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(54) Title: CHLORINE DIOXIDE GENERATION

(57) Abstract: Disclosed herein is an improved method for generating chlorine dioxide that involves reacting a diluted, chilled aqueous solution of sulfuric acid with an aqueous solution of sodium chlorite.



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CHLORINE DIOXIDE GENERATION BACKGROUND OF THE INVENTION

Related Applications

This application claims priority to U. S. Serial No. 61/173,442 filed April 28, 2009, which is incorporated herein in its entirety.

Field of the Invention

[01] The present invention relates to the generation of chlorine dioxide and more particularly relates to an improved method of chlorine dioxide generation wherein the resultant conversion of chlorite to chlorine dioxide is of an efficiency previously unknown for the specific reactants using a two chemical system employing sulfuric acid/sodium chlorite, and in which the precursors can be retained in the reactor for a prolonged time before dilution without loss of chlorine dioxide by reaction with water to form chlorate, as has been reported when hydrochloric acid is used as the proton donor.

General Background

[02] Chlorine dioxide is a powerful oxidant and disinfectant. Applications for chlorine dioxide cover a wide spectrum from disinfection of foods and drinking water, treatment of process water, odor control, zebra mussel eradication, Anthrax destruction, disinfection of medical waste, wastewater treatment, and oil- and injection water well stimulation, paper pulp bleaching, and fabric bleaching.

[03] Chlorine dioxide is not available for purchase or may not be readily available for every application in which it might be used. In certain situations, regulatory and economic limitations suggest that the chlorine dioxide cannot be shipped, but instead must be generated on site at the time of use. The need for generation has spawned a variety of processes in which a relatively small group of precursors are combined in different ways. These can be broken down into groups depending on the precursor and the method of conversion.

[04] Two generally indispensable precursors around which many chlorine dioxide generation methods are built are sodium chlorate, NaClO_3 , and sodium chlorite, NaClO_2 . Sodium chlorate is the less expensive of the two and, as such, has become the precursor of

choice for the paper industry, which uses chlorine dioxide daily in tonnage quantities to bleach and delignify paper pulp, as well as for applications such as wet-end biological control on paper machines. Lowering chemical costs justifies the investment in corrosion resistant, operator-controlled titanium machinery suit to carry-out acidic chlorate conversion. There is a commercially available small-scale, three-chemical method for chlorate conversion U.S. Pat. No. 6,790,427, which is hereby incorporated by reference in its entirety. The method teaches the combination of concentrated sulfuric acid, and a proprietary mix of sodium chlorate and hydrogen peroxide to convert the chlorate to chlorine dioxide.

[05] Other known generation methods employ sodium chlorite, despite its higher cost, because of the relative ease of conversion. Conversion methods can be categorized as one chemical, two chemical, and three chemical, each of which offers a specific advantage. One chemical method includes electrolytic oxidation of chlorite anion, and exposure to ultraviolet light. Current electrolytic methods can generate hundreds of pounds of chlorine dioxide per day, whereas ultraviolet methods are useful in cases where a few pounds per day are adequate.

[06] In view of the shortcomings of the prior art, it would be desirable to have an improved method of generating chlorine dioxide using two precursor chemicals that may result in high conversion rates, be able to be carried-out in situ, when necessary, and be conducted in a scaleable manner, to meet the needs of large users of ClO_2 , such as paper mills, and small users such as private water treatment facilities.

[07] Further, many acid-chlorite methods are known. Such methods that employ hydrochloric acid are known to yield no greater than a theoretical 80% conversion rate of the chlorite used into chlorine dioxide, with practical yields closer to 70%. Diluted (9-15%, by weight) hydrochloric acid is commonly used as the acid in the generation of chlorine dioxide from chlorite. Concentrated sulfuric acid cannot be combined directly with chlorite, as it reacts too violently and generates a significant amount of heat, which lends to volatilization of produced chlorine dioxide and possible damage to plastic generation equipment.

[08] It would, therefore, be desirable to have a method which employs 'dilute sulfuric acid' in the generation of chlorine dioxide and results in higher conversion efficiencies than were previously known for this chemistry with little or no conversion of generated chlorine

dioxide to chlorate even with prolonged residence time in the reactor. This increase in conversion efficiency would result in obvious economic advantages over previously known methods.

