

Municipal Water Disinfection Using Calcium Hypochlorite



February 16, 2010
Zachary Adams
Arch Chemicals

Chlorine Chemistry

Basic Chlorination

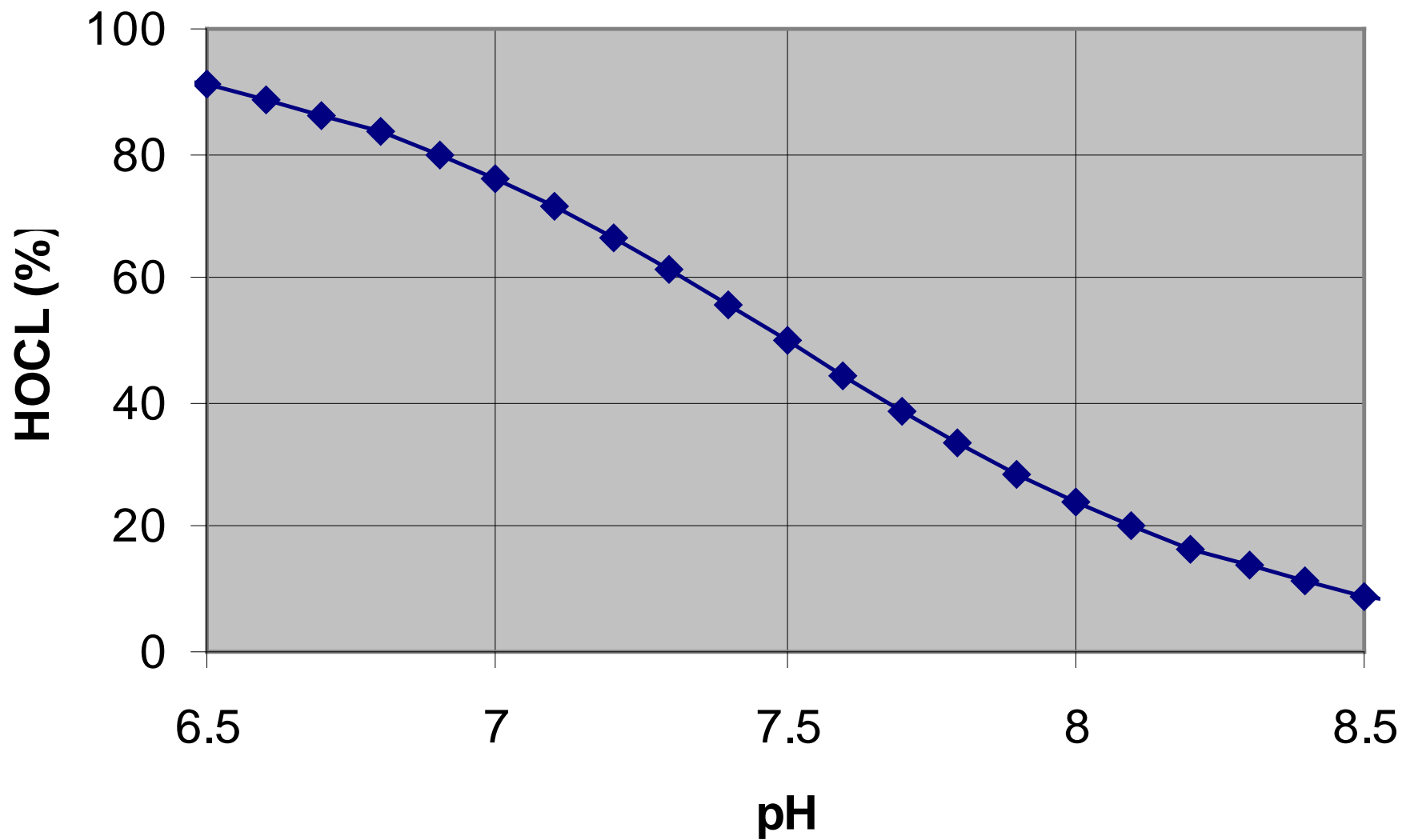
- Any chlorinating chemical added to water will initially form the same active ingredient : hypochlorous acid (HOCl)



