OxyChem Sodium Hypochlorite Handbook

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Foreword

This handbook outlines recommended methods for handling, storing, and using sodium hypochlorite. It also includes information on the manufacture, physical properties, safety considerations and analytical methods for testing sodium hypochlorite. Additional information and contacts can be found at www.oxychem.com

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INTRODUCTION

This handbook provides information concerning sodium hypochlorite or bleach, solutions. An attempt has been made to give comprehensive coverage of the subject. If additional technical information or specific recommendations regarding soda bleach solutions are desired, the Technical Service Group of Occidental Chemical Corporation will be pleased to provide assistance. Requests for such information should be made to your local OxyChem representative.

Some safety and handling information has been taken directly from the Chlorine Institute's Pamphlet 96 with the permission of the Chlorine Institute. Pamphlet 96 also contains additional information on sodium hypochlorite.

For further information regarding caustic soda and chlorine, refer to the appropriate OxyChem handbook.

Sodium hypochlorite solutions have attained widespread use in bleaching operations and as disinfectants, both in the home and in industry.

Scheele, a Swedish chemist, is generally credited with discovering chlorine in 1774. During his experiments, he found that a solution of chlorine in water possessed definite bleaching properties. Since the reaction between chlorine and water forms hydrochloric and hypochlorous acids, early textile bleaching experiments were not successful because of damaged cloth.

In 1789, the French chemist Berthollet succeeded in chlorinating a solution of potash, forming a potassium hypochlorite solution. This solution proved to be a more successful bleach for textiles due to the absence of hydrochloric acid. However, it never gained more than limited usage in the bleaching field, primarily because of the high cost of potash.

In 1798, Tennant of England prepared a solution of calcium hypochlorite by chlorinating a slurry of relatively inexpensive lime. The following year he patented a process for the manufacture of bleaching powder where chlorine gas was absorbed in a dry lime hydrate.

Labarraque succeeded, in 1820, in preparing sodium hypochlorite by chlorinating a solution of caustic soda. Varying concentrations of this solution have found a multitude of applications so that the general public is now well acquainted with the material. This handbook will discuss sodium hypochlorite solutions.

PROPERTIES OF SODIUM HYPOCHLORITE

CHEMICAL PROPERTIES

Chlorine (Cl_2) is the best overall disinfectant, germicide, algaecide and anti-slime agent. Chlorination and filtration of drinking water is responsible for a nearly fifty percent reduction in deaths due to disease in major cities during the late 19th and early 20th centuries and the near elimination of typhoid fever. Infants and children benefiting the most. Calcium hypochlorite was the first chlorinating agent used.

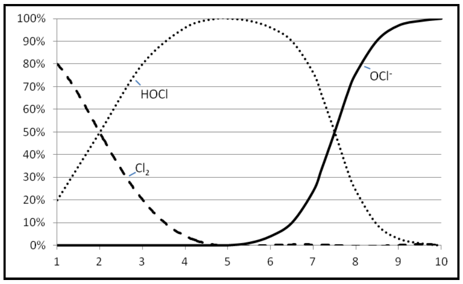
Chlorine also oxidizes and eliminates organic compounds and converts some soluble metallic impurities into insoluble solids that can be removed by filtration.

Chlorine is soluble in water to about 7000 ppm at 68°F. It reacts with water forming hypochlorous acid (HOCl). In alkali solutions hypochlorous acid dissociates forming hypochlorite (OCl^-). Chlorine, hypochlorous acid and hypochlorite exist together in equilibrium.

$$Cl_2 + H_2O \leftrightarrows HOCl \leftrightarrows OCl^-$$

Increasing pH →

The figure below shows the effect pH has on the equilibrium.



Below pH 2 the equilibrium favors chlorine. Between pH 2 and 7.4 hypochlorous acid predominates and above pH 7.4 hypochlorite predominates.

Hypochlorous acid is a significantly more powerful oxidizer and disinfectant than hypochlorite. Best biological control is achieved in the pH range of 5 to 7 where hypochlorous acid is predominate.

Hypochlorous acid is extremely unstable. It is much easier to handle the more stable hypochlorites. The term hypochlorites refers to the salt of hypochlorous acid. One of the best known hypochlorites is sodium hypochlorite, the active ingredient in bleach. The molecular formula for sodium hypochlorite is NaOCl.

Na^+	+	OCl^-	→	NaOCl
sodium cation		hypo-chlorite anion		sodium hypochlorite

The most common method for producing sodium hypochlorite is to react chlorine with sodium hydroxide (NaOH). The reaction by-products are sodium chloride (salt, NaCl) and water (H_2O).

1) $Cl_2 + 2\,NaOH \rightarrow$
$NaOCl + NaCl + H_2O + HEAT$

SYNONYMS

- Hypo
- Hypochlorite
- Bleach
- Chlorine bleach
- Liquid bleach
- Soda bleach
- Javel water

APPLICTIONS

- Disinfection
- Removal of ammonia
- Control taste and odor
- Hydrogen sulfide oxidation
- Iron and manganese oxidation
- Destruction of organic matter
- Color reduction
- Control of slime and algae
- Laundry Bleaching

OXIDIZING POWER

Eq. 2 shows the oxidation of two moles of potassium iodide (KI) with one mole of sodium hypochlorite in a solution of acetic acid to iodine (I_2).

2) $NaOCl + 2\,CH_3COOH + 2\,KI \rightarrow$
$NaCl + 2\,CH_3COOK + I_2 + H_2O$

Eq. 3 shows the oxidation of two moles of potassium iodide with one mole of chlorine to iodine.

3) $Cl_2 + 2\,KI \rightarrow 2\,KCl + I_2$

Given that one mole of sodium hypochlorite can oxidize the same amount of iodide to iodine as one mole of chlorine they have equal oxidizing power. Therefore, the “available chlorine” in sodium hypochlorite equals the amount of chlorine used to produce it and sodium chloride (see Eq. 1) in oxidizing power.

DECOMPOSITION REACTIONS

Sodium hypochlorite is stable above pH 12 where the less reactive hypochlorite is predominant and hypochlorous acid is virtually nonexistent.

Decomposition is by Eq. 4 and 5.

4) $3\,NaOCl \rightarrow NaClO_3 + 2\,NaCl$

5) $2\,NaOCl \rightarrow O_2 + 2\,NaCl$

Eq. 4 is the major decomposition reaction forming chlorate (ClO_3^-) and chloride (Cl^-). This reaction is temperature and concentration dependent; it is not catalytic. Eq. 5 is catalytic, forming oxygen (O_2) and chloride. Trace metals such as nickel, cobalt and copper form metal oxides, which cause catalytic decomposition. Light also catalyzes this reaction.

PROPERTIES OF SODIUM HYPOCHLORITES

STABILITY

Although more stable than hypochlorous acid, sodium hypochlorite is unstable. It starts decomposing immediately. With proper care, the rate of decomposition can be reduced such that relatively stable solutions can be prepared.

The stability and shelf life of a hypochlorite solution depends on five major factors:

- Hypochlorite concentration.
- pH of the solution.
- Temperature of the solution.
- Concentration of certain impurities which catalyze decomposition.
- Exposure to light.

Low concentration hypochlorite solutions decompose slower than high concentration hypochlorite solutions. Fifteen weight percent sodium hypochlorite will decompose approximately 10 times faster than 5 wt% sodium hypochlorite at 25°C.

The pH has a significant effect on the stability of sodium hypochlorite solutions. Below pH 11 the decomposition of sodium hypochlorite is significant due to the shift in the equilibrium in favor of the more reactive hypochlorous acid. A pH between 12 and 13 gives the most stable solution. This equates to 0.4 to 4.0 grams per liter (gpl) excess NaOH. Greater concentrations will not improve the stability. Excessively high alkalinity will damage textiles and retard the bleaching and disinfecting actions of the hypochlorite.

Temperature influences the stability of hypochlorite solutions. Care should be taken to keep solutions away from heat, as higher temperatures increase the decomposition rate. Fifteen percent sodium hypochlorite decomposes five times faster at 45°C than at 25°C. Although low storage temperatures improve the stability of hypochlorite solutions, freezing should be avoided. Sodium hypochlorite solutions will freeze at different temperatures depending on the concentration of the solution. Thirteen wt% sodium hypochlorite freezes at -22.5°C compared to 6 wt% sodium hypochlorite which freezes at -7.5°C.

The quality and stability of sodium hypochlorite solutions can be affected by the concentration of certain impurities. Trace metals such as nickel, cobalt and copper form insoluble metal oxides, which cause the bleach to catalytically decompose by Eq. 5. These trace metals, as well as iron, calcium and magnesium, form sediment and may discolor the bleach solution.

Potential sources for these impurities include raw materials, processing equipment and product storage containers. The most common source for these metals, particularly nickel and copper, is the caustic soda.

Diaphragm cell caustic soda typically contains a higher concentration of these metal catalysts than membrane grade. However, stable bleach can be made from diaphragm grade caustic soda.

Some techniques to minimize the concentration of impurities in the finished product are listed below.

- Polish the finished bleach with a 0.5 to 1 micron filter. This will remove impurities which promote bleach decomposition and/or degrade the visual appearance.
- Use plastic or plastic lined tanks and piping systems to reduce metals contamination.
- Use soft water for dilution.
- Allow finished bleach to settle until clear and decant before packaging.

The most effective of these techniques is polishing the finished bleach with a 0.5 to 1 micron filter. It removes insoluble metal oxides that catalyze decomposition and sediments that affect product appearance. This level of filtration is difficult and expensive to achieve using cartridge type filters. A filter that uses a filter aid such as diatomaceous earth is needed.

