

An Evaluation of an Electrolytic Process for the Removal of Ammonia and Urea from Simulated Spa Water

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A bromine based electrolysis unit was evaluated and compared to chlorine, bromine and ozone addition for urea and ammonia removal in simulated spa water. Systems were evaluated with respect to each other using a test referred to as "total oxidants" by determining DPD reactive materials, a general measure of several oxidants including chlorine, chloramines, bromine, bromamines, ozone and others. Results of the experiments using Cl₂, O₃, Br₂ addition and the electrolytic cell were compared by calculating the ratio of oxidants added or produced, i.e., mass of bromine or chlorine as DPD reactive materials to ammonia or urea loss. Total oxidants formed by the electrolysis unit were determined by measuring accumulation in control systems with no urea or ammonia present. Ammonia and urea removal in the electrolytic unit significantly exceeded that measured in the equivalent chlorine system or with ozone, and averaged higher than that determined in the equivalent bromine system. The addition of ozone did not result in a significant loss of ammonia or urea. Results indicate that oxidants produced by the electrolytic cell are more efficient at removing urea and ammonia than chlorine, ozone and bromine systems alone.

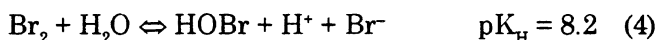
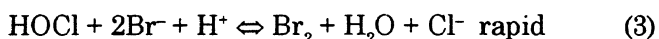
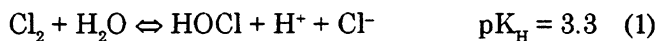
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Introduction

Bromine has been shown to be a more effective disinfectant than chlorine. The increased disinfection effectiveness of un-ionized bromine "species" is due to the different ionization characteristics between the aqueous bromine and chlorine solutions. At any given pH, HOBr [$pK_a = 8.7$, Reaction (5)] ionizes tenfold less than HOCl [$pK_a = 7.3$, Reaction (2)]. The relative high concentration of the un-ionized bromine species at a near neutral pH makes the bromine system much more effective. Typical chlorine and bromine reactions involved in disinfection chemistry are listed below.



Additionally, both HOCl and HOBr can react with ammonia to form mono-, di-, and tri-haloamines. If chlorine is added in sufficient quantity to a system containing ammonia and the proper pH range (6 to 9) is maintained, "breakpoint" chlori-

nation can occur (Appendix A). In the process of "breakpoint" chlorination, the ammonia is converted to haloamines and eventually to nitrogen gas and some other minor nitrogen species. There is also ample evidence in the literature that bromamines will undergo "breakpoint" bromination to ultimately form nitrogen gas. The process of "breakpoint" chlorination has been used extensively for the oxidation of ammonia in wastewater.

The BioQuest system uses a saline solution (NaCl and NaBr) in an electrolysis process for the production of bromine for disinfection of spa waters. Chlorine is produced in the electrolysis cell and quickly reacts with bromide ion to produce bromine (Reaction 3). There is a strong possibility that additional oxidants are also produced in the electrolysis process. If additional oxidants are produced, "breakpoint" bromination in combination with other oxidants may destroy nitrogen (ammonia and/or urea) containing compounds with less bromine. A search of the literature has provided little information on this possibility. Other electrolytic type processes (NaCl solution), evaluated in our laboratory, have produced an "oxidizing environment" well in excess of the chlorine produced.

Objectives

The primary objective of the project was to evaluate the effectiveness of the electrolytic cell for the destruction of ammonia and urea in simulated spa water. Using the electrolytic cell process, "super-bromination" may not be required, yet achieve ammonia and/or urea oxidation and the desired level of bromination for effective spa disinfection. The secondary objective was to compare the electrolytic cell process with other classical disinfection techniques.

Methods

Experimental Methods

The electrolytic cell, bromine, chlorine and ozone were each evaluated for their ability to remove ammonia and urea in simulated spa water. The ammonia and urea loss was evaluated in separate experiments that were monitored for temperature, pH, total oxidants and urea or ammonia. Each oxidant was measured twice in triplicate runs, one set of triplicates for ammonia and another for urea. Results from each experimental condition (i.e. ammonia spiked simulated spa water treated with chlorine) were then reported as the average amount of total oxidants as chlorine (mg/L as Cl_2) required per unit urea or ammonia (mg/L as N) removed.

Experiments with the electrolysis unit were performed with 15 L of solution in 20 L Nalgene tubs. The Nalgene tubs, tubing, tub heaters; electrolytic cells and control units were provided by BioQuest. Chlorination and bromination procedures were per-

formed in 2 L glass flasks with 1 L of solution and heated in a circulating hot water bath. Both the plastic tubs and flasks were constantly stirred during the experimental runs.

For the chlorine/bromine experiments, chlorine and bromine stock solutions were added at appropriate intervals to match the total oxidant production by electrolytic cells at a setting of "5". This resulted in doses of chlorine or bromine added to match the production of oxidants in the electrolytic cell. Chlorine or bromine was added every 30 minutes to match the total oxidant production of the cells as determined in the electrolysis unit controls with no urea or ammonia. Total length of the experiments was typically four hours.

