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Review of Current Bauxite Residue Management, Disposal and Storage: Practices, Engineering and Science

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EXECUTIVE SUMMARY

This report addresses Items 2 and 3 of ATF-06-3 project on the Management of Bauxite Residues for the Department of Resources, Energy and Tourism (DRET), Commonwealth Government of Australia.

Item 2 is a general literature review covering the history, current status, and projected future direction of bauxite residue. It introduces those aspects of Bayer process that relate to the production of bauxite residue, with general comments on how each unit process influences the properties of the residue.

Item 3 is a detailed literature review of current practices and potential future developments in bauxite residue disposal. It examines the associated developments in engineering and science, and provides an overview of the chemistry and practices of residue neutralisation. A set of Research Priorities is provided to address the knowledge gaps identified in relation to the identification, development and deployment of best practice residue management.

The first key issue that was identified in this project was the lack of availability and organisation of the existing knowledge relating to bauxite residue. This gap is being addressed with the creation of the Bauxite Residue and Disposal Database (BRaDD). Version 1 of BRaDD has been an essential enabling tool for the collation and interpretation of information required for this review. Later versions of BRaDD with data input from the industry will provide invaluable support to the development of a global strategy for the future of bauxite residue management. Support for further development and more comprehensive data availability for BRaDD are warranted.

Bauxite residue has been continuously produced since the inception of the alumina/aluminium industry in the late nineteenth century. We have estimated that the global inventory of bauxite residue reached 1 billion tonnes in 1985, 93 years since the establishment of the first Bayer process plant. This inventory grew to 2 Bt by 2000, a doubling time of only 15 years. The inventory was 2.7 Bt by 2007, growing at 119 million tonnes per annum. The prospect of an ever decreasing doubling time, and an inventory of 4 Bt likely before 2015, highlights the urgency of the need to develop and implement improved means of storage and remediation, and to pursue large-volume re-use options.

Prior to 1980, most of the inventory of bauxite residue was held in lagoon-type impoundments. Since 1980 the trend has been towards dry stacking to reduce the potential for leakage of caustic liquor to the surrounding environment, reduce the land area required, and maximise the recoveries of soda and alumina. Further research to optimise dry stacking technology is appropriate.

Hyperbaric steam filtration is an emerging technology which discharges residue as a dry, granular material of low soda content. These properties are beneficial to long term storage, remediation, and re-use. Support to the development and implementation of hyperbaric filtration as a potential breakthrough technology is warranted.

The most important barrier to remediation, re-use and long term sustainability of bauxite residue management is its high alkalinity. The alkalinity of bauxite residue is a result of a complex mixture of solid-state and solution phase interactions. Better understanding of these interactions is required to support progress in the development of sustainable bauxite residue management and re-use options. Continuing research on the chemistry and technology of residue neutralisation is warranted.

The key Research Priorities identified in relation to the identification, development and deployment of best practice residue management, and the APP Objectives which they support, are:

Research Priority	**APP Objectives Supported**
Further development of BRaDD, in particular incorporation of information from industry practitioners	Identification, evaluation and deployment of best practices Evaluation of impacts and trends Development of best practice residue management options
Development of economically viable hyperbaric steam filtration	Development of best practice residue management options More environmentally acceptable storage Improved potential for re-use options Improved raw materials usages
Fundamental chemistry of leaching and neutralisation	More environmentally acceptable storage Improved potential for re-use options
Quantification and validation of carbon sequestration potential of residue carbonation	More environmentally acceptable storage
Development of methods for direct carbonation of residue by stack gas carbon dioxide	More environmentally acceptable storage Improved potential for re-use options Improved raw materials usages

1. INTRODUCTION

1.1 Scope

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 2 (general literature review covering the history, current status, and projected future direction of bauxite residue) and Item 3 (detailed literature review of current practices and potential future developments in bauxite residue disposal) 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 parallel documents that relate to Items 4, 5 and 7:

DMR-3609 Review of bauxite residue reuse options (Item 4)
DMR-3610 Review of bauxite residue alkalinity and associated chemistry (Item 5)
DMR-3611 Priority research areas for bauxite residue (Item 7)

1.2 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.*

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.

2. OVERVIEW OF BAUXITE RESIDUE MANAGEMENT

2.1 The History and Future of Bauxite Residue

We begin this review with a brief overview of the historical development of the alumina industry, the corresponding inevitable growth of the world inventory of bauxite residues, and the ways in which producers have dealt with those residues. This is to help us appreciate the trends in the awareness and perceptions of residue, and the evolution of technologies, management systems and regulation that have shaped the situation as it exists currently. We then move on to an examination of possible future scenarios for the coming 20 to 30 years and how they might be managed towards sustainable rehabilitation and/or productive re-use. Only with a forward-looking approach based on sound knowledge of the past can we hope to minimise the risks and maximise the benefits associated with the production of bauxite residue.

In 1885, Karl Josef Bayer moved from Brno (Czech Republic, then Austro-Hungarian Empire) to St. Petersburg, where he joined the Tentelev Chemical Plant to work on the dying of cotton fabrics using pure aluminium hydroxide, which was a rare and expensive raw material. By 1888 he had discovered that aluminium hydroxide could be precipitated in crystalline form from a cold sodium aluminate ($NaAl(OH)_4$) solution, if a seed of aluminium hydroxide was used. On August 3, 1888, Bayer filed with the German Patent office "A process for the production of Aluminium Hydroxide". Shortly after, he discovered that the required $NaAl(OH)_4$ solution could be prepared by heating bauxite under pressure in concentrated caustic soda (NaOH) solution, a process that he patented in 1892. Bayer's two patents formed that basis of the industrial process of extracting and synthesising gibbsite that now bears his name [1].

The potential for the Bayer process to provide alumina as feedstock for the newly invented process for manufacturing aluminium metal was quickly realised. By 1892 Bayer plants had been established in England, France, Italy and Germany for this purpose. Between 1893 and 1910, two more Bayer plants were built in France, and the Pittsburgh Reduction Company (later Alcoa) built the first Bayer plant in the USA at East St. Louis (Illinois). In the ensuing thirty years, more plants were built in the USA, Germany, Great Britain, Japan and the Soviet Union. Of these early plants, only the plant at Gardanne (France) is still operating.

From these beginnings the aluminium industry grew rapidly. From 6,800 tonnes in 1900, the global production rate of aluminium metal reached 1 million tonnes per annum (1Mtpa) in 1940. The global inventory of bauxite residue at that time can be estimated to have been approximately 22 million tonnes[1] associated with production

[1] 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 [2]) 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 [3].

facilities which were small by today's standards. The available literature up to that time makes little mention of bauxite residue, other than to account for dealing with it as part of the cost of production. It seems that bauxite residue was not seen by the industry, the public or governments as an issue of social or environmental importance.

Technology development and economies of scale have driven the development of increasingly larger production facilities. By the 1980s 1Mtpa was the size of new plants being built in Australia and Brazil. Today Alunorte (Barcarena, Brazil) is targeting a production of 6 Mtpa. By 1985 residue was being produced at a rate of around 48.5 Mtpa and we estimate that in that year the global inventory of residue reached 1 billion tonnes (Bt). In 2007 the annual production of residue was and estimated 119 Mtpa and the global inventory had risen to 2.6 Bt. It took about 90 years to generate the first billion tonnes of residue, but only about 15 years to produce the second billion tonnes. These figures suggest that 3 Bt will be reached some time between 2010 and 2015, and a doubling to 4 Bt is possible by 2015. Our estimates of the growth in the inventory and rate of production of bauxite residue from 1900 to 2007 are shown in Figure 1 below.

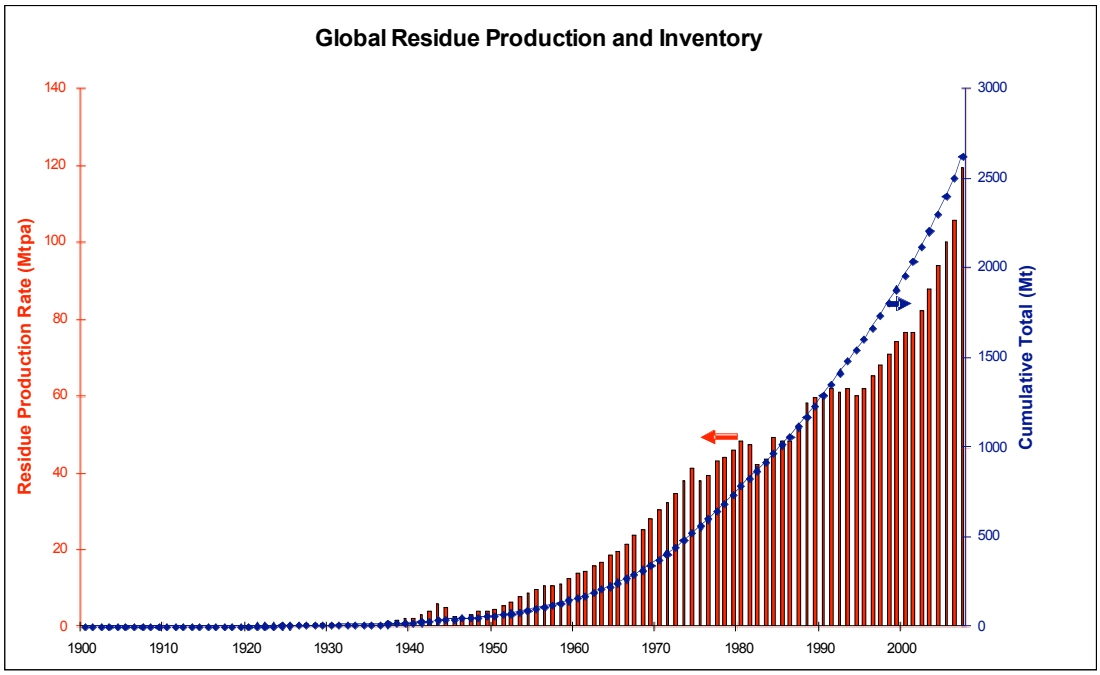

Figure 1: Global production rate and cumulative inventory of bauxite residue[1]

2.2 The Need for a Database: Development of BRaDD

It appears to have been in the early 1980s, when the bauxite residue inventory was approaching the 1 Bt level, that bauxite residue became recognised as an issue of increasing importance to the future of the industry. In 1981, the United Nations Environmental Programme (UNEP) and the United Nations Industrial Development Organisation (UNIDO) jointly sponsored a workshop in Paris to examine the environmental aspects of alumina production. Overviews of the workshop, "Environmental Aspects of Alumina Production", are available as a UNEP pamphlet [2], and in a conference paper by Hamada [3]. The workshop identified bauxite

residue as a key environmental issue for alumina production.

In 1986, The University of the West Indies and The Jamaica Bauxite Institute conducted the first conference and workshop on bauxite tailings in Kingston (Jamaica) co-sponsored by UNIDO, the International Research Development Centre (IRDC) and major producers of alumina and aluminium. A subsequent bauxite tailings workshop was held in Perth (Australia) 1992 under the sponsorship of the Australian bauxite and alumina producers. The proceedings from both of these conferences are available as conference proceedings [4, 5].

Other useful sources of papers relating to bauxite residue storage and disposal have been conference proceedings of the annual Light Metals conferences of the The Minerals, Metals and Materials Society (TMS), the Alumina Quality Workshop held every three years in Australia, and Travaux held in mostly Europe. Literature searches using the Web of Science, one of the best available literature search tools, revealed only a small number of publications in the academic literature (peer-reviewed journal and conference proceedings) relating to bauxite residues and storage. The first publication that was found was from 1977, and the total was only 89 to date (April 2009). This search did not show conference proceedings prior to 1990 and excluded patents. CSA's Aluminium Industry Abstracts lists 220 publications since 1968 including patents, peer-reviewed journal articles, other articles and conference proceedings.

From these initial searches it became clear that being restricted to existing publicly available data resources places a severe limitation to the ability to collect, systematise and interrogate information. Surveys of the accessible literature revealed the following:

1) The relevant information for Items 2-5 are scattered over many public domains: Journals, Conference Proceedings, Patent offices, Company reports, Securities and Exchange Commission reports, newspaper articles, PhD and MSc theses, and other miscellaneous sources;
2) Each source of information provides only a limited amount of relevant data, and the data type is not consistent across publications;
3) The relevant information is published in a variety of languages, principally Chinese, English, French, German, Portuguese, Russian and Spanish;
4) The nature and scope of the information is owner and/ or refinery specific and not consistent in form and content;
5) Each refinery has unique operating details with respect to BR technologies, management and engineering practices;
6) The operating details of each refinery may or may not change in any given year;
7) Therefore, *for every refinery*, a multifactorial data set propagates over time, which must then be combined over all refineries in order to provide a true reflection of technology, storage practices, engineering, science, re-use options and chemistry relevant to bauxite residue.

