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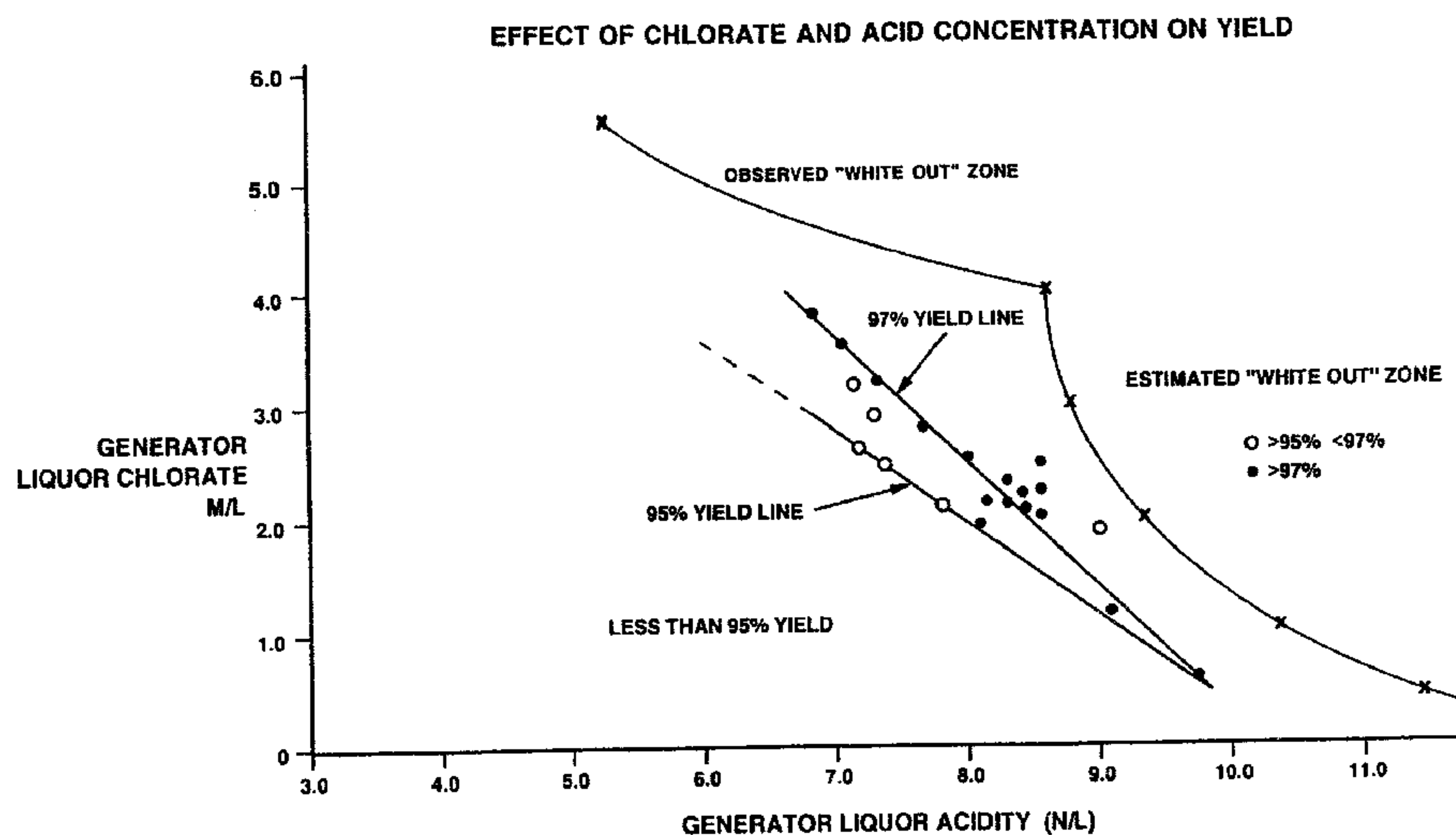
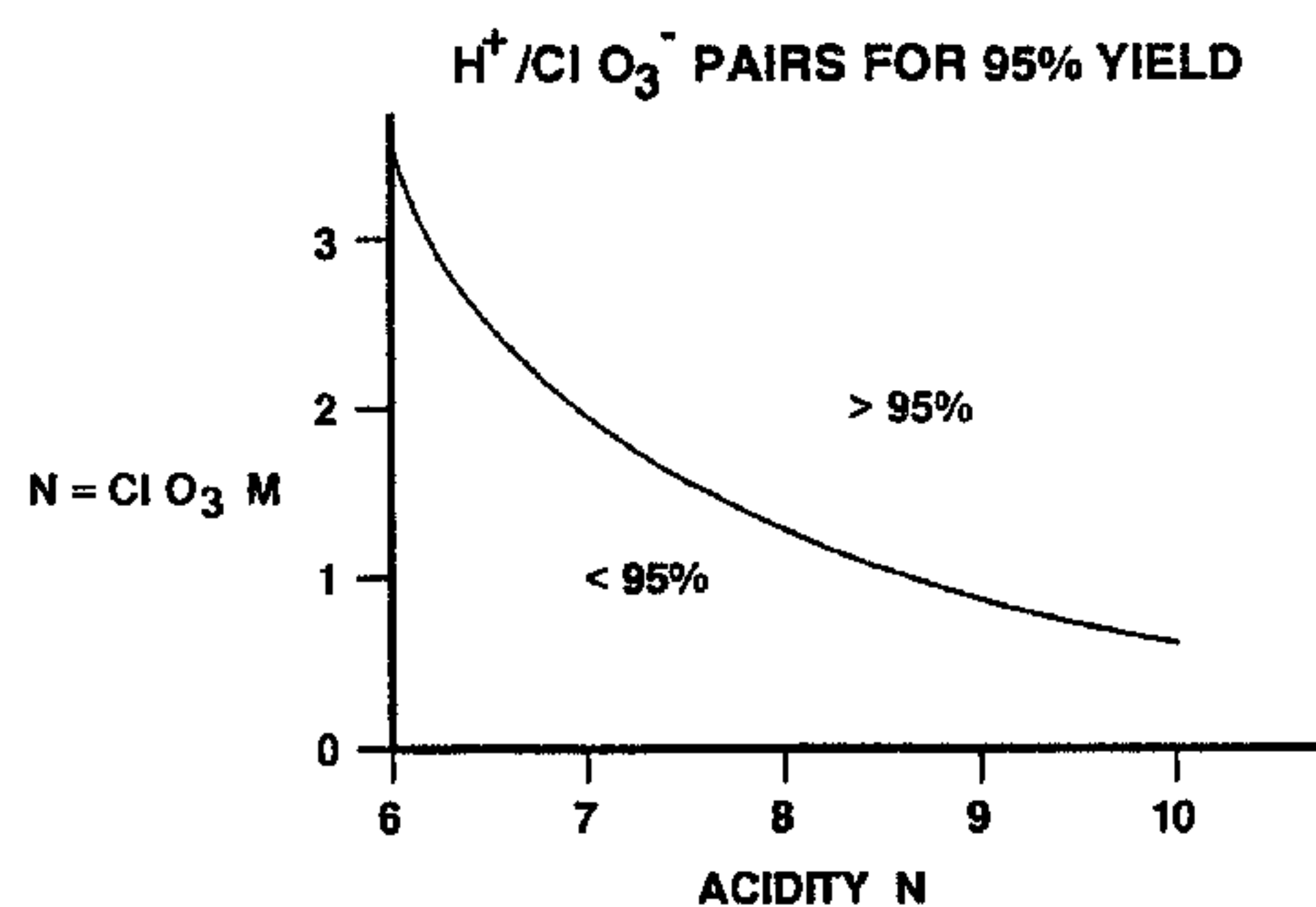
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(54) **PREPARATION DE DIOXYDE DE CHLORE A L'AIDE DE
METHANOL**

