Comparison of Chlorite and Chlorate based Chlorine Dioxide Generation on the Reduction of TTHMs Formation Potential

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Summary

Laboratory and field tests were conducted on drinking water in El Paso Texas to evaluate the performance of chlorine dioxide produced from sodium chlorite and sodium chlorate (a component of Purate®) in reducing Total Trihalomethane Formation Potential (TTHMFP). The chlorine dioxide solutions produced by the two methods contain low levels of unreacted precursors and by-products, which potentially could affect the stability or performance of the key component, chlorine dioxide. Test results showed that equal performance was achieved by both processes.

Introduction

In 1997, Eka Chemicals introduced the SVP-Pure® chlorate-based, chlorine dioxide generator for the municipal and industrial markets. The generator utilizes a chlorine-free chemistry, which does not produce chlorite or chlorine with the chlorine dioxide in the generator solution. By comparison, the chlorite-based generators of chlorine dioxide often contain some un-reacted chlorite and chlorine in the generator solution. Although both systems are capable of 95+% conversion of their precursor chemicals to chlorine dioxide, it is important to compare their capability in actual operation. Is there a difference in performance between chlorine dioxide generated from sodium chlorite and sodium chlorate? To answer that question, a two-year laboratory and plant study was performed in El Paso Texas to determine the effect of the two chlorine dioxide generation methods on the reduction of TTHMs formation potential in drinking water.

The laboratory and plant studies compared the performance of a Rio Linda chlorite/chlorine gas ClO_2 generator to the Eka Chemicals SVP-Pure® chlorate-based ClO_2 generator in reducing TTHMs formation potential of the Rio Grande River water. The following three conditions were evaluated:

1. Chlorine doses to raw river water
2. Rio Linda best trim settings (5-10% excess chlorine) generator solutions
3. Eka Chemicals SVP-Pure® generator solutions.

The experimental hypothesis was that the Rio Linda generator would perform similarly to the Eka Chemicals SVP-Pure® generator in reducing TTHM formation potential. Indeed, the results showed that the Rio Linda best trim settings had essentially the same TTHM reduction capability as the Eka Chemicals generator.

The results from the studies were that:

1. The Eka Chemicals generator reduced TTHMFP by 11.8 µg/L per mg/L of chlorine dioxide compared to 10.9 µg/L for the Rio Linda generator in the chlorine dosage range of 3 to 7 mg/L, pH range of 6 to 9, TOC levels from 3 to 5 mg/L.
2. At chlorine dioxide dosages of less than 2.0 mg/L, the measured TTHM formation potential reductions ranged from zero to less than 10 µg/L per mg/L of chlorine dioxide for each generator. These values were scattered, but within the experimental error of TTHM analyses because the initial chlorine dioxide demand (less than 1 minute) was about 1.5 to 2.0 mg/L, making measurement difficult.
3. At higher dosages, the persistence time of the chlorine dioxide was sufficient to cause TTHMFP reduction to be consistently about 10 µg/L per mg/L of chlorine dioxide.

Laboratory Studies

The raw water source for the studies was the Rio Grande River, which was available for treatment during the period of March through September in El Paso, Texas. The raw water samples were dosed with chlorine dioxide solutions obtained from the existing Rio Linda chlorine dioxide generators utilizing sodium chlorite/chlorine gas and the Eka Chemicals SVP-Pure® chlorine dioxide generator utilizing a sodium chlorate/hydrogen peroxide/sulfuric acid system. In chlorite-based systems for generating chlorine dioxide, chlorine is normally overfed by 5% to 10% to ensure high efficiency conversion of the chlorite to chlorine dioxide. A comparison of these results was made to samples similarly dosed from the Eka Chemicals SVP-Pure® chlorine dioxide generator, which does not contain chlorine or chlorite.

