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(54) Titre : PROCEDE DE PRODUCTION DE DIOXYDE DE CHLORE A L'AIDE D'ACIDE NITRIQUE
(54) Title: NITRIC ACID BASED CHLORINE DIOXIDE GENERATION PROCESS

(57) Abrégé/Abstract:
Chlorine dioxide is generated from a sulfate free aqueous acid reaction medium using nitric acid as the acid source. Highly efficient chlorine dioxide generation at high production rate is achieved in the low acidity range below about 2 N at low concentrations of chlorate below about 3 M, under crystallizing and non-crystallizing conditions.

ABSTRACT OF DISCLOSURE

Chlorine dioxide is generated from a sulfate free aqueous acid reaction medium using nitric acid as the acid source. Highly efficient chlorine dioxide generation at high production rate is achieved in the low acidity range below about 2 N at low concentrations of chlorate below about 3 M, under crystallizing and non-crystallizing conditions.

TITLE OF INVENTION

NITRIC ACID BASED CHLORINE DIOXIDE GENERATION PROCESS

FIELD OF THE INVENTION

The present invention is concerned with the production of chlorine dioxide from chlorate ions using hydrogen peroxide or methanol as the preferred reducing agents and, in particular, with the production of chlorine dioxide where the reaction medium is substantially free of sulfate ions and where the primary source of acidity is nitric acid.

BACKGROUND TO THE INVENTION

It is known to produce chlorine dioxide by reduction of an aqueous acid chlorate solution using various reducing agents, such as methanol, hydrogen peroxide and sulfur dioxide, wherein the acidity required for the chlorine dioxide generation reaction is supplied primarily by sulfuric acid. The process can be carried out either in the crystallizing mode, typically in a single vessel generator-evaporator-crystallizer at subatmospheric pressure with the sodium sulfate being precipitated from the reaction medium, or in a non-crystallizing mode where the conversion of chlorate takes place in at least one but typically two reaction vessels with the secondary vessel yielding a liquid acid effluent containing sulfuric acid and alkali metal sulfate along with unreacted chlorate and other by-products.

The single vessel sulfuric acid-based processes employing methanol as a reducing agent are described, for example, in US Patents 4,081,520 (Swindells et al), 4,473,540 (Fredette) and 4,770,868 (Norell), while the use of hydrogen peroxide as a reducing agent in chlorine dioxide generation is described, for example, in US Patents 5,091,166 (Engstrom et al), 5,091,167 (Engstrom et al) and 5,366,714 (Bigauskas).

One of the deficiencies of sulfuric acid based chlorine dioxide generators is a low production rate at

low acidities. The lower limit of acidity below which the reaction rate becomes commercially unacceptable is somewhat dependent on the type of reducing agent used. Typically an acidity of at least about 2 N sulfuric acid is required with the preferred acidity being at least about 4 N and at least about 5 N in the processes involving the use of hydrogen peroxide and methanol, respectively.

Another problem associated with the sulfuric acid based generators is the cost of disposal of excess saltcake by-product, especially in the case of non-crystallizing generators. There is a need, therefore, to provide a chlorine dioxide generation process operating at a very low acidity, preferably below about 2 N, without a co-production of saltcake by-product. While sulfate-free chlorine dioxide generators have been described in the prior art, none of them offers high efficiency and high production rate at low acidities (i.e., below about 2 N) without the necessity of a significant increase in the chlorate ion concentration.

US Patents 5,174,868 and 5,284,553 (Lipsztajn, et al) describe an operation involving the addition of chloric acid as a sole source of hydrogen ions whereby the high efficiency and production rate are achieved due to the presence of a dead load of sodium chlorate, resulting in the chlorate ion concentration in the reaction medium in the range of about 6 to about 9 M. An analogous process disclosed in US Patent 5,486,344 (Winters et al) requires a preferred range of chlorate ion concentration of from about 2 M up to about 5 M.