(54) **METHANOL-BASED CHLORINE DIOXIDE PROCESS**



(57) On produit le dioxyde de chlore de manière très économique en réduisant du chlorate de sodium à l'aide de méthanol dans un milieu réactionnel acide et aqueux et à une normalité d'acidité totale inférieure à 7, le milieu réactionnel étant à son point d'ébullition pendant qu'on

(57) Chlorine dioxide is produced at high efficiency by reduction of sodium chlorate with methanol in an aqueous acid reaction medium at a total acid normality below 7 with the reaction medium being at its boiling point while a subatmospheric pressure is applied thereto





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lui applique une pression subatmosphérique, et présentant une concentration de chlore d'au moins environ 2,0 molaire. Sous ces conditions, la susceptibilité de la réaction aux arrêts épisodiques de la production de chlore sans apport d'ions de chlorure est éliminée. On peut ainsi éliminer la teneur en chlore de la solution aqueuse de dioxyde de chlore provenant de cette source.

and having a chlorate concentration of at least about 2.0 molar. By employing such conditions, the tendency is eliminated for the reaction to be subject to white-outs in the absence of added chloride ion. In this way, the chlorine content of product aqueous chlorine dioxide solution arising from this source is eliminated.

ABSTRACT OF THE DISCLOSURE

Chlorine dioxide is produced at high efficiency by reduction of sodium chlorate with methanol in an aqueous acid reaction medium at a total acid normality
5 below 7 with the reaction medium being at its boiling point while a subatmospheric pressure is applied thereto and having a chlorate concentration of at least about 2.0 molar. By employing such conditions, the tendency is eliminated for the reaction to be subject
10 to white-outs in the absence of added chloride ion. In this way, the chlorine content of product aqueous chlorine dioxide solution arising from this source is eliminated.

METHANOL-BASED CHLORINE DIOXIDE PROCESS

The present invention is concerned with the production of chlorine dioxide, in particular to the production of chlorine dioxide using methanol.

5 It is known to produce chlorine dioxide by reduction of an acid aqueous sodium chlorate solution using methanol, as described in U.S. Patent No. 2,881,052. The process, however, is quite slow, involves the handling of a large volume of liquid effluent and the efficiency of
10 the process is quite low. More recently there issued U.S. Patent No. 4,081,520, assigned to the assignee hereof, wherein the problems of the prior process were overcome by the use of a single vessel generator-evaporator-crystallizer. The latter process operates at
15 high efficiency, produces no liquid effluent and has an acceptable production rate.

In the commercial implementation of the above-noted process, known commercially as the "R8" process, a periodic random complete loss of chlorine dioxide
20 production has been observed from time to time, known as "white-outs". This problem was overcome, in accordance with U.S. Patent No. 4,465,658 assigned to the applicant hereof, by the continuous addition of chloride ions to the reaction medium. By purposely adding them to the
25 reaction medium, the presence of chloride ions at all times is ensured and the possibility of white-outs is avoided.

