

Testing of Chlorine Generator System

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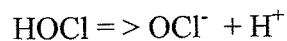
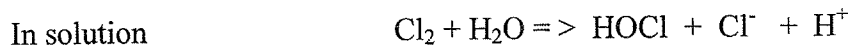
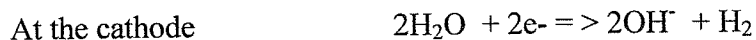
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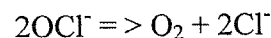
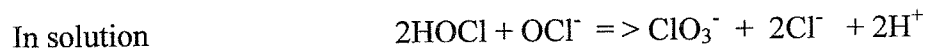
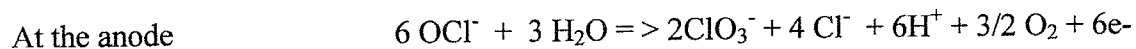
1.0 Background

Hays Water Science, L.L.C. of Washington, IA has developed a portable chlorine generating system that can be used to chlorinate drinking water. The generation of chlorine is based on the electrolysis of the salt water. The Hays technology consists of passing the water over battery powered electrodes multiple times, effectively generating chlorine from sodium chloride solution. When the water is recycled several times through the generator, the chlorine in the water is concentrated.

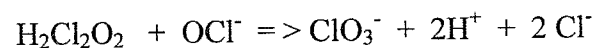
The primary chemical reactions taking place in the electrochemical cell are complicated and involve the following reactions:



Other reactions that are also taking place include:



Also between pH 5 – 7, HOCl decomposes to form chlorate, ClO_3^- .



As can be seen from the various reactions, intermediates such chlorate can be formed but may be difficult to isolate and identify due to their rapid reactions and interactions.

2.0 Objectives of Project

The objective of the project is to analyze the amount of chlorine generated from the chlorine generator developed by Hays Water Science. The project will also assess the amount of chlorine generated for various passes of brine solution through the generator and the measurement of other oxidants generated.

3.0 Materials and Methods

3.1 Materials

The chlorine generator was provided by Hays Water, L.L.C. Salt used in generating the brine solution was purchased from Iowa State University Chemistry Stores. Total chlorine was measured using the sodium thiosulfate titration method for total chlorine purchased from Hach Chemical. Chlorine dioxide was measured using the Accepta 61317 test kit manufactured by Accepta, Manchester, United Kingdom. The test kit is based on a modified method of Lisamine Green method under alkaline conditions. This method as described by the manufacturer can measure a chlorine dioxide range of 0.3 - 600 mg/L without interference from other oxidants. Ozone was measured using the indigo trisulfonate method (Method 4500-O₃) as per Standard Methods for the Examination of Water and Wastewater (APHA, 2005). Because the ozone method is based on the differences in absorbance between the sample and blank, interferences from other oxidants present are highly probable. There are no suitable methods to measure ozone in the presence of free chlorine (Gordon et al., 2002). The only reliable method for measuring ozone and other oxidants is to use a membrane separation method to enhance selectivity of specific oxidants in the liquid samples (Gordon et al., 2002).

3.2 Methods

The brine solution was prepared by adding 280 gm of sodium chloride to 900 mL of water and stirring until the sodium chloride dissolved. The battery for the generator was charged overnight unless specified otherwise. A total of five test runs were conducted. For each test run, the solution was passed through the chlorine generator once as in a flow-through system and three, five and ten times through the generator (a total of 4) as in a recirculation system. Water samples were collected and analyzed immediately. Triplicate samples (or more) were tested.

4.0 Results and Discussion

The average concentrations for the five test runs are presented in Table 1. Total chlorine was tested on all five test runs while chlorine dioxide and ozone were only tested in Aug. 31 and Sept. 14.

Results for total chlorine were highly variable. On Aug. 31, the concentration of total chlorine was lower than during any other test runs, between 542 and 937 mg/L Cl₂. The highest total chlorine concentrations were between 2,620 and 5,273 mg/L Cl₂ for Aug. 15 test run (No samples were tested for one pass through the system for that day). On both Aug. 31 and Sept. 15, the charger was plugged in and fully charged the night before the testing session, yet the concentrations of total chlorine generated were vastly different. The highly variable results were therefore not due to the charge status of the battery charger. This also cannot be attributed to a difference in sodium chloride concentrations. On all occasions, sodium chloride and water were both carefully measured and the salt was dissolved in the water before being used for the tests. On all occasions, the analyses were carried out immediately after passing the salt water through the chlorine generator.