Rio Grande settled water samples were dosed with chlorine dioxide at 1 to 7 mg/L and chlorine at 3 to 7 mg/L. Contact times were 1-hour and 24-hours. The raw water pH was 8.3 but samples were also pH adjusted in the range of 6 to 9 before adding oxidants. Raw TOC levels were from 3 to 5 mg/L. After adding oxidants, the samples were placed in a dark closed container for 1-hour and 24-hour periods, after which they were de-chlorinated and analyzed for THMs, THMFP, bromides, bromates, HAAs, TOC, DOC, pH, chlorite, chlorate, chlorine dioxide, and chlorine. A second set of 1-hour and 24-hour samples were chlorinated at a wide-range of chlorine dosages, de-chlorinated, and then analyzed for the same constituents identified above. The 1-hour contact period was chosen because it approximates the detention period in the primary sedimentation tanks (where chlorine dioxide is applied) at a 20-mgd flow rate. The 24-hour period was chosen to approximate the average detention time in the distribution system from the Water Treatment Plant.

At 3 to 7 mg/L chlorine dioxide dosages, the Eka Chemicals and Rio Linda generators had 11.8 and 10.9 µg/L TTHMFP reduction per mg/L of chlorine dioxide, respectively, in the pH range of 6 to 9, raw TOC levels from 3 to 5 mg/L, chlorine dosages of 3 to 7 mg/L, and at 24 hours contact time. All samples were kept at 23 ºC. In laboratory testing performed 10 years previously on Rio Grande water, the dose response studies showed an average of 10 µg/L TTHM reduction per mg/L of chlorine dioxide over a wider range of chlorine dioxide dosages (1 to 10 mg/L) using optimum Rio Linda generator settings at pH 8.3 with similar TOC levels. The results of this study are consistent with the earlier work.

Plant Studies

There are two 20 MGD surface water treatment plants in El Paso, Texas, which treat Rio Grande River water during the months of March through September. The plants use a physical-chemical treatment process involving screening, silt and mud removal, chlorine dioxide addition to raw water, pre-sedimentation, ferrous chloride addition (chlorite reduction), coagulation/flocculation, secondary sedimentation, granular activated carbon filtration, chlorination and poly/orthophosphate chemical addition for corrosion protection. Since the two plants are similar in design and operation, the conditions for a comparative evaluation of the two chlorine dioxide treatment technologies are ideal.

The plant studies were conducted to verify the laboratory results. Samples were taken from the raw water (Canal), primary effluent (1 hour after chlorine dioxide addition), from the secondary effluent immediately prior to chlorination, and from the product water (filter effluent). The samples were subjected to the same analyses as identified above.

The raw water samples averaged 67 µg/L TTHMFP at 1-hour contact time with 7 mg/L chlorine addition. After adding 2.5-mg/L chlorine dioxide dose at the raw in each plant from the Rio Linda and Eka Chemicals generators, the TTHMFP was 44 µg/L and 41 µg/L, respectively at the secondary effluent in each plant. Therefore, the TTHM potential reduction was 23 µg/L and 26 µg/L, respectively, or 9.2 and 10.4 µg/L per mg/L of chlorine dioxide showing about the same results as the lab study.

Conclusions

Based on the laboratory and plant studies, the following conclusions can be made:

1. Chlorine dioxide from the Eka Chemicals SVP-Pure® chlorate-based chlorine dioxide generator and the Rio Linda chlorite-based chlorine dioxide generator performed equally in reducing TTHMFP on Rio Grande River water.
2. At chlorine dioxide dosages less than 2.0 mg/L from either generator, one should expect TTHMFP reduction to be within the experimental error of TTHMs analyses on Rio Grande River water.
3. At chlorine dioxide dosages from 3 mg/L to 7 mg/L from either generator, one should expect TTHMFP reduction to be about 10 µg/L per mg/L of chlorine dioxide in the pH range of 6 to 9 and at TOC levels of 3 to 5 mg/L on Rio Grande River water.

About the Author

Dr. Douglas Rittmann has a PhD in Environmental Science and Engineering from the University of Texas at El Paso and he is a registered professional engineer in Texas. He has more than 35 years experience in water and wastewater utility operations. In 1993, he developed the first plant use of ferrous chloride to reduce excessive chlorite levels at El Paso Texas.

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