The absence of a means of collecting and managing information on bauxite residue was identified as a key knowledge gap, and prompted the creation of a database that would contain details on refinery practices on bauxite residue storage, disposal, and technologies gathered from a wide range of sources. The aim was to provide a

comprehensive literature resource that could be interrogated in a flexible way to enable data to be compared and analysed in a variety of user-specified ways.

The database, called the Bauxite Residue and Disposal Database (BRaDD), has already been instrumental in enabling collation of the articles and information into a coherent and (re)examinable form for synthesis and analysis. BRaDD addresses the first key knowledge gap identified in this project ([6], Appendix 1). It is the first time an attempt has been made to establish a comprehensive picture of the practices, engineering and science behind bauxite residue management, disposal and storage. Gaps in the database show where key information is missing, and provide direction for requests for information from the industry. The available data organised within the database has for the first time provided a resource, based on verifiable information, to enable the development of a systematic understanding on how current bauxite residue management, disposal and storage has evolved and where it may be heading.

2.3 The Bauxite Residue Production Process

The success of the Bayer process is demonstrated by the fact that, despite enormous technological advances and the need to process a wide range of ore types, the basic chemistry and operational steps of a modern Bayer plant are fundamentally the same as originally described in Bayer's patents. In combination with the Hall-Héroult process for smelting to metal, it remains the only viable process for the production of the metal, a situation which is highly unusual if not unique in the history of metallurgical processes. The chemical and physical nature of bauxite residues are determined by the nature of the bauxite and the effect that the Bayer process has on it. This section provides an overview of the main aspects of a modern Bayer plant that affect the properties of the residue.

2.3.1 Bayer Process Plant Outline: Red Side

The section of the Bayer plant that affects the properties of the residue produced includes a series of unit processes that start with bauxite and finish with bauxite residue. This section of the plant is often referred to as the "red side". A Bayer plant's red side today generally includes the unit processes of bauxite milling, pre-desilication, digestion, clarification, and counter-current decantation (CCD) washering. These may be followed by a further thickening or filtration step prior to discharge, usually to a bauxite residue disposal area (BRDA). A schematic of these basic steps is shown in Figure 2. Each unit process influences the chemical composition of the residues, as well as their physical and mineralogical attributes and the way they behave subsequently in the BRDA.

Bauxite residue management begins at the point of separation of the green liquor from the solids remaining after digestion. This is usually achieved in a settler which separates bauxite residues from saturated sodium aluminate ($NaAl(OH)_4$) solutions. After the green liquor has been separated, the residue underflow is transferred to the counter-current decantation (CCD) washer trains where the residues are washed in several stages in raked settler-washers to recover NaOH and $NaAl(OH)_4$ from the remaining entrained liquor and from the solids that slowly release these constituents into solution. After washing in the CCD, the residue is usually treated in a final

thickener or filter to increase the solids content prior to being transported to the BRDA. Filtration is used in some plants currently, but the majority of plants use thickeners for this purpose. The thickener may be either a deep cone thickener (Alcan) or a Superthickener (Alcoa). Further details of these final stages are given in Section 2 below.

The most important influences of each process in relation to bauxite residue are summarised in Table 1.

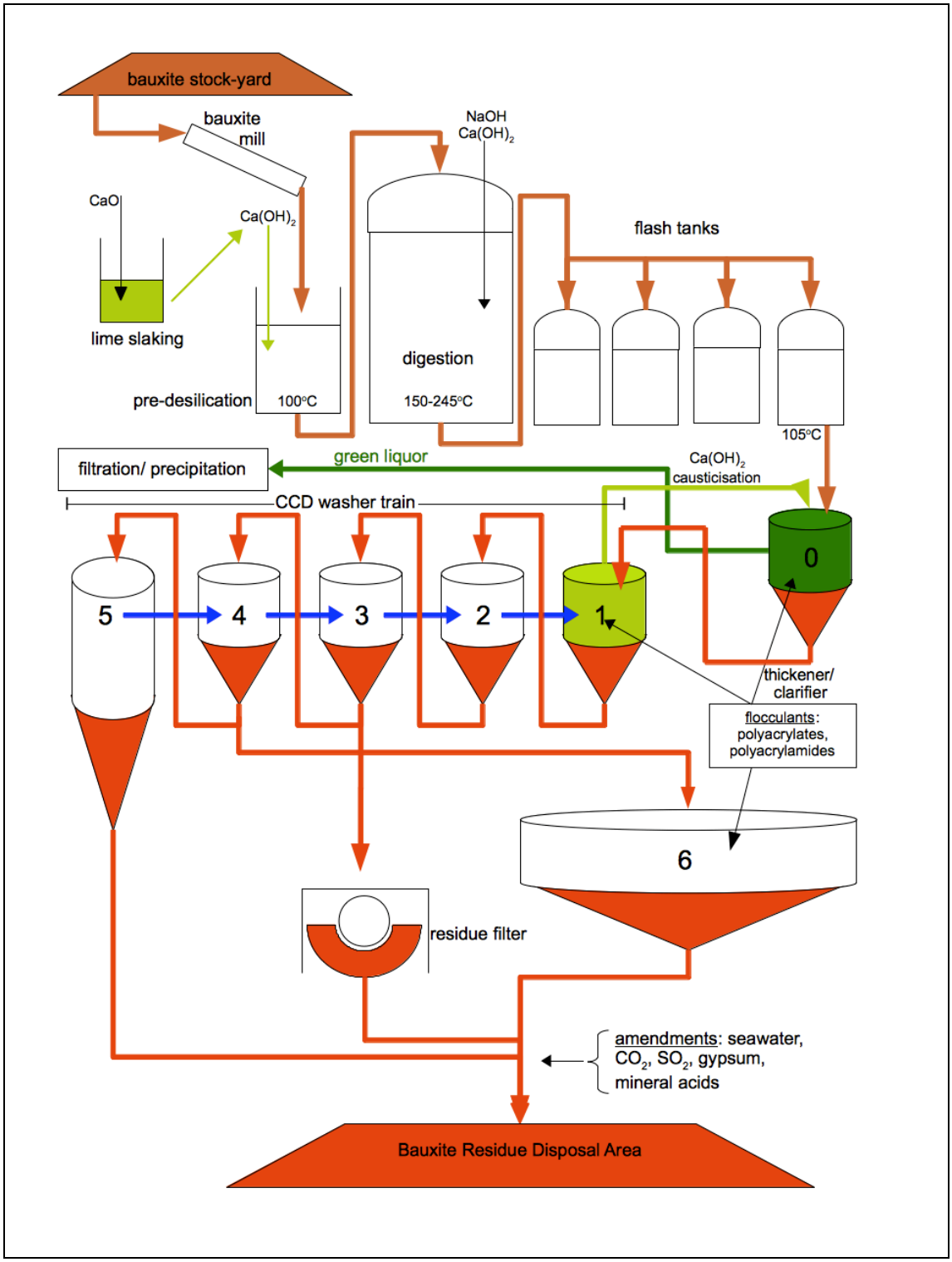

Figure 2: Schematic of Bayer process "red side" highlighting the processes affecting the disposal and storage of bauxite residues. The blue arrows indicate the flow of wash water counter-current to the flow of residue (red arrows). The final residue preparation stage may be a deep cone thickener (5), Superthickener (6) or a filter. (Adapted from Whittington [7] with major modifications.)

Table 1: Bayer plant unit processes affecting bauxite residue characteristics relevant to disposal and storage.

Plant Process	Effects relevant to disposal and storage
Bauxite milling	• Sets the effective particle size distribution and specific surface area of bauxite particles for digestion • Particle size and surface area are key factors in determining physical properties (e.g. settling rates, mud rheology) and chemical properties (e.g. adsorption of flocculants, organics and metal ions, dissolution rates of minerals and precipitates)
Desilication	• Introduces sodium alumino-silicates (desilication products (DSP)) to the residue
Digestion	• High temperature, high pressure environment which alters the elemental and mineralogical make-up of the original bauxite particles into bauxite residues • Nature of the bauxite dictates temperature, pressure and NaOH concentrations (see Table 2 for more detail) • Introduces large amounts NaOH to the solids increasing their pH, alkali and Na^+ content. • Al is solubilised and removed from the solid phase • Mineral transformation reactions occur: less stable minerals dissolve and re-precipitate; other minerals undergo solid-state dehydration reactions which convert them to more stable mineral phases
Settling	• Conducted in high volume raked settlers • Slurry is mixed with chemical additives to promote settling and to clarify the overflow liquor • Bauxite residue is separated from the green liquor
Washing	• Conducted in high volume raked washers • Flocculants added to achieve required underflow densities • Recovery of NaOH and $NaAl(OH)_4$ in the remaining liquor of the residues to be returned to the main Bayer process liquor • The underflow of the last washer is optimised according to the disposal method
Final thickening or filtration	• Increases solids density to meet storage or disposal requirements • Further flocculent or filtration aid added • Additional washing

Table 2: Bayer Digest Variables [8].

Main Al Mineral	**Gibbsite, $Al(OH)_3$**	**Boehmite, AlOOH**
Temperature, ^oC	140 - 150	200 - 240
Pressure, atm	1.0 - 3.0	6.0
NaOH, M	8.7 – 3.5	4.9 – 3.5

3. DETAILED LITERATURE REVIEW OF CURRENT STORAGE PRACTICES, ENGINEERING AND SCIENCE

3.1 Disposal Methods: Overview

The methods currently in use for the disposal of bauxite residues may be classified broadly into the following groups: seawater discharge, lagooning, dry stacking and dry disposal. The main characteristics of each of these are as follows:

3.1.1 Seawater Discharge

The residue slurry from the mud washing circuit is disposed directly into the sea, usually via a pipeline which takes the slurry well offshore for discharge into the deep ocean. Residue disposal is generally preceded by thickening and washing processes which remove caustic liquor and increase solids contents to various degrees.

Key Attributes:

Positive:

i. Eliminates the need to allocate land for residue storage;
ii. Eliminates the need for closure and rehabilitation of storage areas;
iii. Eliminates environmental impacts associated with land-based storage, including potentials for dusting, contamination of surface and ground waters, and leaching of toxic metals;
iv. Generally lower capital and operating costs than for land-based disposal methods;
v. Does not require additional thickening or filtration of the slurry prior to disposal;
vi. Does not return impurities to the Bayer plant liquor; but

Negative:

vii. Covering of sea bed and destruction of associated ecosystem;
viii. Potential for release of toxic metals to marine environment;
ix. Increased turbidity of sea water in the region of the discharge due to dispersion of original mud and the formation of colloidal magnesium and aluminium compounds;
x. Unknown short- and long-term effects on ecosystems in general and food-chains in particular;
xi. Increasing community and regulatory pressure to discontinue the practice; and
xii. Loss of soda and alumina values with entrained liquor.

3.1.2 Lagooning

Without Neutralisation: The residue slurry from the mud washing circuit is pumped into land-based ponds. Such ponds may be formed within natural depressions using dams and other earthworks as appropriate and necessary to ensure secure containment. Alternatively, in the absence of suitable natural topography, ponds exist as fully fabricated structures, generally excavated into the existing land. In either case, best

practice is to line the ponds with sealants to minimise liquor leakage to the underlying ground and ground water. The linings used vary in relation to both the materials used and the complexity of the construction. The simplest is a single layer of compacted clay which separates the residue from the original soil or rock of the storage area, but the integrity of such layers cannot in general be guaranteed [9]. Additional security can be achieved by the use of multiple layers featuring impermeable plastic or geo-membrane materials to form a seal between the residue and the supporting clay or other layer beneath. Minimising the hydrostatic pressure by removing liquor by decanting or under-draining the deposit further contributes to the reliability of the seal [10].

Key Attributes:

Positive:

i. Lowest capital cost land-based disposal method provided suitable land is available at low cost;
ii. Does not require additional thickening or filtration of the slurry prior to disposal;
iii. Dust potential minimised by maintaining a supernatant liquor layer;
iv. Does not return impurities to the Bayer plant liquor; but

Negative:

v. Requires the provision of substantial areas of land for storage;
vi. Requires planning and funds allocation for long-term closure and rehabilitation;
vii. Loss of soda and alumina values with entrained liquor;

And, if not neutralised:

viii. Creates a highly alkaline, poorly compacted mud overlain by a highly alkaline lake;
ix. Involves a range of safety and environmental hazards including potentials for contact of humans and wildlife with caustic liquor and mud, and contamination of surface and ground waters by leaching of caustic liquor and associated toxic metals;
x. Difficult to close and rehabilitate because of the need to remove large amounts of caustic liquor, both supernatant and entrained, and to render the contents of the site benign to the surrounding ecosystems in the long term;
xi. Generally requires significant engineering to eliminate potential for catastrophic failure of impoundments and consequent hazard to surrounding environment and population; and
xii. High construction and maintenance costs;
xiii. Difficulty of eventual closure – possibility of indefinite legacy.

