

Sodium Chlorite / Chlorine Dioxide Neutralization

The Clean Water Act (CWA) regulates pollutants entering surface waters. A basic prohibition of the CWA is that it is unlawful for any person to discharge, without a permit, any pollutant from a point source into navigable waters of the U.S.

Under the CWA, any discharge of sodium chlorite to waters of the U.S. requires a permit. Sodium chlorite users should contact their state regulatory agency to obtain information on applying for a permit consistent with the Clean Water Act requirements. These permits operate under a CWA program called the National Pollutant Discharge Elimination System. (NPDES) and are generally referred to as NPDES permits. Pollutant limitations contained in these permits are, in part, based on federal or state effluent limitations.

If a user of sodium chlorite discharges wastewater effluent, not to waters of the U.S. but to a Publicly Owned Treatment Works (POTW) or Sewer Authority, then the user will need a permit from the POTW which will set concentration limits for pollutants in the wastewater stream. Effluent levels are based on a variety of standards, but must meet established EPA Pretreatment Standards. Pretreatment Standards are established on an industry specific basis.

Application Description

Sodium chlorite neutralization may be required under the following circumstances:

If sodium chlorite is spilled or becomes a waste, neutralization may be needed prior to disposal in accordance with all regulations in either a NPDES permitted outfall or in a permitted hazardous waste treatment, storage, and disposal facility.

When chlorine dioxide or sodium chlorite is used in water treatment and residual levels of either oxidant exceed the limit of their NPDES permit or POTW permit, whichever is applicable.

There are a number of procedures and compounds that can be used to neutralize either chlorine dioxide or sodium chlorite depending on the concentration of each active component in the solution to be neutralized.

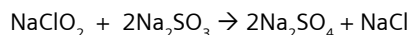


Application Note

Concentrated Sodium Chlorite Solutions

For concentrated solutions of sodium chlorite the use of sodium sulfite is recommended over other reducing agents such as sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), sodium bisulfite (NaHSO_3), and sodium meta-bisulfite ($\text{Na}_2\text{S}_2\text{O}_5$). These other agents may result in acidic solutions and should not be used due to the possibility of generating chlorine dioxide gas.

The reaction of sodium chlorite with sodium sulfite is illustrated below. It is important to note that this reaction is exothermic and liberates a significant amount of heat (ΔH).



$$\Delta H = -168 \text{ kcal/mole NaClO}_2$$

For example, when starting with a 5% sodium chlorite solution, the heat generated from this reaction could theoretically raise the temperature of the solution by 81°C (146°F). Adequate dilution, thorough mixing and a slow rate of reaction are important factors in controlling the temperature increase (ΔT).

The complete neutralization procedure involves three sequential steps: dilution, chlorite reduction, and alkali neutralization. The dilution step lowers the strength of the sodium chlorite solution to 5% or less; the reduction step reacts the diluted chlorite solution with sodium sulfite to produce a sulfate solution, and the neutralization step reduces the pH of the alkaline sulfate solution from approximately 12 to 4-5.

1. Dilution

Due to the potential for heat generation, it is important to dilute the sodium chlorite with water to a solution containing no more than 5% (wt.) sodium chlorite. At 5%, the pH of the solution should be approximately 11.9. When diluting sodium chlorite in a reactor, the reactor should never be filled beyond 75% of its capacity. A reactor that provides good agitation is beneficial.

2. Chlorite Reduction

Slowly and carefully, add dry sodium sulfite at a ratio of 2.8 pounds (1.27Kg) of dry sodium sulfite per pound of active sodium chlorite in the solution and mix thoroughly. For a diluted (5%) sodium chlorite solution, this is equivalent to 1.2 pounds (0.55 Kg) of dry sodium sulfite per gallon of solution (0.197 Kg of active sodium chlorite). The addition of an excess of sodium sulfite will assure the complete reduction of chlorite, and will prevent the generation of chlorine dioxide in the next step. As a precaution, sodium sulfite should always be added slowly to allow for adequate heat dissipation.

Thorough mixing of the sodium sulfite is very important to prevent the generation of chlorine dioxide during the addition of hydrochloric acid in step 3.

