METHOD FOR CONTROLLING THE PRECIPITATION OF ALUMINA

A method for controlling the precipitation of alumina from a Bayer process solution, the method comprising the steps of: contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble; removing sodium ions from the Bayer process solution; reducing the concentration of hydroxide ions in the Bayer process solution; and precipitating alumina in the Bayer process solution.
Method for controlling the precipitation of alumina

Field of the Invention

The present invention relates to a method for controlling the precipitation of alumina from a Bayer process solution.

5 Background Art

The Bayer process is widely used for the production of alumina from alumina-containing ores such as bauxite. The process involves contacting alumina-containing ores with recycled caustic aluminate solutions at elevated temperatures in a process commonly referred to as digestion. Solids are removed from the resulting slurry and the solution cooled to induce a state of supersaturation.

Alumina is added to the solution as seed to induce precipitation of further aluminium hydroxide therefrom. The precipitated alumina is separated from the caustic aluminate solution (known as spent liquor), with a portion of alumina 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 precipitation reaction can be generally represented by the following chemical equation with reference to the precipitation of aluminium hydroxide. A similar equation may be prepared for the precipitation of aluminium oxyhydroxide:

\[ \text{Al(OH)}_4^- (aq) + \text{Na}^+ (aq) \rightarrow \text{Al(OH)}_3 (s) + \text{OH}^- (aq) + \text{Na}^+ (aq) \]

As the precipitation reaction proceeds, the A/TC ratio of the liquor falls from about 0.7 to about 0.4 (where A represents the alumina concentration, expressed as gL⁻¹ of Al₂O₃, and TC represents total caustic concentration ([NaOH] + [NaAl(OH)₄]), expressed as gL⁻¹ of sodium carbonate). At the lower value of A/TC, the rate of precipitation slows substantially due to a decrease in the level of
supersaturation, and an increase in the level of "free caustic" in the liquor, as the system approaches equilibrium.

It is known that the TC and TA (where TA represents total alkali concentration ([NaOH] + [NaAl(OH)₄] + [Na₂CO₃] ), expressed as g L⁻¹ of sodium carbonate) of Bayer process solutions affects the solubility of boehmite and gibbsite in those solutions in a number of ways.

Generally, more than half of the alumina stays dissolved in solution, to be recycled through the digestion circuit of the plant. In principle, if some of the hydroxide formed during precipitation could be removed, the A/TC ratio of the liquor would increase and the equilibrium of the above reaction would be shifted to the right favouring more precipitation of alumina. Further, it is believed that supersaturation could also be induced, and controlled, by reducing the level of caustic in Bayer liquor with the benefit of achieving an increase in yield beyond that which is attainable under current practices.

Liquor carbonation is a technique used in the alumina industry to convert hydroxide to carbonate, and has been used to increase the precipitation yield of alumina. However, apart from producing alumina of inferior quality compared to current practices, liquor carbonation necessitates the excessive purchase cost of lime which is required to regenerate caustic from sodium carbonate. Further, the recausticisation step is inefficient and does not result in complete regeneration of the caustic.

Based on alumina solubility alone, the removal of sodium ions in conjunction with the neutralisation of hydroxide should produce a greater increase in precipitation yield than hydroxide neutralisation by carbonation. This is because the former leads to a reduction in both TC and TA whereas the latter leads to a reduction in TC but TA remains constant (where TC and TA represent the total caustic concentration and the total alkali concentration respectively, both expressed as gL⁻¹ sodium carbonate). For a given value of TC, alumina is more soluble in solutions of higher TA.
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, or anywhere else, as at the priority date of the application.

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, which are intended for the purpose of exemplification only. Functionally equivalent products, compositions and methods are clearly within the scope of the invention as described herein.

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.

In accordance with the present invention, there is provided a method for controlling the precipitation of alumina from a Bayer process solution, the method comprising the steps of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution;
reducing the concentration of hydroxide ions in the Bayer process solution; and

precipitating alumina in the Bayer process solution.

As used herein the term "alumina" shall be taken to include, without limitation, any
form of aluminium hydroxide, aluminium oxyhydroxide or aluminium oxide.

The step of reducing the concentration of hydroxide ions in the Bayer process solution may include removing hydroxide ions from the Bayer process solution or neutralising hydroxide ions in the Bayer process solution.

It will be appreciated that the step of precipitating alumina in the Bayer process solution need not immediately follow the step of reducing the concentration of hydroxide ions in the Bayer process solution.

Alumina is more soluble in alkaline solutions than in water and advantageously, the reduction of sodium ion concentration in the Bayer process liquor can increase precipitation of alumina.

In one form of the invention, the solid support and the extractant are provided in the form of an ion exchange resin. Where the solid support is an ion exchange resin, the method preferably comprises the additional steps of:

exchanging the sodium ions present in the Bayer process liquor with an ion on the resin.

Where the ion on the ion exchange resin is a proton, the step of:

exchanging the sodium ions present in the Bayer process liquor with an ion on the resin,

advantageously reduces the concentration of hydroxide ions in the Bayer process solution.

Ion exchange resins are high molecular weight polymeric materials containing many ionic functional groups per molecule. Cation-exchange resins can be either
a strong-acid type containing sulfonic acids groups (RSθ3H⁺) or a weakly-acidic
type such as those containing carboxylic acid (RCOOH) or phenolic (ROH) groups.

Anion exchange resins contain basic amine functional groups attached to the
polymer molecule. Strong-base exchangers are quaternary amines
(RN(CH₃)₃⁺OH⁻) and weak-base types contain secondary or tertiary amines.

Preferably, the ion exchange resin is a cation exchange resin and in highly
preferred forms of the invention, the cation exchange resin is a weakly-acidic
cation exchange resin.