Ozone was generated using an O_3 Associates ozone generator attached to an AirSep Model AS-12 oxygen generator. Previous experiments had determined that this unit produces between 1500 and 1800 mg ozone/min. Ozone experiments were performed with test solutions in an ice bath to optimize transfer of generated ozone into solution. Simulated spa water was used except NaCl and NaBr were not added to the solution. Due to the lack of ammonia or urea loss under these conditions for ozone, studies were limited to preliminary experiments.

Reagents

To create a water chemistry representative of spa water; 0.168 g NaHCO_3 , 0.168 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 0.221 g CaCl_2 were added to one liter of tap water to obtain a solution with the following characteristics: alkalinity \approx 100 mg/L as CaCO_3 , calcium \approx 150 mg/L as CaCO_3 and magnesium \approx 65 mg/L as CaCO_3 . With the exception of ozone, all experiments were run at a temperature between 38 and 41°C with 1.5 g NaCl added per liter. Cell systems also contained an 0.10 g NaBr per liter. Standardized stock solutions of chlorine and bromine were used for chlorine and bromine addition respectively. All cell systems were run at setting "5" except where noted. Bromine and chlorine sources included Guardex® brominating tablets (referred to as bromine tablets), bromine water (Fisher Scientific) and a sodium hypochlorite solution (Clorox®).

Analytical Methods

All systems were monitored for pH and temperature using probes and meters. Total oxidants were analyzed using Hach® DPD Total Chlorine reagents following a modified Method 4500-Cl G from Standard Methods for the Examination of Water and Wastewater (1998). Ammonia was measured using a modified Indophenol Method also found in Standard Methods for the Examination of Water and Wastewater (1998). A modified Diacetyl Monoxime Method from Clinical Chemistry, Principles and Techniques

(1974) was used to measure urea. Extensive preliminary method development was required to verify method accuracy, matrix effects and/or interferences from the residual oxidants in the spiked simulated spa water.

The total oxidant procedure measured DPD reactive materials, a general measure of several oxidants including chlorine, chloramines, bromine, bromamines, ozone and other oxidants. This method was chosen because of the inclusive nature of the reaction with most oxidants, ease and widespread application to the spa sanitation methods being studied. Limitations regarding measurement of some bromine species and other radicals generated by the elec-

trollysis units should be considered when reviewing the data.

Colorimetric DPD response was calibrated to chlorine, so results presented are as chlorine (mg-Cl₂/L). All urea and ammonia results are reported as nitrogen (mg-N/L).

Results

Electrolytic Cell

Prior to determining the loss of urea or ammonia in the electrolytic cell, the production of DPD reactive oxidants (total oxidants) was determined for

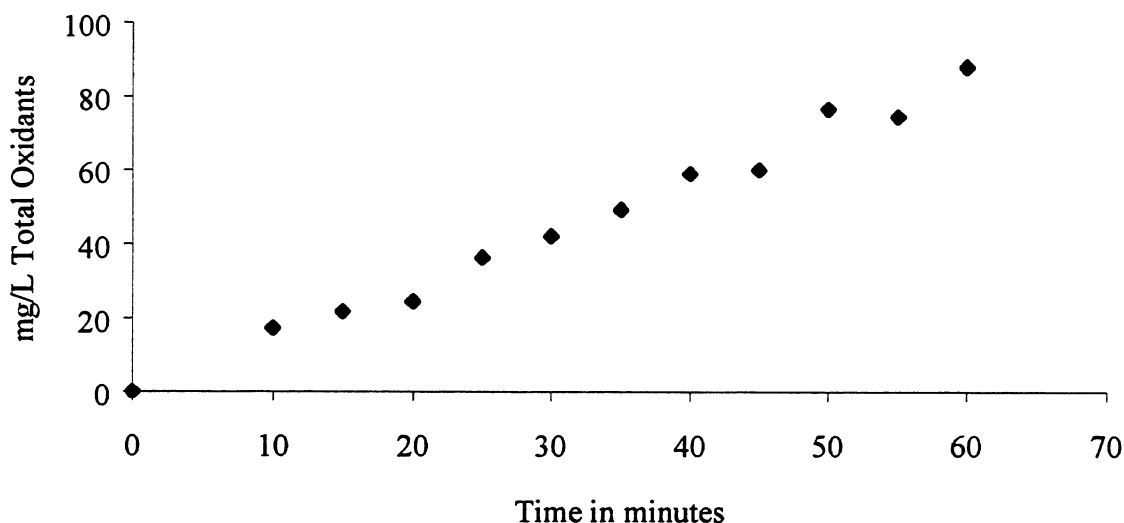


Figure 1 – Concentration of total oxidants versus time in electrolysis unit treated solutions set on “Blast”. The control system contained no urea or ammonia.