Sunlight (ultraviolet light) catalyzes hypochlorite decomposition by Eq. 5. Opaque (non-translucent) containers for hypochlorite solutions will reduce decomposition due to light.

In summary:

1. Low concentration solutions are more stable than high concentration solutions. Diluting soon after receiving will reduce the decomposition rate. Use soft water to minimize impurities. Use cold water to reduce the temperature thus reducing the decomposition rate.
2. A pH between 12 and 13 gives the most stable solution. Less than pH 11 decomposition is significant. Greater than pH 13 there is no improvement.
3. Keep solutions away from heat, as higher temperatures increase decomposition.
4. Filter to remove insoluble metal oxides that catalyze decomposition and sediments that affect product appearance. Use titanium, plastic or plastic lined tanks and piping systems to reduce metals contamination.
5. Store in opaque (non-translucent) containers to prevent decomposition due to sunlight.

SODIUM HYPOCHLORITE CONCENTRATION TERMINOLOGY

Chlorine is the standard against which oxidizers are compared The term “available chlorine” refers to the amount of chlorine equivalent in oxidizing power. It is a measure of strength and bleaching power and is used to express the concentration of bleach solutions. Available chlorine is usually expressed as grams per liter (gpl) or weight percent (wt%). The strength of hypochlorite solutions may also be expressed as wt% sodium hypochlorite.

Trade percent available chlorine is another way to express the strength of hypochlorite solutions. Similar to grams per liter available chlorine except instead of grams per liter its grams per 100 ml. Given that one liter is 1000 ml, trade percent is the gpl available chlorine divided by 10.

It is important to specify the concentration units whenever describing the strength of hypochlorite solutions. For example, 5.25 wt% sodium hypochlorite is equivalent to 5.0 wt% available chlorine or approximately 53.8 gpl available chlorine.

The table below converts from one concentration to another.

Conversions

$$\text{wt\% available } Cl_2 = \frac{\text{gpl available } Cl_2}{10 * SG_{solution}}$$

$$\text{wt\% NaOCl} = 1.05 * \text{wt\% available } Cl_2$$

$$\text{wt\% NaOCl} = 1.05 * \frac{\text{gpl available } Cl_2}{10 * SG_{solution}}$$

Note:
74.44 = MW NaOCl, 70.90 = MW Cl_2
1.05 = 74.44 / 70.90

$$10 = \frac{453.6\text{ g/lb} * 8.34\text{ lb/gal}}{3.7854\text{ l/gal} * 100\%}$$

		gpl available chlorine	40	50	60	80	100	120	140	150	160	180	200
		Trade% available chlorine	4	5	6	8	10	12	14	15	16	18	20
gpl excess NaOH (approximate pH)	0.4 (11.0)	Specific Gravity @ 20°C	1.056	1.069	1.083	1.108	1.133	1.158	1.181	1.193	1.205	1.228	1.250
		% excess NaOH	0.04%	0.04%	0.04%	0.04%	0.04%	0.03%	0.03%	0.03%	0.03%	0.03%	0.03%
		wt% available chlorine	3.79%	4.68%	5.55%	7.23%	8.84%	10.38%	11.87%	12.59%	13.30%	14.68%	16.02%
		wt% NaOCl	3.98%	4.92%	5.83%	7.59%	9.28%	10.90%	12.46%	13.22%	13.96%	15.41%	16.82%
	0.5 (12.1)	Specific Gravity @ 20°C	1.056	1.069	1.083	1.108	1.133	1.158	1.181	1.193	1.205	1.228	1.250
		% excess NaOH	0.05%	0.05%	0.05%	0.05%	0.04%	0.04%	0.04%	0.04%	0.04%	0.04%	0.04%
		wt% available chlorine	3.79%	4.68%	5.55%	7.23%	8.84%	10.38%	11.87%	12.59%	13.29%	14.68%	16.02%
		wt% NaOCl	3.98%	4.92%	5.82%	7.59%	9.28%	10.89%	12.46%	13.22%	13.96%	15.41%	16.82%
	1 (12.4)	Specific Gravity @ 20°C	1.056	1.070	1.083	1.108	1.133	1.158	1.181	1.193	1.205	1.228	1.250
		% excess NaOH	0.09%	0.09%	0.09%	0.09%	0.09%	0.09%	0.08%	0.08%	0.08%	0.08%	0.08%
		wt% available chlorine	3.79%	4.68%	5.54%	7.23%	8.83%	10.37%	11.86%	12.58%	13.29%	14.67%	16.01%
		wt% NaOCl	3.98%	4.91%	5.82%	7.59%	9.27%	10.89%	12.46%	13.21%	13.95%	15.40%	16.81%
	2 (12.7)	Specific Gravity @ 20°C	1.058	1.071	1.085	1.110	1.135	1.160	1.183	1.195	1.207	1.230	1.252
		% excess NaOH	0.19%	0.19%	0.18%	0.18%	0.18%	0.17%	0.17%	0.17%	0.17%	0.16%	0.16%
		wt% available chlorine	3.79%	4.67%	5.54%	7.22%	8.82%	10.36%	11.85%	12.57%	13.27%	14.65%	15.99%
		wt% NaOCl	3.97%	4.91%	5.81%	7.58%	9.26%	10.88%	12.44%	13.20%	13.94%	15.38%	16.79%
	4 (13.0)	Specific Gravity @ 20°C	1.060	1.074	1.087	1.112	1.137	1.162	1.185	1.197	1.209	1.232	1.254
		% excess NaOH	0.38%	0.37%	0.37%	0.36%	0.35%	0.34%	0.34%	0.33%	0.33%	0.32%	0.32%
		wt% available chlorine	3.78%	4.66%	5.52%	7.20%	8.80%	10.33%	11.82%	12.54%	13.24%	14.62%	15.96%
		wt% NaOCl	3.96%	4.89%	5.80%	7.56%	9.24%	10.85%	12.41%	13.17%	13.90%	15.35%	16.76%
	6 (13.2)	Specific Gravity @ 20°C	1.063	1.077	1.090	1.115	1.140	1.165	1.188	1.200	1.212	1.235	1.257
		% excess NaOH	0.56%	0.56%	0.55%	0.54%	0.53%	0.52%	0.51%	0.50%	0.50%	0.49%	0.48%
		wt% available chlorine	3.77%	4.65%	5.51%	7.18%	8.78%	10.31%	11.80%	12.51%	13.21%	14.59%	15.93%
		wt% NaOCl	3.95%	4.88%	5.78%	7.54%	9.22%	10.83%	12.38%	13.14%	13.87%	15.32%	16.72%
	8 (13.3)	Specific Gravity @ 20°C	1.066	1.079	1.093	1.118	1.143	1.168	1.191	1.203	1.215	1.238	1.260
		% excess NaOH	0.75%	0.74%	0.73%	0.72%	0.70%	0.69%	0.67%	0.67%	0.66%	0.65%	0.64%
		wt% available chlorine	3.76%	4.64%	5.50%	7.16%	8.76%	10.29%	11.77%	12.48%	13.18%	14.56%	15.89%
		wt% NaOCl	3.94%	4.87%	5.77%	7.52%	9.20%	10.80%	12.36%	13.11%	13.84%	15.28%	16.69%
	10 (13.4)	Specific Gravity @ 20°C	1.069	1.082	1.096	1.121	1.146	1.171	1.194	1.206	1.218	1.241	1.263
		% excess NaOH	0.94%	0.93%	0.91%	0.89%	0.87%	0.86%	0.84%	0.83%	0.82%	0.81%	0.79%
		wt% available chlorine	3.75%	4.63%	5.48%	7.15%	8.74%	10.26%	11.74%	12.46%	13.15%	14.52%	15.86%
		wt% NaOCl	3.93%	4.86%	5.76%	7.50%	9.18%	10.78%	12.33%	13.08%	13.81%	15.25%	16.65%

MANUFACTURING SODIUM HYPOCHLORITE

There are commercially available continuous bleach systems capable of producing 25 to 150 gpm of 160 gpl available chlorine. These systems come skid mounted, fully instrumented and include all the operating discipline and training. The intent of this section is to provide an overview of the manufacturing process.

Chlorine reacts with sodium hydroxide to produce sodium hypochlorite according to Eq. 6.

Based on the ratio of the molecular weights, 1 pound of chlorine reacts with 1.13 pounds of sodium hydroxide to produce 1.05 pounds of sodium hypochlorite. This does not include the excess sodium hydroxide needed for stability. The exact ratio of chlorine and caustic soda depend on the quality of the dilution water (hard or soft) and amount of excess sodium hydroxide in the final product to name a few.

The approximate amount of raw materials needed to produce a given concentration of bleach can be calculated using Eq. 7 through 14. Caustic soda solutions are not 100% sodium hydroxide; the calculations take this into account. Chlorine is assumed to be 100% (99.5% min).

The table on page 8 shows the raw materials for making 1,000 gallons of bleach in various concentrations from 10 to 200 gpl available chlorine. The table also shows the gallons of bleach that can be produced from a 100 lb cylinder, 150 lb cylinder and ton container of chlorine.

