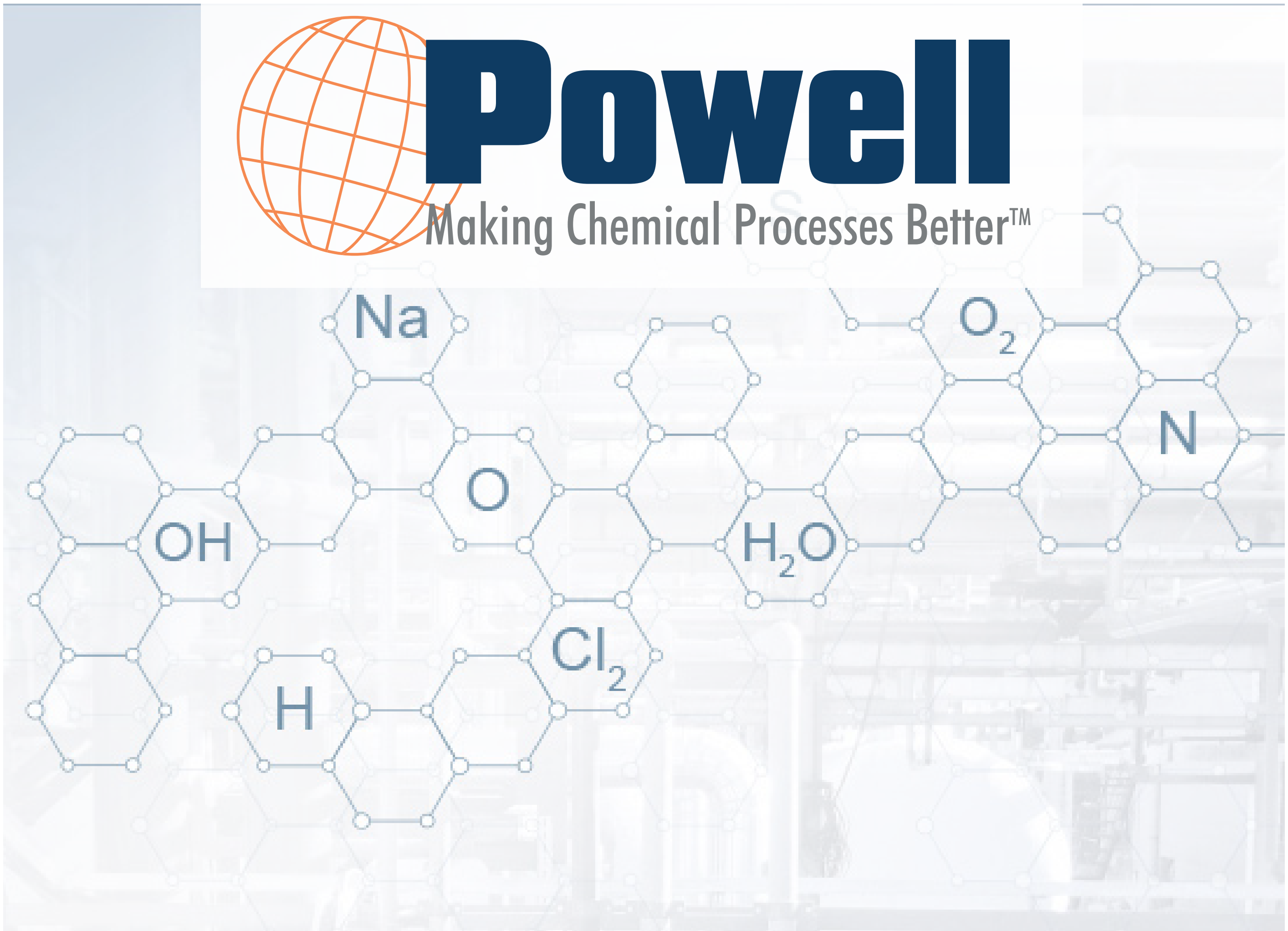

SODIUM HYPOCHLORITE SPECIFICATION

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Issues like low chlorate ion levels, minimal suspended solids and negligible oxygen build-up are important. Specifically, water utilities 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^-.

