

LAYERED DOUBLE HYDROXIDES IN THE BAYER PROCESS: PAST, PRESENT AND FUTURESteven P. Rosenberg¹, Lyndon Armstrong²¹BHP Billiton / Worsley Bauxite and Alumina Technology Centre, PO Box 344, Collie 6225, WA, Australia²Alcan Queensland R&D Centre, PO Box 883, Kenmore 4069, Qld, Australia

Keywords: LDH, hydrotalcite, hydrocalumite, brucite, anionic clay

Abstract

Alumina refiners have been aware of some of the potential uses of Layered Double Hydroxides (LDH's) in the Bayer process for more than a decade. By virtue of their lamellar structure, the ability to adjust the separation of these layers, and the reactivity of the interlayer region, LDH's can be used for the controlled addition or removal of a variety of species, both organic and inorganic. In this paper, we review the history and present use of LDH's in alumina refining, particularly the most commonly used calcium and magnesium aluminate varieties.

We also examine some of the ways in which these LDH's can be produced in the refinery, both intentional and unintentional, as well as some of the possible reasons they have not found more widespread application. Finally, we discuss how LDH technology might be applied to deal with emerging trends and issues in alumina refining, particularly in reducing the environmental impact of alumina refining.

Introduction

Layered Double Hydroxides (LDH's), sometimes referred to as anionic or hydrotalcite-like clays, consist of sheets of the hydroxides of two or more metals of different valence. The metal hydroxide layers are positively charged, so charge neutrality requires that anions must be intercalated between the layers. Water is also usually present, hydrogen-bonded both to the hydroxyl ions of the metal hydroxide layers and to the intercalated anions. This is illustrated conceptually in Figure 1.

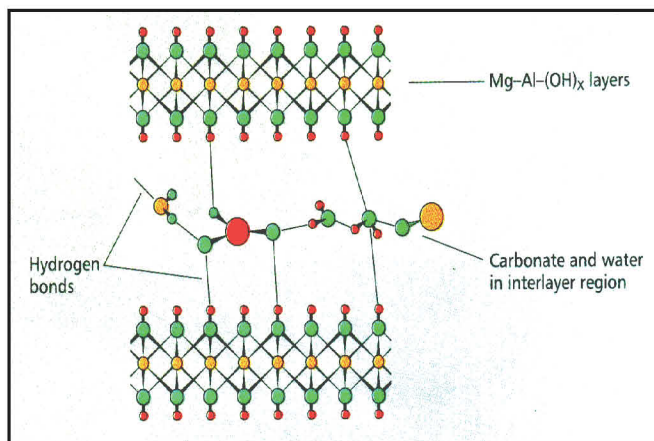


Figure 1: Hydrogen bonding between layers in an LDH [from S. Carlino, "Chemistry between the sheets", *Chemistry in Britain*, 33 (9) (1997), 59-62 - Reproduced by permission of The Royal Society of Chemistry]

This class of compound has a number of interesting and useful characteristics, the most significant of which is that the anions within the interlayer regions of this sandwich structure can be readily exchanged with other anions. Another useful property is that the spacing of the layers can be controlled in a number of ways, and can constrain the size and type of reactants that enter the interlayer region. In many cases, an LDH can be calcined to produce a layered double oxide analogue. When the calcined species is rehydrated, the original LDH structure is re-formed. Some intercalated anions (carbonate, for example) can be driven off during calcination. The original anion can then be replaced by another simply by rehydrating in a solution containing the new anion. Large anions can be intercalated using this technique, which "pillars" the structure, increasing the interlayer spacing.

The best known and most widely studied of the LDH's is hydrotalcite (HT), first discovered in Sweden in 1842. Natural HT has the formula $Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$, with the two metals randomly distributed in the octahedral positions, commonly described as brucite-like $M(OH)_2$ layers, as shown in Figure 2.