Note: Disadvantages viii to xi can be substantially mitigated by neutralizing the slurry prior to discharge, for example by mixing with seawater or by the addition of mineral acids (e.g. sulphuric acid).

3.1.3 Dry Stacking

The residue slurry from the mud washing circuit is thickened to a paste (in the range of approximately 48 to 55% solids) prior to discharge. The paste is thixotropic, and so is amenable to pumping and pipeline transport. Upon discharge from the pipe it will flow down a slope without segregating or settling to form layers of uniform thickness at an

angle of repose in a range of 2^o to 6^o (in non-freezing conditions). The residue deposit is built into a stack by discharging the paste progressively in thin layers which are allowed to dewater and air-dry before being overlain with the next layer. Upon standing, the paste consolidates to a density of 62 to 65% solids, with an accompanying increase in shear strength. Shear strengths of 20kPa or more may be reached [11]. The consolidation occurs as the solids settle and liquor is removed by a combination of decantation and surface evaporation. Modern designs also include under-draining to facilitate the consolidation process. The process is designed such that the dried paste becomes substantially self-supporting so that it can be safely stacked to considerable heights within containment bunds, minimising the physical footprint of the disposal area [10].

Key Attributes:

Positive:

i. The area of land required for storage is minimised;
ii. The structures required for secure containment are minimised;
iii. Soda and alumina values in the liquor are returned to the Bayer plant;
iv. The potential for leakage to groundwater is minimised due to the reduction in hydraulic head;
v. The potential for surface water contamination is minimised by reducing the area of open contaminated water and returning runoff water to the Bayer plant;
vi. Rapid deliquoring facilitates subsequent management of the area, including stabilisation and rehabilitation;
vii. Environmental and safety hazards associated with the presence of open caustic lakes are minimised ;
viii. Recovery of solids for alternative uses is facilitated; but

Negative:

ix. Requires the provision of sufficient areas of land for storage;
x. Requires planning and funds allocation for long-term closure;
xi. Requires an additional stage of thickening or filtration prior to discharge;
xii. Liquor impurities are returned to the Bayer plant, resulting in a variety of negative process (economic) impacts;
xiii. The surfaces of the dry stack are subject to dust lift-off and mitigation processes may be required;
xiv. May be difficult to achieve in areas of high rainfall and low nett evaporation; and
xv. Significant compaction hinders the establishment of vegetation.

Note: The hazards associated with alkalinity may be further reduced by neutralisation of the slurry. Seawater, carbon dioxide, sulphur dioxide, mineral acids and waste gypsum have all been used in this application. Changes in drying and structural characteristics must be taken into account in evaluating alternatives.

3.1.4 Dry Disposal

The residue slurry from the mud washing circuit is filtered to a dry cake (>65% solids). It is assumed that the material is also washed on the filter with water or steam to recover soda and minimise the alkalinity of the residue. The dry residue cake is carried by truck

or conveyor to the disposal site, where it is dumped without further treatment.

Key Attributes:

Positive:

i. The area of land required for storage is minimised;
ii. The risk of collapse of a raised mound or impoundment, and the structures required for secure containment, are minimised;
iii. Soda and alumina values in the liquor are returned to the Bayer plant to the extent possible by filtration (including washing), which reduces the need for washing by counter-current decantation;
iv. The potential for leakage to groundwater is minimised due to the low pore volume of the mass;
v. Environmental and safety hazards associated with the presence of open caustic lakes are avoided;
vi. Material can be recovered from the deposit by standard earthmoving equipment if and when required, for example to be marketed as a raw material for downstream use;
vii. Rehabilitation and closure are facilitated by the ability to mound and landscape the deposit to cover it with a surface layer of soil to establish vegetation, and by its low alkali content; but

Negative:

viii. Requires the provision of sufficient areas of land for storage;
ix. Requires planning and funds allocation for long-term closure and rehabilitation;
x. Requires the installation and operation of a filtration plant capable of filtering the whole mud throughput, preferably with associated washing;
xi. Liquor impurities are returned to the Bayer plant, resulting in a variety of negative process (economic) impacts; and
xii. Surfaces are subject to dust lift-off so that mitigation processes may be required.

Note: The hazards associated with alkalinity may be further reduced by neutralising the filter cake in addition to washing it on the filters. As noted previously, the effect of neutralisation on the physical properties of the cake must also be determined and taken into account.

3.1.5 Historical Evolution of Disposal Methods

Fig 1 shows the distribution of the broad categories of residue disposal methods for 17 refineries for which information could be found in the public domain for each of the years nominated. These 17 refineries accounted for 44% of the 76 million tonnes of alumina produced globally in 2007 [12].

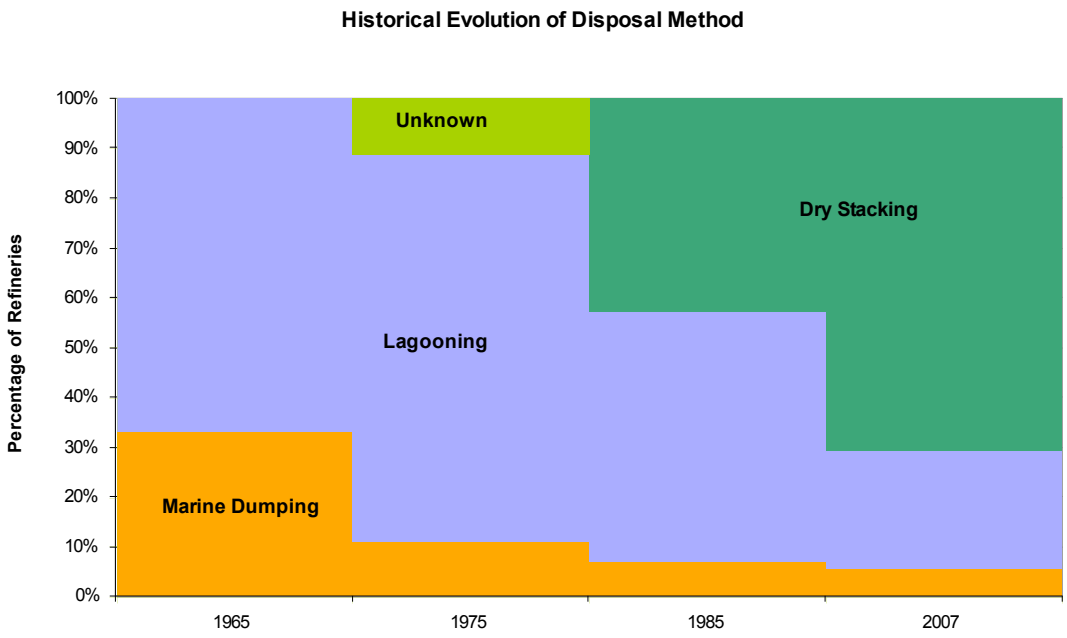

Figure 3: Evolution of storage practices at 17 refineries (representing 44% of global alumina production in 2007) for which information is available over the period 1965-2007 (see Table 3).

Figure 3 indicates a consistent trend away from seawater disposal to land-based disposal, and from wet to dry disposal methods. In 1965, one third of the refineries considered were disposing of residue by marine dumping, and the other two thirds were impounding it in lagoons. In the 1970s research into alternatives led to the development of dry stacking methods. The subsequent increase in the number of plants using dry stacking reflects its emergence as preferred practice in the construction of new refineries, and the conversion of a number of refineries from wet to dry disposal. By 1985 43% of the refineries were using dry stacking, growing to 70% by 2007.

The individual refineries and the associated storage methods are summarised in Table 3.

Table 3: Storage practices at 17 refineries (representing 44% of global alumina production in 2007) for which information is available over the period 1965-2007 (see Figure 3).

Startup date	Refinery	1965	1975	1985	2007
1959	Kirkvine	Lagoon	Lagoon	Lagoon	Lagoon
1963	Kwinana	Lagoon	Lagoon	Dry stack	Dry stack
1965	Aluminium de Grece	Sea disposal	Sea disposal	Sea disposal	Sea disposal
1967	Queensland Alumina Limited		Lagoon	Lagoon	Lagoon
1972	Alcoa Aluminio S.A.		Lagoon	Lagoon	Dry stack
1972	Gove Alumina		Lagoon	Lagoon	Dry stack
1972	Pinjarra		Lagoon	Dry stack	Dry stack
1973	VAW Stade		Unknown	Dry stack	Dry stack
1973	Eurallumina		Lagoon	Lagoon	Lagoon
1980	San Ciprian			Dry stack	Dry stack
1983	Aughinish			Dry stack	Dry stack
1983	CVG Bauxilum			Lagoon	Lagoon
1984	Worsley Alumina			Dry stack	Dry stack
1984	Wagerup			Lagoon	Dry stack
1987	Dhamanjodi				Dry stack
1995	Alunorte Barcarena				Dry stack
2005	Yarwun				Dry stack

The predominance of dry stacking in current practice is a result of economic and environmental factors which drive the need to:

- Reduce the land area required for residue storage;
- Minimise the potential for liquor release to the surrounding environment; and
- Maximise the recovery of liquor to the refinery.

3.1.6 Emerging Technology

Filtration on vacuum drum filters followed by dry disposal has been applied successfully in practice, for example at the Hindalco plant at Renukoot [13]. Recent improvements in filtration technology, in particular the advent of large scale hyperbaric steam filtration, have opened the possibility of a further step change improvement in the removal of fluids and salts from bauxite residue. Hyperbaric steam filtration of bauxite residue has been successfully demonstrated using a Bokela Hi-Bar® in at the pilot plant scale at the Aluminium Oxid Stade plant [14] and with similar technology at the Bauxilium plant in Venezeula [15].

3.1.7 Post-disposal Treatments

For long-term storage or re-use of the residue, it may be necessary to release liquor to the surrounding environment. This will generally require it to be neutralised in some way and diluted prior to discharge. The pore fluids remaining in the stack will generally also need to be diluted and/or neutralised. Solid alkalinity must also be taken into consideration, because it can have a profound effect on attempts to neutralise the pore water. Solid alkalinity is also a major factor to be considered in any evaluation of possible future storage or re-use scenarios. Post-disposal treatments are dealt with in more detail in Section 3.3 below.

3.1.8 Summary

The main factors that determine the choice of disposal method for a given refinery include:

- The grade and mineralogy of the bauxite and the size of the refinery, which together determine the rate of residue production;
- The local rainfall and topography;
- Land availability; and
- Other factors such as the economics of trucking versus pumping.

The current direction for the industry indicates dry stacking as the favoured option for residue disposal [10, 16]. The next step could be to further reduce moisture and soda contents by hyperbaric steam filtration [14,15].

3.2 Disposal Methods: Scientific and Environmental Aspects

3.2.1 Historical Perspective

Prior to the 1970s, there were only two disposal methods in general use, seawater discharge and lagooning. The reasons for the choice of one technology over another were driven by a variety of factors, the main ones being availability of land or proximity to the ocean for disposal, local governmental regulations, and the technology choices of the alumina plant operator. French and Japanese practices have favoured disposal at sea as the best option on economic and environmental grounds. North American practice has favoured land-based disposal in lagoons, even for refineries on the seaboard.

The 1970s saw a major expansion of the alumina industry in response to growth in primary aluminium production, resulting in a rapid growth in the production rate and global inventory of bauxite residue as shown in Figure 1 above.

The demand for expansion of production in the 1970s led to the construction of new refineries throughout the world. In particular, increasingly large refineries were built in the major laterite regions of South America, India and Australia. The distribution and timing of refineries are shown in Figure 4. Apart from a number of refineries which we have been unable to locate in China, we believe this distribution map accurately accounts for the majority of global alumina production.

The rapid expansion in alumina production and increasing environmental awareness and regulation in the developed world from the 1970s onwards led to the development of new approaches to residue management.

