

New Development in Sodium Hypochlorite Manufacturing: High Strength Low Salt Bleach

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Overview and Highlights

The new Powell Fabrication High Strength Low Salt (HSLs) Bleach Technology offers chemically improved bleach that brings significant advantages over traditional bleach:

- HSLs Bleach has 1.7 times longer stability even at outdoor temperatures.
- 64% less salt is produced in HSLs bleach than in a typical 13% wt NaOCl because of a newly developed, patented salt recovery system.
- Lower residual concentrations of chemical impurities such as chlorate and perchlorate (which are currently pending USEPA regulations) are formed.
- Much slower formation of chlorate and perchlorate occurs, which increases the useful shelf life of HSLs bleach as compared to the traditional bleach of equal strength currently available.
- The use of HSLs bleach will prepare utilities for pending chlorate (current HRL at 210 µg/L) and perchlorate (current HAL at 15 µg/L) federal regulations, which maybe more stringent than the current health reference or advisory levels.
- HSLs technology can produce higher strength NaOCl (up to 30% by wt) as compared to existing generators (this saves on shipping costs vs. traditional bleach that is only available up to 16.5% wt).
- Higher concentration HSLs bleach can be shipped and then diluted on site after delivery resulting in even lower formation of chlorate and perchlorate.
- It is more economical and has potentially less impact on the environment due to recycling and/or sale of recovered salt.
- Like regular bleach, HSLs product is equally safer and easier to handle than chlorine gas.

Disadvantages of traditional (typical) bulk sodium hypochlorite (e.g. 13% wt NaOCl):

- Requires cooling and dilution in hotter climates to slow down (minimize) decomposition.
- Relatively rapid (faster) chlorate and perchlorate formation leading to potential contamination of finished water.
- Lower (shorter) shelf life of stored, undiluted bleach.
- Less economical due to stability issues and higher impact on the environment.
- May be difficult for utilities to meet future federal regulations per Safe Drinking Water Act.

Executive Summary

In view of an improved chemical model now available describing hypochlorite ion decomposition products and due to potential health effects that maybe subject to regulations

(USEPA is due to announce perchlorate maximum contaminant level goal (MCLG) in 2013 while chlorate is on CCL3 list, with a Health Reference Level (HRL) of 210 µg/L), drinking water utilities are strongly advised to adopt “best practices” to minimize bleach decomposition during storage, perform routine testing, and select the “cleanest” product available from trusted vendors. Bulk bleach (12.5-16.5% wt NaOCl) is used by approximately one third of drinking water utilities in North America. In light of public health concerns and inevitable hypochlorite decomposition, Powell Fabrication & Manufacturing has developed High Strength Low Salt (HSLs) bleach that provides a significantly safer product for manufacturers and drinking water utilities. While the typical bleach at 13% wt NaOCl also contains approximately 10% wt NaCl, the new HSLs bleach at 30% wt NaOCl has less than 9% wt NaCl. Thus, the HSLs bleach at 13% wt NaOCl contains less than 4% NaCl. This reduction in the amount of NaCl lowers the ionic strength. The typical contribution of chloride ion to the ionic strength in freshly generated commercial bleach is nearly 50%. The HSLs formulation decreases the NaCl content by 64%. This is the main reason behind the improved stability and lower production of chlorate and perchlorate ions in HSLs bleach. By using the AWWA's web model (“Hypochlorite Assessment Tool:” www.awwa.org/hypochlorite), it is possible to assess the benefits of this improved formulation using the established, experimental kinetic parameters. This model shows that the half-life of 13% HSLs bleach is 1.7 times longer than typical bleach (210 days vs. 122 days) at 25 °C. As a result, after 30 days following manufacturer, a utility using HSLs bleach can expect to have 9% higher NaOCl strength, than using typical bleach. This corresponds to 9% savings every month! In addition, according to the model calculations, after 30 days there would be 39% less chlorate and 64% less perchlorate formed in HSLs bleach than in typical bleach! This significantly minimizes contamination of finished drinking water. If we take into account the USEPA HRL of 210 µg/L for chlorate, and assume 5 mg/L (as Cl₂) is used during treatment (primary/secondary disinfection, residual for distribution system), then typical bleach would introduce too much chlorate after as few as 14 days of storage at 25 °C. The HSLs bleach may be used safely for 24 days. Thus, HSLs formulation greatly improves the stability and minimizes formation of unwanted decomposition products, without the required need for cooling and/or dilution. Utilities that experience higher levels of chlorate and perchlorate ions in source water would benefit by switching to HSLs bleach, as well as, by practicing the established recommendations in order to continue safeguarding public health and complying with pending new regulations.