Preferably, the exchangeable ion on the solid support is a proton.

It will be appreciated that the exchange of a cation present in the Bayer process
solution with a proton on the extractant will encompass the exchange of more
than one cation and more than one proton.

Examples of resins that may be used in the present invention include the following
ion exchange resins all in their hydrogen form: Amberlite IRC-86, Amberlite IRC-
50, Lewatit CNP-105, Amberlite CG-50, Lewatit CNP-80, Lewatit CNP-80 WS,
Purolite C115KMR, Purolite C115E, Diaion WT01S, Dowex Mac-3, Duolite® CS-
100, RF Resin and SRL Resin.

Advantageously, the exchange of a cation present in the Bayer process solution
with a proton on the resin will be accompanied by a concomitant neutralisation of
hydroxide ions in the Bayer process solution according to the following equation
where RH represents the hydrogen form of the resin.

\[ \text{NaOH} + \text{RH} \rightarrow \text{R}^+\text{Na}^+ + \text{H}_2\text{O} \]

In a second form of the invention, the solid support and the extractant are
provided in the form of an ion aqueous biphasic extraction chromatography resin.
Examples of this type of resin are ABEC-2000 and ABEC-5000. Such resins
contain polyethylene glycol (PEG) chains tethered to a polymer backbone, such
as polystyrene divinylbenzene backbone. As the PEG chains are not endowed with ion-exchange capability, the expected extraction mechanism is by transfer of NaOH ion pairs into the resin. The high concentrations of sodium and hydroxide ions in the Bayer liquor drive the uptake of the ion pairs into the resin, making possible caustic recovery by elution with water by a simple mass-action reversal of the uptake. ABEC resins operate best at high ionic strengths with hydrophilic inorganic salts, such as NaOH, making Bayer liquor an appropriate medium for use with such resins.

The present invention offers distinct advantages over methods employing carbonation to reduce hydroxide concentrations in Bayer process solutions, as carbonation reduces TC without affecting TA, but the present invention reduces both the TC and TA of the Bayer process liquor. Further, the present invention increases the A/TC of the Bayer process liquor, thereby increasing the precipitation efficiency of alumina.

The present invention offers distinct advantages over methods employing solvent extraction to control the precipitation of alumina in Bayer liquors as the liquor does not need to be contacted with an organic solvent which could result in adverse reactions between constituents of organic phase and constituents of plant liquor as well as solvent loss to the aqueous phase.

The present invention offers distinct advantages over methods employing membrane electrolysis to control the precipitation of alumina in Bayer liquors as the invention does not require the use of external power to drive the ion exchange and does not require the use of expensive membranes with the potential for fouling.

Advantageously, the method of the present invention may be utilised to control the form of precipitated alumina and influence the formation of forms such as boehmite, gibbsite, bayerite, doyleite and nordstrandite. It will be appreciated that the alumina may be a mixture of any of the preceding forms.
Advantageously, by removing sodium and precipitating alumina, impurities in the Bayer process solution are concentrated which may make the solution more amenable to impurity removal techniques such as liquor chilling (to remove carbonate and sulfate as a double salt of sodium).

Preferably, the method comprises the further step of:

seeding the Bayer process liquor with alumina.

In one form of the invention, the step of:

seeding the Bayer process liquor with alumina,

is conducted prior to the step of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble.

In a second form of the invention, the step of:

seeding the Bayer process liquor with alumina,

is conducted after the step of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble.

It will be appreciated that the optimal seeding rate will depend on many factors, including the seed and liquor properties and the design of the precipitation circuit, and may be greater than 50 gL\(^{-1}\) and preferably, in the range of 50 to 1300 gL\(^{-1}\).

Preferably, the step of:

precipitating alumina in the Bayer process solution,
is conducted at temperatures up to the boiling point of the Bayer process solution at that pressure.

Advantageously, the present invention can negate the need to reduce the temperature of a Bayer process liquor to encourage supersaturation. It is known that precipitation rates decrease with temperature. In a gibbsite precipitation circuit, precipitation commences at about 90 °C and ends at about 60 °C at the completion of the precipitation phase. Without being limited by theory, it is believed that the method of the present invention may permit precipitation of alumina at temperatures as high as the boiling point of the liquor at that pressure.

The present invention may be utilised to increase precipitation yields beyond current limits without initially increasing TC in digestion. It may provide a means of inducing supersaturation without appreciable liquor cooling.

Without being limited by theory, it is believed that a sodium/aluminate ion pair exists on or near the surface of precipitated alumina and hinders further deposition of alumina onto the surface. Advantageously, removing sodium from the Bayer process solution may increase alumina precipitation.

Importantly, the present invention does not advocate a measurable reduction in solution pH. Bayer liquor pH is above measurable limits (>14) and it has been discovered that a significant increase in precipitation yield can be obtained by instigating a decrease in caustic concentration by the present invention, whereby liquor pH is still kept well above a value of 14.

Preferably, the steps of:

- contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;
- removing sodium ions from the Bayer process solution; and
reducing the concentration of hydroxide ions in the Bayer process solution;

are conducted at a temperature which is below that used to digest the bauxite.

Preferably, the step of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

comprises agitating the Bayer process solution and the solid support by any means known in the art including shaking, stirring, rolling and sparging.

It will be appreciated that the contact time between the Bayer process solution and the solid support should be sufficient for ion exchange or extraction to occur. Said contact time will be influenced by many factors including the pKa of the ionisable proton on the solid support, the pH of the aqueous phase, the volumes of the aqueous and solid phases, the temperature, the concentration of the sodium ions, the total alkalinity, the total caustic concentration, the extent of agitation and the presence of other species in the liquor.