The manufacturing process for making bleach can be batch or continuous and use gaseous or liquid chlorine. Typically they are continuous and use liquid chlorine. The manufacturing process can be broken down into several unit operations; caustic

6)	Cl_2	+ 2 NaOH →	NaOCl	+ NaCl + H_2O + 24,700 calories
MW	70.91	80.00	74.45	
Ratio	1.00	1.13	1.05	

Chlorine

7a) lb Cl_2 = wt% NaOCl / 1.05 / 100 * SG_{bleach} * 8.34 lb/gal * gal bleach
7b) lb Cl_2 = wt% available Cl_2 / 100 * SG_{bleach} * 8.34 lb/gal * gal bleach
7c) lb Cl_2 = gpl available Cl_2 * 3.7854 l/gal / 453.6 g/lb * gal bleach

Caustic Soda

8) lb NaOH = lb Cl_2 * 1.13 lb NaOH/lb Cl_2
9a) lb XS NaOH = wt% XS NaOH / 100 * SG_{bleach} * 8.34 lbs/gal * gal bleach
9b) lb XS NaOH = gpl XS NaOH * 3.7854 l/gal / 453.6 g/lb * gal bleach
10) lb caustic soda = (lb NaOH + lb XS NaOH) / wt% caustic soda
11) gal caustic soda = lb caustic soda / 8.34 lb/gal / $SG_{caustic\ soda}$

Water

12) lb water = gal bleach * 8.34 lb/gal * SG_{bleach} - lb Cl_2 - lb caustic soda
13) gal water = lb water / 8.34 lb/gal
14) Diluted caustic soda %NaOH = (lb NaOH + lb XS NaOH) / (lb caustic soda + lb water) * 100

Example:
Make 1,000 gallons of household bleach, 5.25 wt% sodium hypochlorite using 20% diaphragm caustic soda.

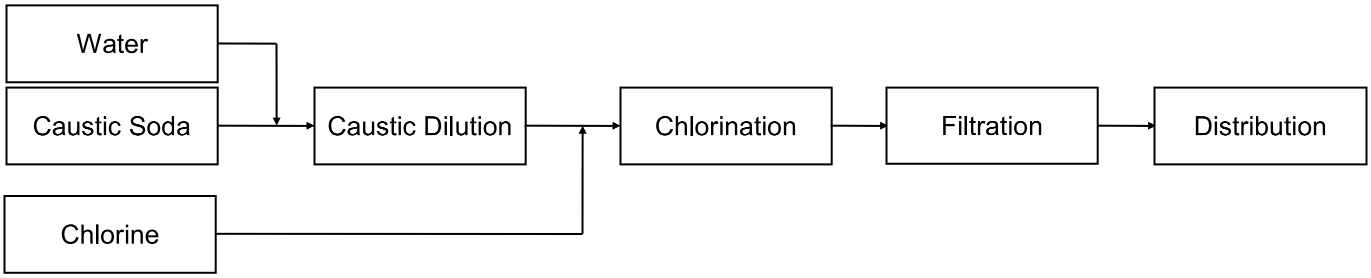
Given:

- 5.25 wt% sodium hypochlorite equates to 5.00 wt% available chlorine, 5.25 wt% NaOCl / 1.05 = 5.00% available Cl_2
- Specific gravity of 20% diaphragm caustic soda is 1.2263 (see chart, pg 17)
- We know a pH between 12 and 13 makes the most stable bleach solutions. This equates to 0.4 to 4.0 gpl XS NaOH.
- Specific Gravity for a 5 wt% available chlorine bleach solution with 2 gpl XS NaOH is 1.076 (see chart, pg 5)

7b) 5.00 wt% available Cl_2 / 100 * 1.076 * 8.34 lb/gal * 1,000 gal bleach = 449 lb Cl_2
8) 449 lb Cl_2 * 1.13 lb NaOH/lb Cl_2 = 507 lb NaOH
9b) 2 gpl XS NaOH * 3.7854 l/gal / 453.6 g/lb * 1000 gal bleach = 17 lb XS NaOH
10) (507 lb NaOH + 17 lb XS NaOH) / (20% caustic soda / 100) = 2,620 lb 20% caustic soda
11) 2,620 lb 20% caustic soda / 1.2263 / 8.34 lb/gal = 256 gal 20% caustic soda
12) (1,000 gal bleach * 8.34 lb/gal * 1.076) – 449 lb Cl_2 – 2,620 lb 20% caustic soda = 5,902 lb water
13) 5,902 lb water / 8.34 lb/gal = 708 gal water
14) (507 lb NaOH + 17 lb XS NaOH) / (2,620 lb 20% caustic soda + 5,902 lb water) * 100 = 6.15% diluted caustic soda

MANUFACTURING SODIUM HYPOCHLORITE

Sodium Hypochlorite Manufacturing Process



dilution, chlorination, filtration and distribution. Above is a simple process flow diagram.

During caustic dilution heat is generated. For instance 50% caustic soda can arrive at temperatures as high as 110°F and after dilution with 70°F water to 20% the final temperature is 130°F.

During chlorination heat is also generated. The amount of heat generated is 24,700 calories. See Eq.6. This equates to 627 BTU/lb of gaseous chlorine. By using liquid chlorine the heat generated is reduced by 109 BTU/lb (heat of vaporization of chlorine @ 70°F) or 518 BTU/lb of liquid chlorine. Using liquid chlorine not only generates less heat, but also eliminates the need for an expensive chlorine vaporizer and everything that goes along with it (maintenance, controls, steam, etc.).

Based on the heat generated from the heat of reaction and specific heat of bleach the temperature will increase about 0.6°F for each gpl available chlorine when using liquid chlorine and 0.7°F for each gpl available chlorine when using gaseous chlorine. When producing 60 gpl available chlorine using liquid chlorine the temperature will increase about 36°F, 0.6°F/gpl available chlorine * 60 gpl available chlorine.

High temperature increases the formation of sodium chlorate. For this reason it is best not to exceed 80°F during chlorination for dilute bleach solutions and 70°F for concentrated bleach solutions.

When making dilute bleach solutions it is possible to cool the diluted caustic soda sufficiently low that no additional cooling is needed during chlorination; 60 gpl available chlorine when using liquid chlorine and 50 gpl when using gaseous chlorine.

The reaction rate is very slow at temperatures less than 30°F. When making concentrated bleach solutions the diluted caustic soda would need to be cooled to less than 30°F, so cooling during chlorination is needed.

Cooling system are sized based on the amount of heat they can remove over time. A one ton system can remove 12,000 BTU/hour. The table on the next page shows the BTU generated when making 1,000 gallons of bleach in various concentrations from 10 to 200 gpl available chlorine using liquid chlorine. The size of the cooling system needed for making 1000 gallons/hour of 150 gpl available chlorine bleach with liquid chlorine is 54 tons, 648,628 BTU / 1 hr / 12,000 BTU/hr/ton. If this chlorination is done in a half hour the size of the cooling system will need to be twice as big, 104 tons. The same amount of heat has to be removed in half the amount of time.

Pumps and heat exchangers made of carbon steel are fine for the diluted caustic soda but in the chlorinator titanium and plastics are the preferred materials of construction.

Good agitation during chlorination is critical to making bleach with low chlorates. This eliminates high concentration areas of chlorine and bleach and hot spots. Static mixers are ideal for this application.

Raw Materials for Making 1000 Gallons of Bleach												Gallons of Bleach		
Available Cl_2		wt% NaOCl	SG	%NaOH (XS)	lb Cl_2	lb NaOH (Stoich)	lb NaOH (XS)	gpl NaOH (XS)	lb NaOH (Total)	%NaOH (Diluted)	BTU (liq Cl_2)	100 lb cylinder	150 lb cylinder	2000 lb container
wt%	gpl													
1.0	10.1	1.05	1.016	0.10	84.7	95.7	8.5	1.0	104.2	1.24	43,875	1,181	1,771	23,613
2.0	20.6	2.10	1.031	0.20	172.0	194.4	17.2	2.1	211.6	2.51	89,096	581	872	11,628
3.0	31.3	3.15	1.046	0.21	261.6	295.6	18.3	2.2	313.9	3.71	135,509	382	573	7,645
4.0	42.4	4.20	1.062	0.25	354.0	400.0	22.1	2.6	422.1	4.97	183,372	282	424	5,650
5.0	53.8	5.25	1.077	0.27	448.9	507.3	24.2	2.9	531.5	6.23	232,530	223	334	4,455
5.25	56.7	5.51	1.081	0.29	473.1	534.6	26.1	3.1	560.7	6.57	245,066	211	317	4,227
5.50	59.6	5.78	1.085	0.31	497.6	562.3	28.0	3.4	590.3	6.90	257,757	201	301	4,019
5.75	62.6	6.04	1.090	0.35	522.3	590.2	31.8	3.8	622.0	7.26	270,551	191	287	3,829
6.0	65.6	6.30	1.094	0.37	547.1	618.2	33.7	4.0	651.9	7.61	283,398	183	274	3,656
7.0	77.7	7.35	1.111	0.45	648.2	732.5	41.7	5.0	774.2	8.99	335,768	154	231	3,085
8.0	90.1	8.40	1.128	0.54	752.3	850.1	50.8	6.1	900.9	10.41	389,691	133	199	2,659
9.0	103.0	9.45	1.145	0.63	859.4	971.1	60.2	7.2	1,031.3	11.87	445,169	116	175	2,327
10.0	116.1	10.50	1.162	0.67	969.0	1,095.0	64.9	7.8	1,159.9	13.30	501,942	103	155	2,064
11.0	129.6	11.55	1.180	0.72	1,081.7	1,222.3	70.8	8.5	1,293.1	14.78	560,321	92	139	1,849
12.0	143.4	12.60	1.197	0.76	1,197.1	1,352.7	75.8	9.1	1,428.5	16.27	620,098	84	125	1,671
13.0	157.6	13.65	1.214	0.80	1,315.6	1,486.6	81.0	9.7	1,567.6	17.80	681,481	76	114	1,520
14.0	172.3	14.70	1.232	0.87	1,437.8	1,624.7	89.4	10.7	1,714.1	19.41	744,780	70	104	1,391
15.0	187.3	15.75	1.250	0.95	1,563.4	1,766.6	99.0	11.9	1,865.6	21.06	809,841	64	96	1,279
16.0	202.7	16.80	1.268	1.00	1,691.4	1,911.3	105.7	12.7	2,017.0	22.71	876,145	59	89	1,182

HANDLING AND STORAGE

HANDLING

Hypochlorite solutions are corrosive to eyes, skin and mucous membranes. Read and understand the SDS and wear all appropriate personal protective equipment.