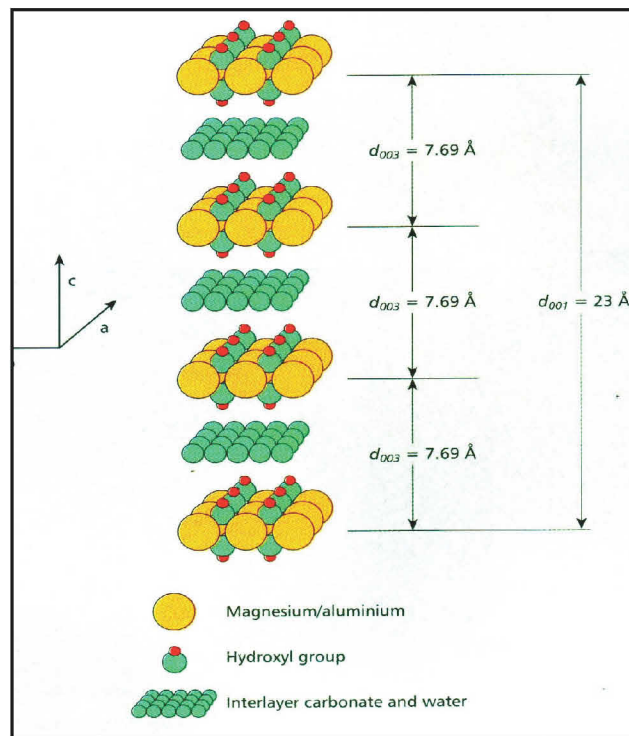
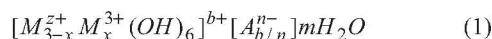


Figure 2: Layering and intercalation in Hydrotalcite [from S. Carlino, "Chemistry between the sheets", *Chemistry in Britain*, 33 (9) (1997), 59-62 - Reproduced by permission of The Royal Society of Chemistry]

The structures of many LDH's subsequently discovered or synthesized are quite similar to hydrotalcite, and it is common for an LDH comprising totally different combinations of metals to be referred to as a "hydrotalcite". It is therefore easy to erroneously assume that the Mg/Al structure is being referred to when the term hydrotalcite is used in a text or patent. The generic formulae for these compounds can be expressed as



where M is a metal, A is an interlayer anion, $0 < x \leq 1$ and $b = x$ or $2x-1$ for $z=2$ or 1 respectively [1].

In the alumina refinery, one of the metals in the above structure is, inevitably, aluminium. The most common LDH's in use are those involving magnesium and calcium, being hydrotalcite and hydrocalumite respectively. Hydrocalumite differs from hydrotalcite in that the hydroxide layers are significantly distorted from the brucite structure, and the Ca and Al are well-ordered. This order apparently extends to the interlayer region [2].

Past and Present Applications

LDH's have been used in alumina refining for the removal of impurities for several decades, although the true nature of the active species was not generally recognised until about 1990. Typically, active magnesium or calcium species were added to the Bayer liquor being treated to effect the removal of anionic contaminants.

For example, in 1977, Schepers et al. [3] proposed an organic impurity removal process in which a magnesium compound was added to an organic contaminated Bayer liquor, with the formation of a brown precipitated mixture. Kieserite ($MgSO_4 \cdot H_2O$) was the preferred material, but they noted that any magnesium compound capable of reacting with aluminate in the liquor was suitable, and that the resulting fine precipitate contained both magnesium and aluminium hydroxides. While this seems to imply a simple mixture of hydroxides, it is probable that the product formed in Schepers' process was in fact an impure hydrotalcite LDH, formed *in-situ* by the reaction of the magnesium salt and the aluminate anion. Humate anions are probably too large to be intercalated without pillaring of the HT layers, so it is likely that a combination of surface adsorption and intercalation of organics occurred. The positive charge of the external surfaces of LDH's makes them effective adsorbents for large anionic molecules.

Poland et al. [4] reported a process in which dry MgO or $Mg(OH)_2$ was added to a clarified Bayer liquor at 40 to 105°C for removal of organics. A precipitated solid containing 31% MgO and 26% Al_2O_3 by weight was formed; this is precisely the compositional ratio found in hydrotalcite. Calcination of the solid at 1000°C then destroyed the organics, giving a refractory material that could be used for other applications.

The use of magnesium compounds for humate removal subsequently became quite widespread in the 1980's. A variant of this was used briefly at the QAL refinery as a prelude to another humate removal process. It was understood that the active species was HT formed *in situ* from addition of an activated magnesium compound. Removal of humates, detected by following the decrease in absorbance of the liquor at specific visible

wavelengths, was thought to be occurring via adsorption at the HT surface.