US Patent 5,523,072 (Falgen et al) teaches a sulfate-free process in which the acidity is provided by phosphoric acid. The latter process requires an acidity of above about 2 N and a preferred range of chlorate ion concentration above about 2 M. The aforementioned US Patent 5,366,714 (Bigauskas) teaches

both a sulfate-based and sulfate-free operation wherein the latter one involves the addition of a strong mineral acid, such as nitric acid, hydrochloric acid, perchloric acid or chloric acid. For a low acidity operation (below about 5 N), this patent suggests the use of a high concentration of chlorate ion, from about 2 M up to saturation, preferably about 3 to 4 M.

SUMMARY OF THE INVENTION

Surprisingly it has been found that by employing nitric acid as a source of acidity a sulfate-free chlorine dioxide generation process can be operated very efficiently and at a high production rate, even in the low acidity range (i.e. below about 2 N) and at low concentrations of chlorate (i.e. below about 3 M, preferably in the range of about 2 to 3 M). Chlorate concentrations higher than about 3 M may also be employed, especially in the process involving the use of methanol as a reducing agent. Such a combination of acidity and chlorate concentration has not been previously disclosed for a nitric acid based chlorine dioxide generation processes.

Accordingly, the present invention provides an improvement in a process for the production of chlorine dioxide by the reduction of chlorate ions in an aqueous acid reaction medium, the improvement being nitric acid providing the acidity to the reaction medium.

GENERAL DESCRIPTION OF INVENTION

As noted above, the present invention provides a chlorine dioxide generating process which utilizes nitric acid as a source of acidity for the process. Such a process has been found to be much less dependent on variations in acidity than other chlorine dioxide generating processes known in the art, thus enabling a very stable, continuous operation to be provided, which is less sensitive to the process upset conditions. In particular, the chlorine dioxide generating process may

be operated at low acid normalities below about 2 N, preferably about 0.5 to about 2 N.

The nitric acid based chlorine dioxide generating process provided herein can be performed both in a crystallizing and non-crystallizing mode at both atmospheric and sub-atmospheric pressures. When operating under subatmospheric conditions, which is the preferred mode of operation, the aqueous acid reaction medium generating the chlorine dioxide is maintained at its boiling point at a temperature of about 50 to about 90°C, preferably about 70 to about 80°C, while a subatmospheric pressure is applied to the reaction zone of about 80 to about 400 mmHg (about 11 to about 53 kPa), preferably about 100 to about 250 mmHg (about 13 to about 33 kPa).

When operating in a crystallizing mode, a by-product nitrate corresponding to the cation of the chlorate reactant is crystallized from the aqueous acid reaction medium in the reaction zone and is continuously or periodically removed therefrom. In the non-crystallizing mode of operation, an aqueous stream is continuously or periodically removed from the reaction zone for processing to remove by-product nitrate salt.

A wide selection from the known reducing agents for reduction of chlorate ions to generate chlorine dioxide can be employed in the process of the invention, with hydrogen peroxide and methanol being the preferred ones. A combination of several reducing agents also may be employed, if desired.

Chlorate ions reduced by the reducing agent to chlorine dioxide in the process of the invention may be provided by an alkali metal chlorate, usually sodium chlorate, although chloric acid and mixtures of chloric acid and alkali metal chlorate may be used. However, in contrast to the prior art processes (see, for example, US Patent 5,296,108 (Kaczur et al)), the

presence of chloric acid is not required in order to achieve high efficiencies at high production rates, when nitric acid is employed as a source of acidity, in accordance with the present invention. The concentration of chlorate ions in the aqueous acid reaction medium depends to some extent on the reducing agent employed. For example, when hydrogen peroxide is the reducing agent, the chlorate ion concentration is generally below about 3 M, preferably about 2 to 3 M. When methanol is employed as the reducing agents, higher chlorate concentration of up to about 4, preferably about 2 to about 3 M may be employed.

When operating the chlorine dioxide generating process in a single vessel generator-evaporator-crystallizer at subatmospheric pressures, it is possible to modify the process conditions used in the process of the invention so that the concentrations in the reaction medium remain below the saturation level with respect to both alkali metal chlorate and alkali metal nitrate.