- HOCl dissociates into H^+ and OCl^- , relative amounts depend on pH



Chlorine Chemistry



Chlorine Chemistry

Chemical Species

- Free Available Chlorine (FAC)
 - Total of HOCl and OCl⁻
- Combined Chlorine (CC)
 - Total chloramines
- Total Chlorine (TC)
 - Total of Free Available Chlorine and Combined Chlorine

Chlorine Chemistry

Biological Activity

- HOCl is the most biologically active form
- OCl⁻ is relatively inactive
- Chloramines are relatively inactive
 - Monochloramine is used in drinking water treatment

Chlorine Chemistry

Physical Forms and Chemistry

Type	Form	Avl Cl	pH
Chlorine	gas	100	1.0
Sodium hypo.	liquid	10 – 15	13
Calcium hypo.	granular	65 – 75	8-12

Evolution of Water Disinfectants

Advantages of the new technology Address the Issues of the former.

Chlorine
Gas

Sodium
Hypochlorite
Liquid

Calcium
Hypochlorite
Solid

Advantages
Disadvantages

- Simple
- Effective
- Reliable
- Low Cost

- Simple
- Effective
- Less Regulated

- Simple
- Effective
- Less Regulated
- Concentrated
- Longer Shelf Life

- Toxic
- Public Concern
- Regulated
- Increased Cost

- Bulky
- Corrosive
- Pumps Cavitate/ fail
- Extra Labor

- Convert Solid to Liquid
- Provide Consistent Performance
- Reduce Failure
- Reduce Maintenance

Chlorine Gas

- Effective
- Simple Application (**vs. Operation**)
- Inefficient: $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$
 $\rightarrow 2\text{HCl} + \frac{1}{2} \text{O}_2$
- Difficult to Transport, Store and Handle
- Higher Capital Cost
 - Carrier, Vacuum Injector, Scales, Scrubbers
- Expensive Annual Maintenance