The introduction of chloride ions in this way causes the formation of small amounts of chlorine along with the
30 chlorine dioxide and that chlorine becomes dissolved in the chlorine dioxide solution. The presence of such chlorine dissolved in the chlorine dioxide is undesirable to some pulp mills.

The prior art has described procedures for forming
35 chlorine dioxide from sodium chlorate, sulfuric acid and

methanol. None of this prior art addresses the problem of eliminating the chloride feed at acid normalities below 7 while maintaining high efficiency of chlorine dioxide production.

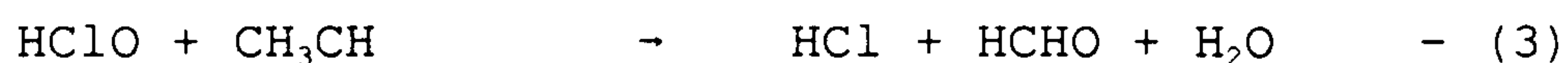
5 EP 357,198 describes a procedure in which chlorine dioxide is generated from sodium chlorate, methanol and sulfuric acid at high acidity in a reactor separate from a crystallizer/evaporator. This procedure permits chlorine dioxide generation also to be effected by
10 reaction of sodium chlorate, sodium chloride and sulfuric acid and production of neutral sodium sulfate in the crystallizer.

 EP 365,501 describes a procedure in which chlorine dioxide is produced from sodium chlorate, methanol and
15 sulfuric acid at a low acidity of 2 to 4.8 N, using certain catalytic agents to speed up the rate of reaction.

 EP 284,577 describes a procedure in which chlorine dioxide is produced from sodium chlorate, methanol and
20 sulfuric acid at a low acidity of 2 to 11 N, wherein the methanol is introduced to the crystallization zone of a cyclic reactor in order to minimize loss of methanol from the reactor in the chlorine dioxide product.

 It has been surprisingly been found that it is
25 possible to eliminate the need for a continuous feed of chloride ions to the reaction medium, so that chlorine resulting therefrom is eliminated from the aqueous chlorine dioxide solution, and yet there is provided a chlorine dioxide generating process which has a continued
30 high yield of chlorine dioxide without being susceptible to white-outs.

 The reactions involved in the production of chlorine dioxide in a methanol-based chlorine dioxide generating process can be represented, as follows:



As may be seen, reaction (1) consumes chloride ion while
5 reaction (3) replenishes it, so that the white-outs can
be controlled by controlling the speed of reaction (1)
relative to relation (3).

In addition, if HClO is produced by reaction (1)
much faster than it is consumed by reaction (3), then the
10 HClO can be lost by the competing reaction:



The present invention provides a novel methanol-
based chlorine dioxide generating process which is able
to satisfactorily operate at high efficiency without
15 white-outs occurring by utilizing a lower total acid
normality for the reaction medium below about 7 and a
chlorate ion concentration generally greater than about
2 molar.

Accordingly, in one aspect of the present invention,
20 there is provided a process for the production of
chlorine dioxide, comprising the combination of steps of
reducing chlorate ions with methanol in an aqueous
reaction medium containing sulphuric acid in a reaction
zone, in the substantial absence of chloride ions added
25 to the reaction medium; the reaction medium having a
total acid normality of from about 5 to less than 7
normal and containing at least about 2.0 molar
concentration of the chlorate ions, the total acid
normality and the molar concentration of chlorate ions in
30 the reaction medium being interrelated to produce
chlorine dioxide from the reaction medium at an
efficiency greater than about 90%; the chlorate ion
concentration being less than about 6.0 molar and no
greater than that which results in a periodic random loss
35 of production of chlorine dioxide from the reaction

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medium; maintaining the reaction medium at its boiling point at a reaction temperature of at least about 60°C while a subatmospheric pressure of about 100 to 300 mm Hg is applied thereto; removing chlorine dioxide from the reaction zone in gaseous admixture with steam; and depositing a by-product acid sulphate in the reaction zone.

In another aspect, the present invention provides a continuous process for the production of chlorine dioxide at an efficiency of at least about 90%, which comprises continuously feeding an aqueous solution of sodium chlorate to a reaction zone containing an aqueous acid chlorine dioxide-generating reaction medium to provide a concentration of sodium chlorate in the reaction medium of at least about 2.0 molar and below about 6 molar and less than that which results in a periodic random loss of production of chlorine dioxide from the reaction medium; continuously feeding sulphuric acid to the reaction medium to provide a total acid normality of from about 5 to below 7 normal in the reaction medium; the continuous feeds of sodium chlorate solution and sulphuric acid being controlled to provide the total acid normality and the sodium chlorate concentration in the reaction medium interrelated to produce chlorine dioxide from the reaction medium at an efficiency of at least about 90%; continuously feeding methanol to the reaction medium in sufficient quantity to effect formation of chlorine dioxide from the reaction medium; continuously maintaining the reaction medium at its boiling point at a temperature of at least about 60°C while a subatmospheric pressure of about 100 to about 300 mm Hg is applied to the reaction zone, continuously withdrawing a gaseous admixture comprising chlorine dioxide and steam from the reaction zone; and continuously depositing sodium sesquisulphate from the

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reaction medium in the reaction zone after the reaction medium becomes saturated thereby after the initial start-up of the process.

