Reducing Perchlorates

by James P. Brennan, Arch Chemicals, Inc.

SWITCHING FROM GAS CHLORINE TO SODIUM HYPOCHLORITE IS NO PANACEA. NOW, ADDING TO THE BURDEN IS PROPOSED EPA REGULATION FOR PERCHLORATE. CONSIDERING THE FACTORS THAT LEAD TO EXCESSIVE PERCHLORATE FORMATION, SWITCHING TO CALCIUM HYPOCHLORITE PROVIDES UTILITIES ANOTHER KEY ADVANTAGE.

The Environmental Protection Agency is proposing to regulate perchlorate. Although the EPA does not currently regulate perchlorate in drinking water, it has published an Interim Health Advisory of 15 ppb for exposure to perchlorate from ingesting drinking water.

There is a growing concern about the impact of perchlorate on human health due to introduction from sodium hypochlorite solutions into drinking water. According to the EPA, the potential effect of perchlorate is secondary, or indirect, meaning that the presence of perchlorate in water may reduce the bioavailability of iodine, thus leading to human nutritional deficiency of that element. Because of this, the emerging EPA strategy is to move forward with proposing a formal rule. If a stringent maximum contaminant level for perchlorate is established, it will impact the way many drinking water utilities handle chlorination.

Perchlorate, Chlorate and Bromate

Unlike chlorine gas, commercial sodium hypochlorite begins to degrade as soon as it is made and can contain undesirable by-products such as perchlorate, chlorate and bromate. These contaminants form during manufacturing or transport and storage.

Chlorine gas (Cl_2) has been effective and inexpensive on a cost per pound basis. Since the early 1990s, however, the growing number of environmental mandates and health and safety requirements associated with Cl_2 have forced many utilities to reduce or eliminate its use and switch to sodium hypochlorite (NaOCl). Whereas 25 years ago virtually all drinking water plants used Cl_2, today it's less than two-thirds. Now a recently proposed 911-related Drinking Water System Security Act will likely reduce its use even further, if passed.

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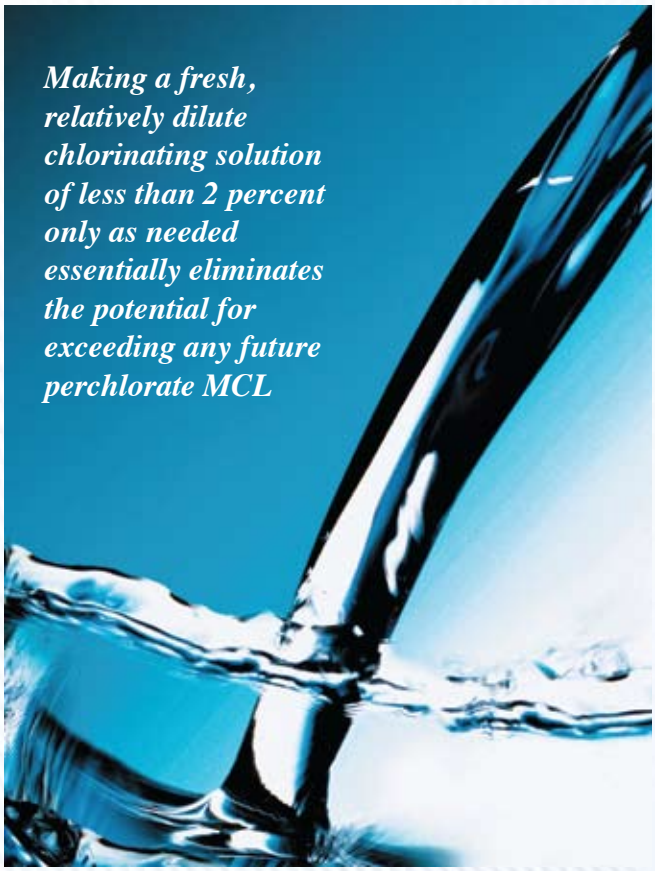
NaOCL No Panacea

