be made use of in agronomic applications. In particular, sandy soils, with little or no nutrient (N, P, K, Ca, Mg, SO₄, etc) or water holding capacity could benefit from the application of bauxite residues. The presence of sodalite, with an estimated cation exchange capacity (CEC) of 645 meq/100g exceeds the CEC of most natural clays, which perform this function in soils. In addition, the alkaline nature of bauxite residues can be used to raise the pH of organic soils, which tend to have pH of 4.5-5.5 and suffer from Al phyto-toxicity [153, 154].

Direct addition of bauxite residue to soils can be beneficial, for example if the soil is acidic and the addition rate is low [131]. In many cases the bauxite residues need to first be modified to reduce their phytotoxicity in order to function as a soil amendment. Principally, the phytotoxicity arises from an alkali pH and excess Na in unamended residues and an increase of free Al(OH)₂⁺ species in neutralized residues, due to the precipitation of partially soluble gibbsite (Al(OH)₃) gels [155, 156]. Zobel

et al. [156] treated bauxite residues from an East German alumina refinery (VEB Aluminiumwerk “Albert Zimmermann”, Lauta - Germany) with sodium-silicate to precipitate $\text{Al}(\text{OH})_4^-$ as a sodium-aluminium silicate and $\text{Ca}(\text{OH})_2$ to remove excess NaOH from the residues. This treatment was designed to achieve:

- A soluble Al concentration of under 1 mg L^{-1} (ppm), which is below the critical concentration of free Al that triggers phytotoxic responses.
- A marked pH reduction (not specified).
- Upon phosphate (PO_4) application, no tie-up of phosphate as insoluble variscite ($\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$).

Bauxite residues treated with sodium-silicate and $\text{Ca}(\text{OH})_2$ increased the water-holding capacity of a sandy soil from 21.7 to 38.9% for an application rate of 1:10 (by weight) of bauxite residues to sandy soil [155, 156]. In addition, the authors claimed an increase of the cation exchange capacity by the formation of sodium-aluminium silicates. Barrow [157] showed that in comparison to a sandy Joel soil (Western Australia), bauxite residues had 15-20% greater water content between wetness potentials of 30 and 1500 kPa (plant available water potential region) and concluded that an amendment of the local sandy soils with bauxite residues would improve their water-holding capacity. When bauxite residues were amended with 5 wt.% gypsum, the water content of Joel sand between 20 and 1500 kPa wetness potential increased by 35-40%. The cation exchange capacity and phosphorous retention capability of Joel sand (Western Australia) was significantly enhanced, when 256 t/ha of bauxite residues treated with gypsum were applied to the Joel sand, suggesting a greater nutrient holding ability of amended sand. Ammonium and phosphate retention increased by 85 and 50% respectively, in comparison to a 0 t/ha application rate [158].

3.2.3.2 Phosphorus

Bauxite residues have high phosphate retention capacities when neutralized below pH 8, owing to the large concentration of iron and aluminium oxides (including hydroxides and oxyhydroxides) in them. These minerals, mainly hematite, goethite, boehmite and gibbsite adsorb phosphate at their edge-sites (Al/Fe-O). Bauxite residue mineralogy and PO_4 's affinity imparts two useful properties with respect to phosphate cycling:

- The ability to reduce phosphate leaching into ground and surface waters, which has the potential to cause eutrophication [134].
- Create a phosphate pool that is available to plants.

These two properties make bauxite residues interesting soil amendments to target phosphate cycling in agricultural areas having sandy soils with low phosphate and other nutrient holding capacities. Such an area is presented by the Peel-Harvey Estuary in Western Australia. A series of research studies conducted by the Western Australian Department of Agriculture have shown the usefulness of bauxite residue applications for P retention and reducing run-off into the Peel Inlet and the Harvey Estuary by up to 75%, while increasing pasture yields by 25% and in well-controlled areas by up to 200% [129, 131, 132, 134, 135]. The fine bauxite residues were commercialised by Alcoa under the tradename Alkaloam[®] and were made available to local horticulturalists and farmers. The Western Australian Department of Agriculture suggested that Alkaloam[®] was the only land management option available

to achieve immediate and significant P runoff reduction and therefore protect the Peel-Harvey ecosystems from the damaging effects of eutrophication caused by phosphate. On the basis of the available literature, we are not aware of any trials or application of bauxite residue to agriculture on a significant scale being practiced anywhere at present since the work by Summers.

Given its potential for environmental and economic benefits, and the potential for large-scale utilization of residue, this is an area of significant interest for research and development. It remains unclear to today whether any negative environmental impact of bauxite residue application would have outweighed the benefits from reducing phosphate runoff in this area, particularly as neither NORMs nor heavy metals were being leached from bauxite residues or bauxite residue amended soils (see section 3.2.3.3 below).