In such a case it is preferred to continuously or periodically withdraw the reaction medium from the single vessel and to subject the withdrawn reaction medium to electrochemical acidification in the anodic compartment of an electrochemical cell, which enables the regeneration of acidity values and at the same time the co-production of alkali metal hydroxide, preferably sodium hydroxide, in the cathodic compartment of the electrochemical cell. The acidified product withdrawn from the anodic compartment can be recycled back to the chlorine dioxide producing reaction vessel.

Such an operation enables there to be achieved the minimization of the quantity of the externally added nitric acid. If desired, all the acidity requirements can be sustained by the acid regenerated in the electrochemical cell from effluent from the chlorine dioxide generator.

Any suitable electrochemical cell can be employed to effect such acidification, including a standard two-compartment cell equipped with a suitable separator, for example, a cation exchange membrane, or a three-compartment cell equipped with two cation exchange membranes. In the latter case, it is preferred to direct the reaction mixture exiting the chlorine dioxide generator into the central compartment of the cell while circulating any suitable mineral acid, for example, nitric acid, sulfuric acid or perchloric acid, in the anode compartment as an anolyte. Hydrogen ions generated in the anode compartment of the three-compartment cell, are transferred through the cation exchange membrane into the central compartment while alkali metal ions are transferred through the second cation exchange membrane from the central compartment into the cathode compartment. By effecting such a three-compartment operation, there is prevented an oxidation of the various components of the reaction medium removed from the chlorine dioxide generator, for example, chlorate ions, chloride ions, hydrogen peroxide, methanol and formic acid, at the anode of the electrochemical cell.

Alternative cell configurations involve the use of both anion and cation exchange membranes, as well as bipolar membranes.

Due to the very high solubility of alkali metal nitrates and the low acidity requirements in the chlorine dioxide generation step, a very high current efficiency for the electrochemical acidification process can be achieved. It is believed that this phenomenon can be attributed to a low concentration ratio of hydrogen ions to alkali metal ions in the acidified stream. The ratio of hydrogen ions to alkali metal ions generally may vary from about 1:100 to about 5:1, preferably about 1:30 to about 2:1.

When operating a subatmospheric type generator in a crystallizing mode for the generation of chlorine dioxide by the process of the invention, it is also possible to combine the chlorine dioxide generation process with the electrochemical acidification process. In such a case, the alkali metal nitrate crystals which precipitate as a by-product of the process and which are continuously or periodically removed from the generator, can be dissolved, optionally with alkali metal chlorate, and the resulting solution can be subjected to an electrochemical acidification step, using one of the electrochemical processes described above, and the resulting acidified solution can be directed to the generator. Such electrochemical acidification may be effected in a manner to coproduce an alkali metal hydroxide, preferably sodium hydroxide, in the electrochemical cell as described above.

The alkali metal nitrate is a high value by-product of the crystallizing mode of operation, which can be readily used, for example, as a nutrient for biological effluent treatment or as a fertilizer. When the alkali metal nitrate comprises sodium nitrate, a further conversion, for example, via metathesis, to other nitrates, for example, potassium nitrate or ammonium nitrate, is also possible.

When compared to the conventional sulfuric acid-based chlorine dioxide generating process, the nitric acid-based process of the present invention offers some additional advantages in terms of the composition of the crystalline by-product precipitated in the generator in the crystallizing mode of operation. While the conventional generators often co-produce an acidic sulfate, such as sodium sesquisulfate, having regard to the operating acid normality the process of the present invention always yields a neutral salt irrespective of the total acid normality of the reaction medium, thus minimizing the acid and alkali consumption. A neutral

by-product stream is also easier to handle due to the lower corrosiveness when compared to conventional procedures.

A non-crystallizing, atmospheric type nitric acid-based chlorine dioxide generation process can be operated in a single reaction vessel or in a multi vessel arrangement. In the latter case, the effluent from a primary reactor is directed to the secondary reactor enabling a further conversion of unreacted chlorate with an additional feed of the reducing agent. The acidity level in the secondary reactor may be increased, if desired, to higher values, typically up to about 7 N, preferably about 5 to about 7 N, in order to ensure a substantially complete conversion of chlorate ions, thus minimizing losses of chlorate with the effluent. The effluent from the primary or secondary reactor may also be directed (cascaded) to a single vessel subatmospheric type process. Alternatively, the effluent from the primary or secondary generator can be subjected to electrochemical acidification in the manner described in more detail above and recycled to the generator. It is possible, if desired, to effect hydrochloric acid addition to the secondary reactor in order to lower the residual chlorate ion concentration.