At about this time, a great deal of fundamental work was being undertaken to synthesise and characterise LDH's and examine their reactivity. Miyata [5], for example, investigated the anion exchange properties of hydrotalcites, finding that monovalent anions were exchanged in the order $OH^- > F^- > Cl^- > Br^- > NO_3^- > I^-$ and divalent anions in the sequence $CO_3^{2-} > SO_4^{2-}$. Small divalent anions are intercalated preferentially to monovalent anions. As with virtually all LDH's, CO_3^{2-} was by far the preferred anion, and when intercalated it is very difficult to exchange with other anions. The HT was synthesised by reacting an aqueous solution of $MgCl_2$ and $AlCl_3$ in sodium carbonate solution, with the pH controlled through addition of sodium hydroxide. The HT carbonate so formed was calcined at 500°C to give the oxide and rehydrated in a solution containing the desired guest anion to form HT with the required intercalate.

Recognition that LDH chemistry may have been playing a part in the early Bayer impurity removal processes increased in the late 80's and early 90's, largely through work conducted by Alcoa.

Misra [6,7] noted that HT could be produced in an impure form by the reaction of magnesia ($Mg(OH)_2$) with Bayer liquors, but that a high purity HT could be formed from activated magnesia, prepared by calcining $MgCO_3$ or $Mg(OH)_2$ at between 500-900°C. Misra and Perotta [8] extended the process with a method for producing pillared HT, using a calcination and rehydration mechanism similar to that used by Miyata [5].

Goheen et al. [9] described a process for improving the whiteness of gibbsite by the addition of calcium compounds, and/or mixtures of calcium and magnesium compounds. The preferred embodiment involved the use of a mixture of Tri-Calcium Aluminate (TCA6) and HT, with the HT made *in situ* in a manner similar to Misra [7]. They postulated that the solids destabilised the ferrate ion or colloidal iron in solution, which then adsorbed on the TCA and HT surfaces, along with organics. Since the HT they used would have contained carbonate as the guest anion, anion exchange with other species in solution was unlikely.

In what was possibly the first Bayer process application to specifically invoke the intercalation of anions into LDH's, Nigro and O'Neill [10] proposed the use of a range of generic HT-like LDH's, with HT itself as the preferred embodiment, to reduce the amount of coloured contaminants in Bayer liquors. The HT was first calcined at 400-650°C to remove carbonate, and either rehydrated in contact with the contaminated Bayer liquor, or separately rehydrated and the resultant slurry mixed with the solution to be treated. They postulated that anionic species such as ferrate are intercalated within the HT structure during this contact. Adsorption was also a likely mechanism: calcination of the HT at temperatures of between 425 and 500°C gave the greatest surface area and pore volume in the dehydrated HT, and also the most effective removal of coloured impurity.

Grubbs and Valente [11] recognised that hydrotalcite containing guest anions other than carbonate could be formed by reacting activated magnesia with a sodium aluminate solution containing the desired guest anion, and from which carbonate had been specifically excluded. This method relies on the preferred order of incorporation of guest anions described by Miyata [5], and also by

ensuring that the guest anion is present in excess. This process clearly demonstrated the important observation that hydrocalcite formation and anion intercalation can occur simultaneously.

Phillips et al. [12] described a similar process, but extended the range of generic LDH's to include calcium, and described a process in which the HT is recycled by calcination and rehydration. Like Nigro and O'Neill [10], the inventors believe that the removal mechanism is a combination of intercalation and adsorption, with the larger humic materials adsorbed at the surface.

Hydrocalcite and its analogues have dominated much of the LDH research literature throughout the latter two decades of the twentieth century. The calcium-aluminium LDH's (hydrocalumites) attracted far less attention, perhaps because of the relative difficulty in synthesising pure forms of the material and the somewhat less efficient calcination / rehydration behaviour.

Much of the early (and continuing) research into the calcium aluminates was conducted by and on behalf of the cement industry (see for example the review by Turriziani [13]), because of its importance in the development and control of the strength and chemical resistance of cement. Unfortunately, the cement literature tends to contain little detail on anion exchange, pillaring and dehydration/rehydration behaviour of the calcium-aluminium LDH species.

Thus, despite the vast quantities of lime consumed by the alumina industry annually, there was little recognition of the potential importance of the calcium-aluminium LDH's until the mid-nineties. Development was again spear-headed by Alcoa.

Perotta and Williams [14] examined the in-situ formation of hydrocalumite (HC) through the reaction of either $\text{Ca}(\text{OH})_2$ or CaO in Bayer liquors. In this study, they found that the formation of HC at temperatures up to 60°C gave an improvement in the removal of sodium oxalate from spent liquor. At higher temperatures, TCA was the major product and there was no improvement in oxalate removal. They concluded that intercalation of oxalate played at most a minor role in its removal, rather depletion of oxalate crystallization poisons by adsorption on the HC surface enhanced sodium oxalate nucleation and precipitation.