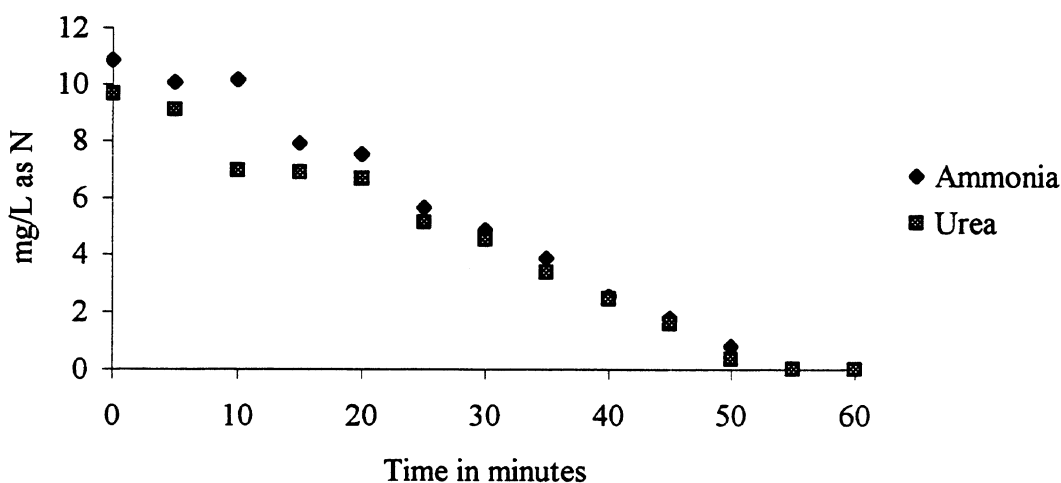


Figure 2 – Ammonia and urea concentration (as N) versus time in electrolysis unit treated solutions set on “Blast” (continuous operation of the cell). The total oxidant concentration remained under 6 mg/L in the presence of urea or ammonia.

control systems with no ammonia or urea. Initial studies using the "Blast" setting, (the cell continuously functioning), resulted in a rate of total oxidant production of 1.4 mg/L-min (Figure 1).

Decreases of ammonia and urea were observed in individual experiments using the electrolysis unit set on "Blast" (Figure 2). The loss of ammonia and urea was comparable to a zero order rate with a ratio of total oxidants produced to ammonia or urea removed of 7.8 and 6.4 respectively.

Total oxidant production rates for the electrolysis unit at setting "5" and "Blast" were similar when rates were based on actual cell on time. The average rate for total oxidant production, using the simulated spa water and no ammonia or urea (control) at a setting of "5", was 0.16 mg/L-min (Figure 3). When this

rate is corrected for the amount of time the cell was actually running (3.3 minutes per 30 minutes), the unit produced 1.4 mg/L for each minute of cell operation, a rate similar to that observed using the "Blast" mode.

Ammonia and urea loss was determined in the electrolysis unit at a setting of "5" (Figures 4 and 5). The loss of ammonia or urea was slower than that measured at the "Blast" setting (continuous operation), presumably due to the reduced "on time" for the cell (3.3 minutes every 30 minutes).

In the electrolysis unit treated solutions without urea or ammonia, the produced oxidants accumulated, reaching a concentration over 80 mg/L (Figure 1). The accumulation of residual total oxidants was reduced in electrolysis unit reactors containing

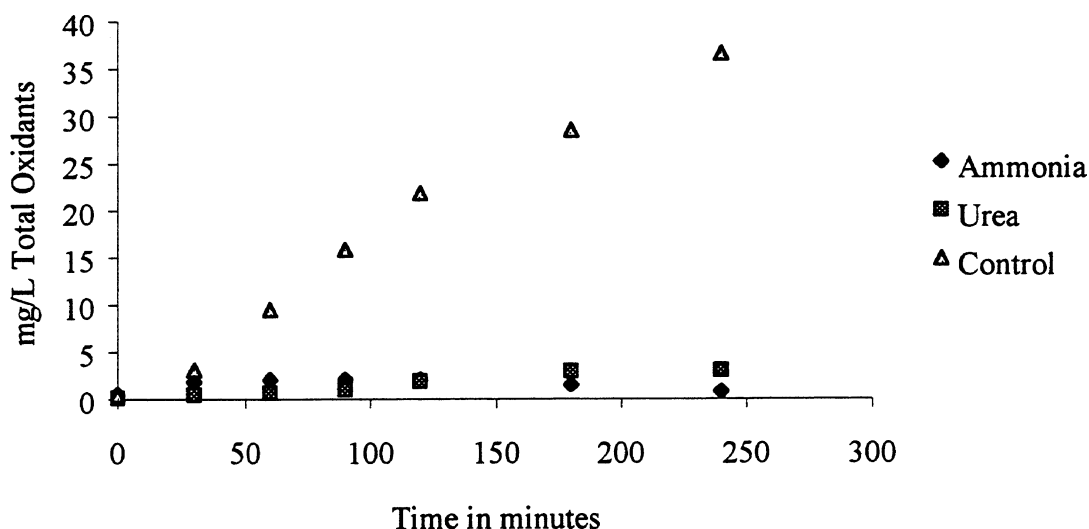


Figure 3 – Total oxidant concentration versus time with the electrolytic cell at setting "5". Values are the means of triplicate experiments.

