METHOD OF REDUCING CALCIA CONCENTRATIONS OF GREEN BAYER PROCESS LIQUORS

Abstract: A method of reducing the calcia concentration of a green Bayer process liquor containing calcia and phosphate, the method comprising the step of: contacting the green Bayer process liquor with a quantity of apatite; thereby inducing the precipitation of further apatite and reducing the calcia concentration of the green Bayer process liquor.
For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.
"Method of reducing calcia concentrations of green Bayer process liquors"

Field of the Invention

The present invention relates to a method of reducing calcia concentrations in liquors generated by the Bayer process for the production of alumina from ores of aluminium. In particular, the present invention relates to a method of reducing calcia concentrations in green Bayer process liquors.

Background Art

The Bayer process is widely used for the production of alumina from alumina-containing ores, such as bauxite. The process is initiated by contacting alumina-containing ores with recycled caustic aluminate solutions, at elevated temperatures, in a process commonly referred to as digestion.

Following digestion, the slurry of insoluble red mud in sodium aluminate solution (green liquor) is passed through a series of pressure-reducing tanks (called blow-off tanks), where the solution is flashed to atmospheric pressure. The next step in the process is to separate the insoluble red mud from the sodium aluminate solution. Coarse material may be removed in crude cyclones called sand traps, while finer residue is settled in raking thickeners with the addition of synthetic flocculants. The red mud is taken as underflow from the thickeners, and then typically washed to recover caustic values and render such suitable for disposal. The overflow, however, typically still contains finely divided red mud particulates, comprising iron oxides, iron hydroxides, silica and the like. The presence of these compounds in the final alumina product is highly undesirable and the settler overflow is often passed through one or more filters to remove such.

The clarified solution is further cooled in heat exchangers, enhancing the degree of supersaturation of the dissolved alumina, and pumped into precipitators before being seeded with aluminium hydroxide to induce the precipitation of further aluminium hydroxide. The precipitated aluminium hydroxide is separated from the caustic aluminate solution, with a portion of the aluminium hydroxide being
recycled to be used as seed and the remainder recovered as product. The remaining caustic aluminate solution is recycled for further digestion of alumina containing ore.

The digestion process consumes caustic, which is typically replenished (at least in part) by the addition of lime. Calcia introduced by way of the lime may be precipitated as calcium carbonate. However, more effective causticisation may be achieved by the addition of an excess of lime, meaning calcia levels in the liquor increase.

Obviously, high alumina concentrations relative to total caustic concentration are highly desirable for efficient precipitation. However, it is equally undesirable for any dissolved alumina to precipitate prior to filtration. As well as reducing efficiency, this decreases the time for which the filters remain operable. Filter maintenance requirements depend on the type of filter employed, but typically involve opening the filter assembly, removing the solids, and back-flushing the filter medium with clean spent liquor. This causes considerable disruption in an otherwise largely continuous process, and demands considerable labour. Accordingly, most refineries typically identify a critical ratio of alumina concentration to total caustic concentration, above which filtration becomes unviable. Elevation of green liquor (or slurry) calcia levels, such as by addition of lime or calcite, or under other circumstances such as an elevated concentration of organic species in liquor, and/or as a side-effect of other plant processes, increases alumina stability, allowing filtration to occur at higher ratios of alumina to total caustic.

However, high liquor calcia levels present a product quality issue: calcia is quantitatively removed by hydrate precipitation, and is retained through calcination, with nearly 100% of the calcia in solution ultimately reporting to product alumina. Accordingly, techniques that result in an increase in liquor calcium levels, such as alumina stabilisation and causticisation with excess lime, cannot be applied to their full potential without adversely affecting product quality.
Accordingly, methods for the reduction of calcia in Bayer process liquors are highly desirable.

The preceding discussion of the background to the invention is intended to facilitate an understanding of the present invention. However, it should be appreciated that the discussion is not an acknowledgement or admission that any of the material referred to was part of the common general knowledge in Australia as at the priority date.

**Disclosure of the Invention**

Those skilled in the art will appreciate that the invention described herein is susceptible to variations and modifications other than those specifically described. It is to be understood that the invention includes all such variations and modifications. The invention also includes all of the steps, features, compositions and compounds referred to or indicated in the specification, individually or collectively and any and all combinations or any two or more of the steps or features.

The present invention is not to be limited in scope by the specific embodiments described herein. These are intended for the purpose of exemplification only.

Functionally equivalent products, compositions and methods are clearly within the scope of the invention.

The entire disclosures of all publications (including patents, patent applications, journal articles, laboratory manuals, books, or other documents) cited herein are hereby incorporated by reference.

Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers.
Throughout the specification, unless the context requires otherwise, the word "apatite" refers to one or more of a family of compounds based on hydroxylapatite Caio(PO$_4$)$_6$(OH)$_2$, including fluorapatite (Caio(PO$_4$)$_6$F$_2$), chlorapatite (Ca$_{10}$(PO$_4$)$_6$Cl$_2$), hydroxylapatite (Ca$_0$(PO$_4$)$_6$OH$_2$), carbonate-apatite, carbonate hydroxylapatite or carbonate fluorapatite. Most forms of apatite can be described by the following formula Aio(XO$_4$)$_6$(OH,F,Cl)$_2$·nH$_2$O, wherein: A may be selected from Ba, Ca, Ce, K, Na, Pb, Sr, Y; X may be selected from As, P, Si, V, and CO$_3$ can be at least partially substituted for PO$_4$.

Throughout this specification, unless the context requires otherwise, the word apatite encompasses mixtures containing apatite, including mixtures containing one or more apatites.

In accordance with the present invention, there is provided a method of reducing the calcia concentration of a green Bayer process liquor containing calcia and phosphate, the method comprising the step of:

contacting the green Bayer process liquor with a quantity of apatite;

thereby inducing the precipitation of further apatite and reducing the calcia concentration of the green Bayer process liquor.

