Title: METHOD OF CATALYTIC WET OXIDATION OF ORGANIC CONTAMINANTS OF ALKALINE SOLUTIONS

Abstract: A method for the catalytic wet oxidation of organic contaminants of an alkaline solution, the method including the step of exposing the alkaline solution to an oxidising agent and a catalyst, under conditions suitable for the catalytic wet oxidation of organic contaminants, the method characterised in that the alkaline solution is exposed to the oxidising agent and the catalyst while the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) is at least approximately 4.
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 Catalytic Wet Oxidation of Organic Contaminants of Alkaline Solutions"

Field of the Invention

5 The present invention relates to a method of catalytic wet oxidation of organic contaminants of alkaline solutions.

Background Art

The application of the present invention will be discussed in the context of the catalytic wet oxidation of organic contaminants of Bayer process solutions, although the scope of the invention encompasses the catalytic wet oxidation of organic contaminants of any alkaline solution. The Bayer process is widely used for the production of alumina from aluminium 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. In some cases, a significant amount of organic material accompanies the bauxite, a portion of which is responsible for the presence of a range of organic compounds in the resulting solution.

After cooling the solution, aluminium hydroxide is added as seed to induce the precipitation of further aluminium hydroxide therefrom. 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 presence of organic contaminants in Bayer process solutions reduces productivity largely through two effects. Firstly, organic contaminants reduce the amount of soda available to dissolve gibbsite and form sodium aluminate in solution. Secondly, the presence of organic contaminants reduces the hydrate precipitation rate, due to crystallization poisoning. Other benefits associated with
removal of organic contaminants from Bayer process solutions include a reduction in the amount of soda in the alumina product, reduced liquor viscosity and improved hydrate agglomeration. Subsidiary disadvantages associated with organic contaminants of Bayer process solutions include reduced boiling point, foaming, liquor and hydrate absorbance and liquor density.

One method of reducing the levels of organic contaminants in alkaline solutions is to oxidise the contaminants. Depending on the degree of oxidation achieved, complex organic compounds may be oxidised to simpler compounds and, in turn, to carbon dioxide. One technique for oxidizing organic contaminants is catalytic wet oxidation, where the alkaline solution is exposed to an oxidizing agent and a catalyst, typically under conditions of elevated temperature and pressure.

For example, again in the context of Bayer process solutions, US patent 4,215,094, July 29, 1980, “Method for the removal of organic substances from alkali metal aluminate solution”, Inao et al., Sumitomo Aluminium Smelting Company Ltd, describes a process whereby liquor is contacted with an oxygen-containing gas under elevated pressure in the presence of copper ions. Sodium sulfide is added to form an insoluble copper sulfide precipitate. The precipitate is filtered and reused as the copper ion source in the wet oxidation step. Incomplete organics destruction is targeted, leaving some solid phase oxalate present to act as a filter aid for the copper sulfide precipitate.

Further, US patent 4,668,486, May 26, 1987, “Method for removing organic substances from caustic aluminate liquors”, Brown et al., Vereinigte Aluminium-Werke Atkiengesellschaft, describes a process whereby liquor is contacted with an oxygen-containing gas under elevated pressure in the presence of copper ions. The copper ions are co-precipitated with boehmite/bayerite. The crystalline co-precipitate (Cu/boehmite or Cu/bayerite) is filtered and recycled, thereby acting as a carrier for the copper catalyst.

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 of the application.

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 "solution" or variations such as "solutions", will be understood to encompass slurries, suspensions and other mixtures containing undissolved solids.

10 Disclosure of the Invention

In accordance with the present invention, there is provided a method for the catalytic wet oxidation of organic contaminants of an alkaline solution, the method including the step of:

exposing the alkaline solution to an oxidising agent and a catalyst, under conditions suitable for the catalytic wet oxidation of organic contaminants, while the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) is at least approximately 4.

Conditions suitable for the catalytic wet oxidation of organic contaminants are known to those skilled in the art and typically involve exposing the solution containing the organic contaminants to the oxidising agent and the catalyst at elevated temperatures and/or pressures. Specific examples of the catalytic wet oxidation of alkaline solutions are provided in the preceding discussion of the Background Art. More generally, Brown, N., "Kinetics of copper catalysed oxidation of Bayer liquor organics", Light Metals (1989), pp. 121-130, provides an overview of the effects of temperature, catalyst concentration, oxygen charge and
level of agitation on the degree of destruction of organic contaminants, and the contents of such are incorporated herein by reference.