In the description which follows, reference is made to the accompanying drawings, in which:

Figure 1 is a schematic flow sheet of a chlorine dioxide generating process provided in accordance with one embodiment of the invention;

Figure 2 is a graphical representation of laboratory data obtained under varying conditions to produce chlorine dioxide; and

Figure 3 is a graphical representation of pulp mill data obtained under varying conditions to produce chlorine dioxide.

As discussed above, the mechanism whereby chlorine dioxide is produced in a methanol-based chlorine dioxide generating process involves three inter-related chemical reactions as well as a fourth competing reaction. The effects of variations of the operating parameters of the process, including reactant concentrations, on the different chemical reactions is unknown and somewhat unpredictable.

As noted above, control of white-outs is achieved by controlling the speed of reactions (1) and (3). So long as reaction (1), which consumes chloride ions, does not exceed reaction (3), which produces chloride ion, then a white-out condition cannot occur. It would appear obvious that lower acidity as well as lower chlorate would slow down reaction (1).

However, using lower or the same chlorate concentration tends to decrease the efficiency as the acidity is decreased. We have discovered that, using lower acidity and higher chlorate still slows down reaction (1) sufficiently that a white-out condition is not experienced in the absence of added chloride and, at

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the same time, high efficiencies of chlorine dioxide production are maintained. Nevertheless, there is an upper level of chlorate concentration at which a white-out condition can still be achieved and hence preferably
5 is avoided.

Accordingly, in the process of the present invention, aqueous chlorate solution is reduced with methanol in the presence of sulfuric acid at total acid normality below about 7 normal and at a chlorate ion
10 concentration above about 2.0 to obtain chlorine dioxide at an efficiency greater than about 90%. In contrast, such efficiencies are obtained in the R8

process at total acid normality greater than 9 normal and a chlorate ion concentrate of about 1 molar.

The aqueous reaction medium is maintained at its boiling point while an appropriate subatmospheric pressure is applied to the reaction zone. The reaction medium usually is maintained at a reaction temperature of at least about 60°C, preferably about 65° to about 80°C. The pressure applied to the reaction zone generally ranges from about 100 to about 300 mm Hg, preferably about 120 to about 200 mm Hg, the actual pressure depending on the reaction temperature.

It may be desirable to provide an air purge to the reaction zone to maintain a low partial pressure of chlorine dioxide in the product gas stream, preferably below about 90 mm Hg.

The aqueous acid reaction medium in the present invention has a total acid normality below about 7 normal, preferably down to about 5 normal, and a chlorate concentration of at least about 2.0 molar, preferably about 3.0 to about 4.0 molar. The chlorate concentration and total acid normality are inter-related to maintain an efficiency of chlorine dioxide production (i.e. the percentage of 1 mole of chlorate which is converted to chlorine dioxide) of at least about 90%, preferably at least about 95%. For example, at a total acid normality of just below about 7 normal, a chlorate ion concentration of about 2.5 molar is required to maintain an efficiency greater than 95%, while the same efficiency is maintained at a total acid normality of about 6 normal and a chlorate ion concentration of about 3.5 molar.

The chlorate ion concentration should not be sufficiently high that a white-out condition is induced by depletion of chloride ions from the reaction medium by operation of reaction (1). The actual upper limit of chlorate ion concentration depends on the other operating parameters and is readily determined.

Generally, the chlorate ion concentration does not exceed about 6.0 molar.

The chlorate employed in the process of the present invention usually is sodium chlorate, but other
5 alkali metal chlorates may be used. The presence of the sodium ions combined with the presence of sulfuric acid results in the formation of by-product sodium sulfate, which builds up in concentration after start up, until it saturates the reaction medium and
10 crystallizes in the generator. The form of the sodium sulfate precipitated depends on the total acid normality of the reaction medium, but generally comprises sodium sesquisulfate i.e. $\text{Na}_3\text{H}(\text{SO}_4)_2$ (or $\text{NaHSO}_4 \cdot \text{Na}_2\text{SO}_4$).

15 By operating under the lower acidity and higher chlorate concentration conditions outlined herein, not only is the necessity for a continuous chloride feed eliminated, so that chlorine arising from this source is eliminated from product chlorine dioxide solution,
20 but the chemical efficiency of chlorine dioxide production is maintained at a high level. In addition, chlorine dioxide production at commercially-acceptable rates is maintained.

Methanol is fed to the reaction medium as the
25 reducing agent for the chlorate and produces chlorine dioxide in accordance with reaction (2). The location of introduction of methanol to the reactor is not critical to the process. When operating under the conditions of the invention, most conveniently the
30 methanol may be introduced to the recycle loop, i.e. following the sodium sesquisulfate crystallization zone in the chlorine dioxide generating reaction zone and prior to the reboiler.

Methanol consumption generally does not exceed
35 about 0.2 tons per ton of chlorine dioxide produced, and is preferably in the range of about 0.13 to about 0.16 tons per ton of chlorine dioxide produced.

DESCRIPTION OF PREFERRED EMBODIMENT

Referring to the drawings, a chlorine dioxide generator unit 10 has an evaporator-crystallizer vessel 12 which has an upper outlet 14 for recovery of product chlorine dioxide from the unit 10. The chlorine dioxide product is removed as a gaseous admixture with steam produced by evaporation of the reaction medium in the vessel 12 and may contain some chlorine, depending on the efficiency of chlorine dioxide production. The vessel 12 is subjected to subatmospheric pressure to maintain the reaction medium therein at the boiling point. The subatmospheric pressure applied to the reaction zone generally ranges from about 100 to about 300 mm Hg, preferably about 120 to about 200 mm Hg. The product gas stream in line 14 is processed to form an aqueous solution of chlorine dioxide for subsequent use, such as in pulp mill bleaching.