The apatite may be provided in the form of any compound having the general formula A$_{10}$(XO$_4$)$_6$(OH,F,Cl)$_2$·nH$_2$O, wherein: A may be selected from Ba, Ca, Ce, K, Na, Pb, Sr, Y; X may be selected from As, P, Si, V, and CO$_3$ can be substituted for PO$_4$.

Preferably, A is Ca and Na and the apatite is provided at least predominantly in the form of a carbonate hydroxylapatite having the general formula Ca-1o-$\chi$Na$_{2x/3}$(P0$_4$)$_{6-x}$(CO$_4$)$_{\chi}$(OH)$_{2-x/3}\cdot xH$_2$O$, where 0<x<3, or any mixture of such compounds.

In one form of the invention, the apatite is provided in the form of Ca$_7$Na$_2$(CO$_3$MPO$_4$M H$_2$O)$_3$(OH).
However, the scope of the invention should not be understood to be limited to carbonate hydroxylapatites, with non-carbonate hydroxylapatites such as Ca$_5$(PO$_4$)$_3$(OH) having been demonstrated to be effective.

Apatite can typically be produced on-site at many Bayer process refineries, affording an additional advantage of the present invention.

For example, apatite may be prepared by the addition of a lime source and a phosphate source to a Bayer process liquor. In one form of the invention, the lime source may be provided in the form of slaked lime, tricalcium aluminate or press mud. The phosphate source and the Bayer process liquor may be provided together in the form of a high-phosphate Bayer process spent liquor. Residence times for the preparation of apatite are low, about 15-30 minutes, at temperatures of about 90°C. The apatite so produced may be separated from the remaining solution before being utilised in the method of the present invention. Alternately, a slurry of the apatite and supernatant solution may be utilised in the method of the present invention.

It has been found that the manner in which the apatite is prepared affects the efficacy of the apatite in the method of the present invention. Specifically, apatite prepared with a stoichiometric excess of phosphate is more effective, with greater excesses affording greater efficacies. Thus, in a preferred form of the invention, the apatite is prepared with a stoichiometric excess of phosphate. However, the residual phosphate concentration after apatite precipitation may cause other process complications. Thus, in a preferred form of the invention, the apatite is prepared with less than 200% stoichiometric excess of phosphate. In a preferred form of the invention, the apatite is prepared with less than 100% stoichiometric excess of phosphate. In a preferred form of the invention, the apatite is prepared with less than 50% stoichiometric excess of phosphate.

Further, it has been found that the efficacy of apatite in the method of the present invention diminishes with time. Accordingly, the quantity of apatite is preferably freshly precipitated, or at least freshly separated from the liquor from which it has been precipitated. In a highly preferred form of the invention, the apatite is
precipitated within 24 hours before it is contacted with the green Bayer process liquor in accordance with the method of the present invention. However, older apatite may be useful under favourable process conditions, such as high feed liquor calcia and phosphate concentrations. Preferably still, the apatite is precipitated within 8 hours before it is contacted with the green Bayer process liquor in accordance with the method of the present invention.

Further, it has been found that the efficacy of precipitated apatite in the method of the present invention may be enhanced by exposing the quantity of apatite to a phosphate solution. The extent to which the activity is replenished has been found to be dependent on the concentration of the phosphate solution and the duration of the exposure, with longer exposure times and more concentrated phosphate solutions effecting greater replenishment. As an example, exposing aged apatite to a 9000 ppm phosphate solution for approximately 15 minutes will restore the activity of such to about one half to one third that of freshly precipitated apatite.

The time for which the Bayer process liquor is in contact with the quantity of apatite (the residence time) has been found to affect the extent of the reduction in calcia concentration, with greater residence times typically resulting in greater calcia reduction. Accordingly, preferred residence times are derived from balancing calcia reduction with the effect of the method of the invention with other elements of the Bayer process. However, effective calcia reduction can be achieved using very short residence times, and in many preferred embodiments of the invention, the method can be implemented in conjunction with existing Bayer process steps without imposing a requirement of additional residence times.

The amount of apatite added to the Bayer process liquor has been found to affect the extent of the reduction in calcia concentration, with larger doses effecting more significant and/or rapid reductions. Furthermore, different doses are appropriate for different approaches to contacting the green Bayer process liquor with the quantity of apatite. Different approaches to contacting the green Bayer process liquor with the quantity of apatite are discussed below. However, apatite doses of the order of 200 - 300 mg per kl of Bayer process liquor should be sufficient for a
range of process conditions. Lower doses may be possible under favourable process conditions, such as high feed liquor calcia and phosphate concentrations.

The concentration of phosphate in the green Bayer process liquor has been found to affect the extent of reduction in calcia concentration, with higher concentrations effecting more significant and/or rapid reductions. However, as would be understood by a person skilled in the art, high phosphate concentrations import process-related disadvantages that may outweigh any advantages achieved in calcia reduction. Typically phosphate concentrations of green Bayer liquors vary considerably, from approximately 40ppm to in excess of 400ppm in high total alkali liquors.

The calcia concentration of the green Bayer process liquor has been found to affect the extent of reduction in calcia concentration, with higher concentrations effecting more significant and/or rapid reductions.

The temperature of the green Bayer process liquor has been found to affect the extent of reduction in calcia concentration, with higher temperatures effecting more significant and/or rapid reductions. However, as would be understood by a person skilled in the art, varying the temperature of a Bayer process liquor is an energy intensive process and the economic advantage gained by varying the temperature of the Bayer process liquor to optimise the method of the present invention may be outweighed by the economic disadvantage of temperature elevation.

The present invention works well at typical Bayer liquor filtration temperatures (100-105°C), but can be applied over a wide range of temperatures (70°C and upwards). Although lower temperatures result in lower rates of calcium removal, these can be compensated by manipulating other process variables (e.g. apatite doses and sizing, feed liquor calcium and phosphate concentrations, residence time).

The sizing of the quantity of apatite has been found to affect the extent of reduction in calcia concentration, with smaller sizes effecting more significant and/or rapid reductions. However, in some forms of the invention, the quantity of
apatite is contacted with the green Bayer process liquor upstream from a solid-solution separation step. Examples of such forms of the invention are discussed below. In these forms of the invention, the solid-solution separation step may provide a lower limit to the desired sizing of the quantity of apatite, in that it is highly desirable that the quantity of apatite be at least substantially separated from the solution in the solid-solution separation step.