It has been discovered that the ratio of the concentration of free caustic to the concentration of organic contaminants in an alkaline solution is a highly significant factor in determining the extent of oxidation of organic contaminants attainable by wet oxidation techniques, with higher free caustic to organic contaminant ratios favouring a greater degree of destruction of organic contaminants, and with ratios in excess of approximately 4 facilitating considerably greater destruction of organics than is enabled by existing methods at comparable conditions, or comparable destruction at less energy intensive conditions.

Without wishing to be bound by theory, it is believed that one action of the higher free caustic ratio is to increase the concentration of catalyst present in active form. It has been demonstrated that copper solubility in alkaline solution is related, amongst other factors, to the concentration of free caustic in that solution. Therefore, solutions with higher free caustic to organic contaminant ratios can potentially have higher concentrations of active catalyst species leading to increased rates of reaction.

When high organic contaminant destruction percentages are achieved, those organic contaminants less amenable to oxidation are being destroyed. Destruction of these organic contaminants is important for obtaining the full range of benefits from oxidation. Without a reduction in organic soda, the solubility derived alumina yield benefit is not achieved. Partial oxidation/destruction of organics can result in increased or unchanged levels of organic soda due to larger molecules being broken down to smaller molecules with similar quantities of negatively charged functional groups.

In a preferred form of the invention, the method includes the step of:

at least maintaining the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants (expressed as
grams per litre equivalent of carbon) at at least approximately 4 while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants.

Importantly, carbon dioxide is produced by oxidation of organic contaminants of alkaline solutions. Carbon dioxide reacts with free caustic to form water and carbonate ions. Thus, although the oxidation process may be reducing the concentration of organic contaminants, the significant concurrent consumption of free hydroxide by the carbon dioxide means that the overall effect is to reduce the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants. This process is represented by equations 1 and 2, below:

\[
\text{Organic contaminants} \rightarrow \text{oxidation} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (1)
\]

\[
\text{CO}_2 + 2\text{OH}^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (2)
\]

Preferably, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 5. In one form of the invention, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 6. In one form of the invention, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 7. In one form of the invention, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 8.

The preferred ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants (expressed as grams per litre equivalent of carbon) is largely determined by balancing the economics of increasing the ratio with the economics of selecting other conditions favourable to destruction of organics, such as elevated temperatures.
In the context of alkaline solutions containing dissolved aluminium, such as Bayer process solutions, the free caustic concentration generally depends on the total caustic concentration at which the refinery operates, the state of evaporation/dilution of the solution, and the amount of dissolved aluminium in the solution. The concentration of organic contaminants is largely related to the organic content of the bauxite used, but also to the state of evaporation/dilution of the stream. The concentration can vary significantly between refineries around the world, perhaps from 2-40g/L.

Obviously, alkaline solutions, including Bayer process solutions, having lower concentrations of organic contaminants are more amenable to economic elevation of the ratio of free caustic to organic contaminant ratio. Equally obviously, alkaline solutions having higher concentrations of organic contaminants are those for which it is more desirable to utilise catalytic wet oxidation. Thus, any upper threshold for the ratio of free caustic to organic contaminants in accordance with any aspect of the present invention is largely of an economic nature.

In one form of the invention, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is between about 4 and about 20.

In one form of the invention, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is between about 5 and about 12.

In one form of the invention, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is between about 5 and about 10.

In one form of the invention, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is between about 6 and about 10.

Alkaline solutions, including Bayer process solutions, may contain sodium carbonate. Increasing the concentration of total sodium in the alkaline solution
decreases the solubility of sodium carbonate. In certain circumstances the precipitation of sodium carbonate may be problematic. In such circumstances, the preferred ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution of the method of the present invention may take account of the effect of the concentration of total sodium on the solubility of sodium carbonate.

Some alkaline solutions may possess a sufficiently high ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution. However, the method may include the preliminary step of:

10 elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution.

The step of elevating the ratio of the concentration of free caustic in the alkaline solution may be performed prior to the step of exposing the alkaline solution to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants, concurrently with the step of exposing the alkaline solution to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants, or both prior to and concurrently with the step of exposing the alkaline solution to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants.

20 The step of elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution may comprise the step of:

adding a first causticising agent to the alkaline solution.

25 In one form of the invention, the first causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof.
The step of at least maintaining the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants at at least approximately 4 while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants may be performed by the step of:

adding a second causticising agent to the alkaline solution.

The second causticising agent may be added whilst the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants. However, in a preferred form of the invention, the step of adding a second causticising agent to the alkaline solution more specifically comprises the step of:

charging the alkaline solution with a quantity of the second causticising agent prior to exposure to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) at at least approximately 4.