3.2.3.3 Agronomy and radioactivity

As noted bauxite, in common with all rocks and minerals, contains trace levels of naturally occurring radioactive materials (NORMs) and other metals. The majority of these do not dissolve in the Bayer digest, and so are more concentrated in the bauxite residue by a factor of about 2 (refining has only two solid outputs; alumina with zero NORM's and residue). Care should be taken to ensure that application of bauxite residues containing naturally occurring radioactive materials (NORMs) above local background concentrations does not result in concentrations exceeding the statutory limits. McPharlin et al. [158] showed for example that an application rate of 256 t/ha, did not increase the concentration of ^{232}Th above statutory limits. The same is required for heavy metals.

This is an area of obvious public concern. Despite the trial successes and favourable scientific results from Alkaloam[®] it ceased to be commercially available after a newspaper article by the Sydney Morning Herald reported on the application of heavy metals and NORMs contained in Alkaloam[®] [59]. Multiple research studies had found that neither NORMs nor heavy metals were being leached from bauxite residues or bauxite residue amended soils [134, 159] or taken up by foodcrops at levels harmful for consumption [158, 160]. Cooper et al [160] show that radiation exposures from radionuclides in vegetables grown in residue amended sandy soils is not significantly different to unamended soils. That study examined ^{238}U , ^{226}Ra , ^{228}Ra , ^{228}Th and ^{40}K (all NORM components of residue) and ^{137}Cs (a nuclear fission fall-out product not present in residue, half-life 30 years). Even at residue applications up to 480 tonnes/hectare there was no uptake of the NORM components; moreover the residue amendment actually lead to a decrease in the ^{137}Cs , in particular for cabbage.

Knowledge of potential leaching and uptake is necessary to support detailed risk assessments for both agronomic and other applications (e.g. urban settings of open fields vs. road strips) for bauxite residues, and such risk assessments are an essential input to more comprehensive evaluation of proposed applications in the future, and will provide a basis for a more informed debate on the issues. In particular:

3.2.4 Research priorities for environmental and agronomic applications

There have been to date very few examples of implementation and ongoing use of bauxite residue in agronomic and environmental applications. The development of a range of products under the Bauxsol™ label is the only example we could find of an independent business based primarily on bauxite residue. We could find no specific information on the amounts of bauxite residue being directed to these products, but there is no indication of a high degree of uptake. There have been examples of the development of products by the alumina companies themselves (e.g. Cajunite™ (USA), Alkaloom® (Australia), Bauxiline® (France)), but none appear to have achieved ongoing success.

The use of bauxite residue for SO₂ scrubbing is an isolated example of a process that has been developed, implemented and marketed as a viable technology, however the number of installations using this technology appears to be small and the neutralised residue has to be disposed of anyway.

In regions with sandy or otherwise infertile soils, bauxite residue applications could improve water and nutrient holding capacities by improving soil structure. This remains a significant utilization option.

Further research is warranted to investigate the solid phase speciation of heavy metals and NORMs in bauxite residues, in conjunction with speciation and adsorption studies of trace and heavy metals on a range of residues various conditions.

3.3 Metallurgical applications

Value Opportunity 3, Metallurgical Applications, includes the following three Key Priority Areas: KPA7, Recovery of Major Metals, KPA8, Steel Making and Slag Additive, and KPA9, Recovery of Minor Metals. 135 patents were filed in this category between 1964 and 2008, which is 17% of the total number of patents relating to bauxite residue utilization in that period. The metallurgical applications in particular illustrate utilization drivers based on overly simplistic interpretations of metal value and processing costs.

3.3.1 KPA 7: Recovery of major metals

The major metals referred to are iron, aluminium, titanium and sodium. The total number of patents in this category is 66 (Figure 13) of which 42 refer to iron recovery, 17 to aluminium, 11 to titanium and 6 to sodium. Four of the patents refer to recovery of Fe and Al together (DE2328674-A, JP50104768-A, JP63286526-A, BR9602530-A), and three refer to simultaneous recovery of Fe, Al and Ti (DE2060766-A, RO91333-A, WO200268331-A).

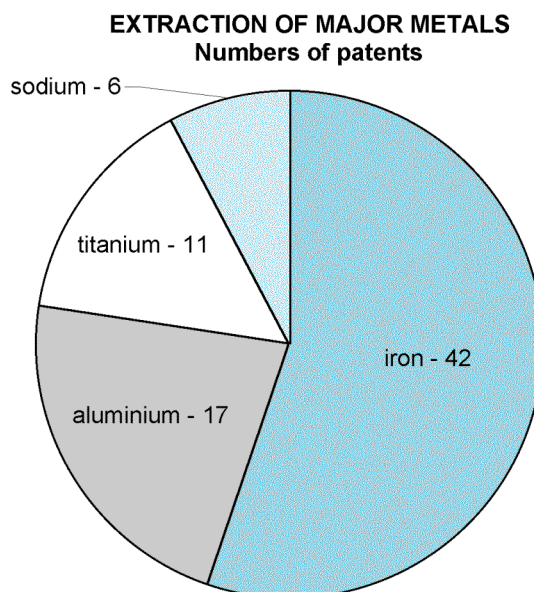


Figure 13: Numbers of patents referring to extraction of each of the major metals.