It will be appreciated that the steps of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution; and

reducing the concentration of hydroxide ions in the Bayer process solution;

may be repeated.

Where the steps of:
contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution; and

reducing the concentration of hydroxide ions in the Bayer process solution;

are repeated, the step of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

may be performed with different solid supports.

Preferably, the method comprises the further step of:

separating the Bayer process solution and the solid support.

It should be appreciated that the step of separating the Bayer process solution and the solid support may be performed by any method known in the art including filtering and centrifugation.

Preferably, the method comprises the further steps of:

contacting the solid support with a stripping solution to regenerate the solid support after the step of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

The stripping solution may be provided in form of water or a Bayer process liquor including condensate or lake water or an acidic solution.
It will be appreciated that the pH of the stripping solution will be influenced by the type of resin employed. For example, carboxylic acid ion exchange resins may require a stripping solution of pH <3, whilst for a phenolic based ion exchange resin or an aqueous biphasic extraction chromatography resin, a stripping solution of pH 5 or higher should be sufficient.

It will be appreciated that the pKa of the ion exchange resin will influence the step of exchanging a metal cation present in the Bayer process solution with an ion on the solid support. Preferably, the ion exchange resin has a pKa of about 9-13.

Preferably, the weak-acid cation exchange resin comprises a phenolic group or a hydroxyl group attached to an aromatic ring.

Advantageously, the stripping solution, after contact with the substantially water-immiscible solution can be re-used in subsequent steps in the Bayer process or in subsequent stripping steps. Depending on the sodium hydroxide concentration, the aqueous solution may need to be pre-treated prior to subsequent use.

In one form of the invention, the steps of:

- contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;
- removing sodium ions from the Bayer process solution; and
- reducing the concentration of hydroxide ions in the Bayer process solution;

are performed in a Bayer process side stream.

In one form of the invention, where the Bayer process includes the steps:

- digestion of bauxite with caustic solution;
- liquid-solid separation to provide a residue and a Bayer liquor; and
precipitation of alumina from the Bayer liquor;

the steps of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution; and

reducing the concentration of hydroxide ions in the Bayer process solution;

are conducted prior to the step of:

precipitation of alumina from the Bayer liquor.

In a second form of the invention, where the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a Bayer liquor; and

precipitation of alumina from the Bayer liquor; and

the steps of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution; and

reducing the concentration of hydroxide ions in the Bayer process solution;

are conducted after the step of:
precipitation of alumina from the Bayer liquor.

Where the steps of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution; and

reducing the concentration of hydroxide ions in the Bayer process solution;

are conducted after the step of:

precipitation of alumina from the Bayer liquor,

the method may comprise the further step of:

precipitation of further alumina from the Bayer process liquor.

In a third form of the invention, where the Bayer process includes the steps:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a Bayer liquor; and

precipitation of alumina from the Bayer liquor;

the steps of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution; and
reducing the concentration of hydroxide ions in the Bayer process solution;

are preferably conducted during the step of:

precipitation of alumina from the Bayer liquor.

The method of the present invention may be performed as a batch process or a continuous process.

In accordance with the present invention, there is provided a method for controlling the precipitation of alumina from a Bayer process solution, the method comprising the steps of:

- digestion of bauxite with caustic solution;

- liquid-solid separation to provide a residue and a green liquor;

- precipitation of alumina from the green liquor to provide a spent liquor;

- contacting the spent liquor with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

- removing sodium ions from the spent liquor;

- reducing the concentration of hydroxide ions in the spent liquor; and

- precipitation of alumina from the spent liquor.

The bauxite may be provided in the form of gibbsitic bauxite, boehmitic bauxite, diasporic bauxite or any combination thereof.
Brief Description of the Drawings

The present invention will now be described, by way of example only, with reference to three embodiments thereof, and the accompanying drawings, in which:

5 Figure 1a is a schematic flow sheet of the Bayer circuit;

Figure 1b is a schematic flow sheet showing how a method in accordance with a first embodiment may be utilised in the Bayer circuit;

Figure 1c is a schematic flow sheet showing how a method in accordance with a second embodiment may be utilised in the Bayer circuit;

10 Figure 1d is a schematic flow sheet showing how a method in accordance with a third embodiment may be utilised in the Bayer circuit;

Figure 2 is a graph showing TC extraction from Bayer liquor using varying amounts of carboxylic acid ion exchange resins;

Figure 3 is a graph showing the drop in pH of an alkaline solution when contacted with varying amounts of different types of ion exchange resins; and

15 Figure 4 is a graph showing the amount of sodium in the aqueous phase of a caustic solution in equilibrium with varying amounts of different types of ion exchange resins.

Best Mode(s) for Carrying Out the Invention

20 The invention focuses on the control of alumina precipitation in the Bayer process by exchange of sodium ions in a Bayer process solution with ions on a solid support. By careful manipulation of the exchange conditions, the precipitation of alumina from aluminate solutions may be controlled.
Figure 1a shows a schematic flow sheet of the Bayer process circuit for a refinery using a single digestion circuit comprising the steps of:

- digestion 12 of bauxite 14 in a caustic solution;
- liquid-solid separation 16 of the mixture to residue 18 and liquor 20;
- alumina precipitation 22 from the liquor 20;
- separation of alumina 22 and liquor 24; and
- recycling liquor 24 to digestion 12.

In accordance with a first embodiment of the present invention and best seen in Figure 1b, the liquor 24 is contacted with an ion exchange resin in an ion exchange apparatus 26. The liquor 28 and the ion exchange resin are separated by filtration and the liquor 28 seeded to induce alumina precipitation 32.