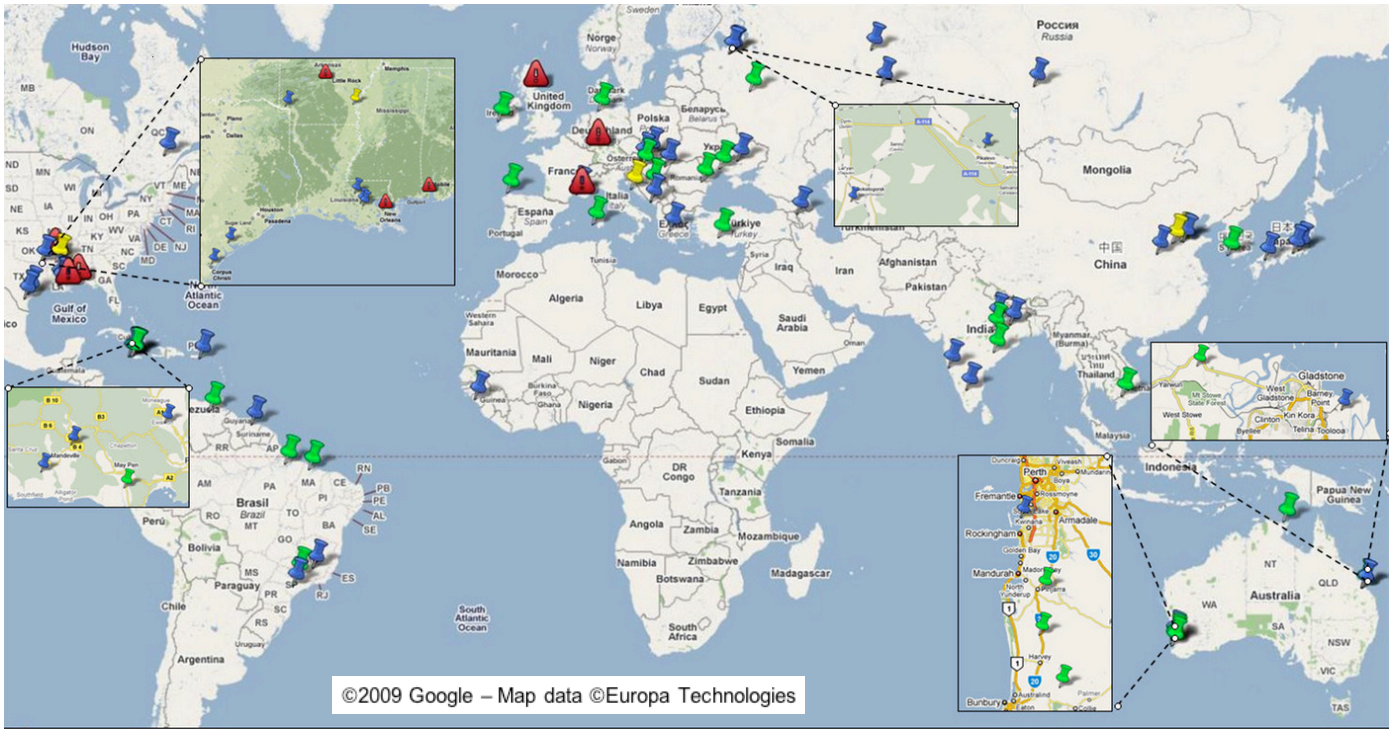

Figure 4: World map showing alumina refineries in existence to our knowledge: before 1970 (blue), after 1970 (green), closed (red) and unknown (yellow). GOOGLE is a trademark of Google Inc.

3.2.2 Marine Disposal

The 1981 UNEP/UNIDO workshop (also see Section 1.3 above) concluded that "disposal [*of bauxite residue*] into rivers has been strongly discouraged and marine disposal regarded as a last resort where suitable land disposal is not available" [2]. This appears to reflect the opinion of the majority of companies involved in alumina refining. There has been a shift away from direct sea water or river disposal as shown in Figure 3 above. To our knowledge no new refineries were built using marine dumping after 1970.

Residue from the Gramercy plant in Louisiana was disposed into the Mississippi River until 1974, at which time a transition was made to lagooning. The operating company, Kaiser, voluntarily removed mud from the river and relocated it to land-based lagoons. Considerable effort was subsequently directed towards dewatering and treating the residue to enable the creation of useful products in order to limit the requirements for additional area for residue disposal [17].

Plants in Japan are particularly restricted in relation to land area available for disposal of residues, and so have historically discharged residue to the deep sea. Environmental and economic factors have increasingly placed pressure on the industry to cease deep sea disposal. One response has been to find beneficial uses for residue, for example as a supplement to cement manufacture, however this has not been sufficient to remove the need for dumping. Another approach has been to avoid the production of bauxite

residue in Japan by importing the intermediate product, aluminium hydroxide ("hydrate") rather than bauxite as the feedstock for the Japanese plants. In this way the bauxite residue disposal issue is effectively exported to the supplier location.

In addition to raw material substitution, efforts are being made to reduce the amount of residue dumped by maximising the grade of the bauxite imported, and seeking ways of utilising the residue as a feedstock to other industries, in particular cement manufacture [18].

In 2005, Japan made a commitment to the International Maritime Organisation that disposal of bauxite residue to the sea would be discontinued by 2015 [18]. Japan reported that in the previous five years residue had been disposed to the sea at two locations at a total rate of 1.0 million tonnes per year. It was further reported that Environmental Impact Assessments had been carried out at both sites. The study observed no impact on water quality and marine organisms in the water column in the region of sedimentation and some differences in the nature of the seabed between the dumping sites and control sites. Overall, only limited impact was observed. It was intended that further monitoring campaigns would be carried out every 2 to 3 years. The plants at Gardanne in France and Viotia in Greece that still use marine dumping are actively pursuing alternatives [19]. A study of the discharge from the Viotia plant into the Gulf of Corinth showed that an extensive deposit has been formed close to the point of discharge from a pipeline at a depth of 100m. The red mud also extends over the sloping shelf of the sea floor and into an abyssal plain to a depth of 860m at distances of up to 17km from the point of discharge. The main mechanism of transport of the residue from the shelf to the abyss was found to be by gravitational flow triggered by seismic events, which are common in the region [20].

Thus, only a small proportion of current global alumina production (in the order of 2 to 3%) results in marine disposal of residue. The strategic direction for each of the companies carrying this legacy appears to be to implement alternatives in the future, however the only firm commitment to this that we were able to find was Japan's commitment to an end-date of 2015.

3.2.3 Dry Stacking

Methods for disposing of residue with prior deliquoring were pioneered in Germany with a view to minimising the land required for disposal and maximising the return of soda and alumina to the refinery. The term "Dry Stacking" appears to have been first used to describe the process developed at the Ludwigshafen/Rh. plant in the 1970s [21-24]. Red mud slurry from the washing stage was filtered on drum filters which discharged a cake at about 55% solids by weight. The cake was fluidised by mechanical agitation for pumping to the drying area where it formed a mound with a shallow angle of repose (approximately 5^{o}). The deposition schedule was managed to optimise surface drying while minimising dusting potential. It was found that:

- The mud consolidates to about 62-67% solids, enabling it to be traversed by machinery minimising the requirements of the containment dykes;
- The degree of fluid decant was minimal, and rainwater could be collected and either discharged to the environment or returned to the Bayer plant according to purity;
- The material compacts on standing to become highly impermeable (permeability

in the order of 10^{-9} cm/sec), removing the necessity to line the disposal area to prevent seepage of impurities into the underlying soil and ground water.

Dry Stacking is a special case of the more general Thickened Tailings Systems that were being developed by the mining and mineral processing industries in that period. A similar system was developed and implemented by Alcan at the Arvida plant in Canada [25-27]. In this case special thickeners were developed to produce a mud of sufficient solids density to behave as a non-segregating slurry. This led to the development of the Alcan Deep Thickener, a new technology for producing densities of over 50% solids suitable for the production of thickened tailings without the need for filtration [28]. In 1996 Alcan entered into a licence agreement with EIMCO for the further development and marketing of deep thickeners. According to the EIMCO (now FLSmidth Minerals) website, there are over 50 Alcan paste thickeners now operating in alumina plants, and the technology has been deployed to other industries including copper and lead/zinc processing [29, 30].

The Thickened Tailings Disposal (TTD) system was recently implemented at the National Aluminium Company (NALCO) plant at Orissa, India, using the Alcan technology [16, 31]. TTD replaced the original wet disposal method. The system was installed as part of a major plant expansion from 0.8Mtpa to 1.575Mtpa. The existing wet disposal method would not have been capable of supporting the projected residue production over the ensuing 20+ years, because of limitations on the availability of suitable land area and environmental concerns associated with wet disposal. The alternative of Dry Disposal (see below) was also considered, but was rejected, primarily on grounds of capital and operating costs. Concerns related to the safety and environmental aspects of trucking the material in hilly terrain were also cited [16]. The TTD system was seen to have the following advantages in relation to wet storage:

- No special requirements for the disposal area;
- No large dams or dike walls;
- Reduced earthquake and erosion risks;
- Lower energy consumption and pipeline requirements; and
- More amenable to reclamation or rehabilitation than is the case for lagoons.

The key to the design of a successful dry stacking system is an understanding of the rheological properties of the residue [32, 33]. In particular, the slurries are thixotropic, such that their flowability increases with the input of mixing energy. Thus, slurry that has been allowed to settle to 50% solids will be firm and seemingly un-pumpable. However if sufficient mixing energy is introduced, the viscosity is decreased as the pore liquids create a network such that the slurry becomes amenable to pumping. If the material is subsequently allowed to sit without mixing, it will slowly revert to a firm condition. These transformations in flow behaviour occur without the solids density of the material changing. This effect and its careful management are fundamental to the success of any dry stacking process. The design must therefore take into account the rheological parameters of the particular mud to be stacked [32].

These principles have been successfully applied also at the MOTIM plant in Hungary, where the mud is filtered on vacuum drum filters to 50% solids, fluidised by high-intensity stirring, and then pumped to the residue storage area where it is stacked in layers to dry. After drying times between 80 days (summer) and 160 days (winter), the solids content rises to around 65%, at which point the material can be mechanically

spread using conventional earth-moving machines [34].

The rheological properties of bauxite residues vary widely from plant to plant. They are a function of the nature of the bauxite, the design of the mud handling and washing circuit, the nature and rates of the chemical additives (in particular flocculants and flowability aids) used, and the amount and manner of introduction of mixing energy applied [35]. The key rheological parameters that must be evaluated in order to design the slurry thickening and transport systems, and to predict the spreading behaviour and slope formation in the tailings area, are yield stress and viscosity as a function of solids content and the shear and compression history of the material [32, 36]. The particle size distribution (in particular the sand content) is also important [37].

Alcoa determined that underflow densities in the region of 50% solids were sufficient as the starting point for a dry stacking system provided with underdrainage for efficient deliquoring [10]. The required solids density was achieved in a specially designed large diameter deep-cone thickener (a "Superthickener") developed in collaboration with EIMCO [38, 39]. This formed the basis for the development of a sophisticated mud stacking system which was adopted through a program of phased implementation in Alcoa's Western Australian refineries between 1985 and 1992. The system integrates close control of the mud slurry properties with a system in which mud is deposited into rectangular cells on a rotational basis to optimise drying and minimise the land area required. The slurry is pumped to specially lined storage areas provided with under-drainage facilities to promote final deliquoring of the deposited paste and return of the recovered liquor to the Bayer plant. In addition to the bottom under-drain, further under-drainage may be introduced progressively as the stack is built. It was found that densities in the region of 70% solids are achievable in the deposit, although the time taken to achieve this was not reported [40]. A schematic of the system is shown in Figure 5.

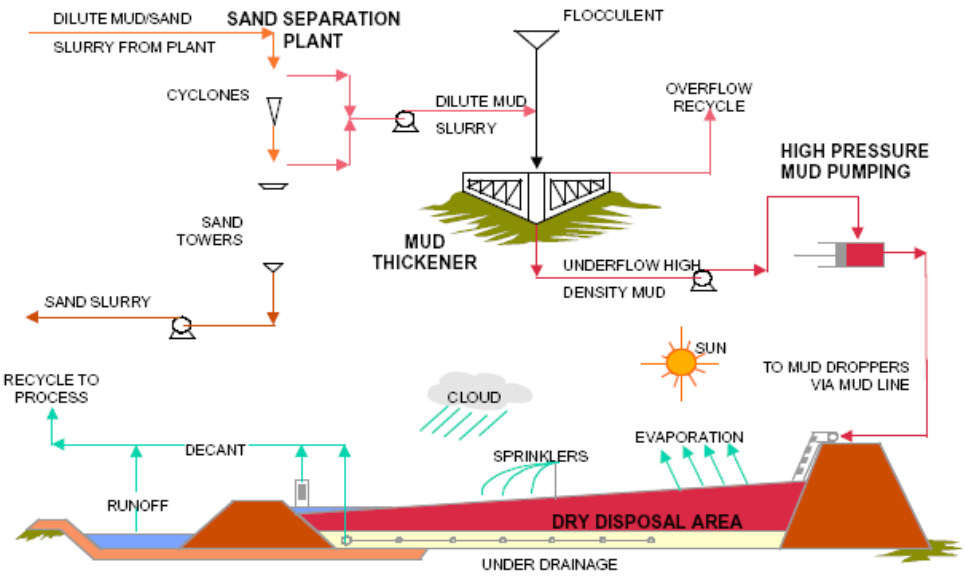

Figure 5: Alcoa dry stacking method – schematic: http://www.alcoa.com/global/en/environment/pdf/Dry_Stacking_Case_Study1.pdf

The choice of this approach was made after extensive pilot-scale testing in which a range of possible technologies were evaluated, in particular vacuum, pressure and belt filters, as well as deep cone and high-rate thickeners. In-situ pumping and dredging techniques were also evaluated. It was found that the optimum economic outcomes were achieved for the first refinery (Pinjarra) with a single large thickener of 90 meters diameter designed to process up to 460 tonnes per hour of mud solids. The yield stress values encountered in this thickener are more than 30 times greater than those found in most thickener underflows resulting from flocculated pulps. This required new rake and rake-shaft mechanism designs to cope with the very high torque requirements. For example it was considered that the raking loads would exceed the capability of any centre-drive design, so a peripheral traction drive was chosen [29].