But utilities that have adopted NaOCl use know that sodium hypochlorite is no panacea. Plant operators, hoping bleach would be as easy and effective to use as chlorine gas, have been generally disappointed. NaOCl use comes with its own set of performance, maintenance and regulatory challenges. Its degradation produces undesirable by-products, inconsistent residuals, and a need for constant dosing corrections. The tendency of NaOCl to off-gas as it degrades often systematically causes chemical metering pumps to become air-bound, resulting in inconsistent dosing and/or failure.



This concentrated bleach releases chlorine vapors resulting in a serious corrosive environment inside equipment buildings and higher maintenance costs. In addition, expensive secondary containment for bulk storage systems is usually required for hazardous solution storage, as well as remote overflow and leakage alarms and, in some cases, transfer point containment.

Potentially adding to this list of negatives is the growing potential for a drinking water standard for perchlorate. The EPA's published Interim Health Advisory of 15 ppb for exposure to perchlorate from ingesting drinking water is meant to provide guidance to state and local agencies to protect public health while the EPA considers setting a MCL for perchlorate. This has resulted in several states already regulating perchlorate in drinking water. In Arizona, for example, perchlorate guidance criteria is 14 µg/L; in Maryland and Mexico, 1 µg/L; New York, 5 µg/L; California, 6 µg/L; and 2 µg/L in Massachusetts.

Research

A research team led by the Southern Nevada Water Authority recently completed a study that investigated the rate of perchlorate and other oxyhalide species formation in hypochlorite solutions. The final report, entitled: *Hypochlorite — An Assessmen of Factors That Influence the Formation of Perchlorate and Other Contaminants*, was jointly funded by American Water Works Association, Water Industry Technical Action Fund, and the Water Research foundation. The research team investigated the factors impacting the formation of perchlorate, bromate, and other contaminants in hypochlorite solutions and developed a set of guidelines to assist utilities in minimizing these contaminants.

In the Southern Nevada Water Authority study, perchlorate was found in five utility bulk hypochlorite samples, in 18 hypchlorite solutions samples taken from 12 onsite generators (OSGs), and in calcium hypochlorite. The sample calcium hypochlorite was provided by Arch Chemicals, Inc., the sole cal hypo manufacturer participating in the study.

If one considers the major factors that the study found leading to excessive perchlorate, and also the advanced chlorination systems developed by Arch Chemicals for making calcium hypochlorite solution on-site, the selection of cal hypo over of commercial bleach will be the optimum choice.

Perchlorate concentration measured up to 14,000 µg/L in bulk sodium hypochlorite and up to 3,100 µg/L in OSG hypochlorite, equating to 0.16 µg/L perchlorate per mg free available chlorine (FAC) in bulk and 0.52 perchlorate per mg FAC in OSG hypochlorite solutions, according to the study.

A comparison was made by normalizing all of the contaminant concentrations by the concentration of FAC. In addition to the bulk and OCG sites, bromate, chlorate, and perchlorate were measured for 3% and 6% (as FAC) Arch calcium hypochlorite solutions immediately after mixing with reagent water. (Note: cal hypo solutions are made fresh and used at less than 2% AvCl, so by-product formattion is less than presented here)/

Figure 1 shows a relative contribution (on a mass of contaminant per mg FAC basis) from each hypochlorite solution.

Samples were also analyzed for contamination and qualification and used in a holding study to examine the rate of perchlorate formation in each solution. All samples tested had measurable concentrations of chlorate, perchlorate, and bromate. The report states that no specific conclusions could be made regarding differences in contamination concentrations in builk, OSG and calcium hypochlorite solutions. The study found that, regardless of hypochlorite type, excessive perchlorate formation can occur in three months with stored hypochlorite solutions.