STORAGE

Few materials of construction will withstand the highly reactive nature of sodium hypochlorite. Improper selection of those materials may result in damage to the handling system and contamination of the product. As a general rule, no metals (with the exception of titanium and tantalum under certain circumstances) should be allowed to come in contact with this chemical.

Warning - sodium hypochlorite solutions must be stored in vented containers, or in containers equipped with adequate relief devices due to O_2 gas generated from decomposition. If venting rate is exceeded by the decomposition rate, swelling or damage to the container may occur.

Bulk Storage Tanks

Tank and lining manufacturer's products and processes vary considerably, therefore, selecting an appropriate storage vessel should be given thorough evaluation. Consultation with tank and lining suppliers is recommended.

Sediments will accumulate in the bottom of the storage tank. To prevent transferring these sediments to the process the nozzle should not be located directly on the bottom of the tank. A low point drain is needed to drain these sediments from the storage tank periodically.

To maintain product quality, minimize the contamination of new material by the remaining material in the storage tank. The storage tank should used to the lowest possible level before new material is received to minimize contamination. Two smaller storage tanks, properly sized, used alternately to their lowest level before any new shipment is received is preferable to one large storage tank.

Storage tanks should have a level indicating device for measuring liquid level.

If possible, locate tank in a shaded area.

If it is necessary to insulate the storage tank to keep the product from freezing or cool to reduce decomposition, a two-inch layer of polyurethane foam or cellular glass should be adequate.

Proper design of a storage system will include adequate containment in case of tank failure. State and local regulatory authorities should always be consulted during the design phase of construction.

Rubber Lined Steel

Tanks of this type are generally custom fabricated for a specific process. They may be any size or shape depending on the needs of the user, but are typically closed vertical or horizontal cylindrical vessels from 1,000 to 30,000 gallons capacity.

Fiberglass

The success or failure of this type of tank when used in sodium hypochlorite service depends upon a large number of variables including resin type and additives, type of reinforcement, fabrication technique, storage temperature, environmental exposure and the characteristics of the solution. While many tanks of this type are currently in use, it is advisable to deal only with fabricators having experience with sodium hypochlorite and who are willing to warranty the vessel for the intended applications. Ensure the tank has adequate UV (ultraviolet) stabilizer or a gel coat outer layer designed for the area of intended use.

Polyethylene Tanks

Although some sodium hypochlorite users have had success with polyethylene tanks, some suppliers will not certify their tanks for this use.

TRANSFER SYSTEMS

Materials Selection

The following materials are compatible with sodium hypochlorite solutions or as linings for non-compatible materials. Some may not be suitable for use in processes that manufacture sodium hypochlorite.

- PVDF (polyvinylidene fluoride)
- PTFE (polytetrafluoroethylene)
- Titanium (Warning: titanium must not be used in contact with dry chlorine)
- Ethylene propylene rubber
- EPDM rubber (ethylene propylene diene monomer rubber)
- Chlorobutylene Rubber
- Polypropylene
- PVC (polyvinyl chloride)
- CPVC (chlorinated polyvinyl chloride)
- Tantalum
- Viton® A with a minimum durometer (hardness) of 70
- FRP

Piping

The two factors which determine the selection of piping materials for sodium hypochlorite solutions are structural strength and chemical resistance. Where piping systems may be subject to physical stress, lined steel pipe should be selected. Lining types include polypropylene, PVDF, PTFE, or similar thermoplastics. In lighter stress situations; fiberglass, CPVC and PVC is suitable. As with the fiberglass tanks, care should be exercised in the selection of the resin for fiberglass piping. Where piping will not be subject to impact, Schedule 80 PVC or CPVC is often used.

- Piping should be dedicated to prevent mixing incompatible materials or using the incorrect materials of construction.

- Locate unloading and unloading connections away from other connections that may contain incompatible materials.

- Loading and unloading piping should be short, visible and well marked so the loader can easily verify the connection is correct.

Valves

PTFE lined or PVC quarter-turn plug or ball valves are recommended for sodium hypochlorite service.

Pumps

Titanium or plastic lined pumps are recommended for sodium hypochlorite service. Magnetic drive pumps are well suited for this application. Size and other specifics should be determined by the pump manufacturer.

SYSTEM DESIGN

Discharge Systems

Where product quality is critical, filter systems are available to remove virtually all sediments. In some applications, the process can tolerate this sediment if it is continually transferred out of the storage tank along with the sodium hypochlorite solution. Cone bottom tanks can facilitate removal of the sediment. In other applications the process cannot tolerate this sediment and it cannot be allowed to accumulate.

Venting/Overflow System

The worst case condition for the vent sizing is usually the venting rate required due to decomposition of the contents of the storage vessel. The vent sizing required for discharging or filling is secondary. To eliminate excessive pressure or vacuum while filling or discharging the tank, a venting system must be provided. As a minimum, this system should contain a nozzle on top of the tank. It should be sized to prevent excessive vacuum or pressure when the tank is discharging or filling. When filling the tank from bulk tank trucks using air pressure, large "air hammers" may occur. Therefore, vent piping should be rigidly secured to prevent vibration. The tank should also have a nozzle on the side near the top. This nozzle should be sized to release the entire filling rate without reaching the tank's vent. Piping should be installed to direct the over flowing solution away from personnel into a containment area.

Gauging Devices

Some tanks are sufficiently translucent to allow for visual gauging from level markers painted on or molded into the side of the tanks. Where lighting conditions or tank construction do not permit this method of gauging, external gauging systems must be provided. Differential pressure systems have been used successfully. Manometers and sight glass gauges are also used but require additional liquid filled connections, thus potential failure points on the tank. An independent, back up level sensor should be used to prevent tank overflow in the event of a level gauge failure.

SAFETY HANDLING OF SODIUM HYPOCHLORITE

Read the SDS before use.

Sodium hypochlorite solution is normally a light yellow liquid with a characteristic bleach odor. Sodium hypochlorite is unstable and can release chlorine gas if mixed with acid. To improve the stability of hypochlorite solutions an excess alkalinity is maintained. Hypochlorite solutions are corrosive to eyes, skin and mucous membranes.

PRECAUTIONS

- Store in corrosion-resistant container.
- Keep container closed when not in use.
- Emergency shower and eyewash facility should be in close proximity to where sodium hypochlorite solution is handled.
- Insure adequate ventilation or use a NIOSH approved respirator with an acid gas cartridge with a dust, fume and mist filter where airborne concentrations are expected to exceed exposure limits or when symptoms have been observed that are indicative of overexposure.
- Avoid breathing fumes.
- Avoid contact with eyes, skin and clothing.
- Wash thoroughly after handling.
- Wear goggles and face shield, chemical resistant gloves, boots and apron or suit.
- Do not allow contact with organic materials such as rags, wood fibers, paper, debris, or with reducing chemicals except under controlled conditions.
- Do not discard indiscriminately. A spontaneous combustion fire could result due to the sodium chlorate generated from decomposition.
- Do no mix with acids, ammonia, heavy metals, ethers or reducing agents. To do so may release hazardous gases.

FIRST AID

Eyes:

IMMEDIATELY FLUSH EYES WITH A DIRECTED STREAM OF WATER for at least 15 minutes, forcibly holding eyelids apart to ensure complete irrigation of all eye and lid tissue. Washing eyes within several seconds is essential to achieve maximum effectiveness.

Skin:

Flush thoroughly with cool water under shower while removing contaminated clothing and shoes. Discard nonrubber shoes. Wash clothing before reuse.

Inhalation:

Remove to fresh air. If breathing is difficult, have trained person administer oxygen. If respiration stops, have a trained person administer artificial respiration.

Ingestion:

NEVER GIVE ANYTHING TO AN UNCONSCIOUS PERSON. If swallowed, DO NOT INDUCE VOMITING, although it may occur spontaneously. Give large quantities of water. If available, give several glasses of milk. Sodium bicarbonate, which would generate carbon dioxide should not be used. Keep airways clear. GET MEDICAL ATTENTION IMMEDIATELY.

FIRE

Use water or other extinguishing medium appropriate for surrounding fire. May release toxic fumes under fire conditions. Wear NIOSH/MSHA approved positive pressure self-contained breathing apparatus and full protective clothing.

SPILL

NEVER FLUSH TO SEWER. Contain the spill with dikes to prevent entry into sewers or waterways. For small spills, absorb with inorganic absorbents. Flush spill area with water ONLY IF water can be collected, and placed in an appropriate container for proper disposal. For large spills, dike and pump into properly labeled containers for proper disposal.

Report release, if required, to the appropriate local, state and federal agencies.