If desired, an effluent from the non-crystallizing chlorine dioxide generating process described above containing unreacted nitric acid and alkali metal nitrate may be used as a nutrient for biological effluent treatment or for pH control in the bleach plant of a pulp mill. Since essentially all nitrates are highly soluble, the use of nitric acid may be beneficial as compared to sulfuric acid due to the absence of scale forming deposits.

Both the crystallizing and non-crystallizing type nitric acid-based chlorine dioxide generation operations provided in accordance with the present

invention, can operate in the substantial absence of added chloride ions. However, small additions of chloride can be made, if desired.

The chlorine dioxide generating process provided herein can operate with the optional addition of a catalyst selected from the group of catalysts known in the art, such as those described in US Patent 4,421,730 (Isa et al) or US Patent 4,770,868 (Norell). Examples of typical catalytic ions which may be employed include Ag, Mn, V, Mo, Pd and Pt. While the premixing of the reducing agent (for example, hydrogen peroxide or methanol) with the other feedstocks to the generator can be employed, it is generally not required.

The above-mentioned embodiments of the process of the present invention involve the generation at either atmospheric or subatmospheric pressures. However, it is also possible to operate the process at super atmospheric pressures, especially in water treatment applications.

In some applications of the process of the present invention, it is possible to replace at least part of the nitric acid with another strong acid, for example, perchloric acid. However, in general, it is preferred to operate the process with nitric acid alone as the source of acidity for the process.

In a case when the entire nitric acid feed is replaced by a perchloric acid feed, it is possible to effect an integration of the chlorine dioxide generator with the sodium chlorate manufacturing plant.

The invention is illustrated by the following Example.

EXAMPLE

A subatmospheric pressure pilot plant chlorine dioxide generator had a maximum volume capacity of 20 L. The chlorine dioxide generator was operated to generate chlorine dioxide under the following conditions:

Reducing agent : hydrogen peroxide
Liquor Total [H^+] : 1.0 to 2.0 N
Liquor [ClO_3^-] : 1.0 to 2.0 M
Temperature : about 70°C
Pressure : about 165 mmHg (about 22 kPa)
Liquor (NO_3^-] : 7.9 to 8.9 M (crystallization of $NaNO_3$ observed).

Chemical feeds were made to the aqueous acid reaction medium (liquor) as the chlorine dioxide generator was operated on a continuous basis at the boiling point of the liquor under the subatmospheric pressure. The chemical feeds were:

70% w/w HNO_3 commercial, reagent grade solution

300 g/L H_2O_2 solution prepared from industrial grade 50% w/w H_2O_2.

6 M $NaClO_3$ solution prepared from crystallized, industrial grade $NaClO_3$

A gaseous mixture of chlorine dioxide, steam and oxygen was removed from the chlorine dioxide generator and an aqueous solution of chlorine dioxide formed from the gaseous mixture. The chemical efficiency of chlorine dioxide production based on gas analysis by gas chromatography, consumption of hydrogen peroxide and rates of chlorine dioxide generation were determined to be as follows:

Chemical efficiency : greater than 95%
H_2O_2 consumption : 0.25 to 0.3 t H_2O_2/t ClO_2
Rate of CLO_2 generation : 1.4 $g.min^{-1}L^{-1}$

As may be seen from these results, highly efficient chlorine dioxide generation is achieved at commercially acceptable production rates.

SUMMARY OF DISCLOSURE

In summary of this disclosure, the present invention provides a process for the production of chlorine dioxide in which chlorate ions are reduced in the presence of nitric acid as at least the primary

source of acidity for the process. Modifications are possible within the scope of this invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A process for the production of chlorine dioxide, which comprises reducing chlorate ions with hydrogen peroxide or methanol in an aqueous reaction medium, said aqueous reaction medium containing nitric acid, having a total acid normality of less than about 2 N and having a chlorate ion concentration of about 2 to about 3 M.