Following the success of this approach at Pinjarra, the Alcoa Dry Stacking process was introduced to the other two Alcoa refineries in Western Australia by (Kwinana 1987, Wagerup 1992) [40]. It has since been deployed to other Alcoa operations including those in Suriname, Spain, and Pt Comfort Texas [41].

Figure 6 is a 2006 Google Earth™ image of the Pinjarra residue area. The labelling of the areas is according to the Pinjarra Long Term Residue Plan [42]. The area is divided into separate rectangular cells. Bauxite residue is pumped into one cell at a time, while the others are left to dry. Once a sufficient layer of fresh bauxite residue has been built up in the active cell, the discharge is moved to the next cell, and so on. The area of open decant water is kept to a minimum – the majority of the open liquid surface is associated with cooling water and fresh water lakes. A series of small circles can be seen on the drying areas corresponding to the arcs of dust suppression sprinklers.

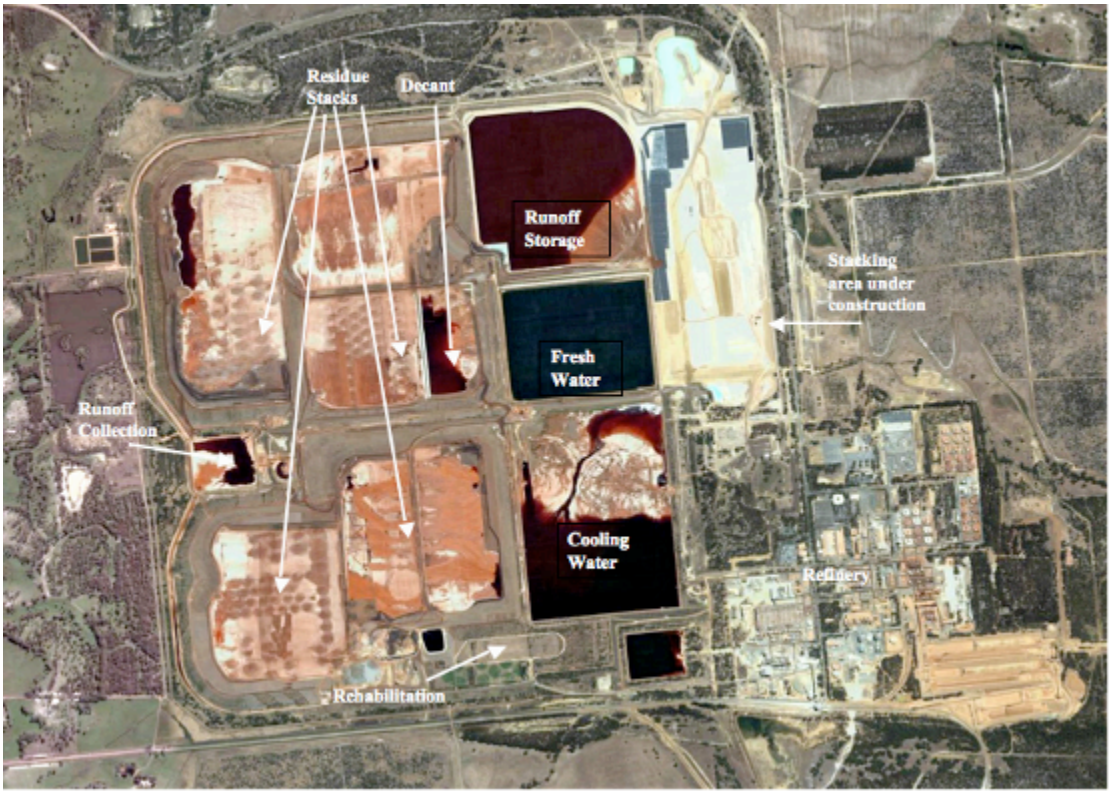

Figure 6: Google Earth™ image of Pinjarra refinery and residue area in 2006. Captions inferred from Pinjarra Long Term Residue Management Plan [42]. GOOGLE is a trademark of Google Inc.

At 70% solids density the shear strength of the stack is > 30 kPa, sufficient to ensure a significant degree of structural integrity. The storage volume requirement for dry stacking is about 60% of the volume required for lagooning. This, in addition to the ability to stack the deposit vertically, results in a greatly reduced area requirement for the residue operation. An interesting aspect of the Darling Range bauxite processed by Alcoa (and the granite-based bauxite portion of the Worsley bauxite) is its unusually high sand content. The thickening operation requires that the sand be removed so that the fine mud fraction can be thickened. Alcoa has turned this to advantage by using the sand for construction of the containment walls, eliminating the need for borrowing local construction materials, which has cost and environmental benefits [10]. A degree of mechanical ploughing of the surface is required to optimise drying rates, and water sprinklers are used on an as needed basis to mitigate dust lift-off. The overall cost (capital and operating) of residue management is significantly less using this technology than for the earlier lagooning approach.

The environmental impact is also significantly less than for lagooning due to:

- Greatly reduced potential for groundwater contamination;
- Reduced land area requirement;
- Reduced alkaline liquor content;
- Improved dust control;
- The use of residue sand for dyke construction; and
- Easier rehabilitation of the final deposit [40].

In addition, the slurry from the Superthickener is suitable for neutralisation by CO_2. The carbonated residue has superior drying and dusting characteristics, is easier to rehabilitate and is more suitable for a range of potential re-use options [43].

3.2.4 Dry Disposal

Dry disposal refers to the practice of mechanically removing as much water as possible from the mud to produce a dry cake with a solids content of 70% or greater prior to disposal. The dry cake is not pumpable, so is generally moved to the disposal area by conveyors or trucks. There is no significant further deliquoring once the residue has been delivered to the storage area. These factors distinguish it from *dry stacking* (above), in which the mud is thickened to a 50-55% solids paste and pumped to the storage area, where it is further deliquored to produce a dry stack whose ultimate solids content is around 70%.

It is not possible to achieve a dry, non-thixotropic cake by means of thickening alone, and so a filtration stage is required. Vacuum filtration is in general not satisfactory for this purpose, fundamentally because it is limited in the available pressure drop across the filter cake to less than 0.75 bar [15]. This is not sufficient to overcome the capillary resistance inside the pores of the red mud to the extent required to fully deliquor the cake. By using pressure filtration it is possible to achieve differential pressures in the order of 6 bar across the cake. This is sufficient to produce a fully deliquored cake. The non-thixotropic nature of this cake is fundamental to the success of the process. It means that the cake can be readily discharged from the filter by air blow-back or mechanical means, and can then be transported to the disposal area by truck or conveyor where it can be stacked with a minimum of additional treatment in relatively simple containment facilities [15, 44, 45].

Recent trials of BOKELA hyperbaric filtration technology at the Stade plant in Germany have demonstrated that solids contents of greater than 75% can be achieved with the application of steam in the filter. This produces soda contents as low as 3 g/kg, which compares to 6 to 12 g/kg by vacuum filtration. The resulting cake is described as "extremely dry and well washed … with a crumbly, sandy-like and non-sticky consistency and a low soda content" [14]. Similar results were also achieved by Machinenfabrik Andritz at the CVG plant in Venezuela [15].

Producing a residue with these characteristics greatly simplifies handling and storage requirements, reduces the potential for environmental impact, and broadens the options for rehabilitation and/or reuse of the material. A number of these advantages have previously been demonstrated by Nippon Light Metals at their Tomakomai works [44]. Given that the technology has been demonstrated at a plant scale, the challenge is to

develop it as an economically attractive alternative to current methods, and then to deploy it to existing and future plants. *This is recommended as a key focus area for research and development.*

3.3 Bauxite Residue Amendment

Bauxite residue leaves the Bayer process plant as a slurry whose high alkaline (pH >11) with a high sodium content favours particle dispersion. In addition, the solids in the slurry contain a high proportion of fine, silt-sized particles. The combination of these chemical and physical factors creates significant difficulties in the handling, storage and remediation or re-use of bauxite residue. The need to amend bauxite residue to mitigate these difficulties grew in the latter half of the 20th century as rapid growth of industry output coincided with increasing levels of environmental awareness and regulation.

Improvements in bauxite residue management will undoubtedly be somewhat site-specific, but significant progress has been made in general with the advent of dry stacking, and a further step change may occur following recent developments in pressure filtration and washing, as described in the previous section. It is likely that some form of additional amendment, probably involving partial pH neutralisation, will be an essential ingredient of any permanent solution. Even with the excellent washing performance offered by hyperbaric steam filtration, significant alkalinity remains associated with the solids because of the complex solution equilibria, incomplete dissolution of solid alkalinity, and kinetic limitations involved.

This section of the report will focus on the ways in which neutralisation has and is being practiced, what the current issues are, and what future directions are anticipated and recommended. The complex chemistry is treated in detail in the accompanying report DMR-3610 (Item 5, [46]), so the discussion here is restricted to an overview of the main principles, with more detail only on the aspects necessary to illustrate specific points of practice and technology.

3.3.1 The Alkalinity of Bauxite Residue

The chemistry of the residue slurry is determined by the interactions between the bauxite and the plant liquor during digestion, followed by the changes that occur after the bulk solids are separated from the digest liquor and progressively washed, usually by a continuous counter-current decantation process, to remove sodium hydroxide, aluminate and carbonate. During the washing process various chemicals are added, most notably flocculants to settle the mud and clarify the solution for return to the Bayer liquor circuit, and lime to remove carbonate ions from the liquor by precipitation of $CaCO_3$ and replacement of carbonate with hydroxide ions in solution.

The object of the digestion step of the Bayer process is to dissolve aluminium-containing minerals while minimising the dissolution of other mineral phases. This is achieved in a strongly alkaline solution at temperatures above 100^oC (mostly in the range 145 to 250^oC), so that minerals such as gibbsite ($Al(OH)_3$) and boehmite (γ-AlO(OH)) are dissolved to produce $[Al(OH)_4]^-$ (aluminate) ions in solution, according to the following reactions:

$$Al(OH)_3(s) + OH^- \Leftrightarrow [Al(OH)_4]^-(aq)$$

$$\gamma\text{-}\ AlO(OH)(s)\ + OH^- + H_2O \Leftrightarrow [Al(OH)_4]^-(aq)$$

The bauxite residue is then separated from the main liquor stream and washed to recover soda and alumina. The resulting residue contains pore water that is much more dilute (by a factor of at least 10) than the main Bayer plant liquor, but is nevertheless highly alkaline. If this residual solution is then neutralised, aluminium hydroxides will re-precipitate. The compounds precipitated depend on the method and conditions of precipitation, but will generally include $Al(OH)_3$ and/or AlO.OH.

Apart from the intended solubilisation of aluminium species, there are a number of other reactions that occur during and prior to digestion. One of the most important is the solubilisation of phyllosilicate-like minerals (clays), for example kaolinite, which has the stoichiometric formula $Al_2Si_2O_5(OH)_4$. The dissolution of these minerals results in aluminate and silicate ions in solution. The digester discharge liquor, which is the solution produced by the digestion process, also contains Na+ ions in high concentration. As a result, the liquor becomes unstable with respect to a range of sodium alumino-silicates, in particular sodalite[2] and/or cancrinite[3]. These sodium alumino-silicates are collectively referred to as "desilication products" or DSPs.