The ion exchange resin is contacted with an aqueous solution to protonate the ion exchange resin. The protonation increases the causticity of the aqueous solution which may then be used, after concentration, in the causticisation of further bauxite or in other places in the circuit as appropriate such as, for example, as a pre-treatment step in the washing of bauxite before digestion to remove impurities or in the washing of seed or oxalate. The ion exchange resin may then be reused in further exchange steps.

In accordance with a second embodiment of the present invention and best seen in Figure 1c, the liquor 20 is contacted with an ion exchange resin in an ion exchange apparatus 26. The liquor 28 and the ion exchange resin are separated by filtration and the liquor 28 seeded to induce alumina precipitation 32.

The ion exchange resin is contacted with an aqueous solution to protonate the ion exchange resin. The protonation increases the causticity of the aqueous solution which may then be used, after concentration, in the causticisation of further bauxite or in other places in the circuit as appropriate such as, for example, as a
pre-treatment step in the washing of bauxite before digestion to remove impurities or in the washing of seed or oxalate. The ion exchange resin may then be re-used in further exchange steps.

In accordance with a third embodiment of the present invention and best seen in Figure 1d, the liquor 20 is seeded and contacted with an ion exchange resin in an ion exchange apparatus 26. The precipitated alumina 27 and ion exchange resin are separated from the liquor and the liquor may be recycled to digestion.

The ion exchange resin is contacted with an aqueous solution to protonate the ion exchange resin. The protonation increases the causticity of the aqueous solution which may then be used, after concentration, in the causticisation of further bauxite or in other places in the circuit as appropriate such as, for example, as a pre-treatment step in the washing of bauxite before digestion to remove impurities or in the washing of seed or oxalate. The ion exchange resin may then be re-used in further exchange steps.

The following Examples serve to more fully describe the manner of using the above-described invention, as well as to set forth the best modes contemplated for carrying out various aspects of the invention. It is understood that these Examples in no way serve to limit the true scope of this invention, but rather are presented for illustrative purposes.

The liquor used in the experiments was Bayer spent liquor from the Applicant's refinery at Kwinana, Western Australia.

Gibbsite was used as seed for all experiments involving precipitation and, unless stated otherwise, the seed loading was at 100 g per litre of solution. Experimental conditions and solution compositions were intended to replicate those conditions and compositions present at the backend of the alumina precipitation circuit of refineries.

The following carboxylic acid resins, all in the H\(^+\) form, were tested:
Amberlite CG-50 obtained from Fluka

Amberlite IRC-50 CP manufactured by Mallinckrodt

Amberlite IRC-86 obtained from Fluka

Lewatit CNP-105 obtained from Fluka

Lewatit CNP-80 obtained from Fluka

Lewatit CNP-80 WS manufactured by ClearTech Industries

Purolite C115KMR manufactured by Purolite SRL

Purolite C115E manufactured by Purolite

Diaion WT01S manufactured by Supelco

Dowex Mac-3 obtained from Sigma Aldrich

The following phenolic resin was tested:

 Duolite® CS-100

The following resorcinol-formaldehyde resins were tested:

 RF Resin manufactured by Boulder Scientific

SRL Resin manufactured by Savannah River Company

The following polyethylene glycol resins were tested:

 ABEC-2000 manufactured by Eichrom Industries Inc.

 ABEC-5000 manufactured by Eichrom Industries Inc.
The following polystyrene resin was tested:

*Rink acid resin obtained from Sigma Aldrich*

The resins were water conditioned prior to use by immersing in distilled water overnight, filtered in a standard manner using funnels and dried in air to constant weight before transfer to sealed containers.

For comparative purposes, soda extraction results are presented as per dry weight of resin. Resin dry weights were calculated by accurately weighing an amount of resin (0.2-4 g), drying in an oven at 120 °C for 1 hr (to constant weight) following by cooling in a desiccator and reweighing.

10 **Part A: Soda extraction from Bayer process spent liquor with carboxylic acid resins**

Spent liquor from the applicant's refinery in Kwinana, Western Australia was vacuum filtered through a Pall A/B glass filter paper and heated to 60 °C in a rotating water bath. The conditioned resins were weighed into 30 ml or 100 ml plastic vials at quantities equivalent to preconditioned charges of 50, 100, 200 and 300 g/L.

A quantity of heated spent liquor (20 ml) was delivered into each plastic vial. The vials were sealed and agitated by vigorous shaking and inverting for 30 s before being placed in a rotating water bath for 15 min. Preliminary work indicated that a contact time of 15 min was sufficient to attain soda extraction equilibrium between the liquor and resins.

Following reaction, the vials were removed from the water bath and the mixtures vacuum filtered through a Whatman Grade No. 1 filter paper. The filtrates were subsampled and passed through a Pall 5µm membrane acrodisc. The filtrates, including a subsample of the stock spent liquor, were stabilised with sodium gluconate (2 drops/10mL) to prevent alumina precipitation and analysed for alumina content (A), total caustic (TC) and total alkali (TA) using the applicant's
proprietary method (ALIAN). The analytical data for the series of experiments are presented in Table 1.