2. The process of claim 1 which is carried out in the substantial absence of sulfate ions.

3. The process of claim 1 or 2 wherein said aqueous acid reaction medium has a total acid normality of about 0.5 to about 2 N.

4. The process of any one of claims 1 to 3 wherein the chlorate ions in said aqueous acid reaction medium are selected from the group consisting of an alkali metal chlorate, chloric acid and a mixture of alkali metal chlorate and chloric acid.

5. The process of any one of claims 1 to 4 wherein said aqueous acid reaction medium is maintained at its boiling point in a reaction zone while a subatmospheric pressure is applied to the reaction zone.

6. The process of claim 5 wherein said reaction medium is maintained at a boiling point of about 50 to about 90°C while a subatmospheric pressure of about 80 to about 400 mmHg (about 11 to about 53 kPa) is applied to the reaction zone.

7. The process of claim 6 wherein said temperature is about 70 to about 80°C and said subatmospheric pressure is about 100 to about 250 mmHg (about 13 to about 33 kPa).

8. The process of any one of claims 1 to 7 wherein said aqueous acid reaction medium is continuously or periodically removed from the reaction zone, subjected to electrochemical acidification in an anodic compartment of an electrochemical cell to at least partially regenerate acidity values consumed in the chlorine dioxide generating process with the cogeneration of alkali metal hydroxide in a cathodic

compartment of the electrochemical cell, and the resulting acidified reaction medium is recycled back to the reaction zone.

9. The process of claim 8 wherein said electrochemical cell is a two-compartment cell wherein said anodic compartment and said cathodic compartment are separated by a cation-exchange membrane.

10. The process of claim 8 wherein said electrochemical cell is a three-compartment cell divided into an anode compartment, a central compartment and said cathodic compartment by two cation-exchange membranes, said removed aqueous acid reaction medium is fed to the central compartment and hydrogen ions generated in the anode compartment are transferred to the central compartment to effect said acidification.

11. The process of any one of claims 8 to 10 wherein the acidified reaction medium recycled to the reaction zone has a ratio of hydrogen ions to alkali metal ions of about 1:100 to about 5:1.

12. The process of claim 11 wherein the ratio of hydrogen ions to alkali metal ions is about 1:30 to about 2:1.

13. The process of any one of claims 1 to 7 wherein a by-product alkali metal nitrate is crystallized from the aqueous acid reaction medium in the reaction zone once saturation is reached after start up.

14. The process of claim 13 wherein said crystallized by-product alkali metal nitrate is continuously or periodically removed from the reaction zone, formed into an aqueous solution, subjected to electrochemical acidification in an anodic compartment of an electrochemical cell to at least partially regenerate acidity values consumed in the chloric dioxide generation process, and the resulting acid solution is recycled back to the reaction zone.

15. The process of claim 14 wherein alkali metal chlorate is added to said aqueous solution of alkali metal nitrate prior to said electrochemical acidification.

16. The process of any one of claims 1 to 7 which is carried out in a non-crystallizing mode of operation wherein aqueous effluent from a primary reaction zone is forwarded to a secondary reaction zone for a further reduction of chlorate unreacted in the primary reaction zone to chlorine dioxide with an additional feed of reducing agent to the secondary reaction zone.

17. The process of claim 16 wherein the aqueous acid reaction medium in the secondary reaction zone has a total acid normality of about 5 to about 7 N.

18. The process of any one of claims 1 to 17 wherein said alkali metal chlorate is sodium chlorate.

19. The process of any one of claims 1 to 18 which is carried out in the substantial absence of chloride ions.

20. The process of any one of claims 1 to 19 which is carried out in the presence of a catalyst for the chlorine dioxide generating reaction.

21. The process of claim 20 wherein said catalyst is selected from the group consisting of Ag, Mn, V, Mo, Pd and Pt.