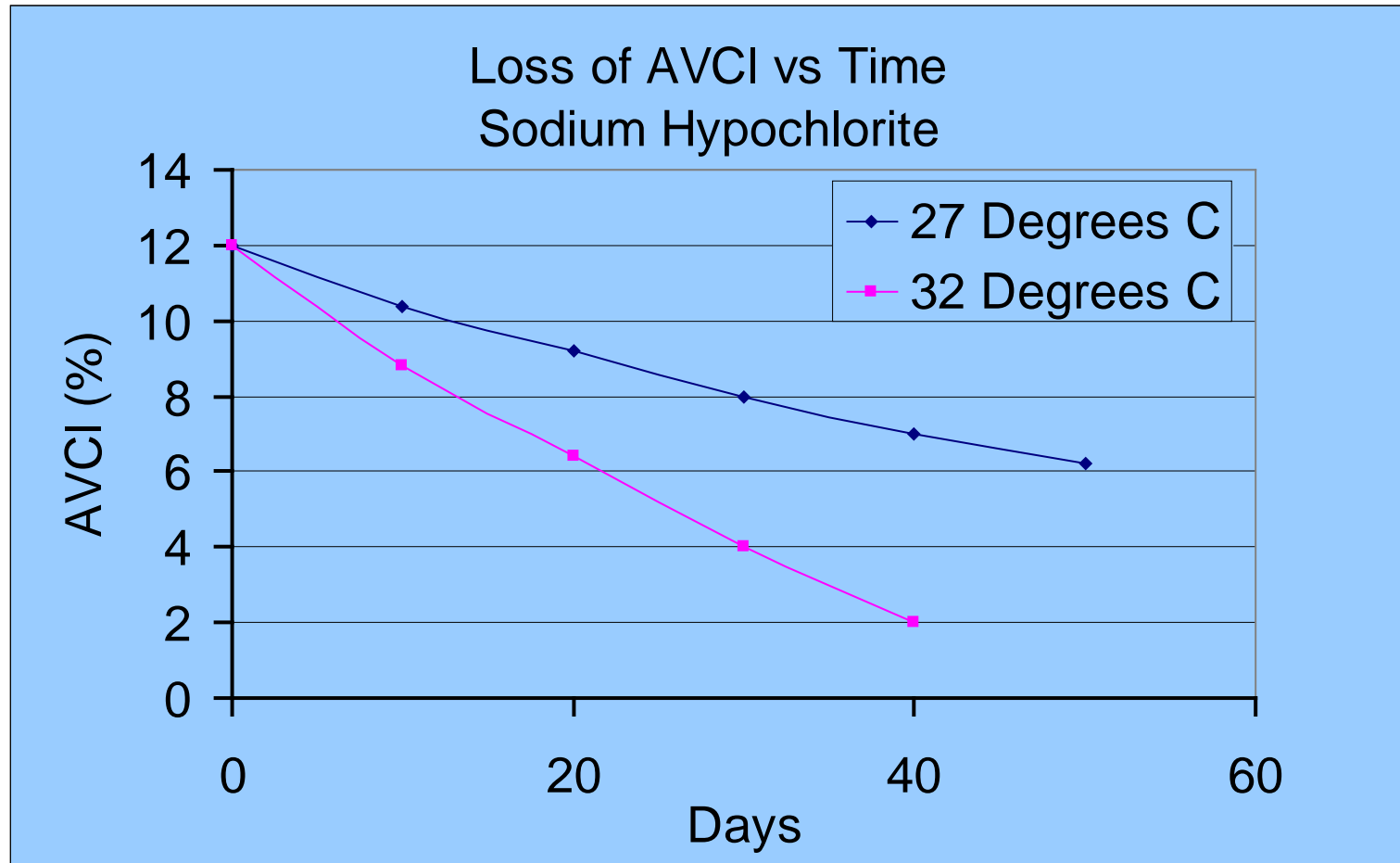


Bleach

- Also a low-price (**low cost**)
- Liquid for **Easy Application**
- Lower Strength, 10%-15% vs. 65%
 - Remote sites pay for shipping 85-90% inert liquid
- Inefficient
 - Short shelf life in solution
 - Variable Strength, dosage rates
- Extremely Alkaline (pH ~ 13)
 - Very Corrosive to Equipment
- High Capital Costs
 - Storage tanks, Containment,



Bleach



Calcium Hypochlorite

- Logistical:
 - Dry solid product: No spills, leaks, etc.
 - Concentrated: Less Handling, Storage, etc.
 - Stable: Longer Shelf Life, Reliable Inventory
- Performance:
 - Reliable Strength, vs. Bleach Loss of Available Chlorine.
 - Less Corrosive to Equipment
- Easy to handle; Lightweight - 55 lbs. Equals 550 lbs. of bleach

Calcium Hypochlorite

Less Chlorate By-product into water

- Hematoxin
 - Interferes with red blood cells ability to carry oxygen.
- Chlorate levels Tested:
 - Bleach:
 - Initial - 15 gm/l.
 - 3 months - 26 gm/l
 - Calcium hypochlorite:
 - Initial - 2 gm/l
 - 3 months – 3 gm/l

Calcium Hypochlorite

- 68% Dry Calcium Hypochlorite
 - Tablets: 3” “pucks”
 - Briquettes: 7gm “pillows”
- Class 3 oxidizer – dry product, and less corrosive than bleach (class 9)
- Scale inhibitor additive to reduce calcium carbonate scale
- Granular is not common for municipal – used in Industrial/Emergency applications

Calcium Hypochlorite - Applications

- **Surface Raw Water**
- **Finished Water**
- **Booster Stations**
- **Reservoirs**
- **Remote Well Sites**
- **Wastewater**
- **Reclaimed Water**
- **Overflow**