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<th>Resin Name</th>
<th>Resin Charge (g/L)</th>
<th>TC</th>
<th>TA</th>
<th>Al₂O₃</th>
<th>A/TC</th>
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<td>218.77</td>
<td>93.36</td>
<td>0.5249</td>
<td>0.8130</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>141.88</td>
<td>180.49</td>
<td>87.69</td>
<td>0.6189</td>
<td>0.7850</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>113.84</td>
<td>150.87</td>
<td>81.90</td>
<td>0.7194</td>
<td>0.7546</td>
</tr>
<tr>
<td>Lewatit CNP 80 WS</td>
<td>50</td>
<td>198.20</td>
<td>237.28</td>
<td>89.82</td>
<td>0.4578</td>
<td>0.8269</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>161.04</td>
<td>219.64</td>
<td>84.50</td>
<td>0.4667</td>
<td>0.8235</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>154.56</td>
<td>188.31</td>
<td>74.73</td>
<td>0.4834</td>
<td>0.8209</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>133.64</td>
<td>162.90</td>
<td>66.79</td>
<td>0.4986</td>
<td>0.8204</td>
</tr>
<tr>
<td>Purolite C115K MR</td>
<td>50</td>
<td>200.68</td>
<td>243.26</td>
<td>96.35</td>
<td>0.4901</td>
<td>0.8250</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>185.22</td>
<td>226.62</td>
<td>95.34</td>
<td>0.5147</td>
<td>0.8166</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>152.20</td>
<td>192.64</td>
<td>91.92</td>
<td>0.6039</td>
<td>0.7901</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>123.50</td>
<td>163.21</td>
<td>87.82</td>
<td>0.7111</td>
<td>0.7567</td>
</tr>
<tr>
<td>Purolite C115E</td>
<td>50</td>
<td>193.07</td>
<td>234.09</td>
<td>92.89</td>
<td>0.4811</td>
<td>0.8248</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>176.76</td>
<td>218.89</td>
<td>91.55</td>
<td>0.5179</td>
<td>0.8150</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>143.72</td>
<td>182.18</td>
<td>86.93</td>
<td>0.6049</td>
<td>0.7899</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>114.92</td>
<td>150.93</td>
<td>81.37</td>
<td>0.7081</td>
<td>0.7614</td>
</tr>
<tr>
<td>Dialon WT01S</td>
<td>50</td>
<td>201.77</td>
<td>246.22</td>
<td>97.74</td>
<td>0.4844</td>
<td>0.6196</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>184.12</td>
<td>228.10</td>
<td>96.50</td>
<td>0.5241</td>
<td>0.8072</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>155.43</td>
<td>198.93</td>
<td>96.16</td>
<td>0.6187</td>
<td>0.7813</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>127.45</td>
<td>170.25</td>
<td>93.43</td>
<td>0.7331</td>
<td>0.7486</td>
</tr>
</tbody>
</table>

Table 1. Solution analyses after Bayer spent liquor contact with varying amounts carboxylic acid resins.

The data in Table 1 clearly shows that all of the resins tested are capable of extracting soda from the Bayer liquor with concomitant neutralization of hydroxide via ion exchange. The extraction and neutralization results in a decrease in both the TC and TA of the liquor and leads to a substantial amount of supersaturation.
with respect to alumina solubility as evidenced by the increase in A/TC ratio. The A/TC ratio of the liquor is independent of volume change and gives a true representation of alumina supersaturation. It has been demonstrated that, from an initial spent liquor A/TC ratio of 0.45, it is possible to extract soda and reach an A/TC ratio as high as 0.80 depending on the type and quantities of resins used. Multiple contacts with resins could be used to increase A/TC ratios further.

To enable a direct comparison of the efficacy of the resins to extract soda from Bayer liquor, a number of factors should be taken into account. Firstly, the conditioned resin weights used need to be converted to dry weights. The procedure for determining resin dry weights is detailed in the preceding section and the results are presented in Table 2.

<table>
<thead>
<tr>
<th>Resin Type</th>
<th>Mass of cond. Resin (g)</th>
<th>Mass of Dry Resin (g)</th>
<th>Moisture content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amberlite CG-50</td>
<td>3.7615</td>
<td>1.2182</td>
<td>67.6</td>
</tr>
<tr>
<td>Amberlite IRC-86</td>
<td>4.0279</td>
<td>1.9321</td>
<td>52.0</td>
</tr>
<tr>
<td>Lewatit CNP-105</td>
<td>3.8812</td>
<td>1.1625</td>
<td>70.0</td>
</tr>
<tr>
<td>Lewatit CNP-80</td>
<td>3.9392</td>
<td>1.6688</td>
<td>57.1</td>
</tr>
<tr>
<td>Lewatit CNP-80 WS</td>
<td>3.9390</td>
<td>1.7398</td>
<td>55.8</td>
</tr>
<tr>
<td>Purolite C115K MR</td>
<td>4.2184</td>
<td>2.1488</td>
<td>49.1</td>
</tr>
<tr>
<td>Purolite C115E</td>
<td>3.8747</td>
<td>1.7780</td>
<td>54.1</td>
</tr>
<tr>
<td>Diaion WTOIS</td>
<td>3.9840</td>
<td>1.6679</td>
<td>58.1</td>
</tr>
<tr>
<td>Dowex MAC-3</td>
<td>4.0544</td>
<td>2.2173</td>
<td>45.3</td>
</tr>
</tbody>
</table>

Table 2. Moisture content of conditioned resins.

Secondly, when the resins are conditioned, additional water is retained on the surface of the resin particles some of which transfers to the liquor when the liquor is contacted with the resins. The net effect is an increase in the volume of liquor and dilution of the dissolved species. Hence, the TC values obtained from the analyses need to be adjusted for this occurrence (this does not affect the A/TC ratios obtained because they are independent of volume). A direct measure of the dilution effect is obtained by the change in concentration of sodium carbonate in the liquor before and after treatment with the resins. The overall amount of sodium carbonate in the liquor should not change and is given by TA minus TC. The percentage change in liquor volume is thus given by the expression:

\[
\% \text{Liquor volume (based on Na}_2\text{CO}_3\text{)} = \frac{\text{Initial TA} - \text{Initial TC}}{\text{Final TA} - \text{Final TC}} \times 100
\]
Based on the above calculations, a graph showing the extraction of TC from spent liquor as a function of dry resin charge, with volume corrections included, is given in Figure 2. The resin performance effectiveness in terms of soda extraction is as follows:

5 Dowex Mac-3 > Amberlite IRC-86 > Purolite C115E > Lewatit CNP-80 > Lewatit CNP-80 WS > Diaion WT01S > Amberlite CG-50 > Lewatit CNP-105 > Purolite C115K MR.