The advantageous effect of decreased particle size is considered to be at least significantly dependent on the increased surface area, with higher surface areas effecting more significant and/or rapid reductions. Thus, in a preferred form of the invention, the quantity of apatite comprises apatite having a high surface area to volume ratio. Increasing the surface area of the quantity of apatite without decreasing sizing, or by at least not proportionately decreasing sizing, affords the advantages of more significant and/or rapid reductions in calcia concentration without attracting, or without attracting to a proportionate extent, the potential disadvantages in subsequent solid-solution separation.

Thus, the efficacy calcia removal according to the method of the present invention has been found to be affected by:

(i) preparation of apatite with stoichiometric excesses of phosphate, with greater excesses affording greater efficacies in terms of the extent of calcia removal, or the time within which a desired degree of calcia removal may be achieved;

(ii) the phosphate concentration of the green Bayer process liquor, with higher phosphate concentrations affording greater efficacies in terms of the extent of calcia removal, or the time within which a desired degree of calcia removal may be achieved;

(iii) the calcia concentration of the Bayer process liquor, with higher calcia concentrations affording greater efficacies in terms of the extent of calcia removal, or the time within which a desired degree of calcia removal may be achieved;
(iv) the dose of apatite contacted with the Bayer process liquor, with higher doses affording greater efficacies in terms of the extent of calcia removal, or the time within which a desired degree of calcia removal may be achieved;

(v) The time for which the quantity of apatite is contacted with the green Bayer process liquor, with longer times affording greater efficacies in terms of the extent of calcia removal;

(vi) the particle size and/or surface area of the apatite contacted with the Bayer process liquor, with smaller particle sizes and/or greater surface areas affording greater efficacies in terms of the extent of calcia removal, or the time within which a desired degree of calcia removal may be achieved;

(vii) the temperature at which the quantity of apatite is contacted with the green Bayer process liquor, with higher temperatures affording greater efficacies in terms of the extent of calcia removal, or the time within which a desired degree of calcia removal may be achieved; and

(viii) the age of the quantity of apatite contacted with the green Bayer process liquor, with freshly precipitated apatites, and/or apatites freshly contacted with a phosphate solution, affording greater efficacies in terms of the extent of calcia removal, or the time within which a desired degree of calcia removal may be achieved.

Requirements dictated by other aspects of the Bayer process place limits on the extent to which any or all of the abovementioned factors may be optimised to achieve a particular extent of calcia removal in a particular Bayer process refinery. The combination and/or optimisation of one or more of the factors for a particular circumstance is considered to fall within the scope of this invention.

Several combinations of phosphate concentration, calcia concentration, temperature, particle size, particle surface area, apatite preparation conditions, apatite age and apatite dose are discussed in the section headed 'Examples',

These combinations are provided by way of exemplification only, and should not be construed as limiting the scope of the present invention.

As explained in the context of the description of the background art, calcia may be present in a Bayer process liquor either as a by-product of a desirable process, such as causticisation, and/or may be added to achieve a desirable outcome such as alumina stabilisation during separation of residual solids (red mud) from green liquor. Thus, the person skilled in the art will understand that calcia introduced into the Bayer process liquor as a by-product of a desirable process may afford additional process benefits such as stabilisation of alumina during separation of residual solids (red mud) from green liquor.

In one form of the invention, the method comprises the steps of:

- dissolving an alumina-containing ore in a caustic solution to provide a slurry of a red mud in a green liquor containing phosphate; then
- adding a quantity of calcia to the suspension of red mud in green liquor to produce a suspension of red mud in green liquor containing calcia and phosphate; then
- separating the red mud from the green liquor; and
- contacting the green liquor with a quantity of apatite.

thereby inducing the precipitation of further apatite and reducing the calcia concentration of the green liquor.

The steps of separating the red mud from the green liquor and contacting the green liquor with apatite may occur simultaneously.

In one form of the invention, the step of separating the red mud from the green liquor comprises the step of passing the suspension of red mud in green liquor through a filter, and the step of contacting the green liquor with a quantity of
apatite occurs immediately prior to the step of passing the suspension of red mud
in green liquor through a filter.

In a preferred form of the invention, the step of separating the red mud from the
green liquor comprises the steps of:

5 passing the slurry of red mud and green liquor through one or more sand traps producing a second slurry of red mud and green liquor, the second slurry containing a lower proportion of red mud relative to green liquor;

passing the second slurry through one or more thickeners, producing a thickener underflow of substantially red mud and a thickener overflow of substantially green liquor; and

10 passing the thickener overflow through a filter.

In this form of the invention, the step of adding a quantity of calcia to the
suspension of red mud in green liquor occurs before the step of passing the thickener overflow through the filter.

15 Where the calcia is added for the purpose of stabilising alumina, the step of adding a quantity of calcia to the suspension of red mud in green liquor may occur after the step of passing the slurry of red mud and green liquor through one or more sand traps producing a second slurry of red mud and green liquor, the second slurry containing a lower proportion of red mud.

20 Further, where the calcia is added for the purpose of stabilising alumina, the step of adding a quantity of calcia to the suspension of red mud in green liquor may occur after passing the second slurry through one or more thickeners, producing a thickener underflow of substantially red mud and a thickener overflow of substantially green liquor.

25 In one form of the invention, the filter is a fixed-bed type filter, such as a sand filter. As will be apparent to a person skilled in the art, a fixed-bed type filter utilises a
bed of at least substantially inert filtration medium, supported by a screen through which the liquor will pass. Using a sand filter as an example, a bed of sand is supported by a metal screen, trapping red mud particles from the feed Bayer process liquor against sand particle surfaces in the bed, as the Bayer process liquor is pumped onto or into the bed (typically through holes in a rotating sparge), and passes through the interstices in the bed under the force of gravity.