Hypochlorite neutralization is a two step process. First the potential to release chlorine due to the lowering of the pH must be eliminated and then pH adjustment. Sodium sulfite, sodium bisulfite, hydrogen peroxide and sodium thiosulfate can be used to reduce hypochlorite; each with it own advantages and disadvantages. Things to consider are safe handling, application, cost, solid or liquid, reactivity and reaction products. A simple test to verify the hypochlorite has been reduced is to use drops of hydrogen peroxide. The mix will release oxygen bubbles if hypochlorite exists. Once the release of chlorine potential has been eliminated a weak acid such as muriatic acid can be used to adjust the pH if needed. A plan should have been created and approved by authority and material should already be a available to carry out the plan when the time comes.

Note: For additional information refer to OxyChem Handbooks on Chlorine and Caustic Soda, in addition to the SDS on Chlorine, Caustic Soda and Sodium Hypochlorite.

SAFELY HANDLING OF SODIUM HYPOCHLORITE

Sodium Hypochlorite is shipped from OxyChem's Niagara Falls, New York plant in tank truck quantities.

Sodium Hypochlorite is regulated by the U.S. Department of Transportation (DOT). The hazard classification is 8, corrosive. The DOT identification number is UN1791.

Sodium Hypochlorite in any concentration must be respected by everyone who handles and uses it. Before starting to work with it, the user should be aware of its properties, know what safety precautions to follow, and know how to react in case of contact. Accidental exposure to sodium hypochlorite may occur under several conditions. Potentially hazardous situations include handling and packaging operations, equipment cleaning and repair, decontamination following spills and equipment failures. Employees who may be subject to such exposure must be provided with proper personal protective equipment and trained in its use. Some general guidelines follow.

- Read and understand the latest Safety Data Sheet.
- Provide eyewash stations and safety showers in all areas where sodium hypochlorite is used or handled. Any sodium hypochlorite burn may be serious. DO NOT use any kind of neutralizing solution, particularly in the eyes, without direction by a physician.
- Move the patient to a hospital emergency room immediately after first aid measures are applied.

FIRST AID MEASURES

Please consult OxyChem's latest Safety Data Sheet for sodium hypochlorite found online at www.oxychem.com for the latest first aid measures.

PERSONAL PROTECTIVE EQUIPMENT

OSHA requires employers to supply suitable protective equipment for employees. When handling sodium hypochlorite, the following protective equipment is recommended:

- Wear suitable chemical splash goggles for eye protection during the handling of sodium hypochlorite at any concentration. The goggles should be close fitting and provide adequate ventilation to prevent fogging, without allowing entry of liquids. The use of a face shield may be appropriate when splashing may occur, including loading and unloading operations.
- Wear rubber gloves or gloves coated with rubber, synthetic elastomers, PVC, or other plastics to protect the hands while handling sodium hypochlorite. Gloves should be long enough to come well above the wrist. Sleeves should be positioned over the glove.
- Sodium hypochlorite causes leather to disintegrate quite rapidly. For this reason, wear rubber boots. Wear the bottoms of pant legs outside the boots. DO NOT tuck pant legs into boots.
- Wear chemical resistant clothing for protection of the body. Impregnated vinyl or rubber suits are recommended.
- Wear hard hats for protection of the head, face and neck.
- If exposures are expected to exceed accepted regulatory limits or if respiratory discomfort is experienced use a NIOSH approved air purifying respirator with high efficiency dust and mist filters.

PROTECTIVE PRACTICES

Keep equipment clean by immediately washing off any spill or accumulation of sodium hypochlorite.

Weld pipelines where practical. Use flanged joints with gaskets made of sodium hypochlorite resistant material such as rubber, PTFE, or EPDM rubber. If a screwed fitting is used, apply Teflon® tape to the threads.

When disconnecting equipment for repairs, first verify that there is no internal pressure on the equipment and that the equipment has been drained and washed.

Provide storage tanks with suitable overflow pipes. Overflow pipes should be directed to a protected overflow area away from operations.

Shield the seal area of pumps to prevent spraying of sodium hypochlorite solutions in the event of a leak.

When releasing air pressure from a pressurized system, take every precaution to avoid spurts or sprays of sodium hypochlorite solution.

In case of a spill or leak, stop the leak as soon as possible. See page 8 for spill clean up.

UNLOADING SODIUM HYPOCHLORITE TANK TRUCKS

GENERAL INFORMATION

Sodium hypochlorite is very corrosive to all body tissues. Even dilute solutions may have a destructive effect on tissue after prolonged contact. Inhalation of mists can cause damage to the upper respiratory tract, while ingestion of sodium hypochlorite can cause severe damage to the mucous membranes or other tissues where contact is made.

It is important that those who handle sodium hypochlorite are aware of its corrosive properties and know what precautions to take. In case of accidental exposure, immediately flush the exposed area with large amounts of water and seek medical attention. For more specific information refer to the Safety in Handling sodium hypochlorite section of this handbook and in the OxyChem SDS for sodium hypochlorite .

CARRIER RESPONSIBILITIES

Tank truck drivers have received instructions regarding equipment and delivery procedures. If an OxyChem arranged carrier, delivering sodium hypochlorite to your plant, fails to adhere to the guidelines, please contact OxyChem so that corrective action can be taken.

Equipment

Equipment must meet Department of Transportation regulations, Code of Federal Regulations (CFR), Title 49.

Tank Truck Specification

Tank trucks should meet the established DOT requirements for hauling sodium hypochlorite. Material of construction is FRP or rubber lined steel. Four DOT “CORROSIVE” 1791 placards must be affixed to the cargo tank. One on each side.

Unloading Equipment

If unloading is by gravity to storage or customer’s unloading pump, no special equipment is needed.

If unloading by pump, the pump must be made from an appropriate material of construction. Use at least a 2-inch unload line.

If unloading is by compressed air, the air must be free of oils, greases and other compounds. The air supply is required to be equipped with: pressure reducing valve, pressure relief valve, pressure gauge, and block valve. The relief valve should be set at a maximum pressure of 20 psig and the pressure reducing valve should be set at 2 to 3 psig lower.

A 40 foot length of air hose is required if the customer’s air supply is used. When compressed air is not available from the customer’s plant, trucks equipped with pumps or air compressors can be provided at the customer’s request.

Unloading Lines

Unloading hoses must be constructed of material resistant to sodium hypochlorite. Hoses should be at least 2 inches in diameter and 15 to 30 feet in length.

Whether the unloading hose is fitted with a union, pipe flange, or a quick type coupler, the truck driver should have available matching fittings and tools to facilitate a connection to a 2-inch or 3-inch threaded pipe.

UNLOADING SODIUM HYPOCHLORITE TANK TRUCKS

TRUCK DRIVER RESPONSIBILITIES

Truck drivers must obtain permission to unload from the proper site personnel and observe any special instructions from the customer.

Truck drivers must wear the protective equipment required by OxyChem or by the customer, whichever is more inclusive, and at all times follow safe handling practices. Customers must not allow truck drivers who do not meet these requirements to unload.

The following unloading procedures are recommended:

Verify the trailer contains sodium hypochlorite by inspecting the shipping papers, placards (UN1791) and/or sampling.

Verify the entire content of the trailer will fit into the receiving tank.

Locate the nearest safety shower and eyewash station and verify its operation. Allow the water to run till it flows clean, free of rust or debris that could accumulate.

Verify the spill containment sump is free of any incompatible material that could react with spilled sodium hypochlorite causing a more serious event.

Connect the unloading hose to the discharge outlet on the tank truck.

Connect the other end of the unloading hose to the customer’s connection. The connection must be clearly labeled for sodium hypochlorite unloading. Have a second person confirm the connection is to the correct tank.

Customer should verify all valves to the storage tank are properly aligned and then open their unloading valve. Consider putting a lock on the unloading valve to prevent unloading into the tank prior to proper verification.

Open the valves on the truck discharge.

If unloading using a pump ensure the manway is open or there is a positive pad pressure. If pressurizing the content to the storage tank a pressure of 15 - 20 psig should be sufficient.

Start the pump or pressurizing the tank, depending on the type of equipment being used.

Verify the level in the tank is increasing. If the level is not increasing the transfer could be going to the wrong tank.

DOT regulations require a qualified person to be in attendance at all times during unloading.

If compressed air is used for off loading, allow the air to blow out the line to the storage tank, then close the air valve, allow the pressure to bled off to the storage tank and then disconnect the air supply.

Close the truck discharge valves and customer unloading valve.

Depressurize the unload hose. Drain the hose to an appropriate container and disconnect it from the tank truck and customer unloading connection.

Reapply any flange covers or caps on the customer line.

Cap the truck unloading hoses and secure both hoses in the carrier tubes or tray.