**Part B: Increased alumina precipitation yield from resin contacted spent Bayer liquor**

10 A sufficient volume of spent liquor was filtered (sub-sample analysed by ALIAN to have an initial TC of 208.4 gL⁻¹) and pre-heated to 60 °C in a water bath. Duplicate volumes of spent liquor (250 mL) were added to 250 mL plastic bottles and conditioned resins Amberlite IRC-50, Amberlite IRC-86 and Lewatit CNP-105 (45 g initial weight) added separately to each bottle. The bottles were shaken vigorously (1 min) and rolled in a water bath for 4 hr at 60 °C. The resins were separated from the liquors using filtration and the liquors analysed. The final liquor TC after contact with each resin was 137.2 gL⁻¹ (Amberlite IRC-50), 140.6 gL⁻¹ (Amberlite IRC-86) and 165.0 gL⁻¹ (Lewatit CNP-105). These results show that the resins can extract sodium ions from Bayer liquor, with the concomitant transfer of a proton to the liquor, leading to a drop in solution TC and an increase in the level of super saturation with respect to soluble alumina.

The contacted liquors (150 mL) were transferred to 250 mL plastic bottles and allowed to equilibrate in a rotating water bath at 70 °C. Gibbssite seed ( > 43 μm) was added at a loading of 100 gL⁻¹ and precipitation allowed to occur for 24 hr. A duplicate control was performed by seeding spent liquor (not contacted with resin) (150 mL) with 15 g of hydrate (15 g). The precipitated hydrate was collected on a Büchner funnel, washed with hot DI water and dried at 60 °C (oven) for 24 hr.
The aqueous filtrate was stabilised by the addition of sodium gluconate to prevent gibbsite precipitation from solution upon liquor cooling to room temperature and analysed for TC and alumina content by ALIAN.

The hydrate yields were determined by subtracting the mass of seed added from the mass of recovered solid after precipitation.

The hydrate yields for liquor treated with Amberlite IRC 50, Amberlite IRC 86 and Lewatit CNP 105 were 63.7 gL⁻¹, 63.1 gL⁻¹ and 27.1 gL⁻¹ respectively compared to the control (untreated spent liquor) which gave a yield of 4.8 gL⁻¹ (see Table 3). All solid samples from the precipitation experiments were analysed by XRD and found to consist of gibbsite only.

<table>
<thead>
<tr>
<th>Description</th>
<th>TC</th>
<th>TA</th>
<th>Al₂O₃</th>
<th>A/TC</th>
<th>TC/TA</th>
<th>Precipitation yield of hydrate (from 160 mL)</th>
<th>Hydrate yield (g/L)</th>
<th>Actual Al₂O₃ yield (g/L)</th>
<th>Theoretical yield (g/L)¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial spent liquor</td>
<td>208.43</td>
<td>259.88</td>
<td>89.44</td>
<td>0.4291</td>
<td>0.8308</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spl no resin contact</td>
<td>209.14</td>
<td>252.00</td>
<td>89.96</td>
<td>0.4362</td>
<td>0.8299</td>
<td></td>
<td>0.8</td>
<td>4.8</td>
<td>3.1</td>
</tr>
<tr>
<td>Amb IRC50 After pptn</td>
<td>213.90</td>
<td>258.55</td>
<td>88.03</td>
<td>0.4127</td>
<td>0.8250</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amb IRC86 After pptn</td>
<td>137.25</td>
<td>179.15</td>
<td>87.00</td>
<td>0.6359</td>
<td>0.7661</td>
<td></td>
<td>10.2</td>
<td>63.7</td>
<td>41.6</td>
</tr>
<tr>
<td>Lewat CNP 105 After pptn</td>
<td>146.09</td>
<td>192.31</td>
<td>51.12</td>
<td>0.3499</td>
<td>0.7597</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>140.61</td>
<td>182.80</td>
<td>88.72</td>
<td>0.6310</td>
<td>0.7692</td>
<td></td>
<td>10.1</td>
<td>63.1</td>
<td>41.2</td>
</tr>
<tr>
<td></td>
<td>149.44</td>
<td>195.98</td>
<td>52.89</td>
<td>0.3539</td>
<td>0.7625</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>165.00</td>
<td>203.16</td>
<td>82.71</td>
<td>0.5613</td>
<td>0.8122</td>
<td></td>
<td>4.3</td>
<td>27.1</td>
<td>17.7</td>
</tr>
<tr>
<td></td>
<td>172.00</td>
<td>213.66</td>
<td>67.59</td>
<td>0.3930</td>
<td>0.8050</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

¹based on change in A/TC

Table 3. Summary of results for soda extraction from LXP using resins and precipitation experiments.

For each of the experiments, the theoretical alumina yield was calculated based on the change in liquor A/TC before and after precipitation. The values which are in close agreement with actual yields obtained are also given in Table 3.

The results clearly show that ion exchange resins can be used to extract soda from spent refinery liquor. The extraction of soda with the concomitant neutralisation of hydroxide leads to an increase in supersaturation of the liquor with respect to alumina solubility. Seeded precipitation experiments on the treated liquor have clearly shown that it is possible to obtain large increases in alumina yields, of the order of ~ 40 g/L, compared to control experiments with untreated spent liquor.
Part C: Soda extraction from Bayer process spent liquor with resorcinol, phenolic and polyethylene glycol grafted resins.