Conceptually, it is difficult to see how bauxite residue containing 40% Fe_2O_3 in combination with aluminium, silicon, soda and a number of other elements and with at least 20% free moisture content could compete with virgin iron ore containing >99% Fe_2O_3 and <5% free moisture. Any process aimed at iron recovery *alone* is not likely to be viable. Similarly, it is difficult to see how recovery of alumina from residue could be viable given that it would require either sintering or acid treatment as a first step, the very processes the avoidance of which is the key to the long standing dominance of the Bayer process itself. Presumably the only way in which processing of bauxite residue for the production of iron and/or alumina could possibly be viable is through the creation of additional value by producing several metals in a single integrated process.

Thakur et al [3] and Paramaguru et al [5] have reviewed processes for the recovery of iron, aluminium and titanium, individually and in combination. The key objectives of the recovery of multiple major metals are to simultaneously maximise the value created and minimise the residual solids produced. All of the proposed flow sheets for complete recovery are technically complex, and would require the establishment of large, capital- and energy-intensive plants (see Figure 14 for an example). Ercag and Apak [19] have also demonstrated a sequential process of smelting and hydrometallurgy to produce pig iron, pigment grade TiO_2 and $\text{Al}_2(\text{SO}_4)_3$ was also possible. This scheme was based on Turkish residue and none of the rare earths could be feasibly recovered. Clearly, to address the volume of the residue then metal recovery needs to include the iron content. Recovery of high value minor components, such as titanium, play a potentially important role in adding value. To be successful, any processing scheme for metals recovery would have to be designed and evaluated for specific residues to maximise opportunities arising from the compositions. For example, some Indian residues have been found to have up to 28 % w/w TiO_2 , so Ti recovery may be of particular interest there. It is technically

feasible to recover the TiO_2 [161] by treatment with a hydrochloric and then sulphuric acid producing 97.5% TiO_2 (white), somewhat above a typical synthetic rutile grade.

Given an efficient process, a natural economic driver would exist for iron recovery as feedstock iron ore amounts to some 30-40% of the cost of pig iron [3]. In terms of iron recovery most effort [5] has been directed in three approaches:

- Smelting
- Solid state reduction
- Magnetic separation

Smelting has an advantage in that it uses existing technology. Reduction of the iron via smelting can also open magnetic separation avenues [17], though for the most part reduction is just part of the metallurgical refining route. In some cases the flow sheets are complex with multiple reduction steps and multiple slags [162]. Magnetic separation can also be applied to the original residue. Methods such as wet high intensity magnetic separation (WHIMS) can work very effectively [87] for the coarser material, such as the sand fraction, but it delivers graded fractions only. The grades are dependent on the extent of mineral liberation and the varying compositions of residues would be expected to impact on the utility of a given metallurgical recovery flowsheet. Atasoy [163] claims on the basis of thermogravimetric comparisons that in a comparison of Seydisheir (Turkey) and Aughinish (Ireland) residues that the Seydisheir residue would be more amenable to iron recovery. As metallurgical recovery is essentially an ore treatment it needs to be remembered that most mineral processing systems are not only tailored to their ore body, they are tailored to variations in their ore body. With the complexity of metal recovery it would be surprising if a single flow sheet could be sufficiently robust to treat all residues, so a solution may be regional. Researching the iron problem goes back over more than 50 years, but no obviously economic solution has been found. Iron recovery also produces additional slag and the issue of further concentration of the heavy metals and the NORM components. Some interest has also been shown in smelting approaches for soda recovery [164, 165]. The question of more conventional mineral processing methods such as flotation has also been raised [166] but realistically, even after soda reduction, flotation would not be cost effective because of low product values.

