Powell
Fabrication & Manufacturing Inc

Sodium Hypochlorite Specifications
Paper presented at AWWA 2000 Annual Conference & Expo

Denver, Colorado
June 14, 2000

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Introduction

With increasing frequency, the purchasers of bleach are requiring a higher quality product. This means that issues like low chlorate ion levels, minimal suspended solids and negligible oxygen build-up are important. Specifically, water utilities are requiring the delivery of high quality bleach (NaOCl) with upper limits on chlorate ion (ClO_3^-) and transition metal ions. The amount of ClO_3^- present in liquid bleach is an indicator of bleach decomposition. The presence of transition metal ions also leads to bleach decomposition however, oxygen is formed instead of ClO_3^-.

Large municipalities are requiring that delivered bleach (9 to 16 wt% NaOCl) have between 0.1 - 0.4 wt% excess caustic, <1,500 mg/L ClO_3^-, <0.5 mg/L iron and <0.05 mg/L nickel and copper. As a consequence, bleach manufacturers are making adjustments to their bleach production facilities. For example, important considerations for minimizing ClO_3^- formation include: pH (i.e. excess caustic), dilution (decomposition is 2nd order with respect to OCl^-), and temperature control.

To minimize the problems caused by the presence of transition metal ions, manufacturers are filtering the bleach. This process not only reduces the concentration of transition metal ions in the bleach but also removes inert sediments that impart off-color and turbidity to the bleach. Filtration with the proper filter-aid materials can be used to remove sub-micron particles of the various species of Fe, Ni, and Cu and help to reduce the coating of pumps/piping and the accumulation of heavy metal sludge on tank bottoms.

Decomposition

Bleach loses its strength by two decomposition pathways. The more dominant pathway leads to the formation of chlorate ion. A second slower bleach decomposition pathway leads to oxygen formation.
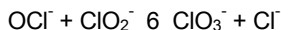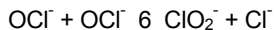
Chlorate Ion (ClO_3^-) Formation Bleach (OCl^-) decomposes between pH 11 and 13 behaves according to a second order rate law:

$$\text{Rate} = k_2 [OCl^-]^2$$

with the following stoichiometry:

$$3OCl^- \rightarrow ClO_3^- + 2Cl^-$$

The decomposition of OCl^- involves chlorite ion (ClO_2^-) as an intermediate in the following generally accepted mechanism:

$$OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-$$

$$OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$$

The stability of bleach can be controlled to prevent the build-up of chlorate ion in the following ways:

1. **Storage pH** Liquid bleach stored in the pH 11 to 13 region is the most stable.

2. **Dilution** is an effective strategy for minimizing NaOCl decomposition. However, it is important that the pH be maintained (adjusted) to be in the pH 11 to 13 region to minimize the rate of ClO_3^- formation.

3. **Temperature Control** Decreasing the temperature of liquid bleach decreases the rate of decomposition.

Oxygen (O_2) Formation The formation of oxygen from decomposing OCl^- is a very slow side reaction in sodium hypochlorite solutions free of transition metal ions. However, in the presence of transition metal ions the rate of bleach decomposition by the oxygen pathway is increased.

$$OCl^- + OCl^- \rightarrow O_2 + 2Cl^-$$
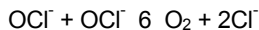
The effect of various metal ions (Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, and Cu^{2+}) on the catalyzed decomposition of OCl^- in basic solution was investigated initially by Lister[1] and more recently by Gordon, Adam and Bubnis[2,3].

The role of transition metal ion catalysis in liquid bleach is complex. In general, nickel ion appears to effectively catalyze decomposition either alone or in combination with other transition metal ions. The maximum concentration of transition metal ions that will not significantly affect the decomposition of bleach is -0.1 mg/L Ni^{2+} and -1 mg/L Cu^{2+}. Ferric ion (Fe^{3+}) and Mn^{2+} when present alone, are not considered to be effective catalysts for bleach decomposition and readily precipitate.

Soluble transition metals are generally present as M^{n+}-hydroxide complexes or as anionic complexes such as phosphates, chlorides, or hypochlorites. The metal complexes also may be present as dimeric (or oligomeric) M^{n+}-hydroxide complexes, which eventually may or may not precipitate. Frequently, the precipitates formed are of unknown (and continuously changing) composition. This complicates an exact understanding of the species present in solution because the chemical form of these complexes can change over time, are frequently difficult to characterize, and are in general undefined.

In the manufacture of bleach, many types of metal complexes undoubtedly form both in solution and as precipitates. Precipitates are frequently observed in holding tanks at utilities using liquid bleach that is mixed with unsoftened water. In addition, dissolved metal ion complexes are most probably also formed. Any or all of these metal-complex species can lower the bleach content in the holding tank resulting from the catalytic formation of oxygen.