Where the filter is a fixed-bed type filter, the steps of contacting the green Bayer process liquor with a quantity of apatite and passing the thickener overflow through a filter comprises combining the thickener overflow with the quantity of apatite then passing the combination through a filter.

Fixed-bed type filters typically operate in cycles: eventually, sufficient particulate material accumulates on the substantially inert filtration medium to substantially decrease the efficiency of the filter. At this point, the filter is renewed, typically by back-washing. The time between filter renewals is typically referred to as a filter cycle.

As discussed above, the reduction in calcia concentration is dependent on a range of factors, including residence time. In a preferred form of the invention, these factors are manipulated such that the desired reduction in calcia concentration is achieved within a residence time that is less than or equal to a single filter cycle. In this case, assuming constant feed conditions, the calcia drops occurring at any given time through each filter cycle should be proportional to the total mass of apatite dosed into the filter bed up to that time point.

In one form of the invention, the filter is a cake-type filter. As will be apparent to a person skilled in the art, a cake-type filter is a filter in which filter aid solids (fine but readily-filterable, chemically inert, particulate solids), are pumped into the filter, to cover the filter leaves (mesh structures covered by open-weave filter cloths) with a filter cake, allowing passage of liquor through its pore structure, but retaining mud solids when green liquor is pumped through the filter, optionally under gravity or vacuum but usually (for green Bayer liquor filtration) under pressure (as in a Kelly filter).
The filter aid solids can be pumped into the filter in either or both of the following ways:

(i) prior to the main filtration flow, to form an initial mud-free filter cake layer on the filter leaves; and/or

(ii) mixed into the filter feed liquor, to progressively grow mud-retaining filter cake layers throughout each green Bayer liquor filtration cycle.

In one form of the invention, where the filter is a cake-type filter, the step of contacting the green liquor with a quantity of apatite comprises the step of:

adding the quantity of apatite to the thickener overflow.

In one form of the invention, where the filter is a cake-type filter, the step of separating the red mud from the green liquor comprises the steps of:

mixing the thickener overflow with a quantity of filter aid; and

passing the thickener overflow through the filter.

Where the present invention comprises the step of mixing the thickener overflow with a quantity of filter aid, the method may comprise the prior additional step of:

mixing a quantity of apatite with the quantity of filter aid;

such that the step of mixing the thickener overflow with a quantity of filter aid effects the step of contacting the green liquor with a quantity of apatite.

In one form of the invention, where the filter is a cake-type filter, the step of separating the red mud from the green liquor comprises the steps of:

applying a layer of filter aid to the cake-type filter; then

passing the thickener overflow through the layer of filter aid and the filter.
Where the present invention comprises the step of applying a layer of filter aid to a filter, the method may comprise the prior additional step of:

mixing a quantity of apatite with the quantity of filter aid;

such that the step of passing the thickener overflow through the layer of filter aid and the filter effects the step of contacting the green liquor with a quantity of apatite.

In one form of the invention, where the filter is a cake-type filter, the step of separating the red mud from the green liquor comprises the steps of:

passing the slurry of red mud and green liquor through one or more sand traps producing a second slurry of red mud and green liquor, the second slurry containing a lower proportion of red mud relative to green liquor;

passing the second slurry through one or more thickeners, producing a thickener underflow of substantially red mud and a thickener overflow of substantially green liquor;

mixing a first quantity of apatite with a first quantity of filter aid to produce a first mixture;

applying a layer of the first mixture to a filter;

mixing a second quantity of filter aid with a second quantity of apatite to produce a second mixture;

mixing the second mixture with the thickener overflow; then

passing the thickener overflow through the layer of the first mixture and the filter;
such that the steps of mixing the second mixture with the thickener overflow and passing the thickener overflow through the layer of the first mixture and the filter each effect the step of contacting the green liquor with a quantity of apatite.

Preferably, the apatite is of a similar sizing to the filter aid. That is, not so fine as to risk significant apatite contamination of filtrate and not so coarse as to lose the surface area needed for sufficient rates of calcia removal. Apatite falling mainly in the 5-15 micron size range would meet both of these criteria. Alternately, and as discussed above, larger particle sizes with increased surface area may be used.

Apatite can typically be produced on-site at many Bayer process refineries, affording an additional advantage of the present invention.

For example, apatite may be prepared by the addition of a lime source and a phosphate source to a Bayer process liquor. In one form of the invention, the lime source may be provided in the form of slaked lime, tricalcium aluminate or press mud. The phosphate source and the Bayer process liquor may be provided together in the form of a high-phosphate Bayer process spent liquor. Residence times for the preparation of apatite are low, about 15-30 minutes, at temperatures of about 90°C. The apatite so produced may be separated from the remaining solution before being utilised in the method of the present invention. Alternately, a slurry of the apatite and supernatant solution may be utilised in the method of the present invention.

International patent application (PCT/AU2006/000140) (Alcoa of Australia Limited) describes methods for the causticisation of and controlling phosphate in Bayer process solutions by the addition of a source of phosphate thereby inducing precipitation of a calcium phosphate precipitate, in one form of the invention as an apatite. The practical utility of these methods is significantly dependent on the cost of the source of phosphate. The method of the present invention thus appreciably facilitates the utilisation of the methods for the causticisation of and for controlling phosphate in Bayer process solutions of (PCT/AU2006/000140) by utilising the primary by-product of such.
Thus, in accordance with the present invention, there is provided a method for the treatment of a Bayer process liquor, the method comprising the steps of:

- adding a source of phosphate to the Bayer process solution;
- adding a causticising agent to the Bayer process solution; and
- forming a calcium phosphate precipitate in the form of a quantity of apatite;
- thereby causticising the Bayer process solution; then
- contacting the Bayer process liquor with at least a portion of the quantity of apatite; and
- thereby inducing the precipitation of further apatite and reducing the calcia concentration of the Bayer process liquor.

As used herein the term "source of phosphate" shall be taken to include, without limitation, any form of phosphorus that provides an orthophosphate anion in Bayer process solutions.