In one form of the invention, the second causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof. The second causticising agent may be identical to the first causticising agent.

Some alkaline solutions, such as Bayer process solutions, contain alumina in the form of the aluminate ion. To maintain the alumina in solution, the ratio of total caustic to alumina must be maintained. As explained above, the oxidation of organic contaminants results in the consumption of free caustic, decreasing the total caustic concentration. Thus, maintaining the ratio of total caustic to alumina allows the increased oxidation of organic contaminants enabled by the method of the present invention to occur without destabilising the Bayer process solution.
Where the alkaline solution contains alumina, prior to the step of exposing the alkaline solution to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants while the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 4, the method includes the step of:

decreasing the alumina to total caustic ratio of the alkaline solution.

In a preferred form of the invention, the step of decreasing the alumina to total caustic ratio of the alkaline solution more specifically comprises the step of decreasing the ratio of alumina in the alkaline solution (expressed as grams per litre Al₂O₃) to total caustic (expressed as grams per litre sodium carbonate) to less than approximately 0.4.

Preferably still, the step of decreasing the alumina to total caustic ratio of the alkaline solution more specifically comprises the step of decreasing the ratio of alumina in the alkaline solution to total caustic to less than approximately 0.35. Further and still preferably, the step of decreasing the alumina to total caustic ratio of the alkaline solution more specifically comprises the step of decreasing the ratio of alumina in the alkaline solution to total caustic in the alkaline solution to less than approximately 0.3.

The step of decreasing the alumina to total caustic ratio of the alkaline solution may more specifically comprise the step of:

adding a third causticising agent to the alkaline solution.

In one form of the invention, the third causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof. The third causticising agent may be identical to one or both of the first and/or second causticising agents.
As already discussed in the context of the ratio of free caustic to organic contaminants, the outcome of the oxidation of the organic contaminants is the consumption of free caustic. Thus, the ratio of alumina to total caustic ratio is also affected by the oxidation of the organic contaminants. In one form of the invention, the method may comprise the step of:

maintaining the alumina to total caustic ratio of the alkaline solution at or below approximately 0.4 while exposing the alkaline solution to an oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants.

Preferably still, the step of maintaining the alumina to total caustic ratio below approximately 0.4 comprises the step of maintaining the alumina to total caustic ratio below approximately 0.35. Further and still preferably, the step of maintaining the alumina to total caustic ratio below approximately 0.4 comprises the step of maintaining the alumina to total caustic ratio below approximately 0.3.

The step of maintaining the alumina to total caustic ratio below approximately 0.4 while exposing the alkaline solution to an oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants may comprise the step of:

adding an fourth causticising agent to the alkaline solution.

The fourth causticising agent may be added whilst the alkaline solution is exposed to an oxidising agent under conditions suitable for the oxidation of organic contaminants. However, in a preferred form of the invention, the step of adding a fourth causticising agent to the alkaline solution more specifically comprises the step of:

charging the alkaline solution with a quantity of the fourth causticising agent prior to exposing the alkaline solution to an oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants, said quantity of fourth causticising agent being sufficient to at
least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4.

In one form of the invention, the fourth causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof. The fourth causticising agent may be identical to one or more of the first and/or second and/or third causticising agents.

The preferred choice of the first and/or second and/or third and/or fourth causticising agents is dependent on other properties of the alkaline solution, most notably sodium balance.

Two or more of the steps of: adding a first causticising agent to the alkaline solution, adding a second causticising agent to the alkaline solution, adding a third causticising agent to the alkaline solution and adding a fourth causticising agent to the alkaline solution, may be performed concurrently by the addition of a one or more quantities of a causticising agent selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof.

Alkaline solutions, including some Bayer process solutions, may contain silica. Where the alkaline solution contains silica, before the step of exposing the alkaline solution to an oxidising agent and catalyst under conditions suitable for the wet oxidation of organic contaminants while the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 4, the method may include the step of:

desilicating the alkaline solution.

The step of desilicating the alkaline solution is preferred where the concentration of SiO$_2$ in the alkaline solution exceeds approximately 0.1 grams per litre.
In one form of the invention, the step of desilicating the alkaline solution more specifically comprises the step of:

adding a desilicating agent to the alkaline solution to induce the precipitation of a silica-containing solid.

5 In one form of the invention, the desilicating agent is selected from the group: lime, slaked lime and mixtures thereof.

In one form of the invention, the desilicating agent is provided in the form of a solid silica-containing phase.