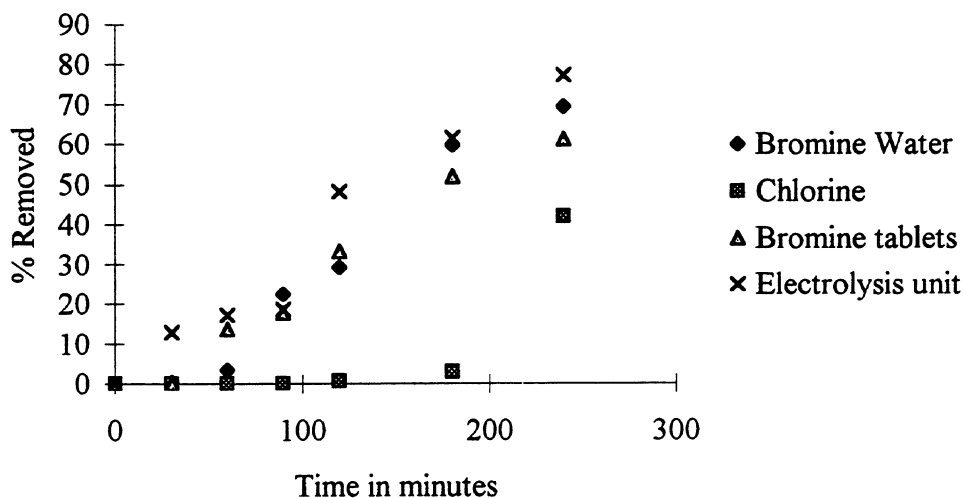


Figure 4 – Percent ammonia removed versus time with various oxidants. Each point is the mean of triplicate tests.

urea and ammonia, as the measured concentration of total oxidants never exceeded 5 mg/L (Figure 3). It is most likely that the oxidants are quickly reacting with urea and ammonia resulting in a lower operating concentration of total oxidants.

Theoretically, a mass ratio of chlorine (as Cl_2) to ammonia (as N) of 7.6 is required for breakpoint chlorination (Appendix A). In practice, the ratio is usually about 10. The total oxidant measurement used for bromine and chlorine determination in this study is reported as chlorine. Following this calibration, bromine addition in this system was calculated as chlorine allowing for the direct comparison of the results of the various oxidant systems. Both bromine and chlorine stock solutions were calibrated using the DPD measurement for total oxidants. In addition, in this pH range, formation of bromamine species would

be expected, allowing for similar mechanisms of ammonia removal by both chlorine and bromine.

Ammonia and urea loss was noted in both the bromine systems (bromine water and tablets) and the chlorine system (hypochlorite). Although differences were noted between the results (Table 1), the values generally followed the range between the theoretical mass ratio of 7.6 and the typical operating mass ratio of 10 (both values for mass of oxidants as chlorine added/mass nitrogen oxidized).

With chlorine, the average ratio of total oxidants (as Cl_2) required per unit urea (as N) removed was significantly lower at the 95% confidence interval than the corresponding ammonia loss. This situation is the reverse for the bromine tablets, where ammonia loss was more efficient than urea loss. There was little difference between the urea and ammonia oxidation

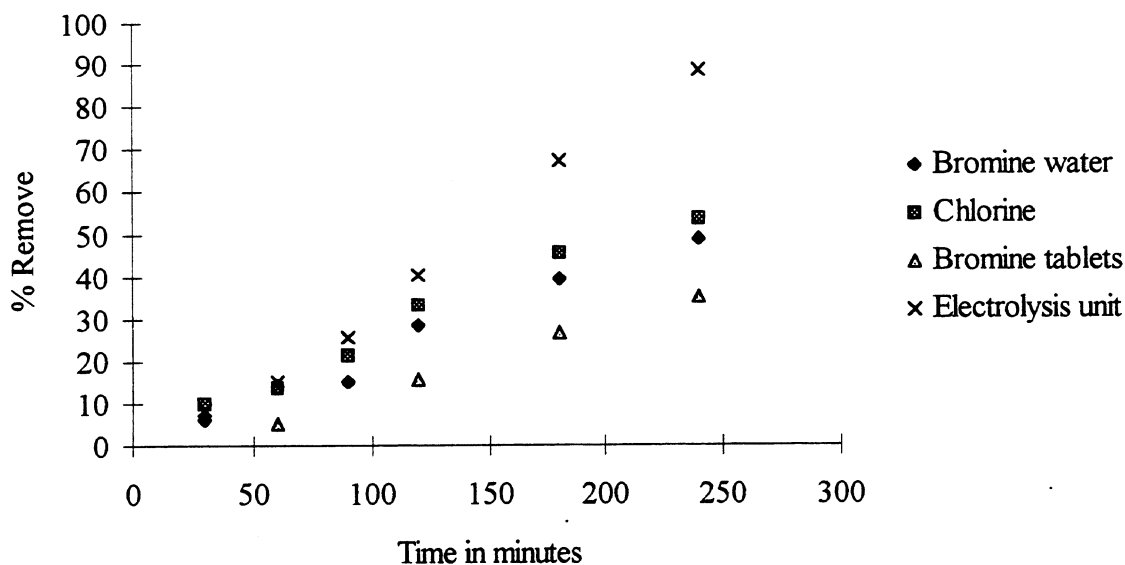


Figure 5 – Percent urea removed versus time with various oxidants. Each point is the mean of triplicate tests.