Advantageously, the method of the present invention permits the causticisation of a Bayer process solution and the simultaneous control of phosphate and calcium concentrations in the solution.

**Brief Description of the Drawings**

The best mode of performing the invention will now be described, by way of example only, with reference to two embodiments and the accompanying Figures, in which:

Figure 1 is a schematic illustration of a Bayer process in which a cake-type filter is employed to separate residual solids (red mud) from green Bayer liquor, showing a first embodiment of the present invention;
Figure 2 is a schematic illustration of a Bayer process in which a fixed bed
filter is employed to separate residual solids (red mud) from green Bayer
liquor, showing a second embodiment of the present invention.

Figure 3 is a graph showing the effect of residence time of carbonate
hydroxyapatite on calcia concentrations;

Figure 4 is a graph showing the effect of carbonate hydroxyapatite and filter
aid concentrations on calcia concentrations;

Figure 5 is a plot showing the effect of carbonate hydroxyapatite on calcia
concentrations in a continuous cake filtration process; and

Figure 6 is a plot showing the effect of carbonate hydroxyapatite and filter
aid on calcia concentrations;

Figure 7 displays the results from a series of experiments in which carbonate
hydroxyapatite was prepared in solutions containing a stoichiometric excess
of phosphate;

Figure 8 displays the results from a series of experiments which
demonstrate the effect of aging of the apatite on the efficacy of calcia
removal; and

Figure 9 compares the amount of calcia removed from solution by the
"refreshed" apatite with that of 1 day old & freshly prepared apatite.

However, this description should not be understood to in any way limit the
preceding general description of the invention.

**Best Mode(s) for Carrying Out the Invention**

Referring to Figure 1, the method of reducing the calcia concentration of a green
Bayer process liquor containing calcia and phosphate of the first embodiment is
employed in the Bayer process in which an alumina-containing ore is dissolved in
a caustic solution (10), providing a slurry of a red mud in a green liquor (12) containing phosphate. The slurry of a red mud in a green liquor containing phosphate is then passed through a thickener (14), producing a thickener underflow (16) of substantially red mud and a thickener overflow (18) of substantially green Bayer liquor.

In addition to phosphate, the thickener overflow (18) contains calcia. The calcia may have originated from any one or more of a number of possible sources. For example, by addition of lime or calcite (such as during a liquor causticisation process), from an elevated concentration of organic species in liquor, as a side-effect of other Bayer processes and/or by deliberate addition such as to stabilise alumina.

The method of the first embodiment is employed in a Bayer process that utilises a cake-type filter (20). A quantity of carbonate apatite (22) in the form of Ca₇Na₂(C0₂)₃(PO₄)₃(H₂O)₃(OH) is combined with a first quantity of filter aid (24) to form a pre-coat (26) then applied as a layer to the cake-type filter (20). A second quantity of filter aid (28) is mixed with the thickener underflow (18) to form a slurry (30) of filter aid and thickener overflow.

The amount of carbonate apatite (22) applied to the cake-type filter (20) depends on a range of factors, not least of which is the desired reduction (and rate of reduction) of calcia concentration, with larger amounts causing greater/more rapid reductions as discussed in the preceding general discussion of the invention. Further, and also as discussed in the preceding general discussion of the invention, the properties of the carbonate apatite (22), such as particle size and surface area, affect the amount required to achieve a given reduction in calcia concentration in a given time. Further, and also as discussed in the preceding general discussion of the invention, the properties of the thickener underflow (18), such as calcia concentration, phosphate concentration and temperature, affect the amount required to achieve a given reduction in calcia concentration in a given time.
These parameters may be varied to balance the effect of the method of the embodiment with other Bayer process-related considerations. There is no one set of optimal parameters. However, it is generally desirable to select a combination of parameters that achieves the desired calcia reduction within the time set by a filter cycle.

Although the quantity of carbonate apatite (22) may originate from any source, conveniently the quantity of carbonate apatite (22) is generated as a by-product of another Bayer process step.

The slurry (30) is then passed through the cake-type filter (20), thereby contacting green Bayer liquor in the form of the thickener overflow (18) present in the slurry (30) to the quantity of carbonate apatite (22) present in the layer applied to the cake-type filter (20). This induces the precipitation of further apatite and reduces the calcia concentration in the Bayer process liquor.

Referring now to Figure 2, the method of reducing the calcia concentration of a green Bayer process liquor containing calcia and phosphate of the second embodiment is applied in a Bayer process substantially similar to the Bayer process in which the method of the first embodiment is applied, and like numbers will be used to denote like parts. However, the Bayer process in which the method of the second embodiment is applied uses a fixed bed filter (32) in place of the cake-type filter.

The thickener overflow (18) is mixed with a quantity of carbonate apatite (34) in the form of Ca₇Na₂(CO₃)₃(PO₄)₂S(H₂O)₉(OH), thereby contacting green Bayer liquor in the form of the thickener overflow (18) with the quantity of apatite, and the mixture held in a filter feed vessel (36) for a predetermined residence time before the mixture of carbonate apatite (34) and thickener overflow (18) is passed through the fixed bed filter (32).

The amount of carbonate apatite (34) mixed with the thickener overflow (18) depends on a range of factors, not least of which is the desired reduction (and rate of reduction) of calcia concentration, with larger amounts causing
greater/more rapid reductions as discussed in the preceding general discussion of the invention. Further, and also as discussed in the preceding general discussion of the invention, the properties of the carbonate apatite (34), such as particle size and surface area, affect the amount required to achieve a given reduction in calcia concentration in a given time. Further, and also as discussed in the preceding general discussion of the invention, the properties of the thickener overflow (18), such as calcia concentration, phosphate concentration and temperature, affect the amount required to achieve a given reduction in calcia concentration in a given time.

These parameters may be varied to balance the effect of the method of the embodiment with other Bayer process-related considerations. There is no one set of optimal parameters.

Results and Examples

Example 1

Table 1 and Figure 3 display the results from a series of experiments with carbonate hydroxylapatite - Ca$_7$Na$_2$(CO$_3$)$_3$(PO$_4$)$_3$(H$_2$O)$_3$(OH) - demonstrating the effectiveness of apatite in removing dissolved calcia from Bayer process solutions.