Where the desilicating agent is selected from the group: lime, slaked lime and mixtures thereof, the step of adding a desilicating agent to the alkaline solution to induce the precipitation of a silica-containing solid may be performed concurrently with at least one of the steps of: adding a first causticising agent to the alkaline solution, adding a second causticising agent to the alkaline solution, adding a third desilicating agent to the alkaline solution and adding a fourth causticising agent to the alkaline solution by the addition of one or more quantities of a causticising agent selected from the group: lime, slaked lime or mixtures thereof.

Where the method comprises the step of adding a desilicating agent to the alkaline solution to induce the precipitation of a silica-containing solid, after this step and before the step of exposing the alkaline solution to an oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants while the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 4, the method comprises the step of:

separating the silica-containing solid from the alkaline solution.

25 Conditions suitable for the catalytic wet oxidation of organic contaminants frequently include elevated temperatures. Conveniently, these elevated temperatures are attained by way of heat exchange apparatus. Aluminosilicate
scale formation rates become increasingly significant as temperature rises, and heat exchange apparatus are typically provided with extensive surface areas, making desilication prior to temperature elevation advantageous.

In a preferred form of the invention, where the method includes the steps of separating the silica-containing solid from the alkaline solution and at least maintaining the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants at at least approximately 4 while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the oxidation of organic contaminants by adding the second causticising agent to the alkaline solution, the step of adding a second causticising agent to the alkaline solution occurs after the step of separating the silica-containing solid from the alkaline solution.

Similarly, where the method includes the steps of separating the silica-containing solid from the alkaline solution and at least maintaining the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4 while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants by adding the fourth causticising agent to the alkaline solution, the step of adding the fourth causticising agent to the alkaline solution occurs after the step of separating the silica-containing solid from the alkaline solution.

Thus, in a preferred form, where the alkaline solution is a Bayer process solution, the method comprises the steps of:

elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the Bayer process solution by adding a first causticising agent to the Bayer process solution;

decreasing the alumina to total caustic ratio of the Bayer process solution by adding a third causticising agent to the Bayer process solution;
desilicating the Bayer process solution by adding a desilicating agent to the Bayer process solution to induce the precipitation of a silica-containing solid;

separating the silica-containing solid from the Bayer process solution;

charging the Bayer process solution with a quantity of a second causticising agent, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution at at least approximately 4;

charging the alkaline solution with a quantity of a fourth causticising agent, said quantity of fourth causticising agent being sufficient to at least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4;

exposing the Bayer process solution to an oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants while the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 4; and

at least maintaining the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants at at least approximately 4 and the alumina to total caustic ratio at or below approximately 0.4 while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants.

Conveniently and preferably, the steps of:

elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the Bayer process solution by adding a first causticising agent to the Bayer process solution;
decreasing the alumina to total caustic ratio of the Bayer process solution by
adding a third causticising agent to the Bayer process solution; and

desilicating the Bayer process solution by adding a desilicating agent to the
Bayer process solution to induce the precipitation of a silica-containing solid;

are performed concurrently by the addition of a single quantity of lime or slaked
lime or a mixture thereof with sodium hydroxide.

Conveniently and preferably, the steps of:

charging the Bayer process solution with a quantity of a second causticising
agent, said quantity of second causticising agent being sufficient to at least
maintain the ratio of the concentration of free caustic in the alkaline solution
to the concentration of organic contaminants in the alkaline solution at at
least approximately 4; and

charging the alkaline solution with a quantity of a fourth causticising agent,
said quantity of fourth causticising agent being sufficient to at least maintain
the ratio of the concentration of alumina in the alkaline solution to the total
caustic concentration in the alkaline solution at or below approximately 0.4;

are performed concurrently by the addition of a single quantity of sodium
hydroxide, lime, slaked lime or a mixture thereof.

The degree of oxidation of organic contaminants of alkaline solutions facilitated by
the method of the invention enables rapid and efficient oxalate destruction, and
the method of the present invention is intended to encompass the destruction of
oxalate, which may be oxalate inherently present or formed in the solution, or
additional oxalate concentrated by some other oxalate removal process.

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

The best method of performing the invention known to the applicant will now be
described, by way of example only, with reference to one embodiment thereof.
The best method performing the invention known to the applicant is described in the context of the catalytic wet oxidation of organic contaminants of Bayer process solutions, although such should not be seen as limiting the generality of the foregoing description.