DSP formation is referred to as "desilication" because it removes silica from solution. It also removes hydroxide ions from solution and incorporates them into the solid; DSP is therefore a form of solid alkalinity. As such it is stable while the solution is alkaline, but decomposes in neutral or acid solutions, releasing sodium, hydroxide, aluminate and silicate ions to the solution. In this way the DSP and other forms of solid alkalinity act as pH buffers.

pH buffers are also present in the form of calcium carbonate, tricalcium aluminate (TCA) and calcium-aluminate carbonate (hydrocalumite). These compounds are present in bauxite residue because lime, usually in the form of $Ca(OH)_2$, is generally added to Bayer process solutions to remove carbonate from solution and replace it with hydroxide, in a process called "causticization". The desired reaction for causticization is:

$$CaO + CO_3^{2-} + H_2O \rightarrow CaCO_3(s) + 2OH^-$$

A number of side reactions can occur between the added lime and the aluminate ions in the Bayer solution. The exact reactions and the nature of the products depend on conditions, but the general reactions may be illustrated by the formation of hydrated calcium aluminate and aluminate carbonate as follows [47]:

$$3Ca(OH)_2 + 2[Al(OH)_4]^- + nH_2O \rightarrow Ca_3Al_2(OH)_{12}.nH_2O(s) + 4OH^-$$

$$4Ca(OH)_2 + 2[Al(OH)_4]^- + CO_3^{2-} + nH_2O \rightarrow [Ca_2Al(OH)_6]_2.CO_3.nH_2O(s) + 4OH^-$$

[2] $Na_6[Al_6Si_6O_{24}]\cdot[2NaOH,Na_2SO_4]$
[3] $Na_6Ca_2[(CO_3,Al_6Si_6O_{24}]\cdot 2H_2O$

Alkaline solids can also be formed with other anions such as phosphate, zincate and titanate, and with other cations such as magnesium and potassium.

There is a detailed discussion of the chemistry of the solid and solution alkalinity in the accompanying report DMR-3610 (Item 5 [46]). Suffice it to say here that bauxite residues are in general not only highly alkaline, but also highly buffered by anions such as carbonate and aluminate in the solution phase in combination with a number of buffering solids which act as a reservoir of hydroxide ions.

The amount and forms of alkalinity both must be taken into account in any process for neutralising the residue. For example, the amount of carbonate in solution determines the buffering capacity of the solution above pH 10. In the region of neutral pH additional buffering is provided by (solid) aluminium hydroxides, and if significant carbonate is present, also by sodium alumino-carbonates, in particular dawsonite.

3.3.2 Remediation with Seawater

Apart from direct marine disposal, such as has been practiced at Gardanne since the very early days of the industry [19], the first example of remediation of residue by mixing with seawater appears to be at the Queensland Alumina refinery. In this case seawater was used as a transport fluid for pumping it to disposal lagoons in order to conserve fresh water [48]. Remediation by neutralisation was not the primary aim of the process in either case, but was a consequence of it.

By adding seawater, hydroxide, carbonate and aluminate ions are removed from solution by reaction with Mg^{2+} and Ca^{2+} ions to form alkaline solids, in particular hydrotalcite ($Mg_6Al_2(CO_3)(OH)_{16} \cdot 4(H_2O)$) and calcite ($CaCO_3$). This buffers the solution in the range of pH 8 to 9.

It has been shown that the phosphate adsorption capacity of the solids is substantially increased by seawater neutralisation [48], and that the solids have a high trapping capacity for trace metals [49]. These features are useful in relation to revegetation of bauxite residue areas, and for creating various re-use products [50].

Seawater is also used to neutralise the decant liquor from ponding operations prior to discharge. Neutralisation by simply mixing the decant liquor with seawater results in the formation of white colloidal precipitates which have the potential to produce contamination downstream of the discharge point [51]. At the Gove refinery hydrotalcite, calcium carbonate and calcium oxalate were identified as the main components of such precipitates along with trace amounts of other salts [52].

Further research has led Alcan Gove to develop a seawater treatment method for decant water to meets stringent standards of purity for discharge to the environment [53]. The purity parameters of particular interest are pH, turbidity and trace metals. In addition to meeting the designated water quality criteria, ecological toxicity testing was done to provide additional confirmation that the treated water was safe for discharge to the marine environment. It was found that a two stage treatment was required in order to meet the design performance requirements, particularly in relation to vanadium levels. The first stage of the process is the mixing of the decant water with a six-times excess of heated seawater (waste cooling water from the plant evaporators) to form the

hydroxide precipitates. The resulting suspension is then mixed with red mud slurry and treated with flocculants in a deep cone thickener to produce a clarified overflow stream for discharge. Continuous flow, bench scale trials have confirmed that the required performance parameters can be met with this design, which has been proposed for implementation at Gove [52]. Successful implementation of this technology would be a significant milestone in the development of sweater neutralisation technology. It would be the first use of a deep cone thickener as a mixer to produce an overflow water suitable for direct discharge. Potentially, this could eliminate the need for the labyrinthine discharge channel currently required to provide residence time necessary for formation and sedimentation of precipitates.

3.3.3 Remediation with Mineral Acids

There are few examples in the literature of neutralisation of bauxite residue by mineral acids. It is addressed in general terms by McConchie et al. [49], but no examples are given. The authors point out that large quantities of acid would need to be available at low cost, opining that this is unlikely to be the case for alumina refineries generally. It is also noted that residue neutralised by mineral acid contains no residual (solid) alkalinity, and so would not be useful as a starting material for the range of applications envisaged by those authors. In addition, neutralisation by mineral acids does not provide any acid-base buffering capacity, nor does it improve the physical properties of the material, both of which occur if either seawater or carbon dioxide is used for neutralisation.

It has been reported that sulphuric acid is used as a supplementary neutralising agent at the Yarwun refinery (Queensland, Australia) due to limitations in seawater supply [54]. The performance of sulphuric acid was assessed in terms of its ability to reduce the level of aluminate in the discharge liquor. It was found that the mineral acid was significantly less effective in removing aluminate from solution because it relies on the precipitation of aluminium hydroxide, whereas if seawater is used the solid phase formed is hydrotalcite ($Mg_6Al_2CO_3(OH)_{16}.4H_2O$)) which is less soluble at the target pH of 8.5.

No references were found in the open literature to the neutralisation of bauxite residue decant waters with mineral acids. Such a practice could be expected to result in the formation of colloidal and/or gelatinous precipitates (primarily aluminium hydroxides and hydroxy-carbonates) requiring a clarification process prior to discharge.

3.3.4 Remediation with Carbon Dioxide

A process for reacting bauxite residue with gaseous carbon dioxide was piloted by Alcan for the Saramenha plant in Brazil in 1983 [55]. The concept has since been developed by Alcoa as a means of reducing the pH of the slurry prior to dry stacking [43]. Extensive laboratory and pilot-scale testing was carried out by Alcoa between 1991 and 1996. This was followed by small-scale field trials in which several mixing devices were tested. Carbonated mud was deposited in layers so that its longer term behaviour could be studied in a dry stacking operation. The optimum rate of CO_2 addition was found to be 25kg CO_2 per kL of mud slurry, at a slurry density of 48%

solids.

It was demonstrated that a pH of 9 could be achieved in the carbonated mud. The pH of the leachate collected from the under-drainage system remained steady at around 10.5 over an extended period, while the pH of the leachate from a non-carbonated drying bed was consistently greater than 13. This difference was sufficient to meet the alkalinity reduction goal. On the basis of these trials, full scale residue carbonation capability was implemented at the Kwinana refinery in 2000 [43].

Although the pH of the leachate from the carbonated residue was consistently lower than from uncarbonated residue as expected, it was nevertheless about 1.5 pH units higher than the pH initially achieved in the residue slurry. This has been explained by the presence of solid hydroxides in the mud slurry that do not react immediately with the carbon dioxide, but which begin to dissolve as the pH of the solution they are in contact with is lowered. Tricalcium aluminate (TCA) was found to be the most important such compound in the Alcoa residue. Over time, TCA dissolves to release hydroxide and aluminate ions to the solution.

The details of the reactions which occur as a result of carbonation have been investigated by Smith et al. [56]. The following section is based on their results and interpretations.

Prior to neutralisation, residue slurries are highly alkaline. The pH of the slurry is generally in the region of 13, equivalent to an OH^- concentration of 0.1 molar. Introducing CO_2 to the solution causes rapid neutralisation according to the following reaction:

$$CO_2(g) + OH^-(aq) \rightarrow HCO_3^-(aq)$$

This reaction causes the pH to drop rapidly until buffering by the carbonate/bicarbonate equilibrium becomes apparent below a pH of 10. At that pH solid hydroxides begin to form, creating additional buffering as they equilibrate with the ions in solution.

The Alcoa trials demonstrated that it was possible to achieve a pH as low as 8.5 by reacting residue slurry with CO_2 under pressure [43]. However it was also discovered that after the CO_2 overpressure was removed, the pH would slowly rise until a final pH of about 10.5 was reached. This was explained by those authors and by Smith *et al* as being due to the dissolution of alkaline solid phases that become soluble in this pH range, for example tricalcium aluminate, TCA. TCA is present in bauxite residue as a result of the use of lime in the Bayer process for control of carbonate levels [47] in the liquor and as an aid to settling and filtration [7]. TCA is a calcium-aluminium hydroxide with the stoichiometric formula $Ca_3Al_2(OH)_{12}$. Dissolution of TCA results in the release of OH^- ions to the solution, thus raising the pH. This is accompanied by the formation of new solid phases, including calcium carbonate (calcite), sodium aluminium hydroxyl-carbonate (dawsonite) and aluminium hydroxide (gibbsite), possibly according to the following equations:

$$Ca_3Al_2(OH)_{12} + 3HCO_3^- + 4Na^+ \rightarrow 3CaCO_3 + 2Al(OH)_3 + 3H_2O + 3OH^-$$

$$2Ca_3Al_2(OH)_{12} + 10HCO_3^- + 4Na^+ \rightarrow 6CaCO_3 + 4NaAl(OH)_2CO_3 + 10H_2O + 6OH^-$$

Due to the buffering effects of these reactions, the pH can be expected stabilise in the region of 10.5. These observations are consistent with recent work by Khaitan et al. [57], who also observed that the amount of TCA present is a major factor in determining the carbon sequestration capacity of a bauxite residue [58].

Alcoa found that carbonation of residue affects the physical properties of the material as well as its chemical composition. Carbonated residue dries more rapidly than uncarbonated residue, probably because of the elimination of surface crusting and improved cracking behaviour which together provide more effective surface area for evaporation. It was also found that the mechanical strength of the residue was enhanced by carbonation. The combination of these effects results in a significant reduction in the drying time required to reach a target minimum strength to ensure long-term stability, which in turn reduces the required cycle time for drying and improves the utilisation of the residue drying area. The elimination of surface crusting also reduces the dusting potential of the surface.

The benefits of carbonation of residue have been summarised along the following lines [43]:

- Reduces risk to containment seal material (clay or synthetic) and therefore reduced risk of contamination of groundwater;
- Improves quality of runoff and drainage water;
- Reduces potential for dusting lift-off;
- Provides a sink for greenhouse gases;
- Reduces risk of future classification of the residue as a hazardous waste;
- Facilitates development of productive uses for the residue in the future; and
- Reduces the impact of residue in the overall life cycle cost of aluminium production.

CO_2 supply is a key issue to be considered in relation to carbonation of residue. The carbonation technology applied at Kwinana requires concentrated CO_2 as the raw material to be mixed with the residue slurry. The Kwinana alumina plant is located within an industrial complex which includes an ammonia plant which produces pure CO_2 as a by-product, which is supplied to the residue area by dedicated pipeline [43]. Such examples of industrial synergy are rare, so alternatives need to be considered if carbonation is to be applied more generally. An alternative is to extract CO_2 from flue gases associated with the alumina refinery. The level of CO_2 in such flue gases is generally in the order of 10%, so a concentration process in which it is separated from the other gases (mainly nitrogen) is needed. The current best technologies for capturing and concentrating CO_2 from flue gases are based on amine scrubbing [59]. Amine scrubbing requires the installation of a significant additional operation to an already complex alumina plant, and carries the potential for amine emissions. A promising amine-free alternative is based on carbonation of residue liquor by contacting it with flue gases in a high-efficiency scrubber. The carbonated solution is then recirculated with residue solids to carbonate the overall residue [60].

3.3.5 Neutralisation with Sulphur Dioxide

The reaction of SO_2 with red mud has been developed as a means of scrubbing SO_2 from flue gases. The technology utilises the reaction of SO_2 with the sodium alumino-silicates in the residue to produce sulphites that can be removed by oxidation by air [61, 62]. The process was patented by the Sumitomo Aluminium Smelting Co [62], and has been used at a number of sites, including Sardinia [63]. The process is aimed at the removal of SO_2 from gas streams and the amount of residue neutralised is minor in relation to the total of amount of residue produced. Reaction of bauxite residue with SO_2 is therefore an example of a beneficial use for bauxite residue, but does it not appear to be a potential treatment for large quantities of residue and so will not be considered in detail here.