Calcium Hypochlorite Feed Equipment

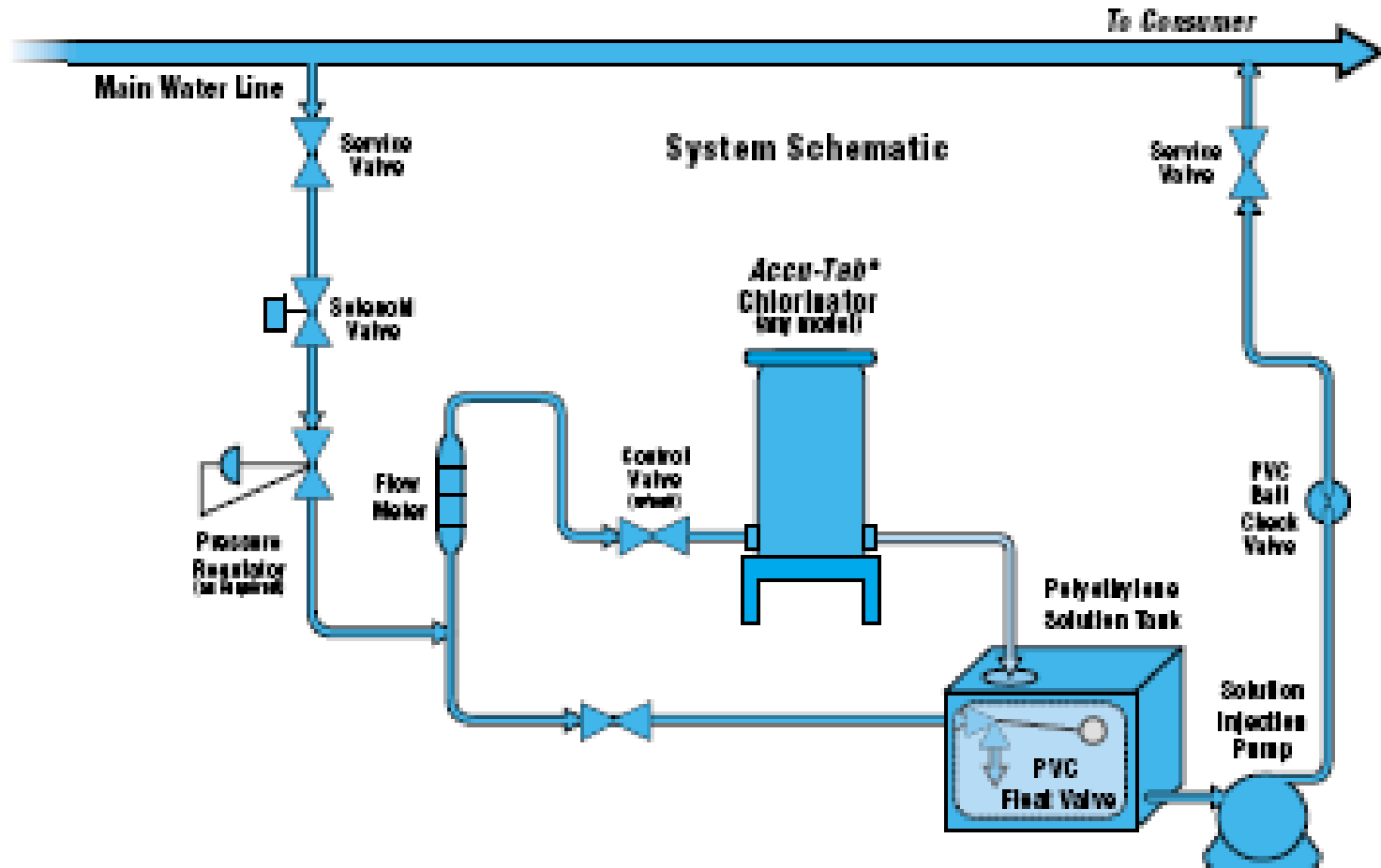
Multiple methods for cal-hypo feed equipment have been developed

Granular – Auger Method (uncommon)

Tablet – Erosion Vortex

Briquette – Vortex and Spray
Technology

PPG Accu-Tab®



PPG Accu-Tab®

- Uses 3" tablets
- Long shelf-life
- Erosion technology
- Concentration output:
~1000 ppm
- Up to 650lbs av
Cl/day