In a follow-up paper, Perotta and Williams [15] concluded that the minor intercalation of oxalate in their earlier work with hydrocalumite was because of preferential intercalation of carbonate. The more recent study focused on reacting magnesia with the liquor to achieve impurity removal. This gave only partial HT formation, with less loss of alumina from solution to form the LDH, but equivalent oxalate removal behavior. This was achieved mostly by adsorption of humates thereby destabilizing oxalate in solution - intercalation was at most a minor effect.

Returning to the hydrocalumite system in 1997, Perotta et al. [16] evaluated the potential to remove anions from Bayer process lake waters. In this solution, carbonate, sulphate and other anions are present at comparatively low concentration, as is the aluminate ion that is required to form the HC in-situ. Treatment with CaO therefore, produced HC with carbonate as the guest anion, and consumed most of the aluminate, preventing the removal of any

further impurities. However, by calcining the HC and returning the calcined product to the treated lake water, hydrocalumite was re-formed and intercalation of other anions such as sulphate and some dicarboxylates took place. The selected calcination conditions (1000°C) produced mayenite (a cubic calcium aluminate) and CaO , rather than a dehydrated HC. In this study, Perotta et al. noted that removal of carbonate was a necessary prerequisite to the removal of other anions.

Studying the chemistry of lime in the re-causticisation of Bayer liquors, Roach [17] more recently found that HC was an important intermediate in the pathway to either calcium carbonate or TCA6 formation.

Similar conclusions had been reached by Rosenberg et al. [18], who described the sequence of reactions in their causticisation patent. By isolating the individual reaction steps, more efficient use was made of the anion exchange properties of the LDH intermediate to intercalate carbonate anions from an already causticised liquor stream. This released hydroxyl ions and increased the liquor causticity to an extent that would otherwise not be possible.

A further outcome of the work by Rosenberg et al. [18] of particular importance to alumina refining was the discovery of a range of additives that helped stabilize the HC structure against undesirable reactions such as the formation of TCA6, substantially broadening the range of conditions under which HC could be formed and used.

In their 2001 paper, Rosenberg et al. [19] described in more detail some of the chemistry of calcium in Bayer liquors, including the formation and reactions of the HC species. A salient aspect of this work was the identification of a dissolved calcium aluminate monomer in equilibrium with the solid phase HC. This equilibrium gives rise to elevated soluble calcium in Bayer liquors, and must therefore be considered in any potential application of HC if the product alumina is not to be unduly contaminated.

The removal of undesirable anions by intercalation into HC from strong Bayer liquors is described in another patent by Rosenberg et al. [20]. Like Perotta et al. [16], the authors recognised that for other impurities to be removed by LDH intercalation, the carbonate concentration must first be greatly reduced. Several schemes for achieving this were described, of which perhaps the most useful is the use of the counter-current causticisation process. This has the advantage that there is potentially no loss of alumina during the carbonate removal step, since the HC is recycled and reacted with the incoming stream to form CaCO_3 , thus releasing the aluminate from the HC back into solution. Alternatively, the stream could be first causticised by intercalation of carbonate into HC, separating the HC and using it elsewhere in the refinery to causticise a separate stream. Using these techniques, they demonstrated that impurities such as sulphate and oxalate could be intercalated into HC, recovering the associated soda as caustic.

Another interesting aspect was the observation that the formation of HC can be used to remove alumina from solution, and this can be subsequently recovered elsewhere in the process by decomposing the HC to, for example, calcium carbonate. The authors made use of this property to remove almost all of the

aluminate from an oxalate-rich Bayer liquor. Addition of further lime to this solution now produced calcium oxalate rather than oxalate-bearing HC. The ability to temporarily “store” the aluminate ion in a solid form and recover it elsewhere has other implications that will be discussed later in this paper.

Future Processing Applications

Many of the applications to date have made use of a single property of the LDH, such as anion exchange. However, as the preceding discussion has shown, LDH's possess some outstanding properties that provide unique capabilities for enhancing the Bayer process when they are used in tandem. In particular, the hydrocalumite family of calcium-aluminium LDH is especially attractive, given the large quantities of material that would be required to treat a typical alumina refinery, as it is cheap and offers a number of advantages over hydrotalcite.