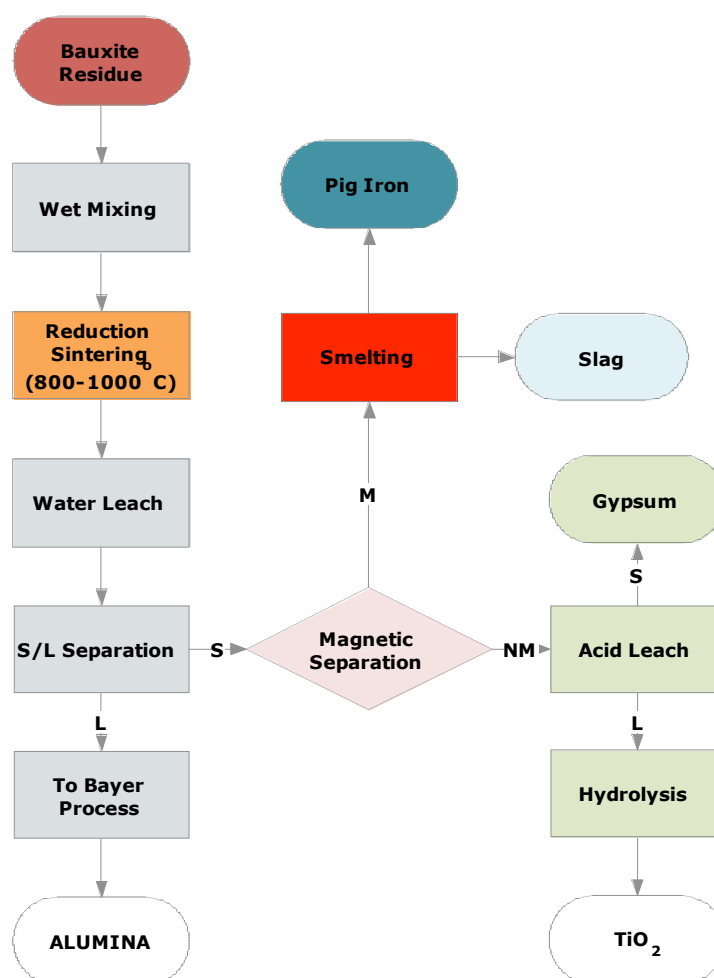


Figure 14: A possible flowsheet for simultaneous recovery of iron, aluminium and titanium from bauxite residue (adapted from Piga et al [167]).

Despite considerable research and the identification of many technical options, no process for the large-scale extraction of metals from bauxite residue has to date been implemented. For this to occur it would first be necessary to demonstrate that it could potentially be viable, both technically and economically, in competition with established processes for the production of the metals concerned. This would require a detailed techno-economic, market and environmental evaluation for specific process schemes in the context of the local and regional conditions.

Support is warranted for a detailed techno-economic, market and environmental analysis of one or more specific schemes for a zero-waste, integrated process for recovering iron, aluminium, titanium and soda from residue.

3.3.2 KPA 8: Steel making and slag additive

Of the 135 patents on Metallurgical Applications, 51 relate to steel making and slag additives. In most of these patents, the bauxite residue is listed as one of a number of possible additives used as a source of aluminium, silicon and calcium to modify the properties of the slag to improve separation, setting and other qualities. Its use in

these applications presumably depends on its relative cost, availability and performance in comparison to other possible additives that include clay, slate and sand. It is not possible to gauge the likely extent of usage of bauxite residue in these applications from the patents, and this area of use has not been discussed to any significant extent in the literature. It therefore would seem that this is not a major area of actual or potential application of bauxite residues, however it may be useful to confirm this.

3.3.3 KPA 9: Recovery of minor metals

Only 16 patents were discovered in relation to the extraction of minor metals from bauxite residue. Of these, 8 referred to extraction of scandium, two to rare earth elements (REEs), and the remainder to a variety including zinc, cadmium, lead, vanadium and silicon.

Russian workers have approached residue as a potential resource, considering it as “a polymetallic raw material with a complex content of oxides of aluminium, iron titanium, silicon and other valuable components, such as scandium, uranium and thorium” [168]. They have investigated treating the material with methods similar to those used for low-grade uranium ores, using direct extraction with mineral acids together with ion-exchange separation of the radioactive and valuable components. The motivation for this work was to recover values and reduce the levels of radioactive elements in the mud to facilitate its use in construction applications. Using a resin-in-pulp method in sulphuric acid media, they demonstrated the feasibility of recovering titanium, scandium, uranium and thorium from residue produced at the Nikolaev alumina plant (Ukraine), which processes bauxites from a number of sources, including Brazil, Guyana, Australia, Guinea and India [169].

The bauxite processed by Aluminium of Greece has a relatively high scandium content of about 130g/t, which is favourable in comparison to naturally occurring Sc resources [170]. Research on the extraction of Sc from the resulting red mud has been taken to the pilot plant stage [170], based on considerable previous laboratory work [171, 172]. This method is based on a nitric acid leach followed by ion exchange separation of the Sc.

The extraction of only minor components from bauxite residue can obviously have no impact on the amount of residue to be stored. Depending on the processing method may render the residue more or less difficult to store or utilise. For example, the Russian work referred to above suggests that the resulting residue would be better for use in building materials because of its lower radioactive element content, but that would have to be considered in combination with other aspects, such as that the residue would then be acidic, and would have quite different properties in relation to leaching of metals, flocculation and consolidation behaviour, etc.

