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(54) Title: METHOD FOR REMOVING ORGANIC CARBON FROM BAYER PROCESS LIQUOR

(57) Abstract: Organic carbon is removed from Bayer process liquor through the addition of a mixture of ozone and oxygen.



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METHOD FOR REMOVING ORGANIC CARBON FROM BAYER PROCESS LIQUOR

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FIELD OF THE INVENTION

This invention relates generally to the purification of Bayer process liquor and, more particularly, to a method for removing organic carbon from Bayer process liquor.

BACKGROUND OF THE INVENTION

10 Alumina trihydrate, the precursor of many alumina-based products, including calcined alumina used for making metallic aluminum by reduction, is most commonly obtained from alumina-containing ores, such as bauxite. Recovery of the alumina content of bauxite is generally accomplished by the well-known Bayer process which involves the digestion of the bauxite with a caustic medium at elevated temperatures and pressures.

15 Digestion of the bauxite results in a saturated sodium aluminate liquor, commonly referred to as "pregnant liquor" from which the alumina content is recovered by precipitation, usually through addition of seed alumina.

 Bauxite is found in many parts of the world and the composition of the ores may vary from place to place. Many bauxites contain organic carbon (also referred to as

20 "organic impurities") that will be co-extracted with the alumina content of the ore during digestion and will contaminate the produced liquor. Most of the organic carbon content found in the ores consists of high molecular weight compounds, a portion of which will decompose to lower molecular weight compounds during the caustic digestion process, thereby producing a whole spectrum of organic salts dissolved in the liquor. Since the

25 Bayer process involves extensive recycling of the used caustic liquor to the digestion stage,

the organic carbon content of the liquor will continuously increase, reaching levels ranging from 5 to 40 g/L carbon depending on the type of bauxite being processed. The accumulation of organic carbon content can reach such high levels so as to seriously interfere with the economic and efficient production of alumina trihydrate unless such
5 accumulation can be prevented or at least controlled.

Since the control of organic carbon levels in Bayer process liquors is an important facet in the production of alumina trihydrate, several methods have already been developed for such organic carbon level control. U.S. Patent No. 4,046,855 (Schepers et al.) suggests that organic impurities can be removed from Bayer process liquors by contacting the liquor
10 with a magnesium compound which will form a precipitated mixture of magnesium and aluminum hydroxides. This precipitate, according to the patent, can remove some of the organic impurities either by adsorption or by chemisorption. The magnesium compound may be added at any stage of the Bayer process, additions prior to digestion or to the digested slurry are preferred. Although this process is capable of removing at least a
15 portion of the organic impurities, the formation of a precipitated hydroxide mixture creates operational difficulties. On the one hand, the precipitated hydroxide mixture will contain aluminum hydroxide and this results in product alumina loss; on the other hand, the precipitated mixture has to be separated from the rest of the treated liquor and this involves additional processing steps and/or a definite increase in the quantity of the total mud load
20 which requires disposal.

In U.S. Patent No. 4,101,629 (Mercier et al.), a barium-containing compound is added to Bayer process liquors. The barium compound precipitates as barium aluminate

and the precipitated material may also include barium salts of organic impurities present in the liquor. As in the previously discussed patent, this process involves precipitation of a compound which has to be removed from the treated liquor requiring settling and/or filtration equipment and additional processing steps. The process allows recovery and
5 reuse of the filtered barium compound by calcination; however, the well-known toxicity of barium salts may create an unacceptable environmental and/or health risk not justifiable by the purification results obtainable by it.

In U.S. Patent No. 4,335,082 (Matyasi et al.), organic impurities are removed from impure Bayer liquors by caustifying the liquor with lime, followed by evaporation of the
10 causticized liquor. Evaporation will result in the precipitation of solids containing a large quantity of the organic impurities from the liquor. The solids are separated and then discarded. This method assures the removal of satisfactory quantities of organic impurities from the liquor, but the problems associated with the process render it impractical and expensive. To achieve good purification, large volumes of liquor have to be treated with
15 lime and evaporated. These involve large quantities of lime and extensive energy input. Also, by treating large volumes, large losses of soda values can be expected. A similar purification process is disclosed in U.S. Patent No. 4,280,987 (Yamada et al.). In this process, Bayer liquor is first evaporated, then calcined at high temperature after its alumina and caustic content is adjusted to a predetermined level. This process, known in the Bayer
20 industry as "liquor burning," is an effective means of organic impurity removal. Its disadvantages are associated with the large volumes to be evaporated and then calcined, which require substantial capital and energy expenditures.