Removal of anionic impurities with recovery of the associated sodium as caustic is the most obvious and likely future application of LDH's in the alumina refinery. Where the impurity content of the liquor streams is small, disposal of the LDH to landfill after use may be economic. However, where large-scale impurity removal is required, the cost of this may be prohibitive, especially when the alumina loss associated with forming the LDH is considered. In this case, some means of recycling the LDH, or at least recovering the alumina content is required.

It has been well recognized that most LDH's can be recycled for further use through calcination to the oxide analogue, provided that the intercalated anions are not refractory. If they are, in many cases an additional processing step can be added that allows the intercalated anion to be exchanged for carbonate before proceeding to calcination [12]. However, regeneration of the LDH through calcination and rehydration is not especially attractive when the volume of material to be treated is large. Further, if the anion must first be exchanged for carbonate, there is the added problem of determining what to do with the solution that now contains the original impurity anion(s).

The above considerations may be at least part of the reason that LDH's have not found more widespread application in the alumina industry.

Hydrocalumite offers an alternative, hydrometallurgical route to re-use. This is discussed in some detail in the patents by Rosenberg et al. [18, 20], but in essence the procedure consists of forming and using the HC to remove the anion in question from one refinery liquor stream, separating the solid and reacting it in an alkaline carbonate solution elsewhere in the refinery. This reaction can be configured to be almost 100% efficient – almost all of the alumina that was consumed in forming the HC is released into solution, and pure calcite is generated. Further treatment of the solution allows recovery of the alumina and disposal of the impurity in a relatively pure form. The calcite, being pure, can be calcined and re-used, if necessary.

One interesting variation on this theme is to form hydrocalumite in the spent liquor stream, and then use this material in the refinery's causticiser circuit in place of lime. This has three beneficial effects: the causticity of the spent liquor returning to digestion is increased, the alumina content is lowered, and the intercalation of water into the HC structure partially dehydrates

the solution, giving the equivalent of additional evaporation. Digestion performance is therefore improved; the alumina and water from the spent liquor is recovered in the causticiser and thus reports to the refinery's pregnant liquor stream, increasing the supersaturation. This process of alumina “shuttling” can be operated even in refineries with relatively low carbonate loading by introducing sodium carbonate ore (eg Trona or Natrite) into the causticiser feed stream.

Uses in Control of Refinery Emissions

LDH's have found widespread use in water treatment outside the alumina industry, to remove organics (humates, phenolics, etc) and other anionic impurities [21]. Within the alumina refinery, they could be used to similar good effect in the treatment of boiler water, or in the purification of brackish water for use in the refinery. Waste or by-product refinery streams from current or future processes may have specific anionic pollutants that allow economic treatment by LDH's for discharge to the environment, with due regard to the order of exchange.

Refinery condensate streams are often odorous, due to the presence of dissolved organic species. Many of these organics are present in anionic form, which suggests that LDH's may well be useful in decontaminating these streams to reduce their odour impact. For some larger anions, it may be necessary to use a pillared form of the LDH, or they may not be able to enter the inter-layer regions for exchange. In practice, the condensate could be passed through a packed bed of the LDH for anion exchange. The intercalated organics would then be destroyed during regeneration of the LDH by calcination in an oxygen-rich environment. Potential advantages of using LDH's over other techniques, such as biofiltration, include the ability to operate at relatively high temperatures and the smaller footprint that a LDH process would require.

LDH's can also be used to treat hot gas streams. For example, the use of LDH's for Flue-Gas Desulphurization (FGD) at temperatures below 400°C was disclosed in a patent by Pinnavaia et al. [22]. In this process a range of LDH's, but preferentially the relatively inexpensive carbonate-bearing HT or HC, are used in a dry contact system to scrub SO₂ from the flue gases of coal-fired boilers. When the sorbent is exhausted, it can be regenerated by heating at above 400°C to evolve SO_x in a concentrated stream that can be used to produce sulphuric acid. The calcined material can then be rehydrated in the usual fashion to regenerate the LDH. The inventors claim the process is more efficient than similar zeolite-based systems, and requires less space and capital investment than conventional limestone-based FGD systems, which require prohibitively high temperatures for regeneration. The sorbent is also recyclable, eliminating the requirement for landfill disposal.

Conclusions

Used in the appropriate way, layered double hydroxides offer a potential for new and efficient options for impurity removal from alumina refinery liquor streams and for control of waste and emissions.