SUMMARY OF THE INVENTION

[09] The present invention provides an improved method of generating chlorine dioxide using two precursor chemicals. The inventive embodiments described herein build on the work that was described in U.S. Patent No. 7,407,642. Through additional experimentation, the inventors have discovered that use of concentrations of sulfuric acid previously thought to be unsafe and unworkable can actually be implemented in a safe manner to achieve higher yields of chlorine dioxide. In particular, the inventors have determined that concentrations of sulfuric acid higher than 50 percent by weight can be reacted with Sodium chlorite solutions of between 7.5 to 20 percent by weight. In one embodiment, a volume of sulfuric acid at 55-75 percent by weight is combined in a reaction chamber with a volume of aqueous sodium chlorite at 7.5-20 percent by weight and allowed to react for a predetermined period of time. In a more specific embodiment, a volume of 60-67 percent, by weight, sulfuric acid is reacted with a volume of 7.5-15 percent, by weight, sodium chlorite. The volumes may be in ratios from 0.1-10.0:10-0.1. In more specific embodiments, the ratio of volumes is 1-10:10-1, 1-5:5-1, 1-2:2-1, 1-1.5:1.5-1 or 1:1.

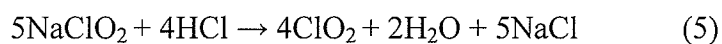
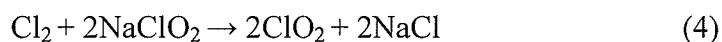
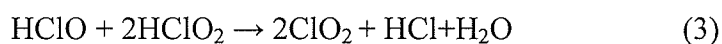
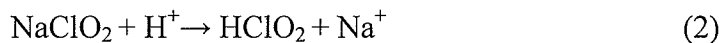
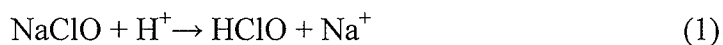
[010] In an illustrative embodiment of the invention, it has been found that by first diluting the concentrated sulfuric acid with water to 55-75 wt.% acid and then allowing the hot acid solution to cool, the resulting acid may be safely combined directly with sodium chlorite to yield chlorine dioxide in a reaction which is ~80% efficient. This results in a number of unexpected advantages over prior art acid-chlorite systems.

[011] In an illustrative embodiment, the present invention relates to the use of 'dilute sulfuric acid' in the generation of chlorine dioxide, resulting in higher conversion rates than would be expected for this chemistry when used with prior-art methods. Further, generation according to the present invention produces ClO_2 with little or no conversion of generated chlorine dioxide to chlorate even with prolonged residence time in the reactor as occurs when hydrochloric acid two chemical generation methods are employed.

DETAILED DISCLOSURE

[012] The subject invention is directed to novel methods for chlorine dioxide generation. In one embodiment, the present methods may utilize a dilute sulfuric acid solution and a sodium chlorite solution as the sole constituents in the generation process.

[013] Two exemplary chemical chlorite conversion methods include two very different reaction routes with different theoretical conversion efficiencies. One method involves combination of chlorite with an oxidizing agent, most commonly aqueous or molecular chlorine, and the other method uses simple acidification to effect conversion. The former has a theoretical conversion efficiency of 100% (equations 3 and 4), whereas the theoretical efficiency of the latter is 80% (equation 5). In practice, actual efficiencies maximize at 95-98%, and 65-75%, respectively.



[014] Of the many methods for chlorine dioxide generation, preparation by mixing acid and chlorite is widely used because of its simplicity and the long-term chemical stability of the two most commonly used precursors, aqueous sodium chlorite and hydrochloric acid. Typical commercially available technology employs 7.5% sodium chlorite and 9% hydrochloric acid (equation 5). These precursors may be pumped into a reaction chamber in the proper proportions and the mix is allowed to remain in concentrated contact for a period of time long enough to give the relatively slow conversion reaction time to take place before being

discharged into the dilution water which carries the chlorine dioxide solution to the point of injection. Pumping rates are adjusted to whatever rate is needed to make the required quantity of chlorine dioxide.