Introduction

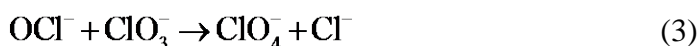
Commercially available solutions of sodium hypochlorite or as they are more commonly referred to as “bleach” are widely used by the water treatment industry, paper manufacturing, agriculture and food industry, pharmaceutical, and chemical industries. It is also used in the household as a product for cleaning and disinfecting purposes. Once added to water, bleach forms varying amounts of hypochlorous acid (HOCl) and/or hypochlorite ion (OCl⁻) depending on the pH of the water, as shown by Equation 1. At pH 7.58, both hypochlorous acid and hypochlorite ion are present, if pH of the water is lower than the pKa value, then there is more hypochlorous acid and significantly less hypochlorite ion. This is important because hypochlorous acid is a more effective disinfectant than hypochlorite ion.



The reactive qualities of sodium hypochlorite and hypochlorous acid and relatively low cost to manufacture, make bleach a practical chemical for various purposes. Since the successful synthesis in late 18th century, bleach has been essential in protecting public health against cholera, Salmonella, Legionella, as well as many other types of bacteria and spores.

According to a recent survey, 63% of water treatment facilities use chlorine as primary disinfectant. As many as 30% of the drinking water treatment facilities (DWTf) in North America switched from chlorine gas to hypochlorite ion solutions in the past 10 years (Routt et al, 2008). Chlorine gas was replaced in more than 80% of the treatment facilities by bulk sodium hypochlorite solutions. Furthermore, 17% of the sites switched to the use of on-site generated (OSG) sodium hypochlorite solutions and about 1% of DWTf use calcium hypochlorite.

Despite its many useful properties bleach decomposes over time, thus it is important to implement proper storage and handling strategies. There are many studies that investigated this chemical and its decomposition pathways (Gordon et al, 1993-1997). It is well known that the main routes of decomposition are: 1) through formation of chloride, chlorite, chlorate, and perchlorate ions and 2) breakdown of hypochlorite ion into molecular oxygen and chloride ion. The first route is the dominant one and proceeds via several reactions that are summarized by Equations 2 and 3. To control the decomposition of hypochlorite ion, bleach manufacturers add caustic (sodium hydroxide) during generation process to obtain sodium hypochlorite solutions at pH 12-13, where the decomposition rate of the hypochlorite ion is slowest.



The second route is a minor decomposition pathway, which is shown by Equation 4. This can become significant when certain metal ions are present (Lister, 1956) and at higher temperatures, lower pH, and exposure to light.



For example, if Ni(II) is present even at 1 mg/L, the decomposition rate will increase by a factor of 10, leading to rapid decomposition of hypochlorite ion and evolution of oxygen gas. Presence of Cu(II) at the same concentration will only increase the rate by a factor of 1.4, however, at 10 mg/L, Cu(II) will increase the rate by a factor of 18 (Gordon et al, 1994; Gordon et al, 1995). In contrast, other metal ions such as Fe(III) and Mn(II) do not have any effect at concentrations up to 1 mg/L for Mn(II) and 40 mg/L for Fe(III). The presence of nickel and copper ions can produce a potential hazards in sealed sodium hypochlorite solutions, piping, valves, and pumps, resulting in bulging (and exploding) of the containers, lost prime of the pumps, and/or exploding of piping and valves. Sodium hypochlorite is also corrosive, so the metal ions can come from other materials that are in contact, such as valves, pump heads, and piping. Thus, it is important not only to minimize the presence of nickel and copper ions in sodium hypochlorite solutions (for example by filtration) but also ensure the use of corrosion resistant materials for handling and transport.