4. SUMMARY AND CONCLUSIONS

4.1 Trends, Future Directions and Knowledge Gaps

The first key issue that was identified in this project was the lack of availability and organisation of the existing knowledge relating to bauxite residue. This gap is being addressed by the creation of the Bauxite Residue and Disposal Database (BRaDD). BRaDD which has been an essential enabling tool for the collation and interpretation of information required for this review. With further programming refinements, and with data input from the industry, BRaDD will be an invaluable tool in the development of a global strategy for the future of bauxite residue management. Support for further development and more comprehensive data availability to BRaDD are warranted.

Bauxite residue has been continuously produced since the inception of the alumina/aluminium industry in the late nineteenth century. We have estimated that the global inventory of bauxite residue reached 1 billion tonnes in 1985, 93 years since the establishment of the first Bayer process plant. This inventory grew to 2 Bt by 2000, a doubling time of only 15 years. The inventory was 2.7 Bt by 2007, growing at 119 million tonnes per annum. The prospect of an ever decreasing doubling time, and an inventory of 4 Bt possibly before 2015, highlights the urgency of the need to develop and implement improved means of storage and remediation, and to pursue large-volume re-use options.

Prior to 1980, most of the inventory of bauxite residue was held in lagoon-type impoundments. This storage method has a number of disadvantages, in particular the large areas of land required and the potential for leakage of caustic liquors to the environment. Since 1980 the trend has been towards dry stacking in bunded areas that are lined with a variety of natural and synthetic barrier materials. Improved methods for thickening and washing of the residues prior to storage, and recovery of decant water during storage, have been developed to increase the recovery of valuable soda and alumina to the Bayer process plants and to minimise the potential for leakage to the surrounding environment.

A range of methods has been employed to neutralise both residue and decant waters. The most established methods to date involve either mixing with sea water to precipitate hydroxide, carbonate and aluminate ions with magnesium and calcium, or with carbon dioxide to produce calcium carbonate and calcium alumino-carbonates. Neutralisation with mineral acids is less successful due to the influence of solid hydroxides in the residue and the deleterious effects that this method of neutralisation has on the physical properties of the residue.

The current trend in residue storage practice is towards increasing use of dry stacking as the preferred technology, and further research to optimise this technology is appropriate. Hyperbaric steam filtration is an emerging technology which produces a dry, granular residue of low soda content. These properties are beneficial to long term storage, remediation, and re-use. Support to the development and implementation of hyperbaric filtration as a potential breakthrough technology is warranted.

The most important barrier to remediation, re-use and long term sustainability of bauxite residue management is its high alkalinity. The alkalinity of bauxite residue is a result of a complex mixture of solid-state and solution phase interactions. Better understanding of these interactions is required to support progress in the development of sustainable bauxite residue management and re-use options. Continuing research on the chemistry and technology of residue neutralisation is warranted.

5. RESEARCH PRIORITIES

Based on the review of bauxite management practices outlined in this report and the knowledge gaps highlighted in the previous section, the research priorities related to bauxite residue management in the context of the APP objectives have been determined. These are summarised in Table 4 below.

Table 4: Research Priorities related to bauxite residue storage technology and practice, and the APP Objectives that they support

Research Priority	**APP Objectives Supported**
1. Further development of BRaDD, with priority on incorporating key information from industry practitioners	Identification, evaluation and deployment of best practices Evaluation of impacts and trends Development of best practice residue management options
2. Development of economically viable hyperbaric steam filtration	Development of best practice residue management options More environmentally acceptable storage Improved potential for re-use options Improved raw materials usages
3. Fundamental chemistry of leaching and neutralisation	More environmentally acceptable storage Improved potential for re-use options
4. Quantification and validation of carbon sequestration potential of residue carbonation	More environmentally acceptable storage
5. Development of methods for direct carbonation of residue by stack gas carbon dioxide	More environmentally acceptable storage Improved potential for re-use options Improved raw materials usages

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APPENDIX: TMS CONFERENCE PAPER 2009

THE ASIA-PACIFIC PARTNERSHIP: AN IMPORTANT NEW INITIATIVE FOR A SUSTAINABLE ALUMINA INDUSTRY.

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Keywords: bauxite residue, red mud, sustainability, re-use

Abstract

The Asia-Pacific Partnership on Clean Development and Climate is an inter-governmental agreement between seven countries, predominantly located around the Pacific Rim: Australia, Canada, China, India, Japan, Republic of Korea and the United States of America. Collectively these countries represent about half the world's emissions and 52% of the world's aluminium production. Aluminium is one of eight key areas covered by the APP and the Task Force is chaired by Australia and co-chaired by the United States of America. Projects within this area are focused on best practice and its deployment across the Partnership economies. Within aluminium there are seven project activities covering benchmarking and linkages to technology providers, plus per-fluorocarbon emissions, bauxite residues, high silica bauxite, fluoride emissions and aluminium recycling. The Partnership program and how it is implemented is described with a particular focus on the bauxite residue management work being undertaken.

Introduction

The Asia-Pacific Partnership on Clean Development and Climate Change (APP) is an inter-governmental non-treaty agreement which brings together Australia, Canada, China, India, Japan, the Republic of Korea and the United States of America to address the challenges of climate change, energy security and cleaner production in a way that encourages economic development. This important initiative engages the key energy intensive economies in the Asia-Pacific region on practical clean development and climate action. It is unprecedented in the way in which business, government and researchers have agreed to work together and to jointly participate in international climate change initiatives [1].

Aluminum production has been identified as a key focus area for the APP because of its current size, projected growth and energy intensity. It has been identified that there is significant potential for improvement across Partnership economies through best practice use of existing equipment, development and deployment of new best practice production processes and technologies, and increased recycling of metal. The APP countries account for about 52% of world aluminum production, and this industry is one of the fastest growing in the region. Accordingly, an Aluminum Task Force has been established to establish and manage the work program for the aluminum sector [2].

The Aluminum Task Force has established a portfolio of seven projects:

1. Aluminium Measuring and Benchmarking:
   Adoption of a standard set of Sustainability Indices for measurement and benchmarking of performance
2. Management of PFC Emissions:
   Achieve substantial reductions in PFC emissions (which have greenhouse intensities of 6,500 to 9,200 CO_2 equivalents) through sharing and development of best practices and technologies
3. Management of Bauxite Residue (Red Mud)
   Detailed review of current practices; recommend priorities for technology sharing and development
4. High Silica Bauxite Processing
   Develop improved ways of processing high silica bauxite to reduce energy intensity and caustic usage
5. Fluoride Emissions Management
   Collect data on fluoride emissions and identify improvement opportunities
6. Aluminium Recycling
   Adopt common recycling indices and agree reporting format
7. Linkages to Technology Providers
   Establish a Technology Register to promote linkages and dissemination of best practice technologies

A full description and the Action Plans for each project are available on the APP website (www.asiapacificpartnership.org). This paper will focus on Project 3, Management of Bauxite Residue, as an example of the work being undertaken within the Aluminum Task Force.

APP Project No. ATF-06-03: Management of Bauxite Residue (Red Mud)

Background and Scope

The Bauxite Residue project is a 3-way partnership between Australia, China and India. The key focus areas for the project are to develop technically and economically sound options for:

- Productive utilization of bauxite residue towards end uses, including application specific to the steel and cement industries (including the extraction of oxides and trace metals);
- Better stabilizing the residue disposal (mechanical stability and chemical inertness);
- Utilizing minimum land for storage and ensuring faster rehabilitation of landfill sites.

Specific objectives for the project are:

- To develop technology and practices for the alternative use of bauxite residues that will reduce the reliance on stockpiling and storage;, and
- To maximise the potential of bauxite reside for the steel and cement industries through the extraction of oxides and trace metals as viable substitutes to existing industrial inputs to production processes [2].

The first part of the project is to undertake a detailed review of currently available technology and research based on publically available information and cross-checked with information from the APP participants. This will enable a priority list of the most promising areas for research and development to be identified, which will form the basis for R&D activities in 2008-9, leading to

pilot testing of the most promising options. It will then be necessary to identify financial mechanisms to implement strategies to enhance bauxite residue utilization, leading to commercial scale trials and exchange of technology among member companies in 2009-10. An ongoing implementation plan and benchmarks for future uptake of the technology and practices will be developed.

Stage 1: Technical Review and Database

Two distinct focus topics are being reviewed:

- The technology and practices of residue disposal and storage, and
- The chemical, physical and mineralogical characterization of residue, and options for beneficial downstream uses.

The core output of the review process will be a comprehensive database which can be queried to produce a flexible variety of outputs, such as summary data tables and graphics, and associated information for inclusion in reports. The database will be designed to facilitate continual improvement, extension and updating, so that it is an up-to-date, comprehensive and accessible source of detailed information, organized on a refinery-by-refinery basis. The database is an essential enabler to progress in a number of areas because it overcomes a major issue of data inaccessibility.

In addition to the creation of the database, the Project will produce written reviews of the current status of the two focus topics based on the information in the database.

Methods and Materials

1. Bauxite residue disposal, technology and engineering practices

Past and present technologies and engineering practices pertaining to bauxite residues were first compiled from the publicly available literature using standard academic search engines, including Web of Science, Aluminium Industry Abstracts, Ph.D and MSc theses, and the Delphion Intellectual Property Index. These searches provided a surprisingly limited amount of data, but did enable identification of sources from which additional data could be obtained, e.g. the United States Securities and Exchange Commission, Tables of Contents of key aluminium industry specific conference proceedings including Light Metals TMS, the International Aluminium Quality Workshop, and ICSOBA. These sources were complemented by information published on company websites and websites on more generic topics ranging from tailings disposal, red mud, and solids-liquid separation.

The collected data were organized into refinery-specific spreadsheet tables. The data in each table are organized chronologically (from current to first year of operation) such that a historic progression of each technology, engineering practice and disposal method can be assessed. The refinery-specific tables were then uploaded to FileMaker Pro (v.9), which serves as a database manager and from which queries about the industry's bauxite residue disposal methods, technology and engineering practices can made. The following types of query are possible:

1. *Overviews* of each refinery individually with the option of creating summary reports regarding specific operating parameters (e.g. residue output vs. alumina production)
2. *Comparisons* between refineries:
   a. individually (e.g. Kwinana vs. Gove)
   b. as groups (e.g. European vs. Australian vs. S. American refineries)
3. *Summary reports* for refinery attributes and operating parameters (e.g. types of thickeners in use):
   a. History of technology and practice (e.g. numbers and types of thickeners used over time)
   b. Current practice (e.g. out of all refineries, how many use Alcan Deep Thickeners, dry-stack, but are not in Australia)
4. *Lists* of refineries against operating parameters (e.g. list of all refineries that used lagooning as a residue storage method between 1990 and 2008).

Figure 1 shows the organization of the Bauxite Residue and Disposal Database (BRADD) and some of the output options. In addition to quantifiable operational parameters, Google Earth™[1] images of each refinery were obtained to provide a visual perspective of the configuration of individual alumina refining and bauxite residue disposal operations around the world.

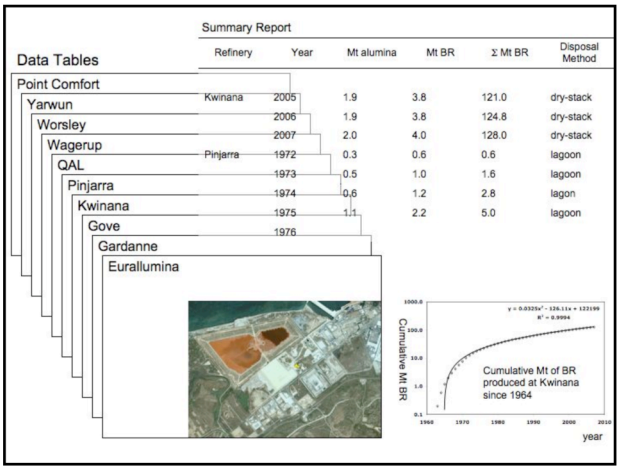

Figure 1. Bauxite residue and disposal database (BRADD): Data organization and output options.

2. Chemical, physical and mineralogical characterization of residue, and options for beneficial downstream uses

Information on the reuse options for bauxite residue is strongly interwoven with the literature on its physical and chemical characterisation, because specific attributes are required for particular downstream uses. Information on these two subject areas was sourced from professional journals and conference proceedings and was noted in BRADD with specific reference to the origin of the bauxite residue and year of publication in order to provide the link to specific technological and engineering practices.