[015] Hydrochloric acid is almost universally used as the acid because chloride ion is believed to be a catalyst for this conversion. The reaction has the disadvantage of producing only four molecules of chlorine dioxide for five reacting chlorite ions (equation 5), but the positive aspects of this method in terms of safety and reliability make it attractive and widely used nonetheless.

[016] While the preceding method has attractive advantages which have given it wide use, there is a fundamental disadvantage which must be considered. The conversion of chlorite to chlorine dioxide first of all occurs with a loss of 20% of the chlorite consumed because of the chemistry involved. This loss is considered acceptable in light of the ease of the method. Properly generated, the conversion efficiency should be 80%; that is every five chlorite ions should generate four chlorine dioxide molecules. This is normally not the case in actual practice. A competitive reaction occurs which reduces the quantity of generated chlorine dioxide.

[017] Acid/chlorite chlorine dioxide generation is not instantaneous, but rather requires the precursors be in concentrated contact for about 1-3 minutes. The reactants are normally retained in the reaction chamber for the period of time necessary to effect this conversion before injection in dilution water. During precursor conversion, at the very high concentration of chlorine dioxide present in the reactor, chlorine dioxide will react with water to form chlorate and reduce the actual yield by whatever amount is lost as chlorate (reference 1)



[018] The reactor is therefore sized for a specific pumping rate to allow complete conversion with the minimum of loss as chlorate. If pumping rates are below those used for reactor sizing, then precursors and generated chlorine dioxide remain in the reaction zone

longer, and more loss of chlorine dioxide to chlorate formation occurs. The reactor volume could then be a compromise between large enough to allow high volume generation, but small enough to limit chlorine dioxide loss at low pumping rates, or if the generator is to be used to produce a constant amount of chlorine dioxide, the reactor will be sized for maximum conversion at the desired rate.

[019] Almost no known commercially available acid/chlorite process uses sulfuric acid as the proton donor. There are several reasons for this lack. First, the chemistry of sulfuric acid conversion is reported to give only 50% conversion of chlorite to chlorine dioxide (equation 7). While chloride is a by-product of this reaction and would be expected to catalyze conversion and change the chemistry to that yielding 80% conversion, the concentration of by-product chloride is apparently insufficient to effect significant catalysis in the brief time the reactants would remain in the reaction chamber before injection into dilution water.



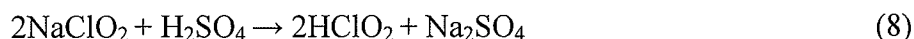
[020] The other reason sulfuric acid is not normally used in chlorite conversion is the difficulty in working with concentrated sulfuric acid, which generates much heat of solution on contact with water and would make the conversion reaction difficult to control and possibly cause thermal damage to the generation equipment, or even explosions. However, the inventors have discovered that controlling the ratios of sulfuric acid and sodium chlorite used, sulfuric acid can be used in a safe manner to produce a surprising yield of chlorine dioxide. The inventors have realized that, when the reaction is controlled, the heat produced actually serves to drive the process in the small three-chemical acid/peroxide/chlorate method referenced above to encourage conversion of the relatively inert chlorate in to chlorine dioxide. The single known European use of sulfuric acid conversion is with the intent of eliminating chloride ion from the final product.

[021] The presently disclosed invention sets forth novel acid/chlorite chemistry using sulfuric acid which has been shown by analysis to produce 75-80% conversion of sodium chlorite to chlorine- and chlorite-free chlorine dioxide.

[022] In the present invention, a solution of 7.5-20%, and all integers in between, aqueous sodium chlorite is combined with previously diluted and cooled 55-70% wt. percent, and all integers in between, aqueous sulfuric acid and allowed to remain in contact for from about 5 to about 300 seconds, although preferable from about 30 seconds to about 60 seconds before injection into dilution water. Four-step iodometric titration (reference 2) has shown the product to be chlorine- and chlorite ion-free, with the conversion ranging from 75 to 80% of theoretical. Thus, the method produces a higher yield of high quality chlorine dioxide than previously described for sulfuric acid chlorite conversion.