Extraction of minor elements from residue can only make sense if it has significant economic benefits. It is for this reason that attention has tended to focus on scandium, partly because it is relatively concentrated in some bauxites, and also because it has been stated to have “high commercial value on the international markets” [173]. The stated commercial value of Sc appears to be based on USGS data for pure Sc metal, which quotes a price of US\$10,000/kg in 1994 [174]. However, it should be noted

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that the product from an extraction as described above would at best be a medium purity scandium oxide, for which the price quoted by USGS for 2007 is US\$700/kg for 99.0% Sc_2O_3 [175]. The economics of minor element production need to be considered carefully before any significant effort is put into the development of technology in this area. The potential for scandium production provides a good illustration of this, as follows. Given that the Greek refinery produces 6M tpa of residue [170], then the potential Sc_2O_3 production is 120 tpa. At \$700/kg this corresponds to a potential revenue stream of \$84M pa, sufficient to justify a significant investment for extraction and purification. However, the current US market (majority of the world market) for Sc_2O_3 is about 10 tpa [175] easily met by domestic tailings. This would mean that the emergence of such a production capacity of 120 tpa would have a significant depressive effect on the price and therefore the viability of the operation. On the basis of this example together with the statement by the researchers that “Sc represents 95% of the economic value of ... the REE” in this residue, it is reasonable to conclude that no project aimed at REE extraction from this (or probably any other) bauxite residue would be justifiable. Of course price depression can also lead to increased demand with new applications. Suggesting residue as source of minor elements should be considered carefully because of these considerations.

4. TRENDS AND RESEARCH GAPS

4.1 Trends and future directions

The global inventory of bauxite residue stored on land currently is estimated to be over 2.7 billion tonnes, with an annual growth rate of over 120 million tonnes. Although this is one of the largest masses of mineral processing residue globally, it does not mean that bauxite residue storage is a global problem in the same manner as are, for example, greenhouse gases, CFCs, or plastic bags. Bauxite residue is not randomly distributed about the globe in an uncontrolled manner, but predominantly exists in discrete locations at which it is generally well contained, closely controlled and subject to strict regulatory requirements. The residue is necessarily managed on a local basis, in terms of geography, jurisdiction, and operating company. Despite a long-standing recognition of the disadvantages associated with such residue storage, it has nevertheless continued to be the preferred solution on balance of economic, environmental and social considerations.

To successfully transition bauxite residue from a waste to be disposed at a cost, to a new product to create overall value, will require more than the development of technological solutions. Arguably a choice of technologies already exists to fully utilise bauxite residue. The barriers that will need to be overcome may be summarised as follows:

Volume

- Reuse options must be high volume

Performance

- Substituting for low cost virgin raw materials – performance must equal
- Effective removal/treatment of soda for some applications

Cost

- Evaluating the economics of current BRDA management
- Economics of additional downstream processing
- Co-use of other by-product waste streams

Risk

- Removal of soda, alkalinity and removal or immobilization of heavy metals and NORM
- Lifetime of the secondary product
- Liability issues covering heavy metals and NORM components

Volume: To make a significant impact on the amount of residue stored, uses that will consume large quantities of residue on an ongoing basis are required. Even for relatively low-technology applications (e.g. road base) this will require a large commitment of resources. For high technology applications (e.g. integrated production of metals towards zero waste) the establishment of major industrial plant would be required, which significantly increases the difficulty of implementation.

Performance: The performance of residue in any particular application must be competitive with the alternatives in relation to quality, cost and risk. For example, residue sand as a building material must be competitive with existing resources of

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mined virgin sand; extraction of iron from residue must compete with established iron ore resources, etc.

Cost: The economic viability for any utilization option must be demonstrated on a case-by-case basis. The overall lack of progress on utilization suggests that no strong economic case has been established to date.

Risk: For any given application, it must be *demonstrated that the risk associated with it is less than the risk associated with continued storage*. These risks include health, safety and environmental issues associated with transport, processing and application, and business risk associated with economic costs, product quality and various liabilities. This is not only an issue of alkalinity, heavy metals and NORMs, but also one of product performance. Critically also, the new utilization product must not compromise the production of alumina, which is the primary objective of the alumina refinery.

Factors surrounding risk are the most difficult to quantify, yet risk minimisation is an imperative of current residue management and underpins the strategies of storage and disposal. Implementation of value-adding utilization options is the alternative to continuous improvement of storage practices. As is the case with the value dimension, risk is a function of local and regional conditions and of the technology in question. The perception of bauxite residue as a waste has been established by historical and current practices. The barrier that this presents should not be underestimated, and stakeholder involvement will be essential for any successful deployment of new products. Whilst the public concern is understandable, the fact remains that very large tonnages of equally (or arguably *more*) hazardous industrial by products such as fly ash are routinely used on a significant scale (31.6 million tons per year in the US as an example). The same outcome should be possible for bauxite residue.