Chlorate and chlorite are well known degradation products and contaminants of hypochlorite solutions that are present in all hypochlorite (Gordon et al, 1993; Gordon et al, 1995). Chlorite ion further reacts with hypochlorite ion to form chlorate at fast enough rate that chlorite ion concentration remains relatively low (at steady state) even in bleach that has been stored for a long time. Chlorite is already federally regulated in drinking water by the USEPA with a Maximum Contaminant Level (MCL) of 0.8 mg/L. Chlorate is currently not regulated at the Federal level (the World Health Organization has a guideline MCL of 700 µg/L), however, it is listed for inclusion in the Third Unregulated Contaminant Monitoring Rule (UCMR3, US EPA, 2012a) with a health reference level (HRL) of 210 µg/L (US EPA, 2011b). The inclusion in UCMR3 list may lead to further investigations by USEPA on whether there is enough exposure risk to warrant regulatory determination and establish preliminary MCL guideline.

Perchlorate ion has been found in sodium hypochlorite and similar to chlorate ion, perchlorate ion concentration increases over time (Greiner et al, 2008; Asami et al, 2009; Snyder et al, 2009; Pisarenko et al, 2010; Stanford et al, 2011). In 2009, the USEPA announced an interim health advisory level (HAL) of 15 µg/L, to provide guidance to state and local officials in their efforts to address perchlorate contamination. In February 2011, USEPA announced Final Regulatory Determination to regulate perchlorate under Safe Drinking Water Act (SDWA). This regulation is due in 2013 (USEPA, 2011a).

Bromate is another contaminant typically associated with ozonation of bromide-containing raw waters, though it can also be found in commercial sodium hypochlorite solutions (Bouland et al, 2005; Asami et al, 2009; Pisarenko et al, 2010; Stanford et al, 2011) likely from a reaction of bromide with hypochlorite analogous to the formation of chlorate. Bromate is currently regulated by USEPA in drinking water at MCL of 10 µg/L. National Sanitation Foundation International established a standard for sodium hypochlorite not to exceed 0.5 µg BrO₃⁻/mg FAC (NSF/ANSI, 2005), so that the contribution of bromate at maximum use level (MUL) of 10 mg/L, would not exceed 5 µb/L in drinking water, also known as single product allowable concentration (SPAC). In January 2013, the SPAC for bromate in sodium hypochlorite was lowered to 3 µb/L (WaterWorks, 2012).

A large amount of detail is known about of the chemistry behind hypochlorite ion decomposition products. Due to potential health effects, chlorate and perchlorate ions are pending USEPA regulations. Utilities are strongly advised to adopt “best practices” to minimize bleach decomposition during storage (Gordon et al, 1993-1997), perform routine testing of treated water, and select the “cleanest” product from trusted vendors.

Sodium Hypochlorite Decomposition and Minimizing Formation of Unwanted products

The rate of decomposition of hypochlorite ion to form chlorate and/or oxygen is well defined in terms of the following rate law (Adam and Gordon, 1999). The rate of the decomposition is dependent on the square of the concentration of the hypochlorite ion and the second order rate constant, as shown by Equation 5. So, for example, if the concentration of the hypochlorite ion is increased by a factor of 2, the rate of decomposition increases by a factor of 4. The kineticists would call this type of reaction second-order.

$$\frac{d[\text{OCl}^-]}{3dt} = k_{\text{obs}}[\text{OCl}^-]^2 \quad (5)$$

The rate of perchlorate formation was recently found in terms of the rate law shown by Equation 6. In this case the rate of perchlorate formation is still second order, as it is dependent on concentration of two reactants: hypochlorite and chlorate ions (Snyder et al, 2009).

$$\frac{d[\text{ClO}_4^-]}{dt} = k_{\text{ClO}_4}[\text{OCl}^-][\text{ClO}_3^-] \quad (6)$$

In both Equations 5 and 6, the rate of hypochlorite decomposition and perchlorate formation are also dependent on second order rate constants. In both cases, it was found that these second order rate constants are strongly dependent on temperature and ionic strength. Equations 7 and 8 show the respective relationships below.

