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High Strength Low Salt (HSLS) Bleach: Chemical Basis for Improved Bleach Quality and Production

Summary

High Strength Low Salt (HSLS) bleach results in better bleach quality. Upon storage, bleach decomposes to form chlorate ion, oxygen and perchlorate ion. Because HSLS bleach has less chloride ion, the ionic strength of the bleach is lowered resulting in slower decomposition rates, increased half-lives, and the formation of less chlorate ion, oxygen and perchlorate ion. This is especially important in the warm summer months when rising temperatures have a pronounced effect on a utilities ability to store bleach for later use.

The chemistry advantages can be summarized:

- Slower decomposition resulting in a longer half-life
- Less chlorate ion formation
- Less oxygen formation
- Less perchlorate ion formation

Introduction

The chemistry associated with bleach production and storage indicates that a low salt product will increase bleach quality and stability. The fact remains that bleach decomposes to form unwanted by-products and lower chlorine concentrations over time. The ability to slow down the decomposition offers a number of advantages for both the bleach producer and the bleach consumer.

High Strength Low Salt (HSLS) bleach is more stable than typical bleach because it contains less salt. Salt (NaCl) increases the ionic strength of the bleach product and thus influences the rate of decomposition. The removal of salt from bleach from a chemistry view results in slower decomposition rates, less unwanted by-products from the decomposition process (chlorate ion, oxygen, perchlorate ion) and a longer shelf-life for the product.

As a practical matter, after the purchase of high concentration bulk bleach storage becomes important. Because HSLS bleach decomposes slower than typical bleach, temperature issues (although important) may become less critical. The slower decomposition rate also helps to minimize chlorate ion, oxygen formation and perchlorate ion, each of which can influence how bleach is stored on-site.

The discussion that follows provides the chemistry basis for why HSLS is a more stable and thus a higher quality bleach product.

Bleach Production and Decomposition

Liquid bleach is manufactured by reacting chlorine with caustic:

$$2NaOH + Cl_2 \rightarrow NaOCl + NaCl + H_2O$$

This means that 1 mole of chloride ion (salt) is produced for each mole of hypochlorite ion produced.

Commercially produced liquid bleach typically has an approximate pH of 13. In basic solution, OCl^- decomposition to form chlorate ion has been shown to be a second-order process over the pH 11 -13 range

$$Rate = k_2 [OCl^-]^2$$

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.

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

This means that chlorite ion is a steady state intermediate that does not build up in bleach during storage. It also means that each chlorate ion that is formed requires three hypochlorite ions. Also, for each mole of chlorate ion produced, two moles of chloride ion (salt) are produced.

Effect of "Salt" on Bleach Quality

The mathematical expression for the ionic strength of liquid bleach is:

$$I = [Cl^-] + [OCl^-] + [OH^-] + [ClO_3^-] + [ClO_2^-] + 3[CO_3^{2-}]$$

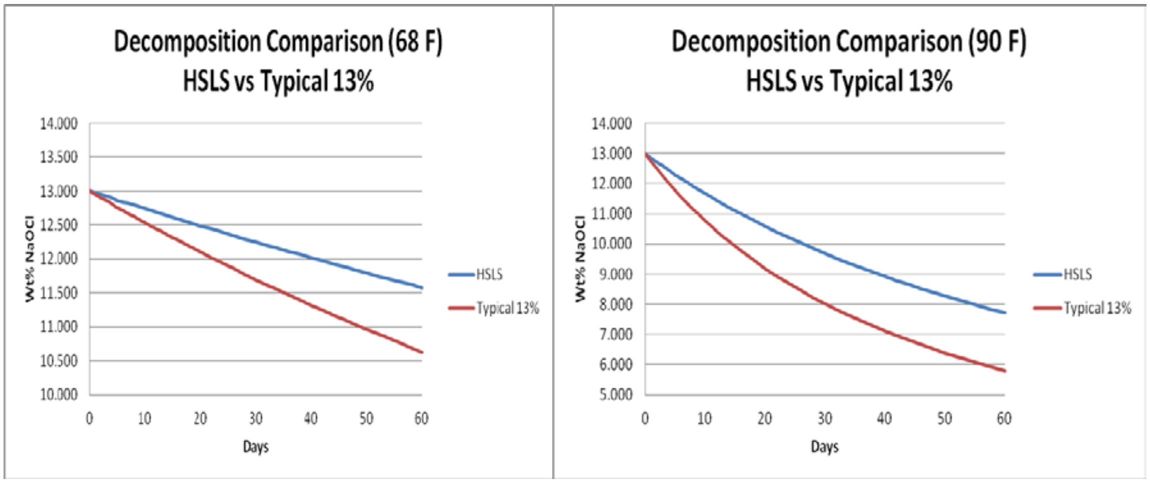
The relationship between ionic strength and the decomposition rate constant is:

$$\log k_2 = 0.146(I) + \log k_\infty$$

This suggests that the presence (or absence) of Cl^- affects the rate of liquid bleach decomposition.