They also provide a number of possibilities to enhance the Bayer process through their ability to “fix” anionic species (particularly

the aluminate ion) in a solid form at one location and then release them into solution again at another location where their presence would be beneficial.

By applying in tandem some or all of the inherent chemistry, the economics of their use might be made quite attractive, overcoming most of the concerns with their use in the past.

Acknowledgements

The authors wish to thank Billiton Aluminium Australia Pty Ltd, Alcan International Ltd, and Queensland Alumina Ltd for permission to publish this work.

References

1. F. Basile and A. Vaccari, "Applications of Hydrotalcite-Type Anionic Clays (Layered Double Hydroxides) in Catalysis", *Layered Double Hydroxides*, V. Rives, ed., (Nova Science Publishers, 2001), 285.
2. A. Terzis et al., *Z. Kristallograph.* 181 (1987), 29.
3. B. Schepers, G. Bayer, E. Urmann and K. Schanz., "Method for Removing Harmful Organic Compounds from Aluminate Liquors of the Bayer Process", US Patent 4,046,855 (1977).
4. H. Pohland, E. Hecht and G. Bayer, "Recovery of Refractory Raw Materials and Simultaneous Removal of Organic Substances from Bayer Process Leachates", European Patent EP 92028 (1983).
5. S. Miyata, "Anion-Exchange Properties of Hydrotalcite-Like Compounds", *Clays and Clay Minerals*, 31(4) (1983), 305-311.
6. C. Misra, "Adsorbent and Substrate Products and Method of Producing Same", US Patent 4,656,156 (1987).
7. C. Misra, "Synthetic Hydrotalcite", US Patent 4,904,457 (1990).
8. C. Misra and A. Perotta, "Method of Making Pillared Hydrotalcites and Associated Products", US Patent 5,075,089 (1991).
9. R.H. Goheen, W.A. Nigro and P.J. Thé, "Process for Producing Aluminium Hydroxide of Improved Whiteness", US Patent 4,915, 930 (1990).
10. W.A. Nigro and G.A. O'Neill, "Method for Reducing the Amount of Colorants in a Caustic Liquor", US Patent 5,068,095 (1991).
11. D.K. Grubbs and P.E. Valente, "Direct Synthesis of Anion Substituted Hydrotalcite", US Patent 5,362,457 (1994).
12. R.B. Phillips, N.M. Fitzgerald and B.L. McCormick, "Method for Improving the Brightness of Aluminium Hydroxide", US Patent 5,624,646 (1997).
13. R. Turriziani, "The Calcium Aluminate Hydrates and Related Compounds", *The Chemistry of Cements*, H.F.W. Taylor, ed., (Academic Press, 1964), 233-286.
14. A.J. Perotta and F. Williams, "Hydrocalumite Formation In Bayer Liquor and its Promotional Effect on Oxalate Precipitation", *Light Metals*, 1995, 77-87.
15. A.J. Perotta and F. Williams, "Layered Double Hydroxide Formation in Bayer Liquor and its Promotional Effect on Oxalate Precipitation", *Light Metals*, 1996, 17-28.
16. A.J. Perotta, F. Williams and L. Stonehouse, "Layered Double Hydroxides for Treatment of Bayer Process Lake Water", *Light Metals*, 1997, 37-48.
17. G.I.D. Roach, "The Equilibrium Approach to Causticisation for Optimising Liquor Causticity", *Light Metals*, 2000, 97-103.
18. S.P. Rosenberg, D.J. Wilson and C.A. Heath, "Improved Bayer Causticisation", WO 00/18684 (2000).
19. S.P. Rosenberg, D.J. Wilson and C.A. Heath, "Some Aspects of Calcium Chemistry in the Bayer Process", *Light Metals*, 2001, 19-25.
20. S.P. Rosenberg, D.J. Wilson, C.A. Heath and W. Tichbon, "Process for the Removal of Oxalate and/or Sulphate From Bayer Liquors", WO00/56660 (2000).
21. S. Amin and G.G. Jayson, "Humic Substance Uptake by Hydrotalcites and Pils", *Water Research*, 30 (2) (1996), 299-306.
22. T.J. Pinnavaia and J. Amaresekera, "Process of Using Layered Double Hydroxides as Low Temperature Recyclable Sorbents for the Removal of SOx from Flue Gas and Other Streams", US Patent 5,358,701 (1994).