PHYSICAL PROPERTY DATA FOR SODIUM HYPOCHLORITE

Sodium Hypochlorite pH Calculated from Excess NaOH
pH = 14 + log(gpl NaOH / 40.00)

gpl NaOH	pH	gpl NaOH	pH	gpl NaOH	pH	gpl NaOH	pH
0.01	10.40	0.85	12.33	1.85	12.67	3.20	12.90
0.02	10.70	0.90	12.35	1.90	12.68	3.30	12.92
0.03	10.88	0.95	12.38	1.95	12.69	3.40	12.93
0.04	11.00	1.00	12.40	2.00	12.70	3.50	12.94
0.05	11.10	1.05	12.42	2.05	12.71	3.60	12.95
0.10	11.40	1.10	12.44	2.10	12.72	3.70	12.97
0.15	11.57	1.15	12.46	2.15	12.73	3.80	12.98
0.20	11.70	1.20	12.48	2.20	12.74	3.90	12.99
0.25	11.80	1.25	12.49	2.25	12.75	4.00	13.00
0.30	11.88	1.30	12.51	2.30	12.76	4.10	13.01
0.35	11.94	1.35	12.53	2.35	12.77	4.20	13.02
0.40	12.00	1.40	12.54	2.40	12.78	4.30	13.03
0.45	12.05	1.45	12.56	2.45	12.79	4.40	13.04
0.50	12.10	1.50	12.57	2.50	12.80	4.50	13.05
0.55	12.14	1.55	12.59	2.60	12.81	4.60	13.06
0.60	12.18	1.60	12.60	2.70	12.83	4.70	13.07
0.65	12.21	1.65	12.62	2.80	12.85	4.80	13.08
0.70	12.24	1.70	12.63	2.90	12.86	4.90	13.09
0.75	12.27	1.75	12.64	3.00	12.88	5.00	13.10
0.80	12.30	1.80	12.65	3.10	12.89	5.10	13.11

Approximate Freezing Point of Sodium Hypochlorite Solution
Data from The Dow Chemical Company

wt% NaOCl	Freezing Pt (°F)	Freezing Pt (°C)
0	32.0	0.0
2	28.0	-2.2
4	24.0	-4.4
6	18.5	-7.5
8	14.0	-10.0
10	7.0	-13.9
12	-3.0	-19.4
14	-14.0	-25.6
15.6	-21.5	-29.7
16	-16.5	-26.9

Molecular Weights:
Sodium Hypochlorite, NaOCl = 74.44
Sodium Hydroxide, NaOH = 40.00
Chlorine, Cl_2 = 70.90

Conversion factors:
3.7854 liters/gallon
453.6 grams/pound

Density of water @ 60°F
8.34 lbs/gal

Specific Gravity of Sodium Hypochlorite Solutions w/ Various Levels of Excess NaOH @ 20°C
SG = SG @ 0 gpl Available Cl_2 + (0.00135 * gpl XS NaOH)

gpl Available	gpl Excess Sodium Hydroxide (NaOH)					
	0	2	4	6	8	10
40	1.055	1.058	1.060	1.063	1.066	1.069
60	1.082	1.085	1.087	1.090	1.093	1.096
80	1.107	1.110	1.112	1.115	1.118	1.121
100	1.132	1.135	1.137	1.140	1.143	1.146
120	1.157	1.160	1.162	1.165	1.168	1.171
140	1.180	1.183	1.185	1.188	1.191	1.194
150	1.192	1.195	1.197	1.200	1.203	1.206
160	1.204	1.207	1.209	1.212	1.215	1.218
180	1.227	1.230	1.232	1.235	1.238	1.241
200	1.249	1.252	1.254	1.257	1.260	1.263

Vapor Pressure of 12.5 wt% Sodium Hypochlorite Solution

Temperature		Vapor Pressure	
(°F)	(°C)	(mmHg)	(psia)
48.2	9	3.7	0.071
60.8	16	8.0	0.15
68.0	20	12.1	0.23
89.6	32	31.1	0.60
118.4	48	100.0	1.93

PHYSICAL PROPERTY DATA FOR SODIUM HYPOCHLORITE

Specific Gravity of Caustic Soda Solutions

wt% NaOH	Dia-phragm	Mem-brane	wt% NaOH	Dia-phragm	Mem-brane	wt% NaOH	Dia-phragm	Mem-brane
1.0	1.0121	1.0120	19.0	1.2152	1.2124	37.0	1.4101	1.4046
2.0	1.0223	1.0230	20.0	1.2263	1.2234	38.0	1.4204	1.4148
3.0	1.0346	1.0342	21.0	1.2375	1.2344	39.0	1.4306	1.4248
4.0	1.0459	1.0453	22.0	1.2486	1.2454	40.0	1.4407	1.4348
5.0	1.0571	1.0564	23.0	1.2597	1.2563	41.0	1.4508	1.4447
6.0	1.0684	1.0676	24.0	1.2708	1.2672	42.0	1.4607	1.4545
7.0	1.0797	1.0787	25.0	1.2818	1.2781	43.0	1.4706	1.4643
8.0	1.0911	1.0899	26.0	1.2928	1.2889	44.0	1.4804	1.4739
9.0	1.1024	1.1010	27.0	1.3037	1.2997	45.0	1.4901	1.4835
10.0	1.1137	1.1122	28.0	1.3146	1.3105	46.0	1.4997	1.4930
11.0	1.1250	1.1234	29.0	1.3254	1.3212	47.0	1.5092	1.5023
12.0	1.1363	1.1345	30.0	1.3362	1.3317	48.0	1.5187	1.5116
13.0	1.1476	1.1457	31.0	1.3470	1.3424	49.0	1.5280	1.508
14.0	1.1589	1.1569	32.0	1.3576	1.3529	50.0	1.5372	1.5298
15.0	1.1702	1.1680	33.0	1.3683	1.3634	51.0	1.5506	1.5388
16.0	1.1815	1.1791	34.0	1.3788	1.3738	52.0	1.5604	1.5476
17.0	1.1927	1.1902	35.0	1.3893	1.3842			
18.0	1.2040	1.2013	36.0	1.3997	1.3944			

DETERMINATION OF SODIUM HYPOCHLORITE, SODIUM HYDROXIDE AND SODIUM CARBONATE IN CAUSTIC SODA BLEACH SOLUTIONS

PURPOSE

To provide a means to quantify the amount of sodium hypochlorite, sodium hydroxide and sodium carbonate in caustic soda bleach solutions.

THEORY

Sodium hypochlorite (NaOCl) is the active agent in caustic soda bleach solutions. Chemically, hypochlorites are the salts of hypochlorous acid (HOCl) and are inherently unstable. The stability of a hypochlorite solution is dependent on five major factors.

1. Hypochlorite concentration.
2. Alkalinity (pH) of the solution.
3. Temperature of the solution, both in production and storage.
4. Concentration of impurities which catalyze decomposition.
5. Exposure to light.

Any one of the above factors or combination of factors can affect the strength of a caustic soda bleach solution. Therefore, reliable methods for determining the sodium hypochlorite and sodium hydroxide concentrations of a caustic soda bleach solution are necessary.

A) Hypochlorite Determination

Hypochlorite concentration is determined by iodometric titration. The hypochlorite ion is first reacted with excess potassium iodide (KI) in an acidic medium to form iodine (I_2).

$$NaOCl + 2\,CH_3COOH + 2\,KI \rightarrow NaCl + 2\,CH_3COOK + I_2 + H_2O$$

Each mole of iodine is then titrated with two moles of sodium thiosulfate to determine the concentration of iodine. The percent hypochlorite is then calculated based on the iodine concentration.

$$I_2 + 2\,S_2O_3^{2-} \rightarrow 2\,I^- + S_4O_6^{2-}$$

B) Sodium Hydroxide and Sodium Carbonate Determination

Sodium hydroxide and sodium carbonate concentrations are determined by a two-step titration with a hydrochloric acid solution. During the first step, the hydroxide is neutralized and the carbonate is converted to bicarbonate.

3) $NaOH + HCl \rightarrow NaCl + H_2O$

4) $Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$

When both of these reactions (Eq. 3 and 4) come to completion, an endpoint is indicated; the solution is then further titrated with acid to convert the bicarbonate to water and carbon dioxide.

5) $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

A second endpoint is indicated at the completion of this reaction. The volumes of acid used in these two steps are then used to calculate the percent sodium hydroxide and sodium carbonate.

APPARATUS

Analytical Balance; 200g capacity, 0.1mg readability (Mettler ML204 or equiv.)
250 ml Erlenmeyer Flask; (Fisher Scientific Cat.# 10-090B or equiv.)
Magnetic Stirrer; (Fisher Scientific Cat.# 14-493-120SQ or equiv.)
Magnetic Stir Bar; (Fisher Scientific Cat.# 14-513-60 or equiv.)
250 ml Volumetric Flask; Class A Volumetric, (Fisher Scientific Cat.# 10-210E or equiv.)
5 ml Pipet; Class A Volumetric, (Fisher Scientific Cat.# 13-650-2F or equiv.)
10 ml Pipet; Class A Volumetric, (Fisher Scientific Cat.# 13-650-2L or equiv.)
20 ml Pipet; Class A Volumetric, (Fisher Scientific Cat.# 13-650-2N or equiv.)
25 ml Pipet; Class A Volumetric, (Fisher Scientific Cat.# 13-650-2P or equiv.)
50 ml Pipet; Class A Volumetric, (Fisher Scientific Cat.# 13-650-2S or equiv.)
50 ml Buret; Class A Volumetric, (Fisher Scientific Cat.# 03-700-22C or equiv.)

REAGENTS

Deionized water
1:1 Acetic Acid Solution; Add 500 ml of ACS reagent grade Glacial Acetic Acid (Fisher Scientific Cat.# A38-212 or equiv.) to 500 ml of deionized water.
10% Potassium Iodide Solution; Weigh 100.0g of KI (Fisher Scientific Cat.# P412-500 or equiv.) into a one liter volumetric flask, add deionized water and mix to dissolve. Dilute with deionized water to volume.
3% Hydrogen Peroxide Solution; (Fisher Scientific Cat.# H312-500 or equiv.)
1% Starch Solution; (Fisher Scientific Cat.# SS408-1 or equiv.)