In U.S. Patent No. 4,215,094 (Inao et al.), a copper-catalyzed wet oxidation process is recommended for the oxidation of organic impurities, followed by addition of a sulfur-containing compound to remove the copper catalyst as a precipitate. The oxidation is accomplished under elevated temperature and pressure conditions in the presence of a catalyst and molecular oxygen. This process has several disadvantages in that a high temperature-pressure digestion has to be applied which involves the use of expensive pressure vessels and substantial energy usage. In addition, the copper catalyst has to be removed from the treated liquor to avoid contamination. Disposal of the removed copper sulfide can create environmental and/or health hazards. Similarly, in U.S. Patent No. 4,663,133 (Malito et al.), organic impurities are oxidized at elevated temperature and pressure by feeding molecular oxygen directly into the bauxite digestion vessels. The amount of oxygen used is limited to below the solubility of oxygen in the liquor and is sufficient to destroy only a portion of the organic impurities. Moreover, there is the potential of explosion due to the high pressures required.

In Japanese Patent No. 53-146,259 (Kazama et al.) various oxidizing agents, such as sodium peroxide powder and 50% hydrogen peroxide, are used to destroy part of the organic impurities. Though effective, these reagents are expensive and hazardous. Also, the color of pregnant Bayer liquor is removed by passing a small stream of air containing 1% ozone through pregnant Bayer liquor. However, this dilute ozone stream only removes color and is not sufficient to oxidize any of the organic impurities.

Accordingly, it would be desirable to provide a method for safely and effectively removing organic carbon from Bayer process liquor.

SUMMARY OF THE INVENTION

The first aspect of the instant claimed invention is a method of removing organic carbon from Bayer process liquor which comprises the step of adding an effective amount of a mixture of ozone and oxygen to the Bayer process liquor.

5 The second aspect of the instant claimed invention is In a composition of matter which is a Bayer process liquor, produced using the Bayer Process, the improvement comprising a Bayer process liquor which comprises ozone in oxygen.

The present invention calls for adding a mixture of ozone and oxygen to Bayer process liquor. This ozone/oxygen mixture safely and effectively removes organic carbon
10 from the Bayer process liquor.

DETAILED DESCRIPTION OF THE INVENTION

For purposes of this invention, the term "Bayer process liquor" means any caustic liquor which is present in the Bayer process. Typical examples of Bayer process liquors include, but are not limited to, pregnant liquor, spent liquor, washer underflow, liquor from
15 oxalate destruction or liquor caustification processes, and slurries containing precipitated alumina trihydrate, as well as the liquor containing dispersed red mud particles or bauxite. Also, those skilled in the art will recognize that Bayer process liquors span a temperature range of approximately 80 °F to 500 °F.

The present invention is directed to a method for removing organic carbon from
20 Bayer process liquor. In accordance with this invention, a mixture of ozone and oxygen is added to the Bayer process liquor.

It is preferred that the amount of ozone in the mixture be in the range of about 1% to about 40% by weight. More preferably, the amount of ozone is from about 5% to about 20% by weight, with about 12% to about 16% by weight being most preferred.

The ozone/oxygen mixture can be added to the Bayer process liquor by any
5 conventional method in an amount which effectively removes organic carbon from the liquor. Typical equipment which may be used for contacting the ozone/oxygen mixture with the Bayer process liquor includes, but is not limited to, batch reactors, packed bed reactors, bubble cap contact towers, gas diffusers in a mixed tank and any other device designed for contacting a gas with a liquid or a slurry. This type of equipment is described
10 in Helble, et al., "Advanced Effluent Treatment in the Pulp and Paper Industry with a Combined Process of Ozonation and Fixed Bed Biofilm Reactors," Wat. Sci. Tech. Vol. 40, No. 11-12, pp. 343-350, 1999, the disclosure of which is incorporated herein by reference. The amount of ozone/oxygen mixture which is added to the Bayer process liquor is dependent upon the particular type of equipment utilized. However, it is preferred
15 that the amount of the ozone/oxygen mixture be in the range of about 1 to about 80 grams of ozone per liter of the Bayer process liquor. Those skilled in the art will recognize that the maximum amount of the ozone/oxygen mixture which can be added is limited by the amount of ozone that can be absorbed by the liquor.

The ozone/oxygen mixture may be added to the liquor at any point in the Bayer
20 process, however, preferred locations include the spent liquor, slurries of spent liquor and bauxite, and slurries containing aluminum trihydrate.

EXAMPLES

The following examples are intended to be illustrative of the present invention and to teach one of ordinary skill how to make and use the invention. These examples are not intended to limit the invention or its protection in any way.