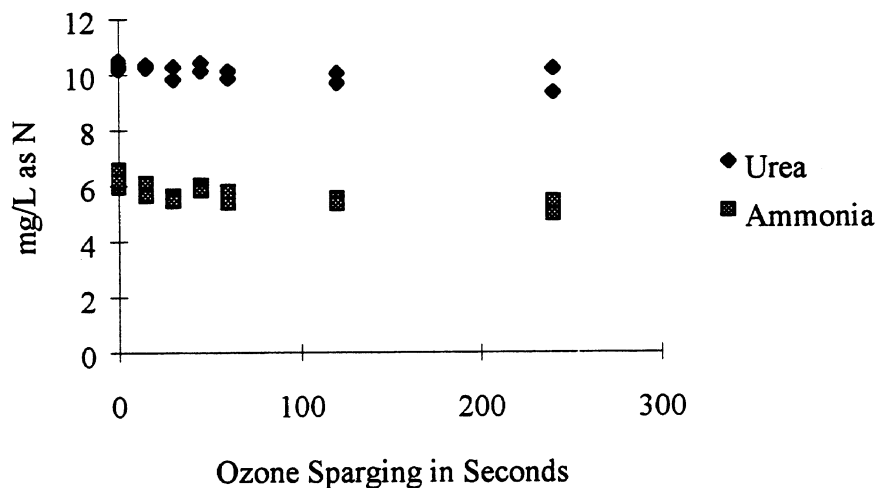


Figure 6 – Urea and ammonia concentration versus ozonation. No significant loss of urea or ammonia was observed.

in the bromine water system.

No loss of urea or ammonia was observed when the system was treated (sparged) with ozone (Figure 6). Conditions such as temperature were modified to enhance the transfer of ozone into solution. NaCl or NaBr were not added to the simulated spa water in the ozone experiments. Due to the lack of ammonia or urea loss under these conditions, no additional experiments were conducted. The rate of ozone generation was previously determined to be approximately 1500 to 1800 mg ozone/min.

The pH decreased with oxidant production and ammonia and urea loss during each of the studied treatments (Table 1). The decrease in pH per mg/L of urea and ammonia as nitrogen oxidized was greatest with bromine tablets and bromine water respectively and least with chlorine. Treatment with the electrolysis unit resulted in a pH change within the range of chlorine and bromine sources for both ammonia and urea. In all cases, buffer capacity in the simulated spa water solution was adequate to maintain a pH between 6.7 and 8.6.

Conclusions

Ammonia and urea loss in the electrolysis unit treated solutions at a setting of "5" exceeded that found in similar chlorine and bromine addition systems (Figures 4 and 5). The low total oxidant to nitrogen oxidation ratios for the electrolysis unit treated solutions not only indicates that the system is more efficient, but that the mechanism for nitrogen oxidation may be different than the other systems studied. Other very short lived oxidants not measured by the methods used in this study but effective in removing ammonia and urea may be produced in the electrolysis process. Ammonia loss in the bromine tablet system, which contains some chlorine, is similar to the value for the electrolysis unit indicating that the combination of chlorine and bromine may be a factor in improved oxidation in the electrolysis unit.

Further study of this system resulting in a better description of the reactions occurring in the electrolysis unit could be used to optimize the system as well as to explore additional applications of this technology. Comparison of the system to current chlorination, ozone and bromination methods indicates the potential of the electrolysis unit

to be offered as a significant advancement for nitrogen removal and possibly other important applications.

Objectives of further research should include:

1. Identification of oxidizing species produced in the electrolysis unit treated solutions to improve the description of possible mechanisms.
2. Evaluate the technology with additional target contaminants for additional applications beyond spa sanitation.
3. Review and possible expansion of optimization studies for application to other contaminants in specific pH and temperature environments.
4. Perform full-scale test.
5. Vary water chemistry to account for additional components and the range of water chemistries found in spas with different water sources, use rates and maintenance levels.

Appendix A Breakpoint Chlorination

It is well known that free chlorine is a strong oxidizer and can react with ammonia. Chlorine reacts with ammonia to form chloramines and eventually, if the chlorine is in sufficient quantity, converts the ammonia to nitrogen gases (N_2 and other minor nitrogen gas species). This phenomenon is typically referred to as breakpoint chlorination. A general breakpoint curve is given in Figure A1.