Solutions of green liquor containing 80, 160 and 250ppm phosphate (expressed as P$_2$O$_5$) were heated to a temperature of 95°C. Carbonate hydroxylapatite was added to the solutions in doses of either 0.2g apatite/L or 1g apatite/L. The mixtures were mixed at temperature for either 1 minute or 10 minutes.

The data given in Table 1 show that contact with carbonate hydroxylapatite reduces the concentration of calcia in liquor. The extent of the reduction of the concentration of calcia in liquor is dependent upon dose, holding time and the concentration of phosphate in liquor.

<table>
<thead>
<tr>
<th>ppm P$_2$O$_5$</th>
<th>Time at 95°C</th>
<th>Apatite Dose (g/L)</th>
<th>CaO Drop (mg/L)</th>
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<tr>
<td>80</td>
<td>1min</td>
<td>1</td>
<td>16.1</td>
</tr>
</tbody>
</table>
Example 2

Table 2 and Figure 4 display the results from a series of experiments in which carbonate hydroxylapatite was mixed with tricalcium aluminate (TCA), to demonstrate the effectiveness of the apatite in removing dissolved calcia from Bayer process solutions in the presence of filter aid.

Neat green liquor solutions and green liquor solutions containing 0.5g TCA/L were heated to a temperature of 95°C. Carbonate hydroxylapatite was added to the solutions in doses of either 0.2g apatite/L or 1g apatite/L. The mixtures were mixed at temperature for either 1 minute or 10 minutes.

The data given in Table 2 show that contact with carbonate hydroxylapatite reduces the concentration of calcia in liquor in the presence of filter aid. The extent of the reduction of the concentration of calcia in liquor is again dependent upon dose and holding time.

<table>
<thead>
<tr>
<th>Time at 95°C</th>
<th>Apatite Dose (g/L)</th>
<th>TCA6 Dose (g/L)</th>
<th>CaO Drop (mg/L)</th>
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</thead>
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<tr>
<td>0</td>
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<td>0</td>
<td>13.1</td>
</tr>
<tr>
<td>1min</td>
<td>0.2</td>
<td>0</td>
<td>20.2</td>
</tr>
<tr>
<td>10 min</td>
<td>1</td>
<td>0</td>
<td>16.9</td>
</tr>
<tr>
<td>1min</td>
<td>0.2</td>
<td>0</td>
<td>23.8</td>
</tr>
<tr>
<td>10 min</td>
<td>1</td>
<td>0</td>
<td>11.9</td>
</tr>
<tr>
<td>1min</td>
<td>0.2</td>
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<tr>
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<td>1</td>
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</tr>
<tr>
<td>10 min</td>
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<td>24.8</td>
</tr>
<tr>
<td>10 min</td>
<td>1</td>
<td>0.5</td>
<td>13.1</td>
</tr>
</tbody>
</table>
Table 2

Example 3

Table 3 and Figure 5 display the results from a pilot scale experiment in which carbonate hydroxylapatite was mixed with tricalcium aluminate (TCA) as filter aid, to demonstrate the effectiveness of the apatite in removing dissolved calcia from Bayer process solutions in a continuous cake filtration process.

500g of carbonate hydroxylapatite was added to a tricalcium aluminate slurry in a dose of 0.04g apatite/g TCA. The filter aid slurry was added to a green liquor and the mixture passed through a Kelly filter over a period of approximately 6 hours.

The data given in Table 3 show that carbonate hydroxylapatite reduces the concentration of calcia in liquor when mixed with filter aid within a filtration cake. The extent of the reduction of the concentration of calcia increases as cake thickness, and hence the amount of carbonate hydroxylapatite within the filter cake, increases.

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</tr>
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<tr>
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<td>10.3</td>
</tr>
<tr>
<td>5:45</td>
<td>11.5</td>
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</table>

Table 3
Example 4

Table 4 and Figure 6 display the results from a pilot scale experiment in which carbonate hydroxylapatite was mixed with tricalcium aluminate (TCA) and applied to the filter medium as a pre-filtration coating layer (pre-coat).

500g of carbonate hydroxylapatite was added to a tricalcium aluminate slurry in a dose of 0.27g apatite/g TCA. The mixture was applied as a coating to the cloth membrane of a Kelly filter prior to liquor filtration. Further filter aid slurry, without carbonate hydroxylapatite, was added to green liquor. The mixture was passed through the Kelly filter, and the apatite/TCA coating, over a period of 5 hours.

The data given in Table 4 show that carbonate hydroxylapatite reduces the concentration of calcia in liquor when mixed with filter aid and applied as a pre-coat. The extent of the reduction of the concentration of calcia throughout the experiment is consistently comparable to that achieved at the end of the experiment in Example 3, when the cumulative amount of apatite in the filter cake was equivalent to that in the layer of pre-coat in the current Example.

<table>
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<tr>
<th>Time Online (h:mm)</th>
<th>CaO Drop (mg/L)</th>
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<tbody>
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</tr>
<tr>
<td>3:00</td>
<td>13.6</td>
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</tr>
<tr>
<td>4:00</td>
<td>13.8</td>
</tr>
<tr>
<td>4:30</td>
<td>14.4</td>
</tr>
<tr>
<td>5:00</td>
<td>14.7</td>
</tr>
</tbody>
</table>

Table 4

Example 5: excess phosphate when apatite is prepared

Figure 7 displays the results from a series of experiments in which carbonate hydroxylapatite was prepared in solutions containing a stoichiometric excess of phosphate, to demonstrate the effect of the excess phosphate on enhancing the activity of apatite with respect to calcia removal.
Na₃PO₄·12H₂O was dissolved in portions of neat spent liquor and the solutions heated to a temperature of 90°C. Slaked lime was added to the solutions in either stoichiometric quantities or in molar proportions such that the concentration of phosphate in solution was in either a 50% or 100% stoichiometric excess, with respect to the stoichiometry of the carbonate hydroxyapatite. The mixtures were reacted at temperature for 15 minutes before the apatite samples were separated from solution by filtration and washed.