KEY FACTORS:
Time, Temperature, Concentration, Ionic Strength

The study concluded that perchlorate formation occurs over time as hypochlorite degrades.

The researchers observed that bromate forms rapidly during hypochlorite manufacturing and does not change significantly over time and that perchlorate is affected by several key factors, including hypochlorite and chlorate concentration, ionic strength, temperature, and concentration of metal ions and bromide ions. Perchlorate formation was first order in hypochlorite and chlorate ion concentration and is highly dependent on ionic strength and temperature, and the rate of perchlorate formation is highest in concentrated hypochlorite solutions and at higher temperatures.

Figure 1.

Relative contribution of specific contaminants on a per-mass FAC basis

		Concentration in hypochlorite solutions				Mass of contaminant added per mg FAC		
		ClO_3 (mg/L)	BrO_3 (mg/L)	ClO_4 (µg/L)	FAC (g/L)	ClO_3 (µg/mg FAC	BrO_3 (µg/mg FAC)	ClO_4 (µg/mg FAC)
	1-A	19,000	14,000	87	220	280	160
	2	5,900	670	150	39	200	4.5
	4	n/a	n/a	n/a	n/a	n/a	n/a
Bulk	5	1,800	220	120	15	75	1.8
	7	2,400	230	120	20	83	1.9
	8	8,000	2,000	130	62	59	15
	1a	140	5.4	9.7	14	420	0.6
	1b	240	16	8	30	480	2.0
	2a	97	8.6	6.8	14	780	1.3
	2b	360	410	6.9	52	480	59
OSG	3	270	7.3	10	27	440	0.7
	4	1,200	40	4.5	270	580	8.9
	5	260	31	8	33	330	3.9
	6	180	22	5.2	35	270	4.2
	7	750	83	7.2	100	280	12
	8	240	740	3.6	67	200	210
	9	760	3500	6.8	110	840	520
	10	780	19	8.7	90	17	2.2
Cal Hypo	Cal 1	390	27	32	12	75	0.8
	Cal 2	830	55	61	14	87	0.9

Based on the findings, several recommendations were given by the researches, including diluting bulk sodium hypochlorite solution by a factor of two upon delivery; reducing storage temperature; controlling pH after dilution; using solutions as soon as possible; and reducing storage time.

Reducing Perchlorate Formation: The Case for Calcium Hypochlorite

Calcium hypochlorite, $Ca(OCl)_2$ has a long history in U.S. drinking water treatment. If one considers the major factors that the Southern Nevada Water Authority study found leading to excessive perchlorate formation in sodium hypochlorite (time, temperature, concentration, and ionic strength), and also the advanced chlorination systems developed by Arch Chemicals, Inc. for making calcium hypochlorite solution on-site, the selection of cal hypo over of commercial bleach will be the optimum choice.

Time

Dry calcium hypochlorite briquettes contain a minimum of 65 percent available chlorine (AvCl) by weight. Solid-state reactions are much slower than liquid-state reactions. In the liquid-state, or solution, ions can move and collide with each other and react much faster. Being in a solid-state, reactions are much slower with calcium hypochlorite as it is being stored, waiting to be made into solution.

According to the recent Southern Nevada Water Authority study, excessive perchlorate formation can occur in three months with bulk hypochlorite.

In 6-month-old commercial sodium hypochlorite, for example, concentration has potentially decreased from 15 percent down to an estimated 5 percent or less free available chlorine, and a large percentage of the solution has gone to chlorate. Looking at half-lives, it is a month or so for bleach, but the half-life of dry cal hypo in storage is years, although producers are held accountable to be within 3 percent of typical in one year.

The study showed that regardless of hypochlorite type, excessive perchlorate formation can occur in three months with stored solutions, including calcium hypochlorite. However, cal hypo solutions are never stored for long periods of time – they are typically used in within hours after they are made.