A slurry of crystallized by-product sodium sulphate in spent reaction medium is removed from the vessel by pipe 16, is passed by line 17 to a filter 18 for removal of the solid phase and the mother liquor is returned by line 19 to the recycle pipe 16. The by-product solid phase sodium sulphate recovered in line 20 usually takes the form of sodium sesquisulphate.

Sodium chlorate is fed to the recycle pipe 16 by line 22 to make up for sodium chlorate consumed in the process. Sodium chlorate is fed as an aqueous solution thereof to said recycle pipe 16, generally having a concentration of about 3 to about 7.5 molar, preferably about 5 to about 6.5 molar.

Feed of the make-up sodium chlorate solution produces a recycle solution generally having a concentration of sodium chlorate of at least about 2 molar preferably about 2.5 to about 4.0 molar. The concentration of sodium chlorate in the reaction medium is co-ordinated with the total acid normality of the reaction medium, so as to obtain an efficiency of

chlorine dioxide production of at least about 90%, preferably at least about 95%.

Methanol is fed to the recycle stream by line 23 in the vicinity of the base of the recycle loop in an amount
5 sufficient to effect generation of chlorine dioxide from the reactants.

The recycle mixture then is pumped through a reboiler 24 by pump 26 to a venturi 28. The recycle mixture is heated by the reboiler 24 to the reaction
10 temperature generally in the range of about 60° to about 90°C, preferably about 65° to about 80°C.

The upstream side of the venturi 28 converges towards the throat 30 and exerts a back pressure on the recycle stream which prevents the mixture from boiling in
15 the reboiler 24.

At the throat 30, sulphuric acid is fed by line 32 into the recycle stream. As a result of the feed of the sulfuric acid, chlorine dioxide is generated and passes along with spent reaction medium through pipe 36 back to
20 the vessel 12.

The sulphuric acid generally is fed by line 32 as concentrated acid to the venturi throat 30, preferably of concentration from about 30 to about 36 normal. Sulphuric acid is fed to the venturi throat 30 at a flow
25 rate sufficient to establish the desired total acid normality of reaction medium in the generator 12, generally about 5 to about 7 normal.

In contrast to the procedure described in U.S. Patent No. 4,465,658, there is no deliberate feed of
30 chloride ions to the reaction medium in the generator 12 and no white-out condition is experienced provided that the chlorate ion concentration is maintained below certain concentrations, generally below about 6 molar.

The invention is illustrated by the following
35 Examples:

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Example 1

A nominal 10 L volume ClO_2 generation was operated at 125 mm Hg absolute at an average of 7.48 N acidity

and 2.06 M NaClO₃, with a boiling temperature of 66°C. Feeds of H₂SO₄, NaClO₃, and CH₃OH were metered in to produce about 15g per minute of ClO₂. A total of 24.3 moles ClO₂ were made from 25.4 moles of NaClO₃ consumed
5 for an apparent yield of 95.6%.

The total Cl atoms fed in vs found as ClO₂ or Cl₂ gave 103.1%. The corrected yield is

$$\frac{95.6}{103.1} \times 100\% = 92.7\%.$$

10 This compares well to the ratio of ClO₂ to Cl₂ produced which indicates 93.7% reaction efficiency.

The above conditions employed in this Example which are not within the scope of this invention, can produce >90% yield but not the preferred 95+% yield.

15 Example 2

A similar run was performed at 125 mm Hg and 66°C boiling point but at an average of 6.47 N acidity and 2.62 M NaClO₃. The yield was 95.2% based on 23.8 moles of ClO₂ made. Thus, the conditions employed in this
20 example, which are within the scope of this invention, can produce >95% yield.

Example 3

The data from many runs in the same equipment as used in Examples 1 and 2 and generally at approximately
25 125 mm Hg and approximately 67°C were plotted to give the pairs of H⁺/ClO₃⁻ required for >95% yield, as seen in Figure 2.

Example 4

A commercial plant of 30 TPD capacity was operated
30 at 25 TPD while varying the acidity from 9 down to 6 normal and while varying the chlorate concentration from 1 up to 4 M. The data was plotted in a similar manner to Example 3 above with additional data plotted on an estimated and observed white-out range. The
35 pressure was kept at 120 mm Hg with the reaction medium boiling at about 70°C. The methanol was fed to the

venturi at the exit of the reboiler. The data is presented in Figure 3.

The above Examples show how acidities at or below 7 N can still give acceptable yields by using chlorate concentrations that are at least 2 M and preferably at least 2.5 M. White-outs can be avoided by using chlorate concentrations that are below 6 M, preferably below 4 M.