A first quantity of lime and sodium hydroxide (relative amounts being dependent on the soda balance) is added to the Bayer process solution to (i) elevate the ratio of the concentration of free caustic to the concentration of organic contaminants to at least 4, (ii) decrease the alumina to total caustic ratio to at most 0.4 and (iii) desilicate the Bayer process solution by inducing the precipitation of a silica-containing solid. Thus, the first quantity of lime and sodium hydroxide comprises (i) the first causticising agent, (ii) the third causticising agent and (iii) the desilicating agent.

The silica containing-containing solid is separated from the Bayer process solution, before heating then charging the Bayer process solution with a second quantity of lime or sodium hydroxide (depending on the soda balance), the second quantity of lime or sodium hydroxide being sufficient to (i) at least maintain the ratio of the concentration of free caustic in the Bayer process solution to the concentration of organic contaminants in the Bayer process solution at at least approximately 4 and (ii) at least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the Bayer process solution at or below approximately 0.4 while the Bayer process solution is exposed to an oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants. Thus, the second quantity of lime or sodium hydroxide comprises (i) the second causticising agent and (ii) the fourth causticising agent.

The Bayer process solution is then exposed to a catalyst and an oxidising agent under conditions suitable for catalytic wet oxidation of the organic contaminants of the Bayer process solution. While the Bayer process solution is exposed to the catalyst and oxidising agent under conditions suitable for catalytic wet oxidation of the organic contaminants, the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline
solution is maintained at least approximately 4 and the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution is maintained at or below approximately 0.4.

The best method of performing the invention may include one or more steps to avoid or manage the precipitation of sodium carbonate. For example, the concentration of organic contaminants in the Bayer process solution may be managed, reactors capable of managing or purging solids may be used or the chemical composition of the Bayer solution may be adjusted to increase solubility of sodium carbonate.

Examples

The following examples serve to more fully illustrate the above-described invention. The examples are discussed with reference to the accompanying drawings, in which:

15 Figure 1 is a plot of organic contaminant destruction as a function of time for wet oxidation at 265°C, 1000kPa O₂ and 1g/L CuO of Bayer process solutions having differing free caustic levels;

Figure 2 is a plot of oxalate formation and destruction as a function of time for wet oxidation at 265°C, 1000kPa O₂ and 1g/L CuO of a range of Bayer process solutions;

20 Figure 3 is a schematic flow sheet showing how an embodiment of the method of the present invention might be utilised;

Figure 4 is a plot of % organic contaminant destruction as a function of the initial free caustic to organic contaminant ratio of the Bayer process solution, for wet oxidation undertaken at 265°C, 1000kPa O₂ and 1g/L CuO; and
Figure 5 is a plot illustrating consumption of the sodium salts of acetate, formate and succinate as a function of time, for wet oxidation undertaken at 265°C, 1000kPa O₂ and 1g/L CuO.

Examples

Bench trials were conducted by adding 2 L of liquor to an Inconel 600 alloy autoclave with a stirring rate of 500 rpm. After the target temperature of 265 °C was reached, catalyst and oxygen were added to the liquor. Oxygen gas was injected into the headspace and maintained at a set partial pressure for the duration of the test. Nitrogen gas was also injected at an equal partial pressure for safety reasons.

TOC (organic contaminant) reductions of up to 94% after four hours treatment time were measured at 265°C, 1000kPa O₂ and 1g/L CuO. TOC reductions were calculated by the drop in total organic carbon concentration of the treated Bayer process solutions relative to the start Bayer process solutions, measured by an oxidation/infrared technique.

Oxalate is both formed and destroyed, hence there is the potential to utilise high temperature catalytic wet oxidation as an oxalate destruction process. The presence of catalyst is important for achieving oxalate destruction at practical temperatures and residence times. As can be seen from Figure 2, tests were run where an extra 30 g/L oxalate was added to the liquor and the results showed that all the additional oxalate was consumed, whilst maintaining high liquor TOC reduction.

Acetate, formate and succinate are also consumed under these conditions. An example of their destruction as a function of time is illustrated in Figure 5.

TOC reduction can be increased by increasing the level of free caustic in the feed liquor or maintaining the free caustic by addition of lime solids. The free caustic can be elevated by the addition of sodium hydroxide and this method has the advantage of reducing the final A/TC of the treated liquor, thus reducing the
potential for hydrate scaling issues. Lime addition also has the benefit of reducing final \( A/TC \), but not to the same extent as sodium hydroxide.