Two resorcinol-formaldehyde (RF Resin and SRL Resin), one phenolic (Duolite® CS-100) and two polyethylene glycol grafted (ABEC 2000 and ABEC 5000) resins were tested to determine their ability to extract soda from caustic solutions. For comparative purposes, the two carboxylic acid resins Amberlite CG-50 and Amberlite IRC-50 were tested alongside.

Prior to testing, the resins were washed with 0.1 M HCl, collected by filtration and rinsed with de-ionized water until the runoff was neutral in pH. They were soaked overnight in de-ionized water, collected by filtration again and air dried before being sealed in containers.

The moisture content of the conditioned resins was determined as previously described and is given in Table 4.

Soda extraction data are presented on a resin dry weight basis.

<table>
<thead>
<tr>
<th>Resin Name</th>
<th>Wet Weight (g)</th>
<th>Dry Weight (g)</th>
<th>Moisture Content</th>
<th>Dry Wt. Conversion Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>LJRL Resin</td>
<td>203.41</td>
<td>57.72</td>
<td>71.24%</td>
<td>3.524</td>
</tr>
<tr>
<td>Cs Ion Exchange (RF)</td>
<td>211.31</td>
<td>38.96</td>
<td>81.56%</td>
<td>5.424</td>
</tr>
<tr>
<td>Amberlite CG-50(IIJ)</td>
<td>209.21</td>
<td>64.72</td>
<td>69.06%</td>
<td>3.232</td>
</tr>
<tr>
<td>Amberlite IRC-50 CP</td>
<td>209.33</td>
<td>104.29</td>
<td>50.18%</td>
<td>2.007</td>
</tr>
<tr>
<td>Duolite® CS-100</td>
<td>205.63</td>
<td>158.78</td>
<td>22.78%</td>
<td>1.295</td>
</tr>
<tr>
<td>Rink acid resin</td>
<td>203.86</td>
<td>164.86</td>
<td>19.13%</td>
<td>1.237</td>
</tr>
<tr>
<td>ABEC-2000</td>
<td>204.18</td>
<td>140.37</td>
<td>31.25%</td>
<td>1.455</td>
</tr>
<tr>
<td>ABEC-5000</td>
<td>201.21</td>
<td>62.93</td>
<td>68.72%</td>
<td>3.397</td>
</tr>
</tbody>
</table>

Table 4. Moisture content of conditioned resins.

Equivalent dry weights of each of the resins were contacted and equilibrated with two milliliters of 0.4 M NaOH (0.368 M as determined by ICP-OES) in 12 x 75 mm VWR plastic tubes fitted with plug closures. The resins and hydroxide solution were intimately contacted and brought to equilibrium by tumbling the tubes end-over-end at ~20 rpm in a 25.2 °C air box using Glass-Col rugged rotators for 15 hr.
Following equilibration, the tubes were centrifuged at 1450 rpm at 25 °C for 6 min in a Beckman Coulter Allegra 6KR centrifuge to isolate the aqueous phase from the resin beds in order to measure the pH and the sodium concentration of the aqueous phase. Due to differences in resin bed sizes and their compressibility upon centrifugation, varying amounts of aqueous phase (that accessible to careful pipette transfer) were passed through 0.45 µm filters and placed in clean 12 x 75 mm plastic tubes for measuring pH. Duplicate samples destined for ICP-OES analyses were treated similarly. The pH measurements were carried out using an Orion model 230A pH meter fitted with an Orion 8103 Ross combination electrode using standard procedures. The results are presented in Figures 3 and 4.

Figure 3 shows the decrease in solution pH upon contact with varying amounts of each resin (presented as dry weight of resin). Notably, and as expected, the two carboxylic acid resins, Amberlite IRC-50 CP and Amberlite CG-50, show the largest fall in solution pH per equivalent dry weight contact. However, there is also a significant fall in solution pH when Duolite® CS-100, SRL Resin and RF (labeled as Cs ion ex in the graph) Resin are used indicating that these resins are also capable of extracting soda from caustic solutions via ion exchange. The two ABEC resins showed little response, although they are expected to perform better under conditions of high caustic strength such as those found in Bayer liquor.

Figure 4 shows the amount of sodium left in equilibrium in the aqueous phase with varying dry weight amounts of each of the resins. This data supports the pH data of Figure 3 in that the phenolic and resorcinol-formaldehyde resins are capable of extracting a substantial amount of sodium from the aqueous phase of a caustic solution via ion exchange with a proton on the resin. They could be used to extract soda from spent Bayer liquor leading to increased supersaturation of the liquor with respect to alumina solubility. Importantly, these three resins would have a greater affinity for stripping with water, due to their expected higher pK_a values in comparison with carboxylic acid resins, to regenerate caustic for recycle if used in this manner.

**Part D: Stripping of soda from a resorcinol-formaldehyde resin after contact with Bayer liquor**
A resorcinol-formaldehyde resin, RF Resin manufactured by Boulder Scientific, was tested.

A previously washed portion (washing procedure described in previous section) of wet RF resin (~1 mL in quantity) was loaded onto a miniature plastic column. Spent Bayer liquor (1 mL), at a temperature of 70 °C, from the applicant's Kwinana refinery was poured into the column to completely cover the resin. After a reaction time of 1 hr at 70 °C, the Bayer liquor was removed by suction through the column.

The resin was rinsed with 1 mL of de-ionized water, to remove traces of residual Bayer liquor and successively eluted with nine 1 mL aliquots of de-ionized water. The 1 mL aliquots were combined in 3 mL batches in successive order of elution for Na analysis and found to contain 2.6 meq (0.86 M), 0.28 meq (0.095 M), 0.073 meq (0.024 M) of Na (1 meq equates to one mmole of Na) respectively. The combined fractions had a total of 2.95 meq of NaOH.