The decomposition of bleach in the presence of transition metal ions shows increased oxygen formation. In solutions containing no transition metal ions, maximum bleach stability is observed. The presence of 1 mg/L of Fe^{3+} or Mn^{2+} results in no increase in the rate of decomposition relative to the absence of any added transition metal. The addition of

1 mg/L Cu^{2+} accelerates the decomposition by a factor of 1.4. The addition of 1 mg/L Ni^{2+} greatly increases the rate of decomposition. After approximately 10 days of storage, a significant deviation in the second-order plot is observed. This demonstrates that a different NaOCl decomposition pathway (*i.e.* oxygen formation) is operating.

Sources of Transition Metal Ions in Commercial Bleach

Bleach quality is directly related to the caustic used in manufacturing. The caustic (diaphragm, mercury, or membrane) used to produce liquid bleach is a major source of transition metal ions. In caustic, the transition metal ions (*i.e.* Fe, Cu, and Ni) can be present as sub-micron particles not visible to the eye or as dissolved anionic complexes.

The metal ions contained in bleach can originate from numerous sources. A few are listed[4] below:

Nickel
The origin of nickel in 50% caustic is from the nickel evaporators used to concentrate dilute caustic from the electrolytic cells. It can also come from nickel containing Na_2CO_3 and NaCl sediments from the bottom of the caustic storage tanks. In terms of quality, nickel in excess of 0.3 ppm results in black residues.

Iron
15% NaOH from cell liquor generally contains 0.6-ppm iron that is concentrated to about 3 ppm in 50% caustic. Iron also will concentrate in the sludge at the bottom of storage tanks resulting in more than 5 ppm Fe in 50% caustic. Caustic is generally transported in lined steel tanks and dilution and storage operations are generally carried out in unlined steel tanks. During these operations, the tank will corrode resulting in iron buildup. Iron in excess of 3 ppm in 50% caustic leads to off colored, brownish bleach.

Calcium and Magnesium
The levels of calcium and magnesium in caustic are low. However, if hard water is used for diluting the caustic, the calcium and magnesium levels will undoubtedly increase. Excessive levels can also result from the sludge at the bottom of storage tanks that are low in caustic. The insoluble species formed when calcium and magnesium are in excess of 6 and 9 ppm respectively also provide additional surface area, which can incorporate transition metal ions (*e.g.* Fe) and result in off-colored turbidity and sediment.

Bleach Filtration

Options are available to bleach manufacturers to reduce or eliminate the problems caused by metal ions. High quality bleach can be produced when careful selections are made for control of raw materials and construction materials for piping and storage tanks.

Filtration essentially removes the 5 to 10 micron size particles in bleach. This means the various species of Fe, Ni, and Cu reacting with OCl^- to form oxygen can be decreased. In addition, inert sediments such as iron oxides, which impart off-color, and Ca or Mg hydroxides, which add turbidity, to bleach are also removed during this operation.

Total Iron and Nickel Removal from 15% Bleach by Filtration

Metal	Initial Concentration (mg/L)	Final Product (mg/L)
Fe	1 - 1.5	0.2 - 0.3
Ni	0.5	<0.01

FILTRATION MEDIA In-line cake filtration is ideally suited for continuous bleach manufacture. In this process, the bleach is forced through a porous filter medium that retains the solid particles. Over time, as more liquid passes through the medium, the solids form a filter cake of retained particles.

Filter aids[5] are generally used to improve the efficiency of in-line bleach filtration. Filter aids are highly porous, inert powders that increase the permeability of the filter cake and help to trap fine solids. Many different materials have been proposed as filter aids. However, only three filter aids are typically used alone or in combination: diatomaceous earth (silica), perlite rock and ground wood pulp.

Diatomaceous earth is a natural material consisting of the skeletal remains of tiny organisms. Their irregular size and shape provides a high surface area with adequate porosity to maintain flow through the filter cake. In a similar way, perlite rock and ground wood pulp have microscopic structures that provide a high surface area and porosity for use when silica is a concern.

The typical application of a filter-aid begins by applying a thin layer of the filter-aid onto a polypropylene filter screen to protect the screen from fouling and to filter a more fine particle matrix. Over time, the filtered particles will build-up and form a filter-cake that will need to be replaced in a routine way.

There are situations during bleach manufacture when transition metal ions do not readily form precipitates but instead remain dissolved in the bleach as complex, partially soluble anionic species. In this case, trace chemicals are added to the body feed to help precipitate the transition metal ion complexes[6].

NAOCL TRANSPORTATION, STORAGE, AND HANDLING

TRANSPORTATION Liquid bleach is delivered by tanker trucks lined with materials resistive to sodium hypochlorite. The liners include rubber, FRP, PVC, Halar®, Tefzel®, and other non-metallic materials. If the tanker liner is steel, the iron content of the bleach will increase over time.

STORAGE The two main types of bleach storage containers are high-density polyethylene and fiberglass reinforced plastic. Other choices include chlorobutyl rubber lined steel, PVC and titanium.

POLYETHYLENE tanks should be of linear construction, typically high density and usually the tanks are vertical cylinders with flat bottoms and a domed top. Cross-linked polyethylene is not recommended because of stress cracking within 5 years. Special resins for NaOCl storage are available from some manufacturers. Outside tanks should have UV protection and should be painted white.