Figure 1 is a plot of organic contaminant destruction as a function of time for wet oxidation at 265°C, 1000kPa \( O_2 \) and 1g/L CuO in Bayer process solutions, demonstrating the efficacy of the addition of lime and/or sodium hydroxide (FC) in the facilitation of the oxidation of organic contaminants. Figure 4 clearly demonstrates the importance of the ratio of the concentration of free caustic to organic contaminants to the achievable %oxidation of the organic contaminants, with a ratio of 4 and above offering marked improvements. Figure 2 demonstrates the efficacy of the method of the present invention in the oxidation of sodium oxalate. Figure 5 demonstrates consumption of the sodium salts of acetate, formate and succinate as a function of time.

Table 1, below, shows the effect of the elevation of the free caustic to organic contaminant ratio, and the reduction of the alumina to total caustic ratio on wet oxidation efficiency at 265degC, 1000kPa \( O_2 \) and 1g/L CuO catalyst.

<table>
<thead>
<tr>
<th>Feed liquor</th>
<th>FC/TOC (initial)</th>
<th>FC/TOC (3hrs)</th>
<th>A/TC (3hrs)</th>
<th>%TOC destruction (3hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated spent liquor</td>
<td>4.0</td>
<td>0.48</td>
<td>1.485 *</td>
<td>69</td>
</tr>
<tr>
<td>Spent liquor +10% v/v of 52% w/w NaOH</td>
<td>7.5</td>
<td>11.1</td>
<td>0.695</td>
<td>89</td>
</tr>
<tr>
<td>Spent liquor +100g/L Ca(OH)2</td>
<td>5.1</td>
<td>24.6</td>
<td>0.575</td>
<td>93</td>
</tr>
</tbody>
</table>

*Assuming no alumina precipitation, which would occur in practice, causing undesirable scaling. A/TC ratios above approximately 0.7 are undesirable.

**TABLE 1**
The claims defining the invention are as follows:

1. A method for the catalytic wet oxidation of organic contaminants of an alkaline solution, the method including the step of exposing the alkaline solution to an oxidising agent and a catalyst, under conditions suitable for the catalytic wet oxidation of organic contaminants, and characterised in that:

   the alkaline solution is exposed to the oxidising agent and the catalyst while the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) is at least approximately 4.

2. A method according to claim 1 characterised in that the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 5.

3. A method according to claim 1 characterised in that the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 6.

4. A method according to claim 1 characterised in that the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 10.

5. A method according to any one of claims 1 to 4 characterised in that the method includes the step of:

   at least maintaining the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants (expressed as grams per litre equivalent of carbon) at at least approximately 4 while the alkaline solution is exposed to the oxidising agent and catalyst
under conditions suitable for the catalytic wet oxidation of organic contaminants.

6. A method according to claim 2 characterised in that the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is maintained at at least approximately 5.

7. A method according to claim 2 characterised in that the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is maintained at at least approximately 6.

8. A method according to claim 2 characterised in that the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is maintained at least approximately 10.

9. A method according to any one of claims 1 to 8 characterised in that prior to the step of exposing the alkaline solution to an oxidising agent and a catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants, the method comprises the step of:

- elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution by adding a first causticising agent to the alkaline solution.

10. A method according to claim 9 characterised in that the first causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof.

11. A method according to any one of claims 5 to 10 characterised in that the step of at least maintaining the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants at at least
approximately 4 while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants comprises the step of:

adding a second causticising agent to the alkaline solution.

12. A method according to claim 11 characterised in that the second causticising agent is added while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants.

13. A method according to claim 11 characterised in that the step of adding a second causticising agent to the alkaline solution more specifically comprises the step of:

charging the alkaline solution with a quantity of the second causticising agent prior to exposure to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) at at least approximately 4.

14. A method according to any one of claims 11 to 13 characterised in that the second causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof.

15. A method according to claim 13 or 14, where the method includes the step of elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution by adding a first causticising agent to the alkaline solution, characterised in that the steps of:
elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution by adding a first causticising agent to the alkaline solution; and

charging the alkaline solution with a quantity of the second causticising agent prior to exposure to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) at at least approximately 4;

are performed concurrently, such that the first causticising agent is identical to the second causticising agent.

16. A method according to any one of the preceding claims characterised in that, prior to the step of exposing the alkaline solution to an oxidising agent, the method includes the step of:

decreasing the alumina to total caustic ratio of the Bayer process solution.

17. A method according to claim 16 characterised in that the step of decreasing the alumina to total caustic ratio of the Bayer process solution more specifically comprises the step of decreasing the ratio of alumina in the alkaline solution (expressed as grams per litre Al₂O₃) to total caustic (expressed as grams per litre sodium carbonate) to less than approximately 0.4.