[023] In a specific embodiment, a volume of 7.5-15 wt. percent, (and all integers in between) sodium chloride is combined with a volume of 60-67 wt. percent (and all integers in between) aqueous sulfuric acid to produce chlorine dioxide. In a more specific embodiment, 64-66 wt. percent aqueous sulfuric acid is used.

[024] A route by which this conversion could take place is by the chlorite first converting to chlorous acid, and then in the highly concentrated environment, the chlorous acid converts to chlorine dioxide in a manner analogous to that which occurs in the hydrochloric acid/chlorite conversion, where 5 chlorous acids yield 4 chlorine dioxide molecules, with one chlorous acid reverting to chloride (equation 9).



[025] Examples are listed in Tables 1 and 2. The ratio of titration 'B' (titrant volume indicating chlorite ion concentration) to titration 'A' (titrant volume indicating chlorine dioxide concentration) is noted as B:A column. Ideal conversion should give a ratio of 4.0 since each chlorine dioxide in step A of the titration produces one chlorite anion, and each produced chlorite anion when acidified in step B reacts with four times the volume of titrant than does chlorine dioxide.

[026] The table also shows that low yields are produced if insufficient acid is employed, but once the proper ratio is achieved, the conversion efficiency is relatively insensitive to the presence of excess sulfuric acid, as well as the residence time in the reactor, where prolonged residence time might be expected to lead to chlorine dioxide loss by reaction with water to form chlorate as it does in the hydrochloric acid/chlorite generators. This decay mechanism apparently does not occur in sulfuric acid/chlorite generation chemistry. Samples have been retained in the reactor for up to 15 minutes without significant loss of chlorine dioxide. In one series of experiments, equivalent volumes of 7.5% sodium chlorite and 64.8% sulfuric acid were reacted for 1, 5, and 15 minutes before dilution. Analysis showed the chlorine dioxide produced in these three experiments to be 37.8, 37.8, and 35.0 ppm, respectively, showing almost no loss when residence time was increased by a factor of 15. This means the reactor used can be fairly large and therefore can accommodate more precursors without product loss, allowing for the scaling up of the generator to higher capacities than typical of chlorite/hydrochloric acid generators.

[027] A number of methods exist to measure or quantify chlorine dioxide in solution. The standard accepted practice to quantify chlorine dioxide is the use of a four step iodometric titration. Table 3 illustrates the yield obtained by reacting 7.5-10% sodium chlorite solutions with various concentrations of sulfuric acid in which the conversion of chlorite to chlorine dioxide exceeds 85%, and in some cases is in excess of 100%. While it is not possible to obtain yields in excess of 100%, no analytical methods are currently available to disprove this conversion of chlorite to chlorine dioxide approaching 100% using these concentrations of sodium chlorite.

[028] The use of chlorine dioxide as a disinfectant and oxidant is widely accepted throughout the world. The present invention teaches a method that offers significant performance and economic advantages over known methods to make the generation of chlorine dioxide more practical for a wide range of applications.

[029] One embodiment of the subject invention is directed to the addition of the cooled diluted sulfuric acid to a sodium chlorite solution.

[030] In the preferred embodiment, the combination of the dilute sulfuric acid with the sodium chlorite solution is carried out in a reaction vessel with a discharge opening into a treatment stream so that the reactants are not diluted until the reaction is complete.