In summary of this disclosure, the present invention provides a novel chlorine dioxide generating process based on methanol which eliminates the necessity for a chloride feed to avoid white-outs by using a total acid normality below 7 normal combined with a chlorate concentration of at least about 2.0 molar at efficiency levels greater than 90%. 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, comprising the combination of steps of:

reducing chlorate ions with methanol in an aqueous reaction medium containing sulphuric acid in a reaction zone, in the substantial absence of chloride ions added to said reaction medium;

said reaction medium having a total acid normality of from about 5 to less than 7 normal and containing at least about 2.0 molar concentration of said chlorate ions, said total acid normality and said molar concentration of chlorate ions in said reaction medium being interrelated to produce chlorine dioxide from said reaction medium at an efficiency greater than about 90%; said chlorate ion concentration being less than about 6.0 molar and no greater than that which results in a periodic random loss of production of chlorine dioxide from the reaction medium;

maintaining said reaction medium at its boiling point at a reaction temperature of at least about 60°C while a subatmospheric pressure of about 100 to 300 mm Hg is applied thereto;

removing chlorine dioxide from said reaction zone in gaseous admixture with steam; and

depositing a by-product acid sulphate in the reaction zone.

2. The process of claim 1 wherein said concentration of chlorate ions is sufficient to form chlorine dioxide at an efficiency of at least about 95%.

3. The process of claim 2 wherein said reaction medium has a chlorate ion concentration of 3.0 to 4.0 molar.

4. The process of claim 2 wherein said subatmospheric pressure is about 120 to about 200 mm Hg.

5. The process of claim 4 wherein said reaction temperature is from about 65°C to about 80°C.
6. The process of claim 1, 2, 3, 4 or 5 wherein said chlorate ions are provided by sodium chlorate.
7. The process of claim 6 wherein methanol is fed to said reaction medium in an amount that does not exceed about 0.2 tons per ton of chlorine dioxide produced.
8. The process of claim 7 wherein methanol is fed to said reaction medium in an amount of 0.13 to 0.16 tons per ton of chlorine dioxide produced.
9. A continuous process for the production of chlorine dioxide at an efficiency of at least about 90%, which comprises:

continuously feeding an aqueous solution of sodium chlorate to a reaction zone containing an aqueous acid chlorine dioxide-generating reaction medium to provide a concentration of sodium chlorate in the reaction medium of at least about 2.0 molar and below about 6 molar and less than that which results in a periodic random loss of production of chlorine dioxide from said reaction medium;

continuously feeding sulphuric acid to the reaction medium to provide a total acid normality of from about 5 to below 7 normal in said reaction medium;

said continuous feeds of sodium chlorate solution and sulphuric acid being controlled to provide said total acid normality and said sodium chlorate concentration in said reaction medium interrelated to produce chlorine dioxide from said reaction medium at an efficiency of at least about 90%;

continuously feeding methanol to said reaction medium in sufficient quantity to effect formation of chlorine dioxide from said reaction medium;

continuously maintaining said reaction medium at its boiling point at a temperature of at least about 60°C while a subatmospheric pressure of about 100 to about 300

mm Hg is applied to the reaction zone, continuously withdrawing a gaseous admixture comprising chlorine dioxide and steam from said reaction zone; and

continuously depositing sodium sesquisulphate from said reaction medium in said reaction zone after the reaction medium becomes saturated thereby after the initial start-up of the process.

10. The process of claim 9 wherein said sodium chlorate concentration is maintained within the range of about 2.5 to about 4.0 molar.

11. The process of claim 9 wherein said reaction medium has a temperature of about 65° to about 80°C.

12. The process of claim 9 wherein said subatmospheric pressure is maintained in the range of about 120 to about 200 mm Hg.

13. The process of claim 9 wherein an air purge is provided to said reaction zone to provide a partial pressure of chlorine dioxide in said gaseous admixture below about 90 mm Hg.

14. The process of claim 9 wherein said sodium sesquisulphate is removed from the reaction zone in a slurry with spent reaction medium, said sodium sesquisulphate is separated from said spent reaction medium, said sodium chlorate and methanol are added to said spent reaction medium, the resulting recycle stream is heated to its boiling point and said sulphuric acid thereafter is fed thereto.

15. The process of claim 14 wherein said methanol is fed to said spent reaction medium at a location following said reaction zone and prior to said heating of said resulting recycle stream to its boiling point.

16. The process of claim 9 which is effected in the substantial absence of chloride ions added to said reaction medium.

17. The process of claim 9, 10, 11, 12, 13, 14, 15 or 16 wherein methanol is fed to said reaction medium in an amount that does not exceed about 0.2 tons per ton of chlorine dioxide produced.

18. The process of claim 17 wherein methanol is fed to said reaction medium in an amount of about 0.13 to about 0.16 tons per ton of chlorine dioxide produced.