18. A method according to claim 16 characterised in that the step of decreasing the alumina to total caustic ratio of the Bayer process solution more specifically comprises the step of decreasing the ratio of alumina in the alkaline solution to total caustic to less than approximately 0.35.
19. A method according to claim 16 characterised in that the step of decreasing the alumina to total caustic ratio of the Bayer process solution more specifically comprises the step of decreasing the ratio of alumina in the alkaline solution to total caustic to less than approximately 0.3.

20. A method according to any one of claims 16 to 19 characterised in that the step of decreasing the alumina to total caustic ratio more specifically comprises the step of:

adding a third causticising agent to the alkaline solution to decrease the alumina to total caustic ratio.

21. A method according to claim 20 characterised in that the third causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof.

22. A method according to claim 20 or 21, wherein the method includes the step of elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution by adding a first causticising agent to the alkaline solution, characterised in that the steps of:

- elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution by adding a first causticising agent to the alkaline solution; and
- adding a third causticising agent to the alkaline solution to decrease the alumina to total caustic ratio;

are performed concurrently such that the first causticising agent is identical to the third causticising agent.

23. A method according to any one of the preceding claims characterised in that the method comprises the step of:
maintaining the alumina to total caustic ratio at or below approximately 0.4 while exposing the alkaline solution to an oxidising agent under conditions suitable for the oxidation of organic contaminants.

24. A method according to claim 23 characterised in that the alumina to total caustic ratio is maintained below 0.35.

25. A method according to claim 23 wherein the alumina to total caustic ratio is maintained below 0.3.

26. A method according to any one of claims 23 to 25 characterised in that step of maintaining the alumina to total caustic ratio at or below approximately 0.4 while exposing the alkaline solution to an oxidising agent under conditions suitable for the oxidation of organic contaminants comprises the step of:

adding a fourth causticising agent to the alkaline solution.

27. A method according to claim 26 characterised in that the step of adding an fourth causticising agent to the alkaline solution comprises the step of:

charging the alkaline solution with a quantity of the fourth causticising agent prior to exposing the alkaline solution to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of fourth causticising agent being sufficient to at least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4.

28. A method according to claim 26 or 27 characterised in that the fourth causticising agent is selected from the group: sodium hydroxide, lime, slaked lime and mixtures thereof.

29. A method according to claim 27 or 28, where the method comprises the step of charging the alkaline solution with a quantity of the second causticising
agent prior to exposure to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) at at least approximately 4, characterised in that the steps of:

charging the alkaline solution with a quantity of the second causticising agent prior to exposure to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) at at least approximately 4; and

charging the alkaline solution with a quantity of the fourth causticising agent prior to exposing the alkaline solution to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of fourth causticising agent being sufficient to at least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4;

are performed concurrently, such that the second causticising agent is identical to the fourth causticising agent.

30. A method according to claim 29 characterised, where the method includes the steps of elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution by adding a first causticising agent to the alkaline solution and adding a third causticising agent to the alkaline solution to decrease the alumina to total caustic ratio, characterised in that the steps of
elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the alkaline solution by adding a first causticising agent to the alkaline solution;

charging the alkaline solution with a quantity of the second causticising agent prior to exposure to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution (expressed in grams per litre equivalent of sodium carbonate) to the concentration of organic contaminants in the alkaline solution (expressed as grams per litre equivalent of carbon) at at least approximately 4;

adding a third causticising agent to the alkaline solution to decrease the alumina to total caustic ratio; and

charging the alkaline solution with a quantity of the fourth causticising agent prior to exposing the alkaline solution to an oxidising agent under conditions suitable for the oxidation of organic contaminants, said quantity of fourth causticising agent being sufficient to at least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4;

are performed concurrently, such that the first, second, third and fourth causticising agents are identical.

31. A method according to any one of the preceding claims characterised in that, before the step of exposing the alkaline solution to an oxidising agent and catalyst under conditions suitable for the wet oxidation of organic contaminants, the method comprises the step of:

adding a desilicating agent to the alkaline solution to induce the precipitation of a silica-containing solid.
32. A method according to claim 31 characterised in that the desilicating agent is selected from the group: lime, slaked lime and mixtures thereof.

33. A method according to claim 32, where the method includes at least one of the steps of adding the first causticising agent to the alkaline solution, adding the second causticising agent to the alkaline solution, adding the third causticising agent to the alkaline solution and adding the fourth causticising agent to the alkaline solution, characterised in that the step of adding the desilicating agent to the alkaline solution to induce the precipitation of a silica-containing solid is performed concurrently with at least one of the steps of adding the first causticising agent to the alkaline solution, adding the second causticising agent to the alkaline solution, adding the third causticising agent to the alkaline solution and adding the fourth causticising agent to the alkaline solution, such that the desilicating agent is identical to at least one of the first, second, third and/or fourth causticising agents.