Neat green liquor solutions containing approximately 50ppm phosphate (expressed as P₂O₅) were heated to a temperature of 95°C. The prepared carbonate hydroxyapatite samples were added to the solutions in doses of approximately 1g apatite/L. The mixtures were mixed at temperature for 10 minutes.

The data shown in Figure 7 demonstrate that the efficacy of calcia removal by carbonate hydroxyapatite in solutions containing low concentrations of phosphate can be increased by preparing the carbonate hydroxyapatite in solutions containing excess phosphate. The effect is proportional to the percentage of excess phosphate in the preparation solution.

**Example 6: aged v fresh apatite**

Figure 8 displays the results from a series of experiments which demonstrate the effect of aging of the apatite on the efficacy of calcia removal.

Orthophosphoric acid was added to neat spent liquor and the solutions heated to a temperature of 90°C. Slaked lime was added to the solutions in stoichiometric quantities with respect to the stoichiometry of the carbonate hydroxyapatite. The mixtures were reacted at temperature for 15 minutes before the apatite samples were separated from solution by filtration and washed. Approximately half of the damp cake was stored at room temperature for 24 hours.
Neat green liquor solutions containing approximately 40 - 60 ppm phosphate (expressed as \( \text{P}_2\text{O}_5 \)) were heated to a temperature of 95°C. The freshly prepared carbonate hydroxylapatite samples were added to the solutions in doses of approximately 0.2, 0.3 and 1 g apatite/L. The mixtures were reacted at temperature for 10 minutes. The experiments were repeated 24 hours later using the stored sample of damp apatite.

The data shown in Figure 8 demonstrate that calcia removal using fresh apatite is proportional to the dose of apatite used, even in solutions containing low concentrations of phosphate. In contrast, the concentration of calcia removed from solution by "aged" apatite is negligible, irrespective of apatite dose, demonstrating that the apatite loses its "activity" upon storage.

**Example 7: reactivated apatite**

Figure 9 displays the results from a series of experiments which demonstrate that the calcia removal activity of old apatite can be regenerated by soaking apatite in solutions containing excess phosphate.

\( \text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O} \) was dissolved in portions of neat spent liquor and the solutions heated to a temperature of 90°C. Carbonate hydroxylapatite was added to the solutions in molar proportions such that the concentration of phosphate in solution was in a 100% stoichiometric excess with respect to the stoichiometry of the carbonate hydroxylapatite. The mixtures were reacted at temperature for 15 minutes before the apatite samples were separated from solution by filtration and washed.

Neat green liquor solutions containing 40 - 50 ppm phosphate (expressed as \( \text{P}_2\text{O}_5 \)) were heated to a temperature of 95°C. The "refreshed" carbonate hydroxylapatite samples were added to the solutions in doses of approximately 1 g apatite/L. The mixtures were mixed at temperature for 10 minutes.
Figure 9 compares the amount of calcia removed from solution by the "refreshed" apatite with that of 1 day old & freshly prepared apatite. The data shown in Figure 9 demonstrate that the activity of old apatite, with respect to calcia removal, can be regenerated by soaking the carbonate hydroxylapatite in solutions containing excess phosphate.

Examples 1 to 7 clearly evidence the efficacy of the method of the present invention in reducing calcia concentrations in Bayer process liquors.

Modifications and variations such as would be apparent to the skilled addressee are considered to fall within the scope of this invention.
We claim:

1. A method of reducing the calcia concentration of a green Bayer process liquor containing calcia and phosphate, the method comprising the step of:

   contacting the green Bayer process liquor with a quantity of apatite;

   thereby inducing the precipitation of further apatite and reducing the calcia concentration of the green Bayer process liquor.

2. A method according to claim 1, characterised in that the green Bayer process liquor containing calcia and phosphate is produced by the steps of:

   dissolving an alumina-containing ore in a caustic solution to provide a slurry of a red mud in a green liquor containing phosphate; then adding a quantity of calcia to the suspension of red mud in green liquor to produce a suspension of red mud in green liquor containing calcia and phosphate; then separating the red mud from the green liquor to produce the green Bayer process liquor containing calcia and phosphate.

3. A method according to claim 2 characterised in that the steps of separating the red mud from the green liquor and contacting the green Bayer process liquor containing calcia and phosphate with apatite may occur simultaneously.

4. A method according to claim 2 or 3 characterised in that the step of separating the red mud from the green liquor comprises the step of passing the suspension of red mud in green liquor through a filter, and the step of contacting the green liquor with a quantity of apatite occurs
immediately prior to the step of passing the suspension of red mud in green liquor through a filter.

5. A method according to any one of claims 2 to 4 characterised in that the step of separating the red mud from the green liquor comprises the steps of:

- passing the slurry of red mud and green liquor through one or more sand traps producing a second slurry of red mud and green liquor, the second slurry containing a lower proportion of red mud relative to green liquor;

- passing the second slurry through one or more thickeners, producing a thickener underflow of substantially red mud and a thickener overflow of substantially green liquor; and

- passing the thickener overflow through a filter;

wherein the step of adding a quantity of calcia to the suspension of red mud in green liquor occurs before the step of passing the thickener overflow through the filter.

6. A method according to any one of claims 2 to 5 characterised in that the calcia is added for the purpose of stabilising alumina, and the step of adding a quantity of calcia to the suspension of red mud in green liquor occurs after the step of passing the slurry of red mud and green liquor through one or more sand traps producing a second slurry of red mud and green liquor, the second slurry containing a lower proportion of red mud.

7. A method according to any one of claims 2 to 6 characterised in that the calcia is added for the purpose of stabilising alumina, and the step of adding a quantity of calcia to the suspension of red mud in green liquor occurs after passing the second slurry through one or more thickeners,
producing a thickener underflow of substantially red mud and a thickener overflow of substantially green liquor.