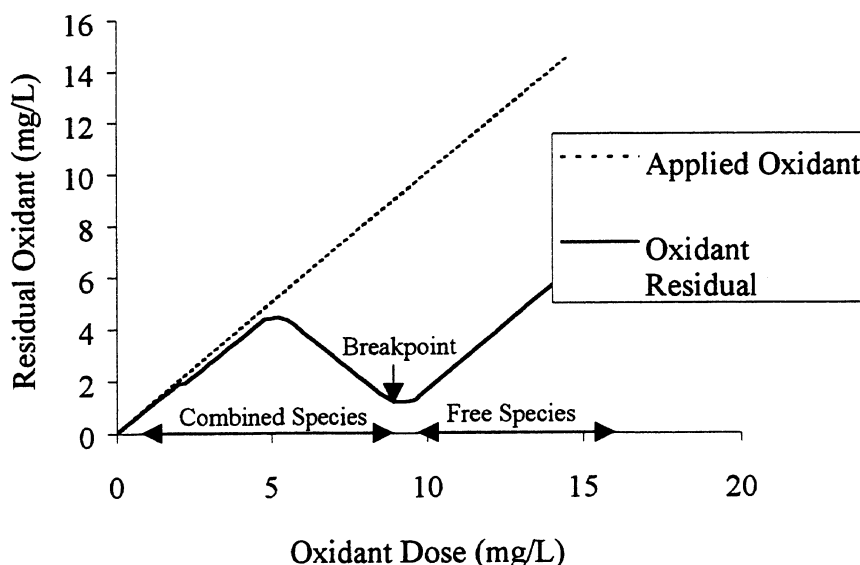


Figure A1 – An example of a breakpoint curve for removal of ammonia with chlorine or bromine as the oxidant. Combined species would include brom- and chloramines. Free species include HOBr and HOCl.

Electrolysis Unit (at setting "S")	Initial/Final		Total oxidants mg/L	Calculated	Tot ox ratio		pH@T _o	pH@T _e	dpH/dConc.	Mean	Std Dev.	Comments
	mg/L	mg/L			Mean	Std Dev.						
NH ₃	8.3	3.3	25.7	5.2			8.2	7.1	-0.22			
NH ₃	8.5	4.3	25.7	6.1			8.2	7.3	-0.22			
NH ₃	6.9	1.8	25.7	5.0	5.4	0.6	8.2	7.1	-0.23	-0.22	0.01	
Urea	5.8	2.1	19.3	5.3			8.5	7.5	-0.27			
Urea	9.9	3.4	37.9	5.8			8.5	7.2	-0.19			
Urea	10.5	4.7	25.7	4.4	5.2	0.7	8.5	7.3	-0.21	-0.22	0.04	
Chlorine (a dilution of Clorox)												
NH ₃	7.8	4.4	36.6	10.9			8.2	7.9	-0.10			(most loss in last hour)
NH ₃	7.3	3.9	36.6	10.5			8.2	7.8	-0.12			(most loss in last hour)
NH ₃	8.0	4.8	36.6	11.4	11.0	0.4	8.2	7.8	-0.12	-0.12	0.01	(most loss in last hour)
Urea	11.1	6.8	36.3	8.4			8.5	8.0	-0.13			
Urea	11.1	7.0	36.3	8.8			8.5	8.0	-0.13			
Urea	11.1	7.0	36.3	8.8	8.7	0.2	8.5	8.0	-0.13	-0.13	0.002	
Bromine Tablets												
NH ₃	8.7	3.6	36.6	7.2			8.2	6.8	-0.29			
NH ₃	8.7	3.1	36.6	6.5			8.2	6.8	-0.26			
NH ₃	8.7	3.4	36.6	6.9	6.9	0.4	8.2	7.1	-0.21	-0.25	0.04	
Urea	10.5	7.8	27.8	10.1			8.6	7.1	-0.57			
Urea	10.4	7.8	27.8	10.9			8.6	7.1	-0.59			
Urea	10.2	7.3	27.8	9.6	10.2	0.6	8.6	7.1	-0.51	-0.55	0.04	
Bromine Water												
NH ₃	5.9	2.1	36.6	9.7			8.3	6.6	-0.44			
NH ₃	6.0	1.7	36.6	8.6			8.3	6.6	-0.39			
NH ₃	6.6	1.9	36.6	7.9	8.7	0.9	8.3	6.7	-0.34	-0.39	0.05	
Urea	10.0	5.3	36.6	7.8			8.6	6.7	-0.41			
Urea	9.9	5.1	36.6	7.6			8.6	6.7	-0.38			
Urea	10.1	5.0	36.6	7.2	7.5	0.3	8.6	6.8	-0.36	-0.38	0.02	
Ozone												
NH ₃	5.9	5.4										Ozone values estimated
NH ₃	6.1	5.8										based on a 1%
NH ₃	6.7	6.3										transfer rate.
Urea	10.5	10.2										
Urea	10.2	9.4										
Urea	11.9	11.7										