Concentration

Again, calcium hypochlorite is in solid-state prior to use, reactions are much slower than bleach. As it is made into solution, cal hypo produces a relatively dilute chlorinating solution of less than 2 percent. Bulk hypochlorite, however, is more concentrated, so there are more ions that are going to collide more often, forming chlorate and perchlorate at a much faster rate.

Dry calcium hypochlorite briquettes contain a minimum of 65 percent available chlorine (AvCl) by weight. Being in solid-state, reactions are much slower with calcium hypochlorite than sodium hypochlorite, allowing for much longer storage periods.

Temperature

Calcium hypochlorite is a solid from the time it is dried to the time it's made into solution. Even solid-state reactions are affected by temperature, however, being a solid, its reactions are much slower than bulk hypochlorite. With bleach, the longer it sits there and the higher the temperature, the faster it goes to chlorate.

No Plant Keeps Bleach For 3 Months! Or Do They?

According to the recent Southern Nevada Water Authority study, excessive perchlorate formation can occur in three months with bulk hypochlorite.

It would seem unlikely that utilities would keep bulk bleach in storage for three months or longer. But they do all the time. Often utilities do not drain their bulk hypochlorite tanks, instead they simply top off the tank. As a result, chlorate generation goes up and keeps getting higher. Even if a utility dilutes their bulk bleach, if they are simply topping off their tank, chlorate generation will climb. In addition, the tank is potentially accumulating metals that further accelerate decomposition.

Utilizing a spare bulk hypochlorite tank (use out of tank A, fill tank B) is excellent advice, however it doubles a utility's capital costs. Same with diluting commercial bleach. If bulk hypo comes into a plant at 12 to 15 percent and the utility wants to dilute it to at least 50/50 to get the concentration down to 6 to 7 percent, the plant will have to double its storage capacity in order to accomplish this.

Perchlorate: Eliminating The Potential

With calcium hypochlorite, making a fresh, relatively dilute chlorinating solution of less than 2 percent only as needed essentially eliminates the potential for exceeding any future perchlorate MCL. Fifteen years ago cal hypo was used primarily as mainly a backup chlorination system for utilities. This was primary because no automatic feeders were available and solutions were prepared manually. However, Arch Chemicals feed systems today are markedly different from calcium hypochlorite feeders of the past, and far superior to the erosion-type feeders currently on the market.

Patented Spray Technology

Calcium hypochlorite is an extremely soluble material. Because of this, adequately controlling solution concentration has been historically difficult. However, that has all changed with Arch Chemicals' development of its patented spray technology specifically engineered to use proprietary calcium hypochlorite briquettes. Today, Constant Chlor® plus briquettes and chlorinator systems are an excellent choice.

The Arch system consists of a chlorinator and proprietary calcium hypochlorite briquettes, each certified to meet NSF standards 61 and 60, respectively. It produces a chlorine solution via a solid-state controlled spray manifold. Based on demand, the motor-driven, positive displacement chemical metering pump is used to inject the chlorine solution into the water system.

Arch Chemicals' Spray Technology, together with its specially engineered Constant Chlor® Plus briquettes have solved the consistency problems that had long been associated with calcium hypochlorite use. This, plus a controlled spray cycle, automatic solution tank refill, pressure relief and mechanical overflow-prevention valves, and full SCADA compatibilities provide for robust, efficient systems to meet the demanding needs for municipal water applications.

Meeting The Trend

Arch calcium hypochlorite is well suited to meet the soon-to-be growing trend of generating fresh, low strength solutions as needed. With the Arch system, excessive perchlorate formation is not an issue, so meeting any future perchlorate MCL is assured.

In numerous drinking water applications, such as wellheads, booster stations, storage facilities and small- to medium-sized surface water treatment plants (3-5 million gallons per day), Arch calcium hypochlorite briquettes and chlorinator systems are providing numerous benefits. In addition, Arch now currently provides chlorinator systems with capacity to feed up to 1,000 lbs AvCl per day, sufficient for large size surface water facilities. ■

About the Author:

James P. Brennan is a Consulting Scientist with Arch Chemicals, Inc., Atlanta, Georgia. He has been working extensively with water chlorination chemistry for the past 30 years.