3. Alkali Neutralization

Once the chlorite has been completely reacted, slowly add a 5% hydrochloric acid (HCl) solution to lower the pH to 4-5, and mix thoroughly to complete the neutralization. HCl should be added at a ratio of 1 gallon of 5% HCl per 10 gallons of reduced 5% sodium chlorite from step 6. Monitor and maintain the solution temperature below 38°C (100°F). Rapid additions of acid will cause excessive temperature increases. Additions of HCl in excess of the 1/10 ratio will contribute to corrosion problems and safety concerns.

The use of strong acid concentrations can result in the generation of extreme heat and material splattering and should be avoided.

4. pH Adjustment

Monitor and maintain the pH of the solution between 4-5. Use acid/base pH test paper with a range of pH 2-10. If too much acid is added, sodium bicarbonate (common baking soda) can be used to raise the pH. Carbon dioxide gas is liberated during the addition of sodium bicarbonate to acid. Appropriate safety precautions may need to be taken if a significant quantity of carbon dioxide gas is generated.

5. Verify Neutralization is Complete

Sample the neutralized product in a clear beaker or equivalent. Maintain a pH of 4-5, monitoring with acid/base pH paper. As a final indicator, test the solution with KI/starch indicator paper.

Neutralization is complete when the paper does not turn black, blue, or brown in color.

If the paper turns black, blue, or brown, neutralization is not complete and chlorine dioxide could be generated. Add additional sodium sulfite, mix and repeat steps 4 and 5.

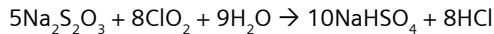
Dispose of the neutralized material in accordance with local, state, and Federal regulations.

Dilute Solutions of Sodium Chlorite and Chlorine Dioxide

Neutralization of very low residual levels of chlorine dioxide and sodium chlorite generated from their use in water treatment may be achieved using either sodium thiosulfate, sodium bisulfite or sodium meta-bisulfite. Actual use quantities of the neutralizing agent will vary depending on the application and the presence of contaminants.

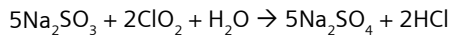
The following equations provide some general guidelines.

1. Sodium thiosulfate reduction of chlorine dioxide:



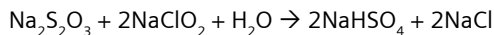
Theoretically 1 mg/L of thiosulfite ion is required to reduce 1 mg/L of chlorine dioxide.

2. Sodium sulfite reduction of chlorine dioxide:



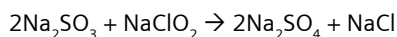
Theoretically 2.96 mg/L of sulfite ion is required to reduce 1 mg/L of chlorine dioxide.

3. Sodium thiosulfate reduction of sodium chlorite:



Theoretically 0.83 mg/L of sulfite ion is required to reduce 1 mg/L of chlorite ion.

4. Sodium sulfite reduction of sodium chlorite:



Theoretically 2.37 mg/L of sulfite ion is required to reduce 1 mg/L of chlorite ion.

Feed Requirements

Dosage level will depend on the residual chlorine dioxide or chlorite ion concentration, competing reactions, the reducing agent used and the local, state and Federal permitted discharge requirements.

The residual oxidant level should be monitored to determine the correct dose rate of neutralizing agent required.

For more information on specific dose rates for your applications contact your Siemens Representative.

Chlorine Dioxide/Sodium Chlorite Analysis

Residual chlorine dioxide and chlorite ion concentrations must be determined by substantiated methods, which are specific for chlorine dioxide.

Three such methods are described in detail in *Standard Methods for the Examination of Water and Wastewater*².

4500-ClO ₂ B	Iodometric Method
4500-ClO ₂ D	DPD-Glycine Method
4500-ClO ₂ E	Amperometric Method II

References

1. Simpson, G.D., "The Reduction of the Chlorite Ion", *Fourth International Symposium on Chlorine Dioxide*, Las Vegas, Nevada, February 15-16, (2001).
2. *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA and WEF, Washington, D.C. (20th Ed., 1998).

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