Data from chemical modeling studies using the Bleach 2001 software[1] show that 13% HSLS bleach decomposes at a slower rate than typical 13% bleach. *After 2 weeks of storage at 68 ^oF, the HSLS bleach stock retains >2% more chlorine than the typical bleach. After 2 months, the difference is >8%. At 90 ^oF, the difference after 2 months is almost 25%.*

[1] Gordon, G.; Adam, L.; Bubnis, B. "Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite Ion Is the Chlorinating Agent", American Water Works Association - Research Foundation (AWWA-RF ISBN 0-89867-781-5) Denver Colorado, **1994**, 195pp



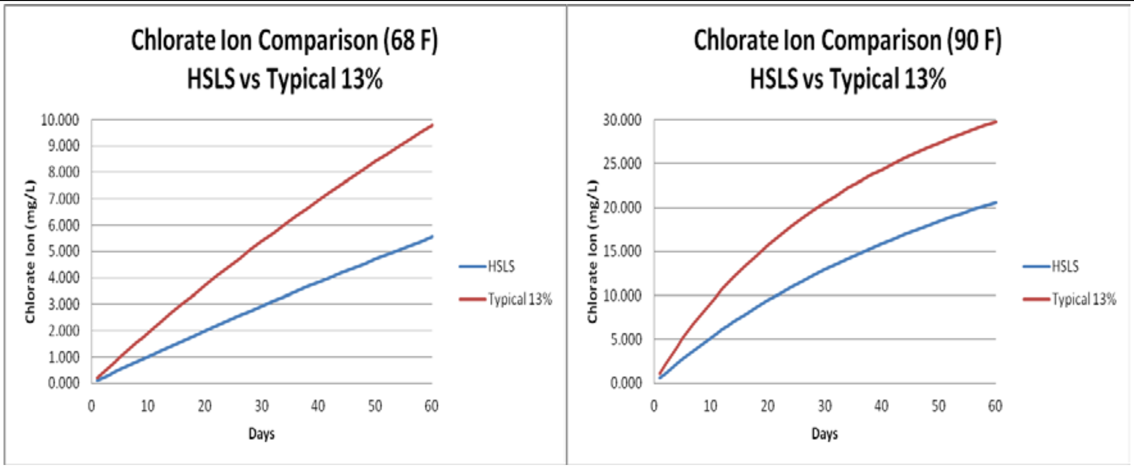
Graphically, it is easily seen that HSLS bleach decomposes slower than bleach containing a higher salt content. The table below shows the half-life of 13% bleach for the same data set. The half-life of HSLS bleach is about 1.8x longer than typically prepared bleach.

	13% Bleach Half-Life ($t_{1/2}$)	
	68 °F	90 °F
13% HSLS Bleach	489 days	88 days
Typical 13% Bleach	269 days	48 days

HSLS Bleach – Chemistry Advantages

The lower salt concentration in HSLS bleach offers a variety of chemistry advantages that result in longer storage times at higher temperatures. *Because HSLS bleach decomposes at a slower rate, bleach concentration is maintained for longer periods, there is less build-up of chlorate ion and oxygen during storage, and because there is less chlorate ion there will be less perchlorate ion buildup in the stored bleach.*

- More chlorine: see discussion above
- Less chlorate ion:

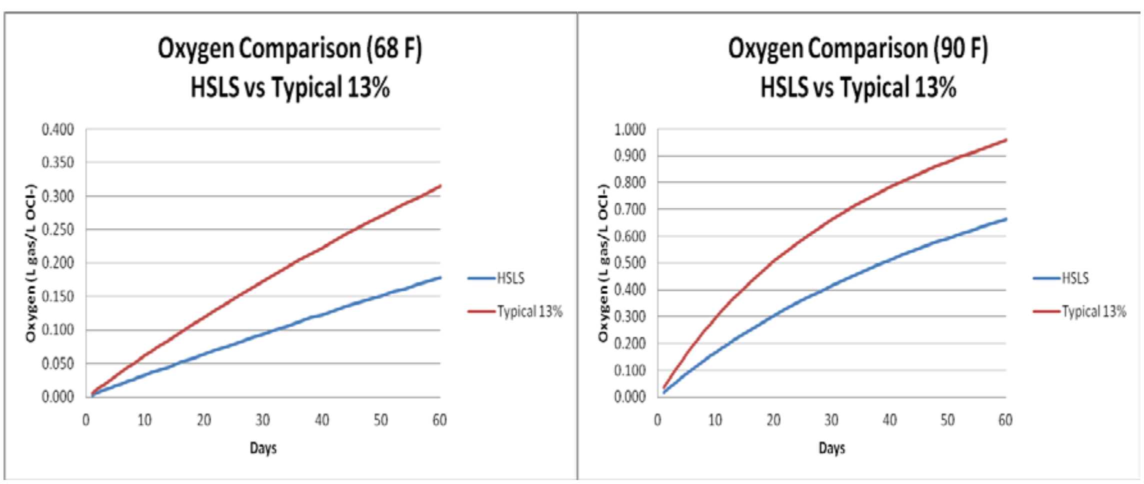


Less salt in the bleach results in a slower decomposition rate which means that less chlorate ion is formed. The chart clearly shows that the difference in chlorate ion between the HSLS and typical bleach increases over time. *After 2 months of storage, the concentration of chlorate ion is substantially less in the HSLS bleach compared to typical bleach at both 68 °F and 90 °F.*