$$\log(k_{\text{obs}}) = 0.146(I) + \log(2.084 \times 10^{10} \times T \times e^{\frac{-1.02 \times 10^5}{RT}} \times e^{\frac{-55.2}{R}}) \quad (7)$$

$$\log(k_{\text{ClO}_4}) = 0.0788(I) + \log(2.084 \times 10^{10} \times T \times e^{\frac{-1.01 \times 10^5}{RT}} \times e^{\frac{-106}{R}}) \quad (8)$$

The rate constant for either hypochlorite decomposition (k_{obs}) or perchlorate formation (k_{ClO_4}) is affected by the same factors: temperature (T) and ionic strength (I). Note that temperature is in degrees Kelvin. R is the gas constant. The ionic strength, which is the sum of dissolved ions, is strongly affected by the concentration of hypochlorite ion and chloride ion. Chloride ion is a byproduct of generation process and is another major decomposition product of hypochlorite ion.

Thus, it is generally recommended to at least store sodium hypochlorite solutions in cool and dark conditions and if possible dilute bleach to further minimize decomposition. Diluting hypochlorite solutions by a factor of two reduces the concentration of hypochlorite ion and ionic strength resulting in decrease of the rate of decomposition by a factor of 4, while the rate of perchlorate formation is decreased by a factor of 6. Cooling also results in significant impacts on the stability: for every 5°C change in storage temperature the rate of decomposition is decreased by a factor of 2. However, it is not always possible to dilute the bleach simply because of lack of large supply of distilled or “metal ions free” water and large quantities of sodium hydroxide to adjust the pH to 12-13 range, where again the rate of decomposition is slowest.

The Benefits of the New Formulation of Sodium Hypochlorite: High Strength Low Salt

Powell Fabrication has been in business since 1964, supplying bleach generation technology (equipment) that is widely used in the United States and Canada, accounting for as much as 80% of the bleach produced in North America. Guided by decades of engineering experience to fabricate more efficient bleach generators Powell has developed a new process that achieves not only economical benefits but also offers a significant improvement in bleach stability producing a product that is improved on a chemical level.

This new process, termed as High Strength Low Salt bleach, allows fabrication of higher strength hypochlorite ion solutions (up to 30% NaOCl by weight) but at lower sodium chloride

content. This is significant for several reasons: 1) improved stability and 2) less unwanted decomposition products.

To determine how this is possible, we can examine the product from this new generation process and compare it to the traditional bleach process, as shown by Table 1. The traditional hypochlorite at 13% strength would contain approximately 10% sodium chloride by weight where as the HSLs product would contain less than 4%. The reduction in the amount of sodium chloride means lower ionic strength. This is the main reason behind the improved stability and lower degradation products, such as chlorate and perchlorate. The HSLs bleach “acts” as if it were diluted, with greater stability over previous generation of 13% bleach. In chemical terms, for every mole of hypochlorite generated there is always one mole of chloride ion, thus the contribution of chloride ion to the ionic strength in freshly generated bleach is nearly 50%! The HSLs formulation achieves a reduction in the amount of sodium chloride by more than 60%.

Table 1. NaOCl strength and NaCl content in traditional (Tradition) hypochlorite (Hypo) and HSLs Hypochlorite.

Traditional Hypo			HSLs Hypo		
NaOCl	NaCl	SG	NaOCl	NaCl	SG
Wt. %	Wt. %		Wt. %	Wt. %	
30.0%	X	X	30.0%	8.5%	1.3459
25.0%	X	X	25.0%	7.1%	1.2936
20.0%	X	X	20.0%	5.7%	1.2391
16.5%	13.0%	1.2622	16.5%	4.7%	1.1997
15.0%	11.9%	1.2382	15.0%	4.3%	1.1824
13.0%	10.4%	1.2052	13.0%	3.7%	1.1592
10.5%	8.3%	1.1610	10.5%	3.0%	1.1296
8.0%	6.3%	1.1210	8.0%	2.3%	1.0994
6.0%	4.7%	1.0920	6.0%	1.7%	1.0750
3.0%	2.4%	1.0490	3.0%	0.9%	1.0376