Table 1

Sulfuric acid %wt	Sodium chloride %wt	Time (sec)	1		2		3		AVE		ppm A	ppm B	B:A	% Yield ₁
			A	B	A	B	A	B						
64.8	20	3.0	146	562	134	551	147	548	142	554	136	132	3.89	63
		30.0	159	590	156	591	172	639	162	607	155	145	3.74	72
		60.0	162	626	170	657	167	555	166	613	158	146	3.68	74
		100.0	191	697	167	646	170	637	176	660	168	157	3.75	78
		200.0	167	624	162	619	160	622	163	622	155	148	3.81	72
		300.0	157	606	186	680	167	641	170	642	162	153	3.78	75
		600.0	163	578	165	617	151	573	160	589	152	140	3.69	71
64.8	15	3.0	119	482	119	446	128	535	122	488	116	116	4.00	74
		30.0	131	446	120	480	149	493	133	473	127	113	3.55	80
		60.0	158	568	174	610	144	574	159	584	151	139	3.68	96
		100.0	139	519	154	559	134	425	142	501	136	119	3.52	86
		200.0	150	554	151	552	143	542	148	549	141	131	3.71	89
		300.0	149	536	147	531	142	500	146	522	139	124	3.58	88
		600.0	136	504	137	523	133	513	135	513	129	122	3.79	82
64.8	10	3.0	95	441	100	436	86	434	94	437	89	104	4.67	87
		30.0	113	434	111	438	112	435	112	436	107	104	3.89	104
		60.0	112	418	114	433	113	415	113	422	108	101	3.73	105
		100.0	112	436	112	423	107	406	110	422	105	100	3.82	102
		200.0	110	410	104	395	116	441	110	415	105	99	3.78	102
		300.0	111	412	116	445	111	419	113	425	107	101	3.78	104
		600.0	114	423	99	381	117	332	110	379	105	90	3.44	102
64.8	7.5	3.0	79	381	69	386	81	390	76	386	73	92	5.05	96
		30.0	93	366	100	367	100	378	98	370	93	88	3.79	122
		60.0	105	377	97	359	94	362	99	366	94	87	3.71	124
		300.0	93	351	98	324	96	341	96	339	91	81	3.54	120

Table 2

Sulfuric acid %/wt	Sodium chlorite %/wt	Time (sec)	Titration 1		Titration 2		Titration 3		AVE		ppm A	ppm B	B:A	% Yield 1
			A	B	A	B	A	B						
17	20	300.0	110	538	109	558	112	542	110	546	105	130	4.95	49
17	15	300.0	88	438	93	504	91	500	91	481	86	114	5.30	55
17	10	300.0	63	399	59	420	60	421	61	413	58	98	6.81	56
17	7.5	300.0	55	374	58	350	53	370	55	365	53	87	6.59	69
31.5	7.5	300.0	82	325	81	324	86	327	83	325	79	77	3.92	104
44.1	7.5	300.0	90	319	89	334	94	348	91	334	87	79	3.67	114
55.1	15.0	3.0	83	643	76	626	88	647	82	639	78	152	7.76	50
55.1	15.0	300.0	122	483	134	502	123	581	126	515	120	123	4.08	76
55.1	7.5	3.0	46	455	50	447	55	450	50	451	48	107	8.95	63
55.1	7.5	300.0	86	339	89	335	78	306	84	327	80	78	3.87	106
73.4	15.0	3.0	explodes											
73.4	10.0	3.0	114	410	103	412	121	430	113	417	107	99	3.70	104
73.4	7.5	3.0	100	372	118	352	102	391	107	372	102	89	3.48	134

Claims

1. A two chemical conversion method for preparing chlorine dioxide, comprising: reacting a 7.5-25 weight % aqueous sodium chlorite solution with a 55-75 weight % aqueous sulfuric acid in a reaction chamber sized to allow the aqueous sodium chlorite solution and the aqueous sulfuric acid to react for about 5 seconds to about 300 seconds to form a reaction mixture comprising chlorine dioxide in which 75% or more chlorite ion in the sodium chlorite solution is converted to chlorine dioxide.
2. The method of claim 1, wherein the reaction mixture comprising chlorine dioxide in which more than 85% of chlorite ion in the sodium chlorite solution is converted to chlorine dioxide when concentrations of aqueous sodium chlorite solution are used comprising a 7.5-10 weight %.
3. The method of claim 1, further comprising: diluting a concentrated sulfuric acid with water to 55-75% by weight and cooling the diluted aqueous sulfuric acid to remove heat of reaction and using the cooled 55-75% by weight aqueous sulfuric acid in the reacting step.
4. The method of claim 1, wherein the aqueous sodium chlorite solution and the aqueous sulfuric acid are contacted for about 30 seconds to about 60 seconds.
5. The method of claim 1, wherein a prolonged time of storage of the reaction mixture prior to diluting the reaction mixture with water does not result in a significant loss of the produced chlorine dioxide by reaction with water to form chlorate.
6. A method for generating chlorine dioxide, comprising: introducing an aqueous sodium chlorite solution and an aqueous sulfuric acid separately into a reactor as sole constituents, and reacting the aqueous sodium chlorite with the aqueous sulfuric acid to form a reaction mixture by converting 75% or more and 85% or less of chlorite ions to chlorine dioxide, wherein the aqueous sodium chlorite solution has a concentration in the range of 7.5-25% by weight, and the aqueous sulfuric acid has a concentration in the range of 55-75% by weight.