- Less oxygen:

The formation of oxygen in bleach is primarily the result of the presence of transition metal ions. This process is referred to as the "catalyzed" pathway. In addition, decomposing bleach forms oxygen independent of transition metal ions. This is a minor pathway described by the following:

$$OCl^- + OCl^- \rightarrow O_2 + 2Cl^-$$



Note: The solutions in the oxygen comparison are assumed to contain identical transition metal ion concentrations

Thus, because of the slower decomposition rate in HSLS bleach, less oxygen is formed during storage. Similar to the previous chart for chlorate ion buid-up, the chart clearly shows that the difference in oxygen formed in the HSLS and typical bleach increases over time. *After 2 months of storage at 68 °F, the amount of oxygen* *formed is ≈ 40 % less in the HSLS bleach. Similarly, at higher temperatures (90 °F), one can expect to see less oxygen formed compared to bleach containing more salt.*

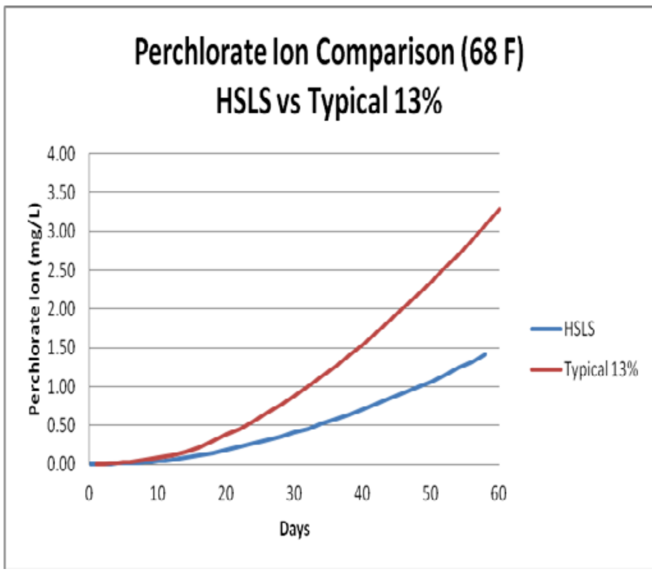
- Less perchlorate ion:

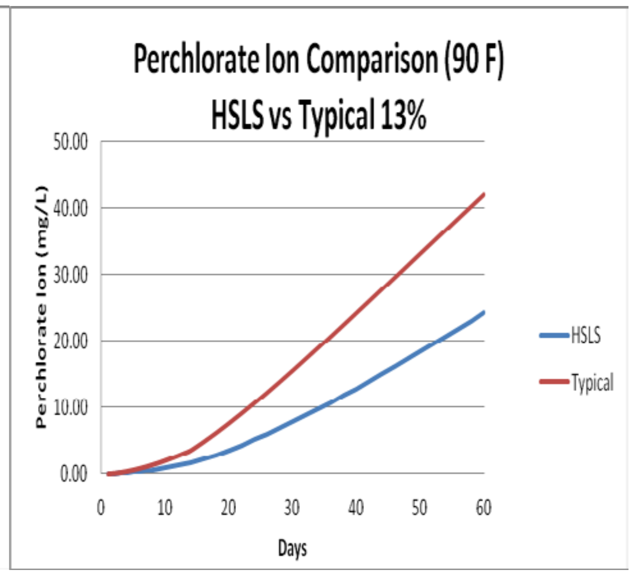
Perchlorate ion formation in stored bleach is largely a function of the concentration of the bleach, the concentration of chlorate ion and the storage temperature. The simplified rate law is

$$\text{Rate} = d\text{ClO}_4^-/dt = k_{calc}\,[\text{OCl}^-]\,[\text{ClO}_3^-]$$

Where the rate constant (k_{calc}) has a dependency on the ionic strength

$$\log(k_{calc}) = 0.0788\,(I) + \log(2.084 \times 10^{10} \times T \times e^{-1.01\text{x}10\text{^}5/RT} \times e^{-106/R})$$





This means that HSLS bleach helps to minimize perchlorate ion formation at any temperature by virtue of having less chlorate ion available to react and by having a lower than average (or normal) ionic strength.