Delivered bleach (9 to 16 wt% NaOCl) 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 have important considerations for minimizing ClO_3^- formation. It includes pH (i.e. excess caustic), dilution (decomposition is 2nd order with respect to OCl^-), and temperature control.

Filtering the bleach to minimize the problems caused by the presence of transition metal ions is a recommendation. This 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 are 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 in tanks.

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 Rate = k_2 $[OCl^-]^2$ with the following stoichiometry $3OCl^-$ 6 $ClO_3^- + 2Cl^-$.

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

$OCl^- + OCl^-$ 6 $ClO_2^- + Cl^-$ $OCl^- + ClO_2^-$ 6 $ClO_3^- + Cl^-$

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

- Storage pH Liquid bleach stored in the pH 11 to 13 region is the most stable.
- 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.
- Temperature Control Decreasing the temperature of liquid bleach decreases the rate of decomposition.

The formation of oxygen from decomposing OCl^- is a very slow 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. $OCl^- + OCl^-$ 6 $O_2 + 2Cl^-$

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 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 Mn^+-hydroxide complexes or as anionic complexes such as phosphates, chlorides, or hypochlorites. The metal complexes also may be present as dimeric (or oligomeric) Mn^+-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 generally 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 water. In addition, dissolved metal ion complexes are 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 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& 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 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 .

NaOCl Transportation, Storage, & Handling

Transportation

They line liquid bleach tanker trucks with materials resistive to sodium hypochlorite. The liners include rubber, FRP, PVC, Halar®, Tefzel®, and other non-metallic materials. If the liner is steel, the iron content of the bleach will increase.

Storage

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

Titanium

Commercial pure Grade 2 storage tanks are the best choice for bleach storage. The cost is prohibitive unless there is a very unusual requirement for unlimited service life with no failures allowable. Thus, use titanium tanks only for process tanks to handle special applications.

Rubber-Lined Steel

Use rubber-lined steel tanks with a 1/4" thick chlorobutyl lining for NaOCl storage. They require a skilled applicator and heat curing. Depending on the brand of rubber and the skill of the applicator, the service life is less than 6 years before you need a total replacement.

Polyethylene

Linear construction tanks are high density and vertical cylinders with flat bottoms and a domed top. Using cross-linked polyethylene can cause stress cracking within 5 years. Special resins for NaOCl storage are available from some manufacturers. Paint outside tanks white and make sure they have UV proteciton. The major problems with polyethylene tanks are the outlet fittings below the liquid level. Use titanium bulkhead fittings with titanium bolting below the liquid level. And PVC bulkhead fittings above the liquid level.

Fiberglass

FRP storage tanks are common if designed and are the best choice for bleach storage. A well specified 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. The corrosion barrier of filament wound will cause the NaOCl wicking around the continuous strands of glass. This weakens the structural portion of the tank, which can cause a catastrophic failure. Use vinyl resin for both the corrosion barrier and structural layers of the tank with the inside starting with 2 nexus veils. They catalyze the last corrosion barrier with a BPO/DMA cure and a 4-hour post cure. There is success with dual laminate FRP tanks using PVC and other materials.

Piping

PVC is typically used for low-pressure piping. Threaded joints are not recommended. At pressures above 40 lbs, certain precautions should be taken to prevent failures. When high pressures 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 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 unless the proper materials and corrosion barries are in place.

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 us flanged or socket welded valves. When low torque is required for non-metallic systems, use Viton® gaskets. EPDM also works. Harder Teflon® gaskets should not be used in a low torque application. These 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.

Compatible Materials

For metals in contact with NaOCl, use titanium. Acceptable non-metallic materials include: PVC, Teflon®, Tefzel®, Kynar®, polyethylene and FRP. Do not use CPVC because it becomes brittle and increases the potential for failure. Any non-metallic material exposed to the sun must have a UV barrier. Paint designed for UV protection is the least expensive solution. A gel coat is used for FRP.

Incompatible Materials

Do not use incompatible materials for construction in the process stream, product contamination occurs. This situation leads to accelerated bleach decomposition. Avoid all metals except titanium, silver, gold and platinum. Also avoid metals such as stainless steel, Hastelloy®, Monel®, brass or copper in pumps, pump seals, water flush lines, electrodes in magnetic flow tubes, diaphragm seals for gauges and switches, temperature wills, and common piping elements.

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. he 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.

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