8. A method according to any one of claims 4 to 7 characterised in that the filter is a fixed-bed type filter, and the steps of contacting the green Bayer process liquor with a quantity of apatite and passing the thickener overflow through a filter comprises combining the thickener overflow with the quantity of apatite then passing the combination through a filter.

9. A method according to any one of claims 4 to 7 characterised in that the filter is a cake type filter.

10. A method according to claim 9 characterised in that the step of contacting the green liquor with a quantity of apatite comprises the step of:

   adding the quantity of apatite to the thickener overflow.

11. A method according to any one of claims 9 or 10 characterised in that the step of separating the red mud from the green liquor comprises the steps of:

   mixing the thickener overflow with a quantity of filter aid; and

   passing the thickener overflow through the filter.

12. A method according to claim 11 characterised in that prior to the step of mixing the thickener overflow with a quantity of filter aid, the method comprises the step of:

   mixing a quantity of apatite with the quantity of filter aid;

   such that the step of mixing the thickener overflow with a quantity of filter aid effects the step of contacting the green liquor with a quantity of apatite.
13. A method according to any one of claims 9 to 12 characterised in that the step of separating the red mud from the green liquor comprises the steps of:

mixing a quantity of apatite with the quantity of filter aid;

applying a layer of filter aid to the cake-type filter; then

passing the thickener overflow through the layer of filter aid and the filter.

such that the step of passing the thickener overflow through the layer of filter aid and the filter effects the step of contacting the green liquor with a quantity of apatite.

14. A method according to claim 2 characterised in that the step of separating the red mud from the green liquor comprises the steps of:

passing the slurry of red mud and green liquor through one or more sand traps producing a second slurry of red mud and green liquor, the second slurry containing a lower proportion of red mud relative to green liquor;

passing the second slurry through one or more thickeners, producing a thickener underflow of substantially red mud and a thickener overflow of substantially green liquor;

mixing a first quantity of apatite with a first quantity of filter aid to produce a first mixture;

applying a layer of the first mixture to a cake type filter;

mixing a second quantity of filter aid with a second quantity of apatite to produce a second mixture;
mixing the second mixture with the thickener overflow; then

passing the thickener overflow through the layer of the first mixture
and the cake type filter;

such that the steps of mixing the second mixture with the thickener
overflow and passing the thickener overflow through the layer of the first
mixture and the filter each effect the step of contacting the green liquor
with a quantity of apatite.

15. A method for the treatment of a Bayer process liquor, the method
comprising the steps of:

adding a source of phosphate to the Bayer process solution;

adding a causticising agent to the Bayer process solution; and

forming a calcium phosphate precipitate in the form of a quantity of
apatite;

thereby causticising the Bayer process solution; then

contacting the Bayer process liquor with at least a portion of the
quantity of apatite; and

thereby inducing the precipitation of further apatite and reducing the
calcia concentration of the Bayer process liquor.

16. A method according to any one of the preceding claims characterised in
that the apatite has the general formula \( \text{Ai}_0(\text{XO}_4)_6(\text{OH, F, Cl})_2 \cdot n\text{H}_2\text{O} \),
wherein: A may be selected from Ba, Ca, Ce, K, Na, Pb, Sr, Y; X may be
selected from As, P, Si, V, and CO\(_3\) can be substituted for PO\(_4\).

17. A method according to claim 16 characterised in that A is Ca and Na and
the apatite is provided at least predominantly in the form of a carbonate
hydroxylapatite having the general formula $\text{Ca}_{1-x}\text{Na}_{2\chi/3}(\text{PO}_4)_6\chi(\text{CO}_4)\chi(\text{OH})_{2-x\chi/3}\cdot\chi\text{H}_2\theta$, where $0 \leq \chi \leq 3$, or any mixture of such compounds.

18. A method according to claim 16 characterised in that the apatite is provided in the form of $\text{Ca}_7\text{Na}_2(\text{CO}_3)\chi(\text{PO}_4)\chi(\text{H}_2\text{O})\chi(\text{OH})$.

19. A method according to any one of the preceding claims characterised in that the apatite is prepared with a stoichiometric excess of phosphate.

20. A method according to any one of the preceding claims characterised in that the apatite is freshly precipitated.

21. A method according to any one of the preceding claims characterised in that the quantity of apatite is 20-25 grams per kL of Bayer process liquor.

22. A method according to any one of the preceding claims characterised in that the phosphate concentration of the Bayer process liquor is between about 50 and 400ppm.

23. A method according to any one of the preceding claims characterised in that the temperature of the Bayer process liquor is between about 70°C and 120°C.

24. A method according to claim 23 characterised in that the temperature of the Bayer process liquor is between about 100°C and 105°C.

25. A method according to any one of the preceding claims characterised in that the quantity of apatite comprises apatite having a high surface area to volume ratio.
Figure 3
Figure 4
Figure 5

Apatite Addition to Filter Aid

Ca(OH)₂ drop (mg/L)

Time On-line (h)
Figure 6
Figure 7
Ca Removal in Low P₂O₅ Liquor: Old vs Fresh Apatite

Figure 8
Figure 9

Old vs "Refreshed" Apatite

ΔCaO (ppm)

Old Apatite  "Refreshed" Apatite  "Refreshed" Apatite  Fresh Apatite  Fresh Apatite
INTERNATIONAL SEARCH REPORT

Internationa] application No
PCT/AU2007/000460

A CLASSIFICATION OF SUBJECT MATTER
Int Cl
COIF 7/04 (2006.01) COIF 7/06 (2006 01) COIF 7/46 (2006 01)
According to International Patent Classification (IPC) or to both national classification and IPC

B FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
apids, japo, caplus; Keywords, BAYER, ALUMINA, LIQUOR, ?APATIT?, ?PHOSPH'?

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Further documents are listed in the continuation of Box C

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* Special categories of cited documents
'P' document published prior to the international filing date but later than the priority date claimed
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'Y' document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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'&' document member of the same patent family

Date of the actual completion of the international search
03 May 2007

Date of mailing of the international search report
2 1 MAY 2007

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Telephone No (02) 6283 3130

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INTERNATIONAL-SEARCHREPORT

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Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

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