Finally, the resin was eluted with ten 1 mL aliquots of 0.1 N HCl to remove all remaining Na from the resin. The aliquots were combined in two 5 mL fractions, in order of elution, for analysis. The first 5 mL fraction contained 0.24 meq (0.047 M) and the second 5 mL fraction contained 0.091 meq (0.018 M) of Na. The combined acid fractions had a total of 0.33 meq of NaOH.

The results show that greater than 90 % of the soda can be extracted back from the resin, as caustic, by elution with water only. Potentially, using multiple contacts, it is possible to recover caustic from the resin suitable for recyle back into the Bayer process by contact with refinery condensate or lake water.

Modifications and variations such as would be apparent to a skilled addressee are deemed to be within the scope of the present invention.
The Claims Defining the Invention are as Follows:

1. A method for controlling the precipitation of alumina from a Bayer process solution, the method comprising the steps of:

   contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

   removing sodium ions from the Bayer process solution;

   reducing the concentration of hydroxide ions in the Bayer process solution; and

   precipitating alumina in the Bayer process solution.

2. A method for controlling the precipitation of alumina according to claim 1, wherein the solid support and the extractant is provided in the form of an ion exchange resin.

3. A method for controlling the precipitation of alumina according to claim 1 or claim 2, wherein the ion exchange resin is a cation exchange resin.

4. A method for controlling the precipitation of alumina according to claim 1 or claim 2, wherein the cation exchange resin is a weakly acidic cation exchange resin.

5. A method for controlling the precipitation of alumina according to any one of claims 2 to 4, wherein the ion exchange resin has a pKa of about 9-13.

6. A method for controlling the precipitation of alumina according to claim 1, wherein the solid support and the extractant is provided in the form of an aqueous biphasic extraction chromatography resin.
7. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein the method comprises the further step of:

seeding the Bayer process liquor with alumina.

8. A method for controlling the precipitation of alumina according to claim 7, wherein the step of:

seeding the Bayer process liquor with alumina

is conducted prior to the step of:

contacting the Bayer process solution with the solid support.

9. A method for controlling the precipitation of alumina according to claim 7, wherein the step of:

seeding the Bayer process liquor with alumina

is conducted after the steps of:

removing sodium ions from the Bayer process solution; and

reducing the concentration of hydroxide ions in the Bayer process solution.

10. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein the step of:

precipitating alumina in the Bayer process solution,

is conducted at temperatures up to the boiling point of the Bayer process solution at that pressure.
11. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein the steps of:

- contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

- removing sodium ions from the Bayer process solution; and

- reducing the concentration of hydroxide ions in the Bayer process solution;

are conducted at a temperature which is below that used to digest the bauxite.

12. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein the step of:

- contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

comprises agitating the Bayer process solution and the solid support by any means known in the art including shaking, stirring, rolling and sparging.

13. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein the method comprises the further step of:

- separating the Bayer process solution and the solid support.

14. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein, the method comprises the further steps of:
contacting the solid support with a stripping solution to regenerate the solid support after the step of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble.

15. A method for controlling the precipitation of alumina according to claim 14, wherein the stripping solution is provided in form of water or a Bayer process liquor including condensate or lake water or an acidic solution.

16. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein the method comprises the steps of:

digestion of bauxite with caustic solution;

liquid-solid separation to provide a residue and a Bayer liquor; and

precipitation of alumina from the Bayer liquor;

and wherein the steps of:

contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

removing sodium ions from the Bayer process solution; and

reducing the concentration of hydroxide ions in the Bayer process solution;

are conducted prior to the step of:
17. A method for controlling the precipitation of alumina according to any one of claims 1 to 15, wherein the method comprises the steps of:

- digestion of bauxite with caustic solution;

- liquid-solid separation to provide a residue and a Bayer liquor; and

- precipitation of alumina from the Bayer liquor; and

and wherein the steps of:

- contacting the Bayer process solution with a solid support comprising an extractant, wherein the solid support is substantially water insoluble;

- removing sodium ions from the Bayer process solution; and

- reducing the concentration of hydroxide ions in the Bayer process solution;

are conducted after the step of:

- precipitation of alumina from the Bayer liquor.

18. A method for controlling the precipitation of alumina according to claim 17, wherein the method comprises the further step of:

- precipitation of further alumina from the Bayer process liquor.

19. A method for controlling the precipitation of alumina according to any one of the preceding claims, wherein the method is performed as a batch process or a continuous process.

20. A method for controlling the precipitation of alumina substantially as hereinbefore described with reference to the Examples.
A method for controlling the precipitation of alumina substantially as hereinbefore described with reference to the Figures.
INTERNATIONAL SEARCH REPORT

PCT/AU2008/001025

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

COI 7/02 (2006.01)  COI 7/47 (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)

WPIDS, CAPLUS, JAPIO, EPDOC, TXTE; Keywords: Bayer, alumin, ion exchange, exchange resin, chromatograph, precipitat, sodium, hydroxide, C01F007/IC, remov, extract

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>WO 1994/002417 A2 (DAVY MCKEE (STOCKTON) LIMITED) 3 February 1994 Page 4, paragraph 3-page 11, paragraph 3</td>
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* Special categories of cited documents:

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Date of the actual completion of the international search: 11 August 2008

Date of mailing of the international search report: 1 AUG 2008

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## DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>CA 1108319 A (GIULINI CHEMIE GMBH) 1 September 1981 Claims</td>
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This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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JP 57149805 NONE
CA 1108319 NONE

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

END OF ANNEX