By using the recently released web model “Hypochlorite Assessment Tool” (www.awwa.org/hypochlorite, that is available to AWWA members), which is based of the “Bleach 2001” predictive model (Adam et al, 2001) and includes perchlorate formation calculations (Stanford et al, 2012), it is possible to assess the benefits of this improved formulation using the published kinetic parameters and relationships. As such, relevant parameters for typical bleach (e.g. NaOCl strength, NaCl level, temperature, etc.) as well as for the HSLs bleach can be used to compare the decomposition of hypochlorite ion as well as formation of chlorate and perchlorate ions at typical storage conditions. As an example, we used three storage scenarios: 20, 25, and 30°C for typical and HSLs 13% wt bleach. Figure 1 shows overlaid plots based on the output of the “Hypochlorite Assessment Tool” model.

This model shows that the half-life of the 13% HSLs bleach is 1.7 times longer than the traditional hypochlorite (431 days vs. 250 days). This trend can be seen by following the changes in wt% NaOCl in Figure 1 for the HSLs Hypo-NaOCl vs. Traditional Hypo-NaOCl, which drops off more quickly over time. As a result, after 30 days a utility using HSLs bleach can expect to have 4.7% higher hypochlorite ion concentration, than using traditional bleach. That’s 4.7% savings in one month!

We can also consider the storing scenario at 25°C, as shown by Figure 2. In this case, the half-life of HSLs bleach again is 1.7 times longer than the traditional hypochlorite (210 days vs. 122 days). As a result, after 30 days a utility using HSLs bleach can expect to have at least 9% higher hypochlorite ion concentration, than using traditional bleach. The resulting savings are 9% in one month!

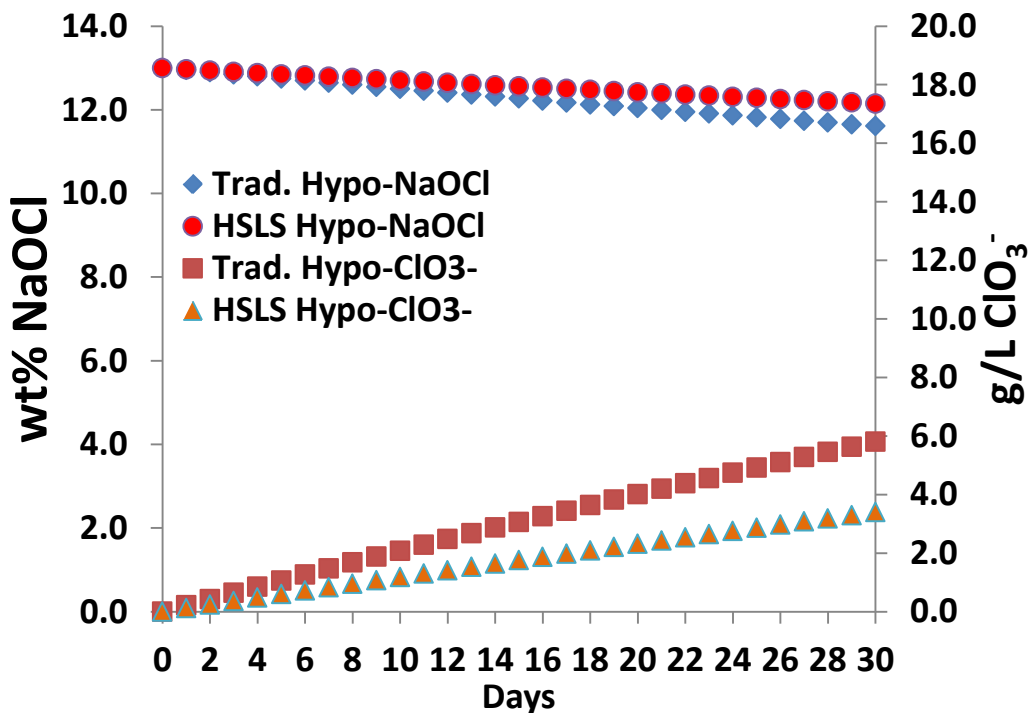


Figure 1. Decomposition of HSLs bleach and Traditional (Trad.) bleach at 20 °C.