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Example 1

Bayer process liquor (17 liters) was heated to 160 °F and charged to a batch reactor through a fill line and a valve. The liquor was circulated through the reactor by a pump at a total flow rate of 10 L/min. Part of this flow (2 L/min) was diverted to a spray nozzle for the purpose of controlling any foam that was generated in the reactor. The flow was
10 adjusted using a flow valve and monitored with a flow meter. The foam phase completely disappeared 30 minutes from the start of the reaction, at which point the flow through the nozzle was discontinued. The rest of the liquid was directed to the reactor through a radial diffuser, and was controlled by a flow valve and monitored by a flow meter. The liquid level in the reactor during operation was maintained at about 40% of the total reactor
15 volume. Ozone was produced in a corona discharge ozone generator using oxygen supplied from a gas cylinder. The ozone/oxygen mixture, containing approximately 13% ozone, was injected into the liquor at an ozone flow rate of 51 g/h through a venturi designed to disperse the gas into fine bubbles. Reaction with the organic carbon in the liquor was very rapid and occurred almost to completion within the reactor tube between
20 the venturi and the radial diffuser. Any unreacted gas was vented through the reactor vent and was sampled continuously for the determination of excess ozone using a UV photometer tuned at 253.7 nm. The absorption efficiency of the ozone was 98.8% or

greater. Any excess ozone was destroyed by passing the vent gases through a thermal ozone destruction unit. The temperature of the liquor was maintained without control between 135 °F and 142 °F over the 5 hour duration of the test.

A 0.1 L sample was collected every 30 minutes for the determination of total organic carbon (TOC), given as the difference between the total carbon and total inorganic carbon, as determined by the DIN (Deutsches Institut für Normung eV) EN 1448 method. The results are shown below in Table 1.

Table 1. Reaction of Ozone with Bayer Spent Liquor at 140 °F

Absorbed Ozone (g/L)	TOC (g/L carbon)
0	8.40
1.43	8.03
2.82	7.89
4.30	7.68
5.79	7.45
7.30	7.40
8.82	7.26
10.4	7.06
11.9	6.87
13.5	6.39
15.1	6.10

10 Contacting the spent liquor with a mixture of ozone and oxygen resulted in a significant reduction in the organic carbon content. The ozone was essentially completely absorbed into the liquid phase, with an average absorption efficiency of 99%. In this example, an average of 0.13g of carbon were removed per gram of ozone absorbed.

Example 2

The ozone/oxygen mixture was contacted with Bayer spent liquor in a manner identical to Example 1, except that the liquor was not preheated before charging the reactor. The temperature during the reaction climbed from 98 °F to 125 °F over the total
5 reaction period of 3 hours. Liquor samples were collected every 20 minutes and analyzed as indicated in Example 1. The results are shown below in Table 2.

Table 2. Reaction of Ozone with Bayer Spent Liquor at 98 °F to 125 °F

Absorbed Ozone (g/L)	TOC (g/L carbon)
0	8.07
0.94	7.82
1.85	7.76
2.76	7.61
3.68	7.25
4.60	7.24
5.52	6.71
6.51	6.76
7.54	6.39
8.56	6.14

Example 2 shows that organic carbon can be effectively removed even at the lower
10 temperature of 98 °F to 125 °F. In this example, an average of 0.21g of carbon were removed per gram of ozone absorbed.

While the present invention is described above in connection with preferred or illustrative embodiments, these embodiments are not intended to be exhaustive or limiting of the invention. Rather, the invention is intended to cover all alternatives, modifications
15 and equivalents included within its spirit and scope, as defined by the appended claims.

WHAT IS CLAIMED IS:

1. A method of removing organic carbon from Bayer process liquor which comprises
the
step of adding an effective amount of a mixture of ozone and oxygen to the Bayer process
5 liquor.
2. The method of claim 1 wherein the amount of ozone in the mixture ranges from
about 1%
to about 40% by weight.
10
3. The method of claim 1 wherein the amount of ozone in the mixture ranges from
about 5%
to about 20% by weight.
- 15 4. The method of claim 1 wherein the amount of ozone in the mixture ranges from
about
12% to about 16% by weight.
5. The method of claim 1 wherein the mixture of ozone and oxygen is added to the
20 Bayer
process liquor in an amount from about 1 to about 80 grams of ozone per liter of the Bayer
process liquor.

6. In a composition of matter which is a Bayer process liquor, produced using the Bayer Process, the improvement comprising a Bayer process liquor which comprises ozone in oxygen.

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7. A Bayer process liquor of Claim 6 which is a pregnant liquor.

8. A Bayer process liquor of Claim 6 which is a spent liquor.

10

9. A Bayer process liquor of Claim 6 which is a washer underflow.

10. A Bayer process liquor of Claim 6 which is a liquor from oxalate destruction.

15 11. A Bayer process liquor of Claim 6 which is a liquor from a liquor caustification process.

12. A Bayer process liquor of Claim 6 which is a slurry containing dispersed red mud particles.

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13. A Bayer process liquor of Claim 6 which is a slurry containing bauxite.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/24354

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C01F 7/00
US CL : 423/130, 121

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)

U.S. : 423/130, 121

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONE

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

WEST: bayer, ozone, oxygen, o2, o?sub.2, aluminate

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SU 1,057,423 A (NIKOLAEV et al) 30 November 1983, abstract.	1-13
X,T	US 2003/0161769 A1 (JENNY) 28 August 2003, abstract.	1-13
A	US 6,555,077 B1 (ROSENBERG et al) 29 April 2003, col. 2.	
A	US 4,046,855 A (SCHEPERS et al) 06 September 1977, col. 2.	



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:	
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