34. A method according to claim 33 characterised in that after the step of adding a desilicating agent to the alkaline solution to induce the precipitation of a silica-containing solid and before the step of exposing the alkaline solution to an oxidising agent and catalyst under conditions suitable for wet oxidation of organic contaminants, the method comprises the step of:

separating the silica-containing solid from the alkaline solution.

35. A method for the catalytic wet oxidation of organic contaminants of a Bayer process solution comprising the steps of:

- elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the Bayer process solution by adding a first causticising agent to the Bayer process solution;
- decreasing the alumina to total caustic ratio of the Bayer process solution by adding a third causticising agent to the Bayer process solution;
desilicating the Bayer process solution by adding a desilicating agent to the Bayer process solution to induce the precipitation of a silica-containing solid;

separating the silica-containing solid from the Bayer process solution;

charging the Bayer process solution with a quantity of a second causticising agent, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution at at least approximately 4;

charging the alkaline solution with a quantity of a fourth causticising agent, said quantity of fourth causticising agent being sufficient to at least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4;

exposing the Bayer process solution to an oxidising agent and a catalyst under conditions suitable for the catalytic wet oxidation of organic contaminants while the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 4; and

at least maintaining the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants at at least approximately 4 and the alumina to total caustic ratio at or below approximately 0.4 while the alkaline solution is exposed to the oxidising agent and catalyst under conditions suitable for the oxidation of organic contaminants.

36. A method according to claim 35, characterised in that the steps of:
elevating the ratio of the concentration of free caustic to the concentration of organic contaminants in the Bayer process solution by adding a first causticising agent to the Bayer process solution;

decreasing the alumina to total caustic ratio of the Bayer process solution by adding a third causticising agent to the Bayer process solution; and

desilicating the Bayer process solution by adding a desilicating agent to the Bayer process solution to induce the precipitation of a silica-containing solid;

are performed concurrently by the addition of a single quantity of lime or slaked lime or a mixture thereof with sodium hydroxide.

37. A method according to claim 35 or 36 characterised in that the steps of:

charging the Bayer process solution with a quantity of a second causticising agent, said quantity of second causticising agent being sufficient to at least maintain the ratio of the concentration of free caustic in the alkaline solution to the concentration of organic contaminants in the alkaline solution is at least approximately 4; and

charging the alkaline solution with a quantity of a fourth causticising agent, said quantity of fourth causticising agent being sufficient to at least maintain the ratio of the concentration of alumina in the alkaline solution to the total caustic concentration in the alkaline solution at or below approximately 0.4;

are performed concurrently by the addition of a single quantity of sodium hydroxide, lime, slaked lime or a mixture thereof.
Figure 1. Effect of free caustic addition on TOC destruction as a function of time under wet oxidation conditions.
Figure 2. Oxalate formation and destruction as a function of time for a range of wet oxidation conditions.
Figure 3. Proposed full-scale plant design

- Feed liquor
- Tricalcium aluminate hexahydrate solids
- Oxidant
- Lime
- Catalyst
- Liquid cooling
- Liquor heating
- Catalytic Wet Oxidation reactor
Figure 4. Percentage organic contaminant destruction as a function of the initial free caustic to organic contaminant ratio of the Bayer process solution.
Figure 5. Consumption of the sodium salts of acetate, formate and succinate as a function of time.
**INTERNATIONAL SEARCH REPORT**

**A. CLASSIFICATION OF SUBJECT MATTER**

Int. Cl. 7: C01F 7/04, 7/06

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)

IPC: C01F 7/-

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

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

WPAT, JAPIO

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>US 4668486 (Brown e al.) 26 May 1987 Whole document.</td>
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<td>A</td>
<td>GB 2037722 A (Magyar Aluminiumpapi Troszt et al.) 16 July 1980 Whole document.</td>
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![ ] Further documents are listed in the continuation of Box C  

[X] See patent family annex

* Special categories of cited documents:

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**L** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

**O** document referring to an oral disclosure, use, exhibition or other means

**P** document published prior to the international filing date but later than the priority date claimed

**T** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

**X** 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

**Y** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

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Date of the actual completion of the international search  
26 September 2005

Date of mailing of the international search report  
4 OCT 2005

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

END OF ANNEX