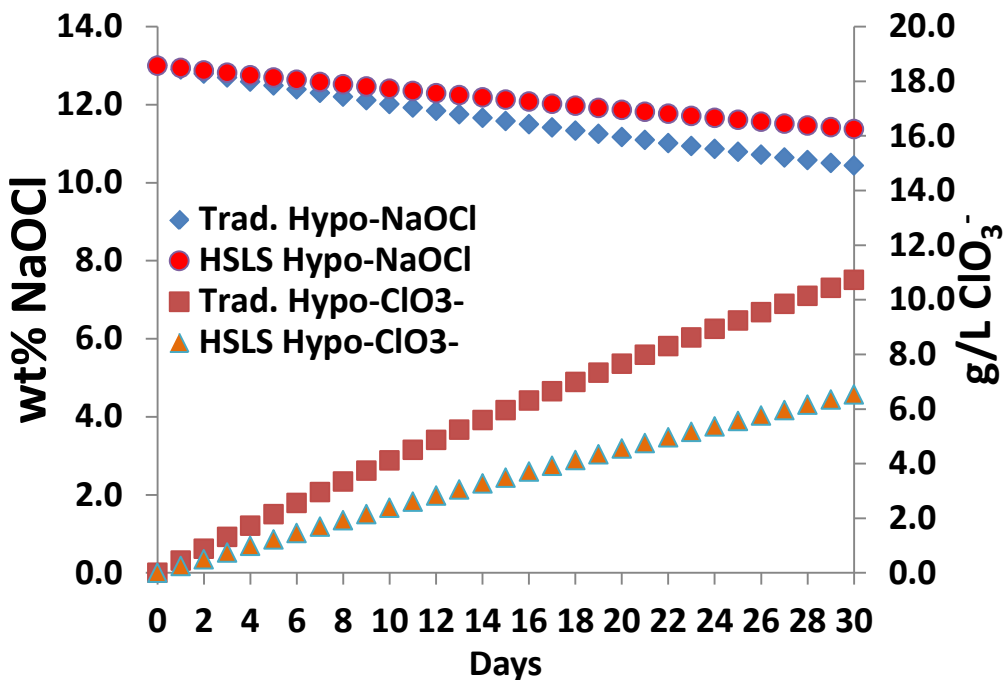


Figure 2. Decomposition of HSLs bleach and Traditional (Trad.) bleach at 25 °C.

Finally, we can compare a more extreme scenario of storage at 30°C, which may be applicable of to utilities in hotter climates. Decomposition of hypochlorite and formation of chlorate are shown by Figure 3.