As well as overcoming these intrinsic barriers, utilization will probably also require incentives to initiate change on a case-by-case basis. These could be provided through direct government support and/or regulation, collaborative arrangements between industry, community and government, industrial synergy projects, or any combination of former.

To provide a framework to move forward, utilization has been organized into three Value Opportunities and these are each further divided into three Key Priority Areas (KPAs).

Value Opportunity 1: Construction and Chemical Applications

KPA1: Civil and building construction

KPA2: Catalysts and adsorbents

KPA3: Ceramics, plastics, coatings and pigments

Value Opportunity 2: Environmental and Agronomic Applications

KPA4: Waste water and effluent treatment

KPA5: Waste gas treatment

KPA6: Agronomic applications

Value Opportunity 3: Metallurgical Applications

KPA7: Recovery of major metals

KPA8: Steel making and slag additive

KPA9: Recovery of minor metals

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The Research Priority recommendations and associated Knowledge Gaps are tabulated below along with a list of suggested Implementation Support Priorities. The latter recognises that technology is only one dimension of a successful utilization industry. A possible process for addressing these aspects as part of an overall implementation of bauxite residue utilization is described in DMR-3611.

4.2 Knowledge gaps and research priorities

Based on the review of bauxite management practices outlined in this report and the knowledge gaps highlighted in the previous section, specific Research Priorities related to bauxite residue utilization in the context of the APP objectives have been determined. In addition, a more general list of Implementation Support Priorities had been identified, recognising that the availability of technology is only one dimension of the requirements for successful development of bauxite residue as a resource.

Knowledge Gap	Research Project
The development of environmental and agronomic applications of bauxite residues depends on a detailed knowledge of the speciation and physicochemical behaviour of metal ions and complexes as a function of composition and environment. Such knowledge is lacking and it is a critical adjunct to conventional environmental/agronomic research.	Detailed speciation studies on a range of bauxite residues across a variety of conditions and applications. Entails metal ions and complexes, with particular attention to leaching and general physicochemical behaviour of toxic species and naturally occurring radioactive materials (NORMs).
The actual cost (ongoing and future) of current residue storage practices is unknown. This critically impacts on the economics of utilization.	A detailed cost analysis of current residue storage practice including future liabilities. This should be undertaken for several generic refinery locations.
The manufacture of geopolymers based on bauxite residue has been identified as an area of major potential, but the technology has not been developed.	Develop processes for the manufacture of geopolymers based on bauxite residue. This should also include the option of controlled low strength materials. A parallel cost/benefit analysis should also be undertaken.
The potential for high volume utilization exists in civil construction areas for residue and/or residue components. Local industrial synergies are the key driver but technical gaps exist.	The area of utilization for civil engineering and construction should be reviewed in more detail. Both in terms of technical requirements for product substitution and opportunities for regional synergies.
A number of processes have been proposed, but never implemented, for the simultaneous recovery of the major metals from bauxite residue (towards “zero waste” objective).	A detailed cost/benefit analysis, of one or more specific process proposals, is needed to establish economic viability. This could range from true zero waste to regional opportunities such as the production of titania from high Ti residues in India.

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Accurate information on historical and current storage utilization (types and rates of deposition) on a site-by-site basis is not available.	Establish and maintain a database of the amounts of bauxite residue produced, stored and utilised on an individual refinery basis.
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4.3 Support priorities

Implementation Opportunity	Support Requirement
<p>A number of opportunities have been identified for the application of bauxite residue in construction and materials applications. Implementation of specific opportunities in the APP region could have a significant impact on the rate of residue utilization and conservation of virgin resources. Specific applications include:</p> <ul style="list-style-type: none"> • Additive to Portland cement • Component in light-weight aggregates • Development of sand fraction as a construction material • Component of bricks and blocks • Generic filler & pigment for various materials 	<p>Support may include some or all of the following:</p> <ul style="list-style-type: none"> • Research to refine the technology • Evaluation of product substitution opportunities to create regional synergies • Techno-economic, environmental impact and risk analysis • Product and market development • Development of standards and regulations • Specific incentives to progress
<p>There are many references, particularly patent literature, to applications of bauxite residue as a fluxing agent in steel making. There is however no information on the amount to which this has been implemented or what potential it may have for the future.</p>	<p>A detailed review on the application of bauxite residues as an additive in steel making. Evaluate current usage, technical issues and future potential.</p>

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GLOSSARY

Alkaloam® - bauxite residue product (Alcoa World Alumina) [138] for use as a soil amendment for phosphorus retention. Dewatered red mud fraction (as opposed to red sand) of bauxite residue.

AMD – acid mine drainage, the property of sulphidic ore bodies, when exposed to air, to generate large quantities of sulphuric acid through microbially induced oxidation. A major environmental problem, closely related to ASS.

ASS – acid sulphate soils, sub-surface soil horizons, mainly pyritic, which when exposed to air, to generate large quantities of sulphuric acid through microbially induced oxidation. A major environmental problem, closely related to AMD, but usually occurring in coastal (or previously coastal) wetland areas disturbed through development activities.