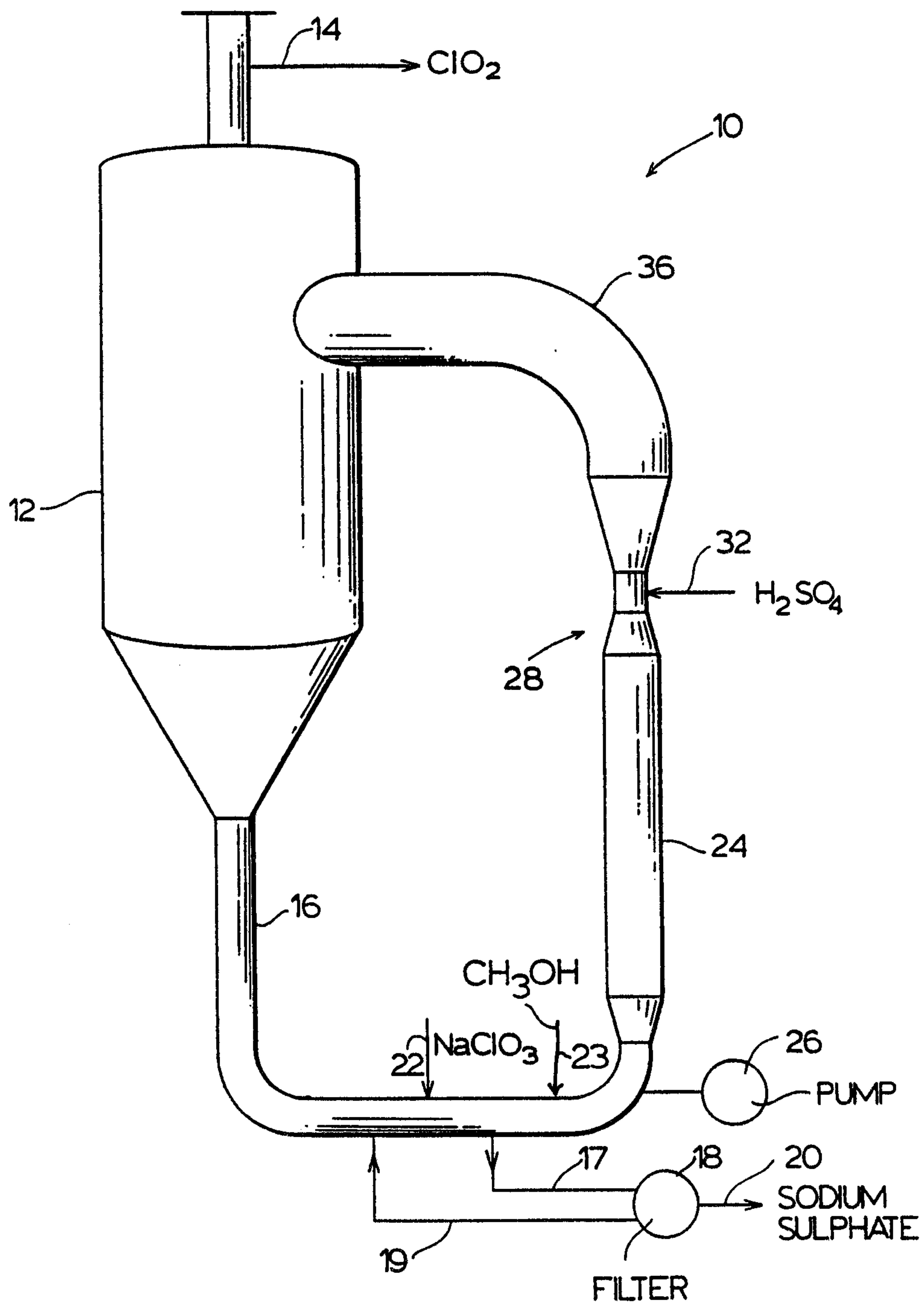
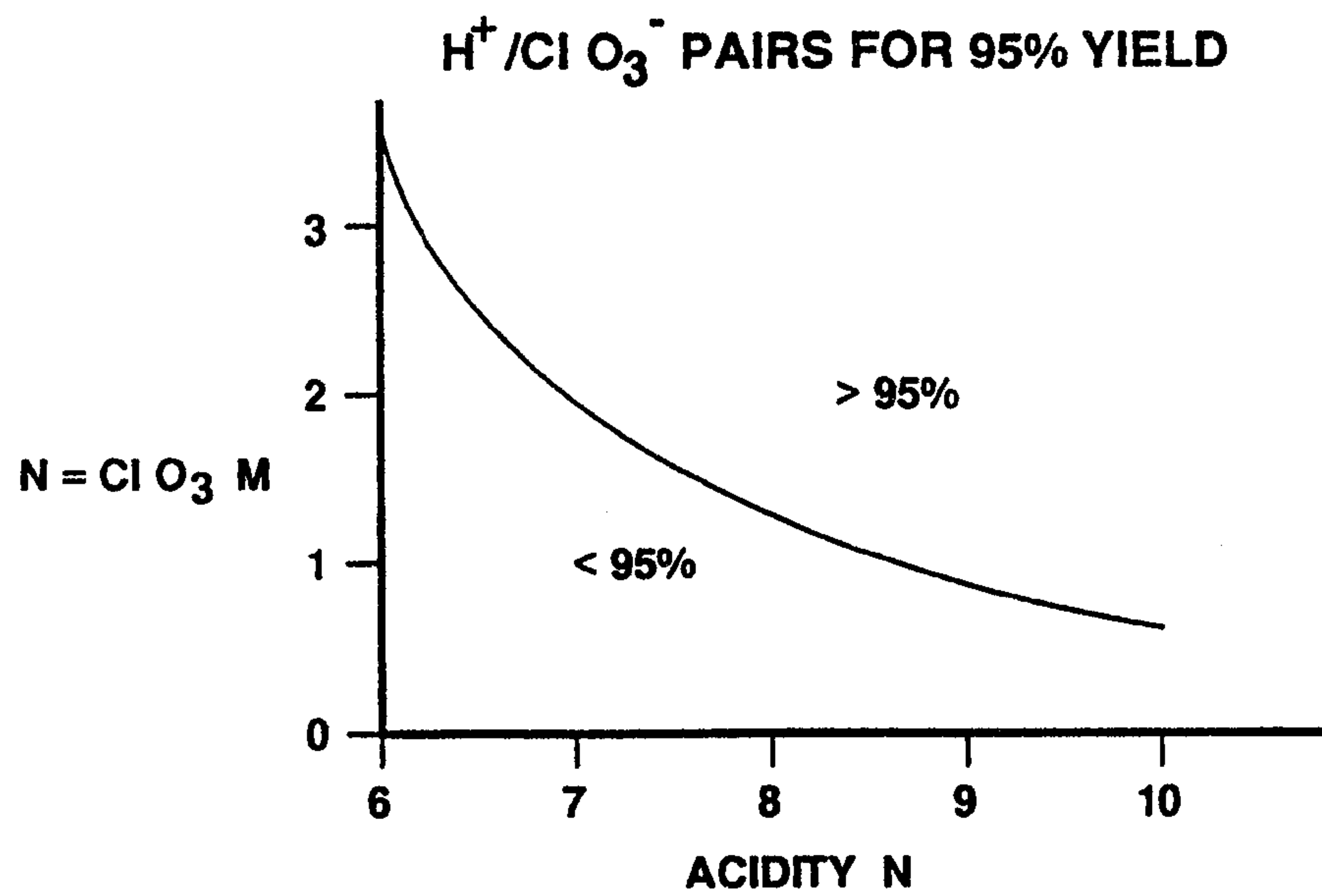