Ammonia and urea, mg/L as N and Total Oxidants, mg/L as Cl₂

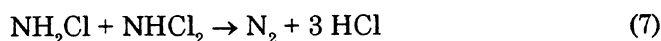
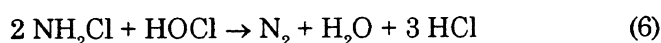
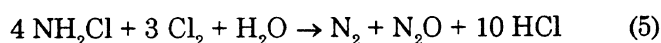
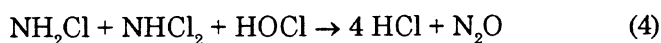
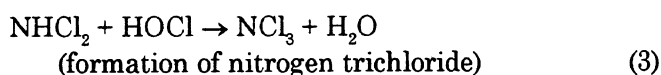
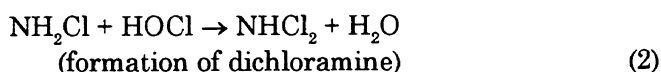
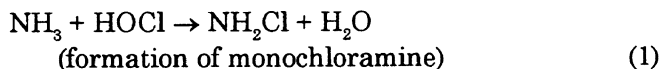
Tot ox ratio – Total oxidants generated or added/urea or ammonia oxidized

T_o = time zero, T_e = time end (~ 4 hours), dpH = change in pH, dConc = change in concentration.

Std. Dev. – standard deviation

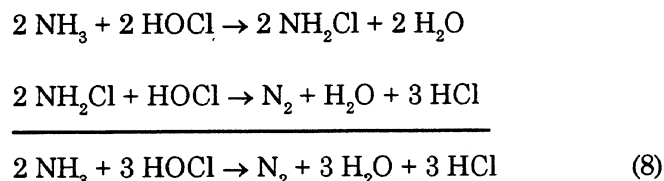
Table 1 – Data Summary

There are several equations that describe the disappearance of ammonia and the formation of nitrogen gases. The mechanism consist of two general phases, the formation of combined species, chloramines, and the oxidation of ammonia to nitrogen. Equations 1-4 describe the formation of chloramines and equations 5-7 describe the formation of nitrogen and nitrogen compounds that are released to the gaseous phase, removing the nitrogen from solution.



If chlorine is added beyond the breakpoint (Figure A1), the free available chlorine will increase proportionally to the amount added. The breakpoint is equal to the concentration of chlorine required to meet the ammonia demand, the amount of chlorine needed to oxidize ammonia to nitrogen releasing the ammonia from solution in the form of nitrogen.

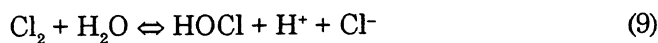
Theoretically, what is the amount of chlorine required to achieve breakpoint chlorination? It is the amount of chlorine required to convert all of the ammonia to nitrogen. To calculate this amount, first look at a general simplified overall reaction (Equation 8) by combining a couple equations from above.



The resulting equation gives an expression in which 3 moles of hypochlorous acid (HOCl) are required to react with 2 moles of ammonia (NH₃). If a stoichiometric weight ratio (mass of Cl₂ to mass of N) is desired, it is necessary to convert the mole ratio to a mass ratio. This can be accomplished by expressing the molecular weight of ammonia (NH₃) as N and expressing the hypochlorous acid (HOCl) as Cl₂ (Equation 9).

tion 9).

$$\frac{1 \text{ mole NH}_3}{1 \text{ mole NH}_3} \times \frac{1 \text{ mole N}}{1 \text{ mole N}} \times \frac{14 \text{ g N}}{1 \text{ mole N}} = 14 \text{ g N}$$



$$\frac{1 \text{ mole HOCl}}{1 \text{ mole HOCl}} \times \frac{1 \text{ mole Cl}_2}{1 \text{ mole Cl}_2} \times \frac{70.9 \text{ g Cl}_2}{1 \text{ mole Cl}_2} = 70.9 \text{ g Cl}_2$$

The mass ratio can now be calculated.

As shown in Equation 8, it takes 3 moles HOCl to react with 2 moles NH₃.

Or, expressed as a mass ratio of Cl₂ to NH₃-N,

$$\frac{3 \text{ moles HOCl} \times 70.9 \text{ g Cl}_2}{1 \text{ mole HOCl}} \text{ to } \frac{2 \text{ moles NH}_3 \times 14 \text{ g N}}{1 \text{ mole NH}_3}$$

$$3 \times 70.9 \text{ (as g Cl}_2\text{)} : 2 \times 14 \text{ (as g N)}$$

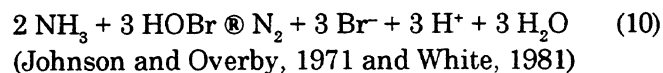
Or,

$$\underline{7.6 : 1} \quad \text{g Cl}_2 : \text{g N}$$

The ratio as calculated will vary depending on the "actual" reactions involved. In practice, the ratio has been found to vary from 8:1 to 10:1.

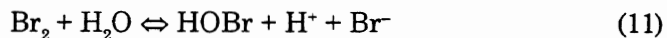
Note: As can be observed from the above equations, hydrochloric acid is formed during chlorination. This acid will react with the alkalinity in the system and the pH may decrease. Stoichiometrically, 14.3 mg/L of alkalinity, expressed as CaCO₃, will react with the hydrochloric acid generated with each 1.0 mg/L of ammonia that is oxidized in the breakpoint process.