Chlorine dioxide was tested twice. On Aug. 31, the average concentrations were between 0.2 and 0.3 mg/L ClO₂ with total chlorine concentrations between 542 and 937 mg/L Cl₂. On Sept. 14, the average concentrations of chlorine dioxide and total chlorine were slightly higher and varied between 0.3 and 0.8 mg/L ClO₂ and between 865 and 1916 mg/L Cl₂, respectively. With respect to ozone concentrations, the "concentrations" measured on Aug. 31 were between 871 and 1,164 mg/L

which were higher than the total chlorine concentrations of between 542 and 937 mg/L. However, for Sept. 14, the “ozone concentrations” were between 893 and 936 mg/L which were less than the total chlorine concentrations of 865 and 1,916 mg/L. Since the indigo method is a colorimetric method based on absorbance, the data cannot indicate that there is ozone present in the water.

There are several patents indicating generation of ozone in a chlorine generator by using different electrode materials such as iridium oxide (US Patent, 1988; US Patent, 1994; and US Patent 1995). In one of the patents (US Patent, 1988), free chlorine was measured using the amperometric titration method while ozone was determined by differences in dye decolorization over 4 hours. The dye method as indicated in the Standard Methods is subjected to interference in the presence of chlorine. A review by Gordon et al. (1998; 2002) on different test methods to analyze ozone with minimum interference of chlorine showed that false positive are observed when dye methods are used. They advocate using a gas diffusion apparatus to separate the gases. Results of their study indicated that it was unlikely ozone would be generated in an electrolytic chlorine generator (Gordon et al., 2002).

Table 1. Test Results Summary

Date:	# of passes Thru chlorine generator	Total Chlorine (Cl₂) (mg/L)	Chlorine Dioxide (ClO₂) (mg/L)	Ozone (O₃) (mg/L)
Aug. 31, '06	1	630	0.3	1164
	3	937	0.2	871
	5	728	0.3	929
	10	542	0.2	893
Sept. 12, '06	1	909	Not tested	Not tested
	3	2833	Not tested	Not tested
	5	no data	Not tested	Not tested
	10	no data	Not tested	Not tested
Sept. 13, '06	1	863	Not tested	Not tested
	3	2,077	Not tested	Not tested
	5	2,726	Not tested	Not tested
	10	2,433	Not tested	Not tested
Sept. 14, '06	1	1,038	0.7	936
	3	1,916	0.8	893
	5	1,354	0.5	921
	10	865	0.3	893
Sept. 15, '06	1	no data	Not tested	Not tested
	3	2,620	Not tested	Not tested
	5	4,318	Not tested	Not tested
	10	5,273	Not tested	Not tested

Aug. 31, '06, Sept. 12, '06 and Sept. 15, '06: Charger plugged in overnight the night previous to testing.

Sept. 13, '06: Charger was used the day on Sept. 12, '06 for 10 minutes total, so it was not charged previous to this testing session.

Sept. 14, '06: Charger plugged in overnight the night previous to testing. However, during the tests, the charger was briefly plugged in for approximately five minutes and then unplugged.

5.0 Conclusion

Total chlorine produced in the generator was highly variable ranging from 630 to 1,038 mg/L for a single pass and between 540 and 5,273 mg/L for ten passes. The causes of the variability were not determined during this study. It is apparent that the generator will produce at least 500 mg/L of Cl₂ with just one pass across the electrodes. All the five test runs except for one test on Sept. 15, a drop in the total chlorine concentration was found between 3 and 5 passes. This may be due to the loss of chlorine as the water is poured back into the chlorine generator. Chlorine dioxide concentrations were less than 1 mg/L. Using current test methods, it was not possible to measure ozone in the chlorinated water.

6.0 References

American Public Health Association (APHA), 2005. Standard Methods for the Examination of Waste and Wastewater, 21st Ed., APHA, Washington D.C.

Gordon, G, Emmert, G, Gauw, R, and Bubnis, B., 1998. Can Ozone and Ozone Oxidative By-Products Be Formed During the Electrolysis of Salt Brine? *Ozone: Sci. Eng.*, 20 (3): 239-249.

Gordon, G, Bolden, R, and Emmert, G, 2002. Measuring oxidant species in electrolyzed salt brine solutions, *J. Am. Water Works Assoc.*, 94(10):111- 119

US Patent, 1988, No. 4,761,208. Electrolytic method and cell for sterilizing water.

US Patent, 1994, No. 5,316,740. Electrolytic cell for generating sterilization solutions having an increased ozone content.

US Patent, 1995, No. 5,385,711. Electrolytic cell for generating sterilization solutions having an increased ozone content.