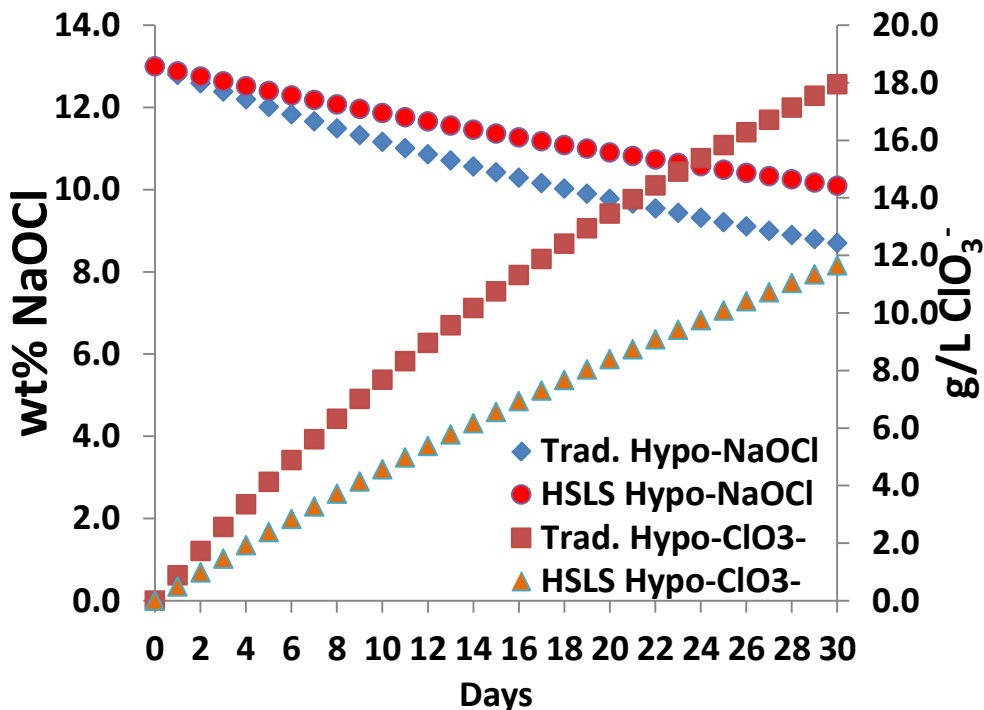


Figure 3. Decomposition of HSLS bleach and Traditional (Trad.) bleach at 30 °C.

In this case, the half-life of HSLS bleach is still 1.7 times longer than the traditional hypochlorite (104 days vs. 61 days). As a result, after 30 days a utility using HSLS bleach can expect to have at least 16% higher hypochlorite ion concentration, than using traditional bleach. This corresponds to 16% savings in one month! This is especially significant when bleach must be transported over long distances and it is not possible to control the temperature.

In addition to reduced costs due to the better stability of the HSLS, there is significantly less formation of chlorate (as can be seen from Figures 1, 2, and 3) and perchlorate (not shown, for brevity). In all cases, after 30 days, there was significantly less chlorate and perchlorate in HSLS bleach than in traditional bleach! At 20°C and after 30 days of storage it can be expected that there will be 41% less chlorate and 63% less perchlorate formed in HSLS bleach. Similarly, at 25°C there still will be 39% less chlorate and 63% less perchlorate formed in HSLS bleach. At 30°C, which now significantly increases the decomposition rate, even then there will be 35% less chlorate and 61% less perchlorate formed in HSLS bleach. This additional benefit significantly minimizes contamination of finished water.

If we take into account the USEPA Health Reference Level (HRL) of 210 µg/L for chlorate ion, and assume 5 mg/L (as Cl₂) is used during drinking water treatment (primary/secondary disinfection, residual for distribution system) then the traditional bleach would introduce too much chlorate in as little as after 28 days during storage at 20°C, whereas HSLS bleach maybe used for 50 days of storage at this temperature. At 25°C, the traditional bleach would introduce too much chlorate in less than 14 days, whereas HSLS bleach maybe used for 24 days of storage

at this temperature. At 30 °C, the traditional bleach would introduce too much chlorate in just 7 days, whereas HSLs bleach can be used for 12 days of storage at this temperature. This is even more significant when bleach must be transported over long distances and it is not possible to control the temperature. In light of more stringent pending USEPA regulations, HSLs technology allows a customer to have a bleach product that has lower concentration of impurities and decomposes significantly slower, thus minimizing contamination of treated drinking water.

Conclusions

This new process to manufacture sodium hypochlorite introduced by Powell Fabrication chemically improves the stability of hypochlorite ion and minimizes formation of unwanted decomposition products, without the required need for cooling and dilution. Utilities that already experience higher levels of chlorate and perchlorate ions in their source raw water would benefit by switching to HSLs bleach as well as by practicing the established recommendations in order to continue safeguarding public health and complying with new regulations under SDWA.

Furthermore, the new process can provide other significant economical benefits not only to bleach manufacturers but for consumers as well. Due to enhanced stability, HSLs bleach is more cost effective to produce, handle, and ship than traditional bleach. It is also possible to recover high purity sodium chloride, which can be sold or reused by other manufacturing process. These savings lower the final cost per gallon, resulting in a new product that has all the benefits due to improved chemistry and yet is price competitive for the consumers.

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