Now, what about breakpoint bromination? If the same logic is applied to the bromination process, Equation 10 is appropriate:



Following the mechanism described for chlorine, bromine also forms combined species, (bromamines) which then result in the oxidation of ammonia to nitrogen. Thus, 3 moles of HOBr are required to react with 2 moles of NH₃. If a stoichiometric weight ratio (mass of Br₂ to mass of N) is desired, it is necessary to convert the mole ratio to a mass ratio. This can be accomplished by expressing the molecular weight of ammonia (NH₃) as N and expressing the hypobromous acid (HOBr) as Br₂ (Equation 11)

$$\frac{1 \text{ mole NH}_3 \times 1 \text{ mole N} \times 14 \text{ g N}}{1 \text{ mole NH}_3 \quad 1 \text{ mole N}} = 14 \text{ g N}$$



$$\frac{1 \text{ mole HOBr} \times 1 \text{ mole Br}_2 \times 159.8 \text{ g Br}_2}{1 \text{ mole HOBr} \quad 1 \text{ mole Br}_2} = 159.8 \text{ g Br}_2$$

The mass ratio can now be calculated.

As shown above, it takes 3 moles HOBr to react with 2 moles NH₃.

Or, expressed as a mass ratio of Br₂ to NH₃-N,

$$\frac{3 \text{ moles HOBr} \times 158.9 \text{ g Br}_2}{1 \text{ mole HOBr}} \text{ to } \frac{2 \text{ moles NH}_3 \times 14 \text{ g N}}{1 \text{ mole NH}_3}$$

$$3 \times 158.9 \text{ (as g Br}_2) : 2 \times 14 \text{ (as g N)}$$

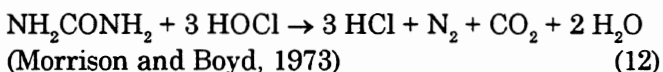
Or,

$$17 : 1 \quad \text{Br}_2 : \text{N}$$

If one wished to compare chlorination and bromination, it is necessary to compare these processes in like terms. To accomplish this, convert the "bromine numbers" to "chlorine numbers". This is done by evaluating the mole ratios. For chlorination, it takes 3 moles HOCl to react with 2 moles NH₃. For bromination, it takes 3 moles HOBr to react with 2 moles NH₃. Thus, the mass ratios can be easily converted using the above calculations.

To provide standardization, bromine is sometimes expressed as "chlorine" or similar term. This is a convenient method to express results since chlorine solutions are often used to standardize the test for total oxidants that measure both bromine and chlorine. For a known bromine solution, multiply the "chlorine" amount by the molecular weight ratio of Br₂ to Cl₂ (158.9/70.9 or 2.24) to convert to mass of Br₂.

Urea will also react with hypohalites to form nitrogen and carbon dioxide given by the following simplified equation:



Equation 12 gives an expression in which 3 moles of hypochlorous acid (HOCl) are required to react with 1 mole of urea (NH₂CONH₂). A stoichiometric weight ratio (mass of Cl₂ to mass of N) can be calculated by converting the mole ratio to a mass ratio. The calculations are similar to those of the reaction of chlorine with ammonia. Express the molecular weight of urea (NH₂CONH₂) as N and hypochlorous acid (HOCl) as Cl₂.

$$\frac{1 \text{ mole NH}_2\text{CONH}_2 \times 2 \text{ mole N} \times 14 \text{ g N}}{1 \text{ mole NH}_2\text{CONH}_2 \quad 1 \text{ mole N}} = 28 \text{ g N}$$

$$\frac{1 \text{ mole HOCl} \times 1 \text{ mole Cl}_2 \times 70.9 \text{ g Cl}_2}{1 \text{ mole HOCl} \quad 1 \text{ mole Cl}_2} = 70.9 \text{ g Cl}_2$$

The mass ratio can now be calculated.

As shown in Equation 12, it takes 3 moles HOCl to react with 1 mole NH₂CONH₂.

Or, expressed as a mass ratio of Cl₂ to NH₂CONH₂ as N,

$$\frac{3 \text{ moles HOCl} \times 70.9 \text{ g Cl}_2}{1 \text{ mole HOCl}} \text{ to } \frac{1 \text{ mole NH}_2\text{CONH}_2 \times 28 \text{ g N}}{1 \text{ mole NH}_2\text{CONH}_2}$$

$$3 \times 70.9 \text{ (as g Cl}_2) : 28 \text{ (as g N)}$$

Or,

$$7.6 : 1 \quad \text{g Cl}_2 : \text{g N}$$

Note: From Table 1, the experimentally determined mass ratios (*Total ox ratio*) for the electrolysis process of ammonia and urea are 5.4 and 5.2, respectively. These experimentally determined mass ratios are somewhat less than the theoretical value of 7.6 indicating the possibility of another mechanism for ammonia and urea oxidation occurring in addition to the classical breakpoint process.

References

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