Basecon™ – bauxite residue neutralization technology (Virotec Global Solutions Pty. Ltd.)

Bauxsol™ – bauxite residue product (Virotec Global Solutions Pty. Ltd.) sea water neutralized and proprietary treated residue.

Bauxaline® - bauxite residue product (Aluminium Pechiney/Alcan) [176, 177]. Simply de-watered residue, ranging in grades from 48% to >99% solids. Uses are stated as “agronomic support, artificial reefs, ceiling of industrial waste, injection filling, coloration, building and materials application (coloration of concrete, paints etc.)”.

Bayer liquor definitions – these vary with company and relate primarily to process liquors, but are also important in the context of waste liquor disposed of to the BRDA. Alumina in solution (A) is expressed as equivalent g/L Al_2O_3 ; Caustic or Total caustic (C or TC) is the combination of the aluminate and excess hydroxide expressed as equivalent g/L of Na_2CO_3 ; Soda or Total Soda or total alkali (S or TA) is the combined caustic and carbonate concentration, again expressed as equivalent g/L (Na_2CO_3).

Bulk density – generally this is the overall dry packed solids density as would be relevant in (for example) transport of the solids or definition of soil properties. This figure is dependent on factors such as extent of pre-washing, drying, constituent particle size distribution and the packing pressure. Due to the entrained porosity bulk densities are always lower the densities of the constituent particles. See specific gravity.

BRDA – bauxite residue disposal area, usually an engineered dam repository for bauxite residue or red mud.

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Cajunite™ – bauxite residue product (Kaiser Aluminum & Chemical Co.) [22] for landfill and as an absorbent, consisting of dried residue plus a binder. Note that the Cajunite™ has a higher pH than the Gramercy residue feed.

CLSM – controlled low-strength materials. Also known as plastic soil-cement and is typically used in back-fill operations without compaction, i.e. it flows and self-compacts.

CPI or Chemical Patents Index Manual Codes – Also known as Derwent classification codes. Proprietary alpha-numeric patent classification code applying to the Derwent World Patents Index® (DWPI). There is also an Electrical Patents Index (EPI).

Drilling fluid – a lubricant for drilling into the earth's crust, usually a water based material consisting of bentonite clays plus additives.

Dry disposal - bauxite residue disposal method in which the residue slurry is filtered to a dry cake (>65% solids) prior to trucking or conveyor transport to an impoundment. See also lagooning and dry stacking.

Dry stacking - bauxite residue disposal method in which the residue slurry is thickened prior to pumping into an impoundment. Solids levels typically in the range of 48 to 55%, close to the limit for pumpable residue. See also lagooning and dry disposal.

Fly ash – finer fraction (0.5 to 100 µm) of coal ash, the residue left after the combustion of coal, substantially SiO₂, Al₂O₃, Fe₂O₃ and CaO but with a wide variety of minor (and often toxic) components. A large percentage is used in industrialized economies.

Geopolymer – synthetic aluminosilicate material suggested as a replacement for traditional Portland cement, a calcium silicate material.

Hyperbaric – pressure in excess of one atmosphere.

KPA - Key Priority Area. Sub-category used in this review to describe a useful utilization area.

Lagooning – bauxite residue disposal method in which the residue slurry is pumped into an impoundment without thickening. Solids level can be as low as 20%. See also dry stacking and dry disposal.

NORM – naturally occurring radioactive material, material containing radionuclides of terrestrial origin (as opposed to those radionuclides created via the nuclear industry within reactors and weapons programs). Exposure of the public to NORM is widespread from house construction materials and location through to coal-fired power stations.

mSv – millisievert or 10⁻³ Sv. The sievert is an SI based unit of radiation dose equivalent that approximately reflects the biological effects of radiation, the unit

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importantly incorporates the biological effectiveness of different radiation types through weighting factors. Doses received through natural background radiation vary with geographical location but typically is $\sim 2.4 \text{ mSv y}^{-1}$.

PRB – permeable reactive barrier. A sub-surface barrier, in any one of a number of geometries, containing a permeable material that removes contaminants from sub-surface aquifer flows, thereby preventing or curtailing the movement of pollution plumes.

Red LimeTM – residue from the causticisation step in the Bayer process, normally added to the bauxite residue stream. Primarily tricalcium aluminate, calcium carbonate and a hydrocalumite (mono carbonate) (Alcoa World Alumina) with an initial utilization focus as an agricultural liming product [16].

Red sand – simply the coarse fraction ($>100 \mu\text{m}$) of the bauxite residue. For typical world bauxites this is $\sim 5\%$ of residue, but some bauxites can produce up to 50% by weight coarse material.