0.1N Sodium Thiosulfate Solution; Weigh 25g of $Na_2S_2O_3$ (Fisher Scientific Cat.# S445-500 or equiv.) into a one liter volumetric flask, add deionized water and mix to dissolve. Dilute with deionized water to volume. Store the solution in a tightly capped amber bottle. Standardize the solution before use (see Standardization section). Standardized 0.1N $Na_2S_2O_3$ is also available (Fisher Scientific Cat.# SS368-1).
1% Phenolphthalein Solution; (Fisher Scientific Cat.# SP62-500 or equiv.)
0.1% Methyl Orange Solution; (Fisher Scientific Cat.# SM54-500 or equiv.)
0.1N Hydrochloric Acid Solution; Transfer 8.3 ml of ACS reagent grade hydrochloric acid (Fisher Scientific Cat.# A144-500 or equiv.) into a one liter volumetric flask containing deionized water, add additional deionized water to bring to volume. Standardize the solution before use (see Standardization section). Standardized 0.1N HCl is available (Fisher Scientific Cat.# SA54-1).

SAFETY

Refer to the MSDS for the proper handling procedures for all chemicals being analyzed by this method.

Caustic soda bleach solutions are irritating to the eyes and skin. Potassium iodide is toxic and sodium thiosulfate is an irritant, both should be handled with care. Acetic acid and hydrochloric acid are extremely corrosive. If any of these chemicals comes in contact with the eyes or skin, the affected area should be flushed with plenty of clean water for a minimum of 15 minutes. **Seek medical attention immediately.**

PROCEDURE

Sodium Hypochlorite Determination

1. Pipet 25 ml of caustic soda bleach solution into a 250 ml volumetric flask. Record the weight to the nearest 0.01g. Add deionized water to the 250 ml mark and mix thoroughly. This sample solution will be used as a stock solution for the determination of %NaOH, %NaOCl, and %Na_2CO_3.
   Note: This sample size is for commercial strength bleach solutions (approximately 5.25% NaOCl). For bleach with solution strengths different from commercial grade products, adjustments to sample size or aliquot size may be necessary.
2. Pipet a 10 ml aliquot of the stock solution into a 250 ml Erlenmeyer flask containing 50 ml of deionized water.
3. Add 25 ml of 10% potassium iodide solution. The sample solution will change from clear to an intense yellow color.
4. Add 10 ml of 1:1 acetic acid solution. Addition of acetic acid to a solution containing iodide liberates iodine which results in a further color change to amber brown.
5. Place the mixture on a magnetic stirring apparatus and gently stir.
6. Titrate using 0.1N sodium thiosulfate solution to a straw yellow color, taking care to not over-titrate the sample to clear.
7. Add 5 ml of starch solution. The starch solution reacts with iodine to form a very intense blue/purple color. Continue the titration until the blue color disappears.
8. Record the volume (ml) of 0.1N sodium thiosulfate solution used. This volume will be used to calculate the %NaOCl in the sample.

Sodium Hydroxide and Sodium Carbonate Determination

1. Pipet a 50 ml aliquot of the stock solution (see Step 1 of sodium hypochlorite determination) into 250 ml Erlenmeyer flask containing 50 ml of deionized water.
2. Add 20 ml of 3% hydrogen peroxide solution and cool the sample to 0° to 5°C. The addition of peroxide is necessary to neutralize the sodium hypochlorite in the sample aliquot.
3. Add 3 drops of 1% phenolphthalein solution and titrate with 0.1N hydrochloric acid solution until the pink color disappears.
4. Record the volume of acid used to the nearest 0.02 ml. This volume will be used to determine the %NaOH present in the sample solution.
5. Add 3 drops of methyl orange solution to the same sample solution and continue to titrate with 0.1N hydrochloric acid solution until the yellow color changes to red. Take care to titrate slowly since very little acid will be required to produce the second endpoint.
6. Record the volume of acid used to the nearest 0.02 ml. This volume will be used to determine the %Na_2CO_3 present in the sample solution.

CALCULATIONS

A) %NaOCl Determination

W = Weight (g) of original sample
V = Volume (ml) of 0.1N sodium thiosulfate solution
N = Normality of sodium thiosulfate solution
10/250 = Dilution factor from stock solution, i.e. 10 ml aliquot taken from 250 ml stock
0.03723 = milliequivalent weight of NaOCl
0.03545 = milliequivalent weight of Cl_2

The sodium hypochlorite content can be calculated as wt% NaOCl or as wt% Available Chlorine.

$$\%NaOCl = (V)(N)(0.03722)(100)/(10/250)/(W)$$

$$\%\text{Available Chlorine} = (V)(N)(0.03545)(100)/(10/250)/(W)$$

B) %NaOH and Na_2CO_3 Determination

W = Weight (g) of original sample
V_1 = Volume (ml) of 0.1N HCl needed to reach the phenolphthalein endpoint
V_2 = Volume (ml) of 0.1N HCl needed to reach the methyl orange endpoint
N = Normality of the hydrochloric acid solution
50/250 = Dilution factor from stock solution, i.e. 50 ml aliquot taken from 250 ml stock
0.040 = milliequivalent weight of NaOH
0.053 = milliequivalent weight of Na_2CO_3

V_1 is the amount of acid required to neutralize the hydroxide and convert the carbonate to bicarbonate as shown in equations 3 and 4.

$V_2 - V_1$ is the amount of acid required to convert the bicarbonate to carbon dioxide and water as shown in equation 5.

The overall titration of sodium carbonate with hydrochloric acid requires two moles of HCl for each mole of Na_2CO_3 since one mole is needed to convert Na_2CO_3 to $NaHCO_3$ and another mole is required to convert the $NaHCO_3$ to CO_2.

Therefore
$2(V_2 - V_1)$ = Volume of acid that reacted with Na_2CO_3
and
$V_2 - 2(V_2 - V_1)$ = Volume of acid that reacted with the NaOH

$$\%NaOH = [V_2 - 2(V_2 - V_1)](N)(0.040)(100)/(50/250)/(W)$$

$$\%Na_2CO_3 = 2(V_2 - V_1)(N)(0.053)(100)/(50/250)/(W)$$

QUALITY ASSURANCE

Clean all apparatus before use to eliminate contamination.

Duplicate analysis should be performed on a minimum of 10% of samples analyzed. Results should be reproducible within 0.025%.

Concentrations of sodium hypochlorite, sodium hydroxide, and sodium carbonate found in samples should be compared with the manufacturers specifications (if available) to ensure the product meets these standards.

Hydrochloric acid and sodium thiosulfate solutions should be standardized at least monthly.

REFERENCES

1. ASTM Volume 15.04, D 2022 with Modifications
2. Vogel, Arthur I., A Textbook of Qualitative Inorganic Analysis, 3rd edition, 1961

STANDARDIZATION OF 0.1N HCl SOLUTION USING SODIUM CARBONATE AND MODIFIED METHYL ORANGE INDICATOR

APPARATUS

Analytical Balance; 200g capacity, 0.1mg readability (Mettler ML204 or equiv.)
250 ml Erlenmeyer Flask; (Fischer Scientific Cat.# 10-090B or equiv.)
Magnetic Stirrer; (Fisher Scientific Cat.# 14-493-120SQ or equiv.)
Magnetic Stir Bar; (Fischer Scientific Cat.# 14-513-60 or equiv.)
100 ml Buret; Class A Volumetric, (Fischer Scientific Cat.# 03-700-22D or equiv.)
Weighing Dish; disposable (Fischer Scientific Cat.# 02-202-100 or equiv.)

REAGENTS

0.1N Hydrochloric Acid Solution; Transfer 8.3 ml of hydrochloric acid (Fisher Scientific Cat.# A144-500 or equiv.) into a one liter volumetric flask containing deionized water; add additional deionized water to bring to volume.
Sodium Carbonate Anhydrous; 99.5% min., (Fisher Scientific Cat.# S263500 or equiv.) Dry at 250°C in a platinum or porcelain crucible for 4 hrs.
Deionized water; Water should be carbon dioxide free (freshly boiled and cooled or purged with nitrogen for two hours).

Modified Methyl Orange Indicator; Dissolve 0.14g of Methyl Orange, (Fisher Scientific Cat.# M216-25 or equiv.) and 0.12g of Xylene Cyanole FF (Fisher Scientific Cat.# BP565-10 or equiv.) in water and dilute to 100 ml.

SAFETY

Refer to MSDS for the proper handling procedures for each of the chemicals listed in this procedure.

Hydrochloric acid is a strong acid, it is corrosive to body tissue and can cause immediate and severe burns to eyes. Wear proper gloves, proper eye protection and other protective clothing when handling.

When handling sodium carbonate, avoid inhalation or contact with skin.

Xylene Cyanole is a flammable solid. Use proper ventilation, avoid prolonged breathing of vapors or prolonged or repeated contact with skin.

STANDARDIZATION PROCEDURE

1. Weigh 1.0g of sodium carbonate to the nearest 0.0001g into a weighing dish. Carefully transfer this material to an Erlenmeyer flask, add 75 ml of deionized water and swirl to dissolve.
2. Add 3 drops of the modified orange solution.
3. Place the mixture on a magnetic stirring apparatus and gently stir.
4. Titrate with the HCl solution to a magenta color change. Record the volume of HCl solution used to the nearest 0.02 ml. Theoretically 188.68 ml of HCl solution should be required.
5. Repeat the titration two more times.

CALCULATIONS

The following formula is used to calculate the normality of the hydrochloric acid.