Results and Discussion

1. Bauxite residue disposal, technology and engineering practices

The initial objective of Project ATF-06-3 was to identify knowledge gaps in the three main research areas. In the area of

[1] GOOGLE is a trademark of Google Inc.

bauxite residue management, technology and engineering practice, it was noticed early on that the key knowledge gap was a comprehensive review of the industry itself. Whereas bauxite residue reuse and characterization have each been the subject of several reviews published over the past 30 years, reviews of alumina industry residue disposal methods, technologies and engineering practices are scarce. Those that do exist are best described as generic and anonymous, i.e. details are described without direct reference to specific refineries, and mainly describe existing not emerging technologies [3]. In addition, published reviews quickly become outdated. Surveys of the accessible literature revealed the following:

1. The relevant information is scattered over many public domain areas, including journals, conference proceedings, patent offices, company reports, Securities and Exchange Commission reports, newspaper articles, academic theses, and other miscellaneous sources;
2. Each source of information provides only a limited amount of relevant data;
3. The relevant information is published in a variety of languages, principally Chinese, English, French, German, Portuguese, Russian and Spanish;
4. The nature and scope of the information is owner and/ or refinery specific.
5. Each refinery has unique operating details with respect to bauxite residue technologies, management and engineering practices; and
6. The operating details of each refinery may or may not change in any given year.

Therefore, *for every refinery*, a multifactorial data set propagates over time. This must then be integrated over all refineries in order to provide a true reflection of disposal methods, technologies and engineering practices for bauxite residues. Despite these difficulties, the information which was available pointed to a limited number of common parameters:

- country of location, refinery name and owners;
- type (laterite, karst, Tikhvin), origin and tonnes of bauxite processed per year and origin;
- tonnage of alumina and bauxite residue produced;
- final thickeners, presence of rakes, use of flocculants, and underflow densities (% solids) achieved; and
- disposal method, sand fractionation, sealants, drains, and neutralization steps for bauxite residue and associated liquors.

The aim of assembling these details was to establish how the practice of bauxite residue disposal has evolved over the years in order to provide a detailed review of the industry without bias towards any particular region or ownership. *An authoritative review on the alumina industry as a whole, however, must be able to quantify actual industry practices that can back-referenced to real refineries, not technology providers.* In addition, it is important to understand how these practices may influence physical, chemical and mineralogical properties of bauxite residues. For example, any flocculants used during counter-current decantation washing are likely to be adsorbed on the residues modifying the surface properties of the residues. Lagooned residues settling out and thickening from an initial 30% solids density over extended periods will have different pore space distributions than pre-thickened muds of ≥ 50 % solids and disposed of as thickened tailings with a repose slope of 6 %. Information at this level of site-specific detail is essential to support the achievement of objectives such as the development of new strategies for inerting, rehabilitating or utilising bauxite residue areas on a global basis.

BRADD at work

The graphical examples given below are based on 10 refineries, 7 from Australia plus Eurallumina, Aluminium de Grèce and VAW Stade in Europe. These are the refineries for which mostly complete datasets existed in BRADD at the time of writing. As noted previously, only data, which are publicly available are used in this compilation.

The first example of an output provided by BRADD is the history of disposal methods shown in Figure 2.

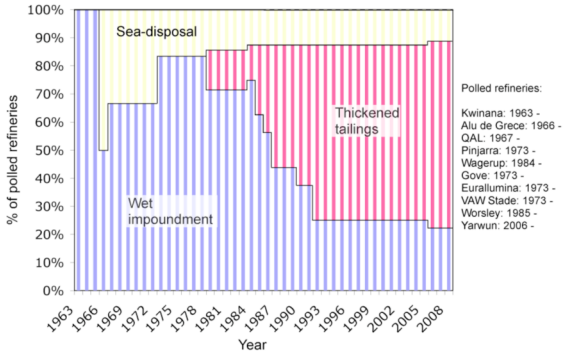

Figure 2. History of bauxite residue disposal methods in Australia and by selected European alumina refineries. The first year of operation of each refinery is provided on the right.

Kwinana (Alcoa World Alumina Chemicals (AWAC), Western Australia) commenced production in 1963. For the first 22 years of operation bauxite residues were lagooned at *circa* 37% solids concentration [4]. In 1985, with the development of superthickeners, Alcoa of Australia residue operations transitioned from lagooning to thickened tailings disposal with average solids concentration of around 50%. Aluminium de Grèce (AdG) adopted the Pechiney method practiced at Gardanne for disposing bauxite residues at sea [5, 6]. In contrast, VAW Stade, within 5 years of starting operations, disposed of their bauxite residues at *circa* 55% solids concentration using vacuum drum filters [7, 8].

As more refineries are being assessed and included in BRADD, Figure 2 will also become more comprehensive. Nevertheless, the general trend towards the adoption of thickened tailings disposal is clear. This is in response to limited disposal areas and the availability of technology that can produce and pump bauxite residues at increased (≥ 50%) solids concentration. Not shown in Figure 2 are various neutralisation steps that are practiced in Australia and elsewhere. For example, Queensland Alumina (QAL, Gladstone – Queensland, Australia) and Eurallumina have used seawater to neutralise and enhance the settling of their bauxite residues since the mid 1970s [9-12]. Once sufficient data have been entered into BRADD it will be possible to generate a graph similar to Figure 2 showing the history of bauxite residue neutralisation can be generated by seawater, CO_2, SO_2, lime, and other additives introduced over the years.

The second example of a BRADD output is the history of bauxite residue production and its correlation to alumina production as shown in Figures 3 to 5.

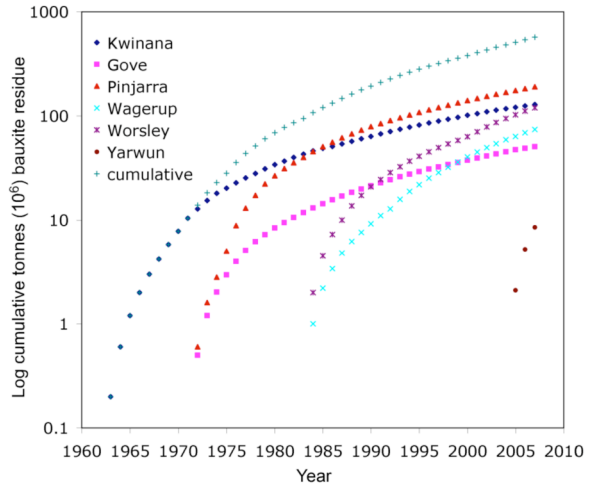

Figure 3: Cumulative bauxite residue output in Australia, in million tonnes, excluding QAL. As of 2007, we estimate that at least 572 million tonnes of bauxite residues are stored in Australia. In 1991/2, 6000 dry tonnes of bauxite residue were discharged on average per day at QAL, which equates to *circa* 2.37 million tonnes per year or 72 % of annual alumina production [9].

Cumulative bauxite residue output provides a measure of the extent of environmental liability and responsibility associated with each refinery, and essential information for ongoing management and regulation. It also provides a measure of the potential resource that the residue deposits represent.

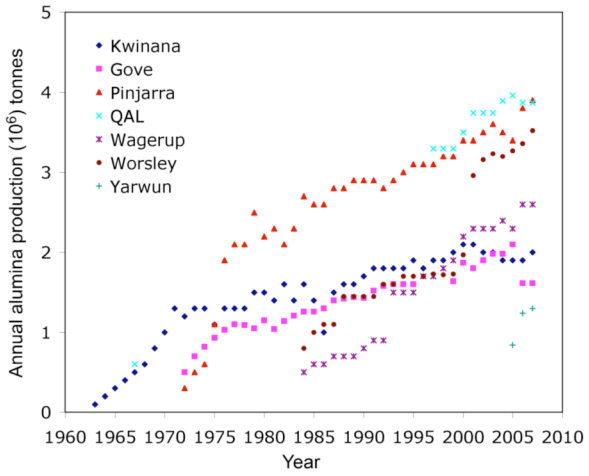

Figure 4: Annual alumina production in Australia. A cumulative representation of the data is not useful at this moment as the data is not continuous and in some cases only nominal capacities of the refineries could be obtained.

The rate of bauxite residue accumulation is increasing as world alumina production increases. Figure 4 shows that since the first year of production, each of the refineries surveyed so far has been continually increasing its alumina production capacity since start-up.

Due to the proximity of the three AWAC refineries to each other and their common ownership, it was instructive to look at the developments of bauxite residue disposal for Kwinana, Pinjarra and Wagerup (Figure 5). It can be seen that Pinjarra began exceeding Kwinana's bauxite residue disposal rate at the same time as superthickeners were introduced in 1984/5, which is also the point in time in which Alcoa's third refinery in Western Australia (Wagerup) commenced production. At Wagerup, bauxite residues were disposed of as slurries (37% solids) only in the first three years of operation, after which the refinery switched to thickened tailings disposal similar to Kwinana and Pinjarra [4].

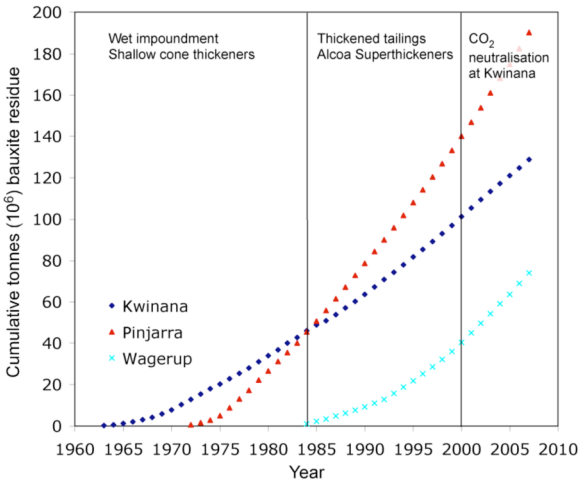

Figure 5: History and development of bauxite residue storage at the three Western Australian Alcoa alumina refineries: Kwinana, Pinjarra and Wagerup.

In the last example, we make use of Google Earth™ images to provide visuals of bauxite residue disposal areas (BRDAs) and managerial practices. QAL uses seawater to neutralise bauxite residues, which results in improved settling properties of the residues. The supernatant liquor enters a labyrinth for removal of suspended solids by settling prior to discharge [9]. A similar feature is in operation at Gove, where the labyrinth is used to mix supernatant liquor with seawater to precipitate hydrotalcite and inorganic contaminants before discharging the supernatant water to the adjacent bay [13]. A this time, the bauxite residue slurry is not treated with seawater at Gove, only the supernatant liquor. According to a recent communiqué [14], Rio Tinto Alcan plans to employ full bauxite residue treatment with seawater in the future. In terms of managerial practices, it is noticeable that BRDAs tend to be compartmentalised as can be seen from images of the Kwinana, Eurallumina and Gove. At Eurallumina, the division of the disposal area is directly related to regulating dust development on the dry residue beds. Supernatant liquor in the smaller area is used to wet the surface of the larger area [11, 12].

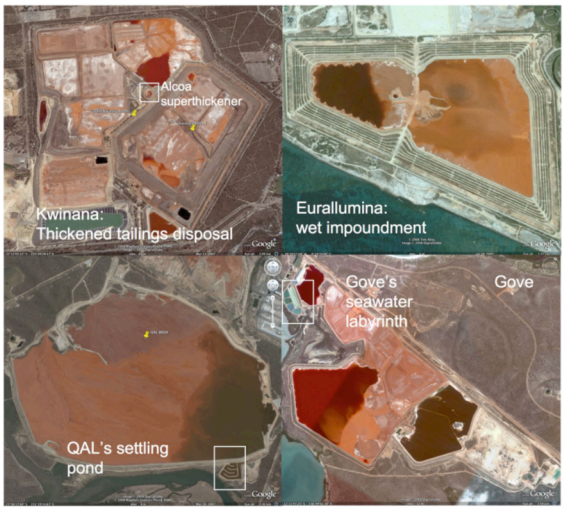

Figure 6: Google Earth™ images of selected BRDAs in Australia and Europe.

Conclusions

The above examples, though based on only a limited number of refineries, underline the usefulness of the data compilation in providing a systematic means by which to review industry practices.

BRADD operates at present solely on publicly available data. In order to assess the industry from a more comprehensive dataset direct input from owners and operators would be needed. It would be desirable if this could be done without restricting access, but it is acknowledged that this may not be possible due to commercial sensitivities. Possible solutions to this include a protocol for holding specified information classified for a set time period, and quarantining data for access only to specified clients while allowing aggregated data to be used for the preparation of trends and reports.

CSIRO, as both a scientific and industrial research organization, is well situated to broker, manage and provide access to the information.

With direct industry input, BRADD will become the first database that comprehensively and transparently documents residue disposal practices by a major sector of the minerals industry, and provides the information in a readily accessible and flexible form. This will provide a means of correlating bauxite residue properties to disposal technologies, treatment and methods, an tool for assessing residue management approaches on a situational basis, and will facilitate identification of potential reuse options.

Once the database has been populated, BRADD will become an information resource of unprecedented flexibility and completeness which will be invaluable to the task of identifying the most promising areas for research and development in relation to bauxite reside. In this way it will make a significant contribution to the Asia-Pacific Partnership's mission of assisting the development and deployment of sustainable industry practices.

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