FIG. 1

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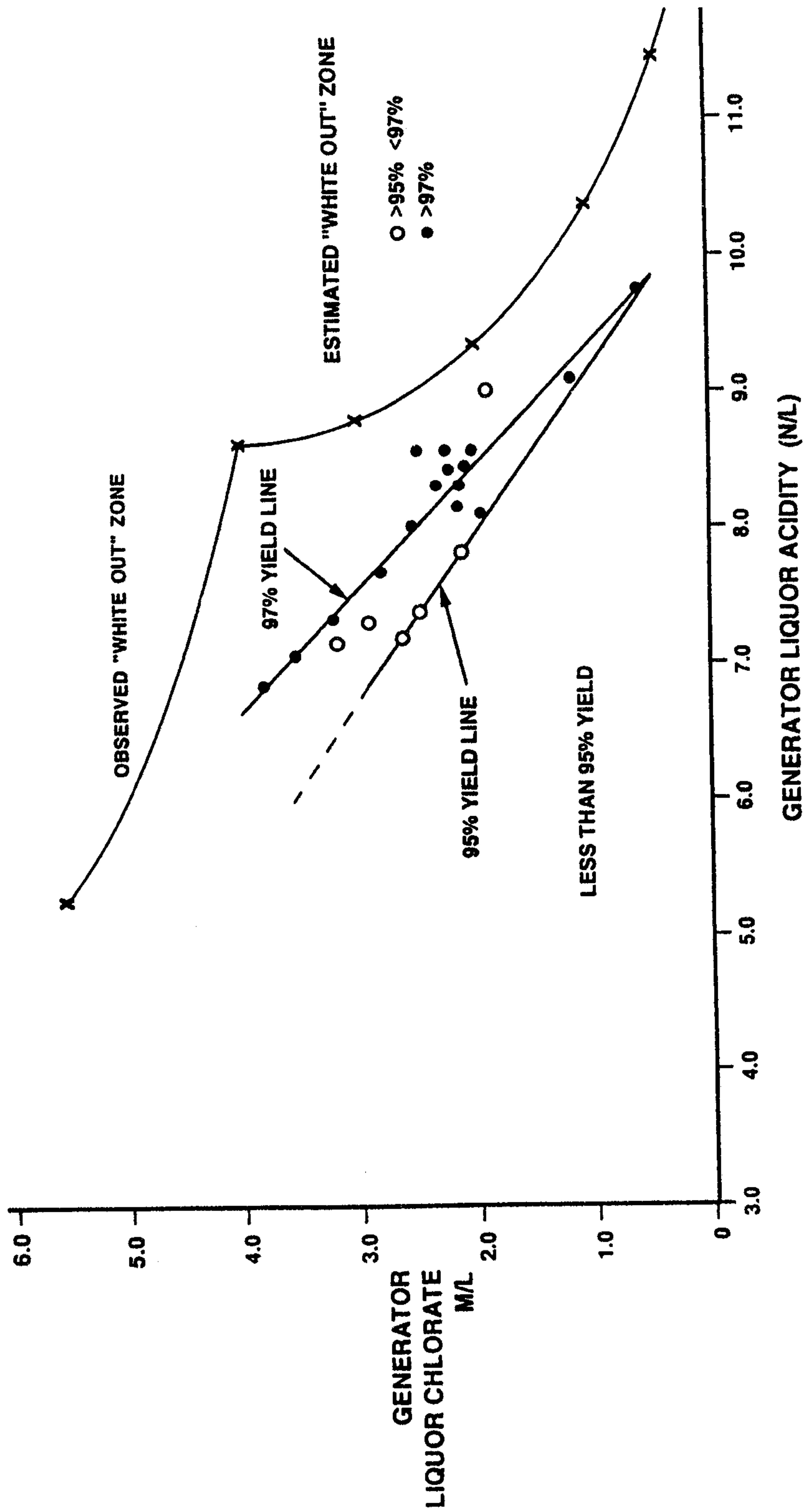
FIG. 2



Sim; M. Bunn

FIG. 3

EFFECT OF CHLORATE AND ACID CONCENTRATION ON YIELD



Sim: M. Baum