W = Weight (g) of Na_2CO_3 used
V = Volume of HCl required
N = Normality of HCl
0.053 = milliequivalent weight of Na_2CO_3

$$N = (W)/(V)/(0.053)$$

Calculate the average normality of hydrochloric acid from the individual values. Also calculate the standard deviation and percent relative standard deviation (%RSD) for the standardization procedure.

STABILITY

Restandardize monthly or sooner.

STANDARDIZATION OF 0.1N SODIUM THIOSULFATE WITH POTASSIUM IODATE

THEORY

A solution of sodium thiosulfate can be standardized by titrating it into an acid solution containing a known amount of potassium iodate and a starch indicator. The acid reacts with the iodate to form iodine. The iodine is stoichiometrically reduced by the thiosulfate. The endpoint of the reaction is indicated when the solution changes from a blue color to colorless. Six moles of $Na_2S_2O_3$ are required to react with 1 mole of KIO_3.

$$IO_3^- + 5\,I^- + 6\,H^+ \rightarrow 3\,I_2 + 3\,H_2O$$

$$2\,S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2\,I^-$$

APPARATUS

Analytical Balance; 200g capacity, 0.1mg readability (Mettler ML204 or equiv.)
250 ml Erlenmeyer Flask; (Fisher Scientific Cat.# 10-090B or equiv.)
Magnetic Stirrer; (Fisher Scientific Cat.# 14-493-120SQ or equiv.)
Magnetic Stir Bar; (Fisher Scientific Cat.# 14-513-60 or equiv.)
250 ml Volumetric Flask; Class A Volumetric, (Fisher Scientific Cat.# 10-210E or equiv.)
2 ml Pipet; Class A Volumetric, (Fisher Scientific Cat.# 13-650-2C or equiv.)
5 ml Pipet; Class A Volumetric, (Fisher Scientific Cat.# 13-650-2F or equiv.)
50 ml Buret; Class A Volumetric, (Fisher Scientific Cat.# 03-700-22C or equiv.)

REAGENTS

Deionized water

1N Sodium Thiosulfate Solution; Weigh 25g of $Na_2S_2O_3$ (Fisher Scientific Cat.# S445-500 or equiv.) into a one liter volumetric flask, add deionized water and mix to dissolve. Dilute with deionized water to volume. Store the solution in a tightly capped amber bottle.

Potassium Iodide; iodate free (Fisher Scientific Cat.# P410-100 or equiv.)

Potassium Iodate; dried at 120°C for at least one hour (Fisher Scientific Cat.# P253-100 or equiv.)

2N Sulfuric Acid Solution; Weigh 55.6g of ACS reagent grade sulfuric acid (Fisher Scientific Cat.# A300-500 or equiv.) into a one liter volumetric flask containing 500 ml of deionized water, mix, allow to cool and diluted to volume with deionized water.

1% Starch Solution; (Fisher Scientific Cat.# SS408-1 or equiv.)

1% Phenolphthalein Solution; (Fisher Scientific Cat.# SP62-500 or equiv.)

0.1% Methyl Orange Solution; (Fisher Scientific Cat.# SM54-500 or equiv.)

SAFETY

Refer to the MSDS for the proper handling procedures for all chemicals being analyzed by this method.

Potassium iodate is an oxidizer, potassium iodide is toxic, sodium thiosulfate is an irritant and sulfuric acid is extremely corrosive. If any of these chemicals comes in contact with the eyes or skin, the affected area should be flushed with plenty of clean water for a minimum of 15 minutes. **Seek medical attention immediately.**

PROCEDURE

1. Weigh 0.15g of dried potassium iodate to the nearest 0.0001g, transfer to a 250 ml Erlenmeyer flask and dissolve in 50 ml of deionized water.
2. Add 2.0g of iodate free potassium iodide and 5 ml of 2N sulfuric acid. Note: To determine if the KI is iodate free, dissolve a small portion of the reagent in 2N sulfuric acid solution. No immediate yellow color should be observed. Add 1-2 ml of starch solution, if no immediate blue color is produced, the potassium iodide is iodate free.
3. Place the mixture on a magnetic stirring apparatus and gently stir.
4. Titrate using 0.1N sodium thiosulfate to a straw-yellow color, taking care to not over-titrate the sample to clear.
5. Add approximately 100 ml of deionized water and 2.0 ml of starch solution and continue the titration until the blue color disappears. To achieve accurate results, the addition of the sodium thiosulfate should be done very slowly. The endpoint of the titration is very sharp (color changes from dark blue or purple to clear) and dropwise addition is recommended. Record the volume of sodium thiosulfate used to the nearest 0.02 ml. Theoretically 42.06 ml of sodium thiosulfate solution should be required.
6. Repeat the titration two more times.

CALCULATIONS

The following formula is used to calculate the normality of the sodium thiosulfate.

W = Weight (g) of potassium iodate
V = Volume (ml) of 0.1N sodium thiosulfate needed to reach the clear endpoint
N = Normality of the sodium thiosulfate solution.
0.03567 = milliequivalent weight of KIO_3

$$N = (W)/(V)/(0.03567)$$

Average the values obtained from the three titration and also calculate the standard deviation and percent relative standard deviation (% RSD) of the standardization procedure.

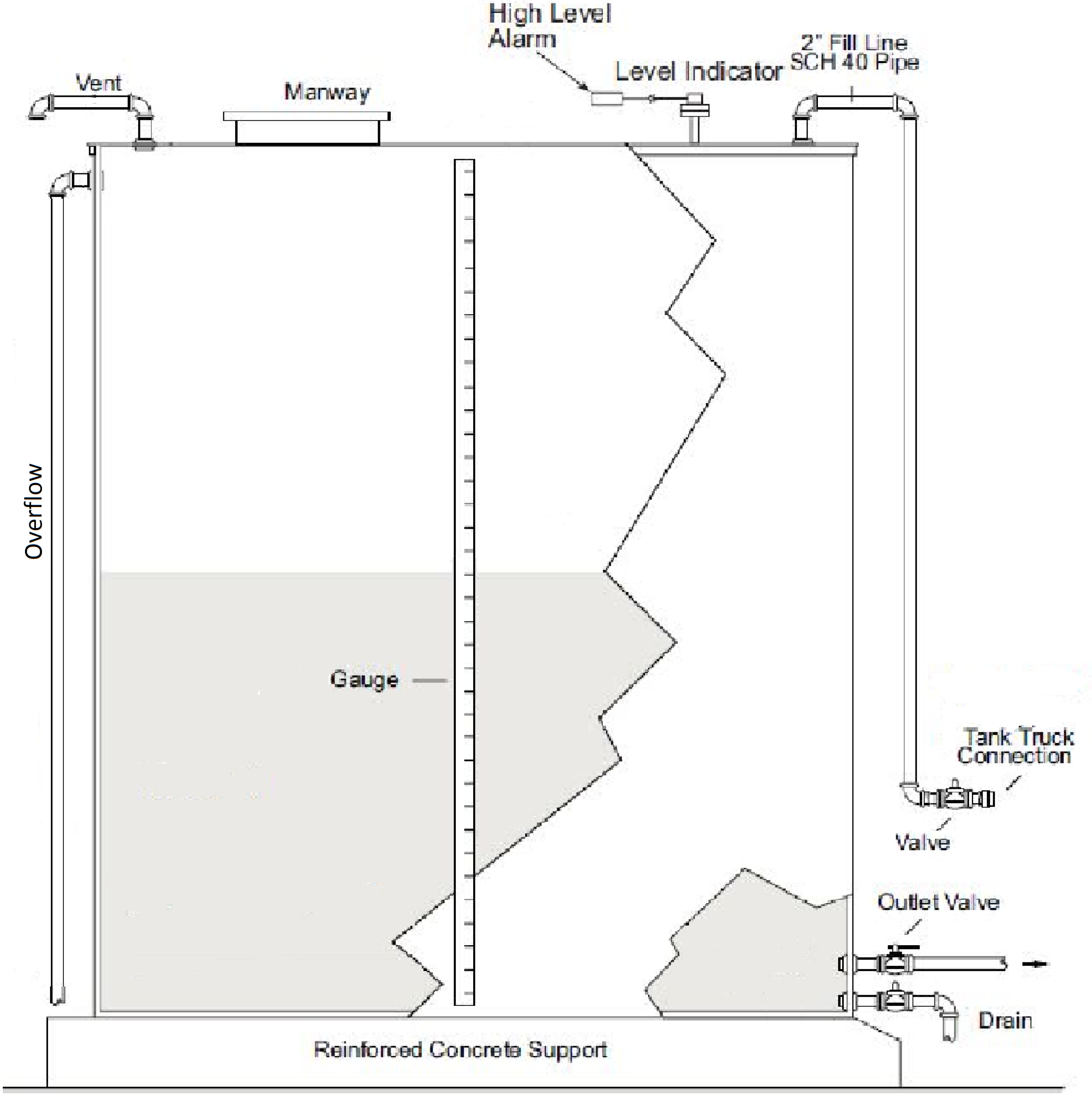
STABILITY

Sodium thiosulfate solutions are relatively stable, but do decompose over time. Exposure to air (especially carbon dioxide), light and airborne bacteria will accelerate the decomposition reaction. Therefore, restandardization should be performed on monthly basis or sooner.

REFERENCES

1. ASTM 15.04 D 2022 with modifications
2. Vogel, Arthur I., A Textbook of Qualitative Inorganic Analysis, 3rd edition, 1961.

TYPICAL STORAGE TANK INSTALLATION



NOTES

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