The major problems with polyethylene tanks are the outlet fittings below the liquid level. Below the liquid level, titanium bulkhead fittings should be used with titanium bolting. Above the liquid level, PVC bulkhead fittings are acceptable.

FIBERGLASS storage tanks are common and if designed properly are the best choices for bleach storage. A well specified and properly constructed FRP tank can last for 30 years or more. An improper design will fail in 3 to 5 years.

FRP specifications should include hand laid "ortho wound" construction. Filament wound is not recommended because the corrosion barrier in a filament wound tank will result in the NaOCl wicking around the continuous strands of glass. This weakens the structural portion of the tank and can result in a catastrophic failure.

Vinyl resin is used for both the corrosion barrier and the structural layers of the tank with the inside of the tank corrosion barrier starting with 2 nexus veils. The final corrosion barrier is catalyzed with a BPO/DMA cure and a 4-hour post cure.

There has been success with dual laminate FRP tanks using PVC and other materials for a corrosion barrier.

RUBBER-LINED STEEL tanks have been successfully used for NaOCl storage using chlorobutyl lining of ¼ -inch thickness. These linings require a skilled applicator and heat curing. Unfortunately, depending on the brand of rubber and the skill of the applicator, the service life is normally less than 6 years before a total replacement is needed.

TITANIUM (commercial pure Grade 2) storage tanks are the best choice for bleach storage. The drawback to using titanium tanks is the cost. Typically, the cost is prohibitive unless there is a very unusual requirement for virtually unlimited service life with no failures allowable. Thus, titanium tanks are only used for process tanks to handle special applications.

INCOMPATIBLE CONSTRUCTION MATERIALS When materials incompatible with bleach are used for construction in any portion of the process stream, product contamination occurs. This situation leads to accelerated bleach decomposition.

All metals should be avoided except titanium, silver, gold and platinum. Metals such as stainless steel, Hastelloy®, Monel®, brass or copper should be avoided at all costs in pumps, pump seals, water flush lines, electrodes in magnetic flow tubes, diaphragm seals for gauges and switches, temperature wills, and common piping elements such as hose connections and valves.

COMPATIBLE CONSTRUCTION MATERIALS For metals in contact with NaOCl, the construction for all process equipment should be titanium. For non-metallic materials, acceptable materials include: PVC, Teflon®, Tefzel®, Kynar®, polyethylene and FRP. CPVC is not recommended because it becomes brittle in a few years and increases the potential for failure. Any non-metallic material exposed to the sun must have a UV barrier on the exterior components. Paint designed for UV protection is the least expensive solution. A gel coat is typically used for FRP.

PIPING PVC is typically used for low-pressure piping. Threaded joints are not recommended. At pressure above 40 lbs, certain precautions should be taken to prevent PVC failures. For example, when high pressure are required, soft start motors on pumps and slow opening/closing valves should be used. Velocities should not exceed 7 feet/second (preferably < 5 ft/second).
Lined Teflon® piping is generally used for high-pressure applications. Systems using PTFE and fittings are expensive but can result in 20-30 years of service life.

Lightweight schedule 5 and 10 titanium pipe can be used for very long runs of bleach. The piping should be a welded system with carefully designed expansion joints.

Standard FRP piping is usually not successful in bleach applications unless the proper materials are specified and corrosion barriers are in place.

In general, valve materials should match the piping system. However, the first tank valve on the outlet of the storage tank should be of very high quality. A lined steel plug, ball or butterfly valve should be considered. Seats should be of Teflon® and rubber compounds.   O-rings and diaphragms should be Viton®. Only flanged or socket welded valves should be used.
When low torque is required for non-metallic systems, Viton® gaskets should be used. EPDM also works. Harder Teflon® gaskets should not be used in a low torque application. Teflon® gaskets are a good choice for lined pipe systems mating to a titanium flange (e.g. in pumps and heat exchangers).

The composition of monitors and instruments in contact with bleach is very important. For pH and ORP monitors, only silver, platinum and gold electrodes should be used. Because small amounts of nickel decompose sodium hypochlorite rapidly, Hastolloy (which contains Ni^{2+}) must never be used.

Conclusions

Bleach decomposes to form ClO_3^- and O_2. The formation of oxygen from decomposing OCl^- is due to the presence of transition metal ions. The removal of transition metal ions (iron, copper and nickel) leads to improved bleach stability and clarity. Typical utility specifications for delivered bleach are

C pH >11

C Ni^{2+} and Cu^{2+} < 0.05 mg/L

C specific gravity >1.14

C ClO_3^- concentration <1.5 g/L

C delivery within 72 hrs of manufacture

Bleach filtering minimizes the potential for the catalytic formation of oxygen and pressure build-up in bleach containers. The removal of transition metal ions and inert sediments helps to eliminate the sources of turbidity in bleach. Filter-aid materials provide additional surface area for promoting transition metal ion precipitation. This process results in the removal of sub-micron particles of the various species of Fe, Ni, and Cu and helps to reduce the coating of pumps/piping and the accumulation of heavy metal sludge on tank bottoms.

References

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