Reference

Benjamin D. Stanford, Shane A Snyder, and Aleksy N Pisarenko, Gilbert Gordon, Mari Asami. *"Hypochlorite — An Assessmen of Factors That Influence the Formation of Perchlorate and Other Contaminants",* American Waterworks Association. (2009).

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Effective & Efficient

New Constant Chlor® Plus MC4-150 feed system serves larger treatment facilities

Arch Chemicals, Inc.'s new generation Constant Chlor® Plus calcium hypochlorite briquette feed systems provide increased capacity and accuracy that exceeds its first generation system, plus new capabilities and features that further enhance operation, maintenance and safety.

The new model MC4-150 system retains all of the key features that made Constant Chlor® the system of choice for years, such as optimum solution consistency and a small footprint; but its loading and feed rate capacities are much higher – *supplying up to 150 lbs. of AvCL/day* — allowing for its effective service to larger treatment facilities.

Major Advantages

Maintaining constant hypochlorite residual levels is now even easier with this second generation feeder system. The MC4-150 model features an HMI with touch screen for easier functionality, plus full SCADA capabilities. The new feeder uses NSF Standard 60 listed Constant Chlor® Plus dry calcium hypochlorite briquettes and patented spray technology to produce fresh liquid chlorine solution as needed.

The fresh made reservoir is filled with approximately 1.7% available chlorine solution and volume is maintained via an electronically controlled spray manifold. The hypochlorite disinfection solution is injected into the application with an appropriate, highly accurate positive displacement chemical metering pump specified for the application. Most metering pumps can be mounted directly to the pump mounting plate on the Constant Chlor® skid.

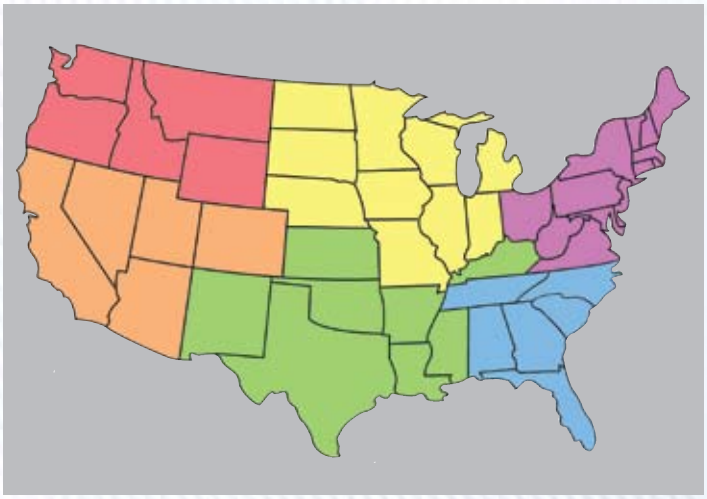
Constant Chlor® Plus MC4-150

Additional MC4-150 Features:

- Large hopper provides a dry chemical capacity of 225 lbs.
- Pre-plumed and skid mounted for simple installation
- All external parts make for easy PM.
- Comes with secondary containment skid
- Convenient AvCl solution sample feature.
- Automatic solution tank refill
- Separate fill cycle switch allows maintenance without service interruption.

Chlorination operations become even more effective and efficient with Arch Chemical's new MC4-150 Constant Chlor® feed system. Most importantly, a steady, constant dose of hypochlorite disinfection solution is always there when you need it. ■

Large Capacity. *The Arch Constant Chlor® Plus Model MC4-150 provides a dry chemical capacity of 225 lbs., supplies up to 150 lbs. of AvCL/day, and is pre-plumed and skid mounted for simple installation.*



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