Solids density – weight percent of dry solids in a liquid slurry. Generally this is filterable solids dried to constant mass and does not include the majority of the total dissolved solids (TDS). Pre-washing to remove soluble components can give a different figure for the solids density.

Specific gravity – density of a material relative to water (at 4°C and one standard atmosphere). Specific gravity is dimensionless. Usually actual densities (mass/unit volume) are preferred. Numerically the two densities match. A specific gravity or actual density of a material will generally be higher than its bulk density. In the case of bauxite residue the differences between bulk densities and the densities of the constituents can be substantial.

TCA – tricalcium aluminate.

TENORM – technologically enhanced naturally occurring radioactive material, material containing radionuclides of terrestrial origin (as opposed to those radionuclides created via the nuclear industry within reactors and weapons programs). The TE prefix relates to an industrial process that increases the concentration, such as with bauxite residue and coal ash.

Thickening – a generic mineral processing unit of operation in which a process stream is (partially) dewatered by the use of thickeners. The thickener combined with flocculation chemistry accelerates the settling of fines leading to a higher solids density underflow and a clarified overflow. Alternative to filtering.

TSF – tailings storage facility.

VO - Value Opportunity. Category used in this review to describe an overall industry area in which residue utilization might be applied.

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APPENDIX

Sorption is the general term that refers to one or more reactions that transfer ions, molecules and other entities from solution or gas phase into the solid state [178]. As metals and metalloids occur as ions in bauxite residue solutions, we will focus the discussion on ion sorption. Ion sorption can occur by several mechanisms [179]:

In surface adsorption reactions, ions bind to the external and internally accessible surface of a mineral phase. At least two forms of surface adsorption are recognized: (i) *Outer-sphere adsorption*, by which the ion retains a sphere of hydration and does not form an ionic and/ or covalent bond with surface atoms. (ii) *Inner-sphere adsorption*, by which the ion sheds the sphere of hydration and forms one or more ionic/covalent bonds with surface atoms.

- As a rule of thumb, inner-sphere surface complexes are retained more strongly than outer-sphere complexes, and the surface complex with the larger number of covalent bonds is more stable as more bonds have to be broken to release the adsorbed metal or metalloid. A typical example of inner-sphere surface adsorption is that of phosphate on iron oxides. Outer-sphere complexes form by electrostatic means or other weak physical forces such as van der Waals forces or hydrogen bonding and are therefore more easily displaced. A typical example of an outer-sphere adsorption is that of Na⁺ in bauxite residues.

Precipitates form from two or more ions in solution that reach a critical level of supersaturation such that the forces of hydration can be overcome and a critical mass can be formed (nucleus) from which a precipitate will grow. A classic example is putting increasing amounts of salt into a glass of water and observing NaCl to settle out eventually at the bottom of the glass. Among precipitates, two general mechanisms are recognized: (i) *surface or co-precipitates* form on the surface of a mineral and the host mineral metal is involved to some extent in the neo-precipitate. Surfaces lower the Gibbs free energy of precipitation by lowering the energy of hydration that has to be overcome for a nucleus to form (heterogeneous nucleation). The nucleus forms at the surface and either begins to spread along the surface (compatible surface geometry) of the host mineral or grows epitaxially away from the surface (less compatible surface geometry). (ii) *homogeneous nucleation*, whereby the precipitate forms due to a critical state of oversaturation in the absence of an external mineral surface. In this scenario, no external surfaces help lower the energy of hydration and only the energy gained from making bonds contributes to nucleus formation.

- As a rule of thumb, precipitates are less soluble than surface adsorption complexes, because the number of bonds needed to be broken is greater and the strength of these bonds increases over time (Ostwald ripening), however, surface adsorption complexes under most scenarios form before precipitates because their Gibbs free energy is more negative and the rates of reaction are not surface, but diffusion limited. Conversely, the rate of nucleation and precipitate growth are directly related to ion concentration in solution and the degree of oversaturation.

Since the development of modern spectroscopic tools (in particular X-ray absorption spectroscopy, Fourier transform infrared spectroscopy (FT-IR) in various forms, Raman spectroscopy, and X-ray photoelectron spectroscopy) from the 1980s onwards,

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it has become possible to define the surface complexes of metals and metalloids in pure mineral-solution environments. In the last decade this has also become possible for complex mineral mixtures to be identified, where multiple *sorption* complexes coexist. Knowledge over the solid phase speciation of *sorbed* metals and metalloids is essential in developing reaction path models and predicting solubilities under varying environmental conditions. A good example of this is the elucidation of the arsenate and selenate adsorption mechanisms on Fe-oxides [180-182] and the speciation of selenium on iron oxides, one of the most important sequestration mechanisms at work in arsenic and selenium contaminated areas. In the context of bauxite residue and its use as a metal/metalloid sequestrant, no such work has been conducted to determine the speciation of either pre-existing or newly introduced metals/metalloids.



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