7. The method of claim 6, further comprising storing the reaction mixture in the reactor for about 1 to 15 minutes without a significant conversion of the chlorine dioxide to chlorate.
8. The method of claim 6, wherein the reaction mixture is substantially chlorine and chlorite free.
9. The method of claim 6, wherein the reactor has a discharge opening which communicates with a treatment stream, and the reaction mixture is not diluted until the reaction is complete.
10. The method of claim 6, further comprising: diluting a concentrated sulfuric acid to 55-75% by weight with water and cooling the diluted aqueous sulfuric acid to remove heat of reaction and using the cooled 55-75% by weight aqueous sulfuric acid in the reacting step.
11. The method of claim 1, further comprising discharging the reaction mixture from the reactor via a discharge opening of the reactor to a treatment stream.
12. The method of claim 3, wherein the concentrated sulfuric acid is diluted with water to approximately 55-75% by weight and cooled.
13. The method of claim 1, wherein the aqueous sulfuric acid has a concentration of approximately 65% by weight.
14. The method of claim 1, wherein the percent conversion of chlorite ion to chlorine dioxide is determined by four step iodometric titration.
15. A method for preparing chlorine dioxide, comprising: reacting a 7.5-25 weight % aqueous sodium chlorite solution with a 55-75 weight % aqueous sulfuric acid solution as constituents in a reactor for 5 to 300 seconds to obtain a reaction mixture in which at least 75 % of chlorite ion in the aqueous sodium chlorite solution is converted to chlorine dioxide.

16. The method of claim 15, wherein the lower concentrations of sodium chlorite (7.5-10%) result in a reaction mixture in which more than 85% of chlorite ion in the aqueous sodium chlorite solution is converted to chlorine dioxide.
17. The method of 15, further comprising: diluting a concentrated sulfuric acid to approximately 65% by weight aqueous sulfuric acid solution and cooling the aqueous sulfuric acid solution and using the resulting cooled, diluted sulfuric acid in the reacting step.
18. The method of 15, further comprising storing the reaction mixture in the reactor for about 1 to 15 minutes without a significant conversion of the chlorine dioxide to chlorate.
19. The method of 15, further comprising discharging the reaction mixture to a treatment stream via a discharge opening of the reactor.
20. The method of claim 15, wherein at least 84% of the chlorite ion is converted to the chlorine dioxide in the reaction mixture.
21. The method of claim 17, further comprising discharging the reaction mixture from the reactor via a discharge opening of the reactor to a treatment stream.
22. The method of claim 1, wherein volumes of the sodium chlorite solution respective to the sulfuric acid solution are provided according to a ratio of about 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 or 2:2, 1.9, 1.8, 1.7, 1.6, 1.5, 1.4, 1.3, 1.2, 1.1, or 1.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 09/53275

A. CLASSIFICATION OF SUBJECT MATTER

IPC(8) - C01B 11/02 (2009.01)
USPC - 423/477

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)
USPC - 423/477

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 423/477 (words only)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
WEST (PGPB, USPT, USOC, EPAB, JPAB); Google
Chlorine dioxide, sodium chlorite, sulfuric acid, wt, weight, chlorine, chlorite free, cool, cooled, cooling, discharge, react, reactor, and aqueous

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2007/0212292 A1 (Mussari et al.) 13 September 2007 (13.09.2007); para [0002], [0011], [0013], [0019], [0022]-[0023], [0025]-Table 1, [0026], and [0029]	1-22
Y	US 2003/0003015 A1 (Roensch et al.) 02 January 2003 (02.01.2003); para [0062]	1-22

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