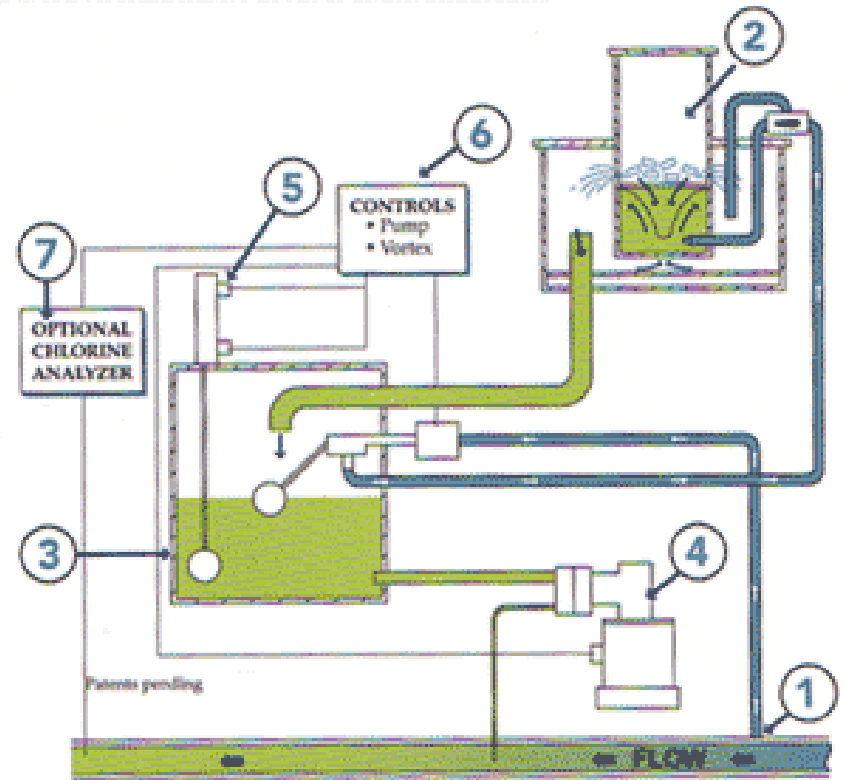
Hammonds Vortex

- Concentration: 1000-1500 ppm
- By recirculating a portion of the erosion water, a consistent and predictable solution strength is produced
- Utilizes DryTec Briquettes (7gm)



Hammonds Vortex

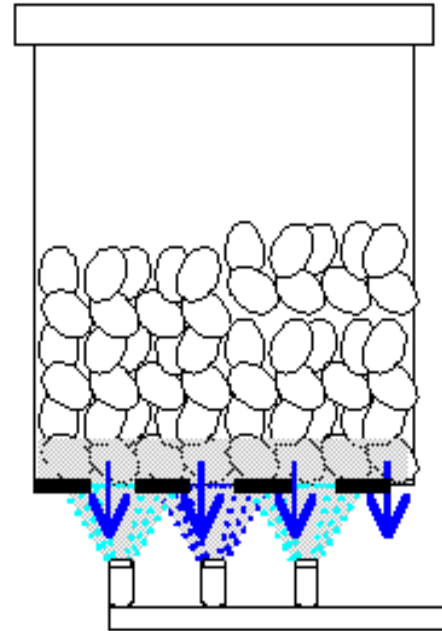
1. Water enters system at a fixed rate of 8 gallons per minute
2. Vortex feeder generates desired solution strength
3. Solution storage ready for injection
4. Variable speed pump injects solution at appropriate rate
5. Level control calls for additional solution as required
6. System controls either manual or automatic operation
7. Optional chlorine analyzer automatically controls variable speed pump and maintains set point chlorine residual



Spray Technology

- Independent Control of:
 - Water Flow
 - Pressure
 - Duration of Contact

- Well-Packed Tablet Bed
 - Small Size
 - Briquette Shape



Resulting In:

- Consistency
- Reliability

Spray Technology

- Spray technology enables more accurate control over erosion type feeders (~10x more concentrated solution)
- Cal-Hypo is very soluble, and continual immersion can vary the feed rate
- Spray technology prevents continual immersion, and promotes more consistent feed rate

Spray Technology

- Spray technology allows for a more concentrated solution, 1.7% or 17,000ppm
- Controlled contact time enables consistent solution strength
- Briquette packing more efficient, higher surface area



Hebron, IL Trial



Hebron, IL Trial

- Team:
 - Apex Pumping Equipment
 - Arch Chemicals, Inc
 - Village of Hebron
 - Applied Technologies
- 60 Day Trial with 30 Data Points
- Replaced Gas System
- IL EPA Approved Application 1/6/09
 - Pilot Study for Calcium Hypochlorite System 1-2008-1500

Hebron, IL Trial

The data points for the test included:

- Daily recordings of the inlet water flow meter to the Constant Chlor®
- Load cell readings (lbs)
- Chemical Dosing pump totalizer readings
- Constant Chlor® reservoir available chlorine solution strength
- Residual total and free chlorine in the finished water
- Daily well run times and output (gal)
- Operator's daily notes

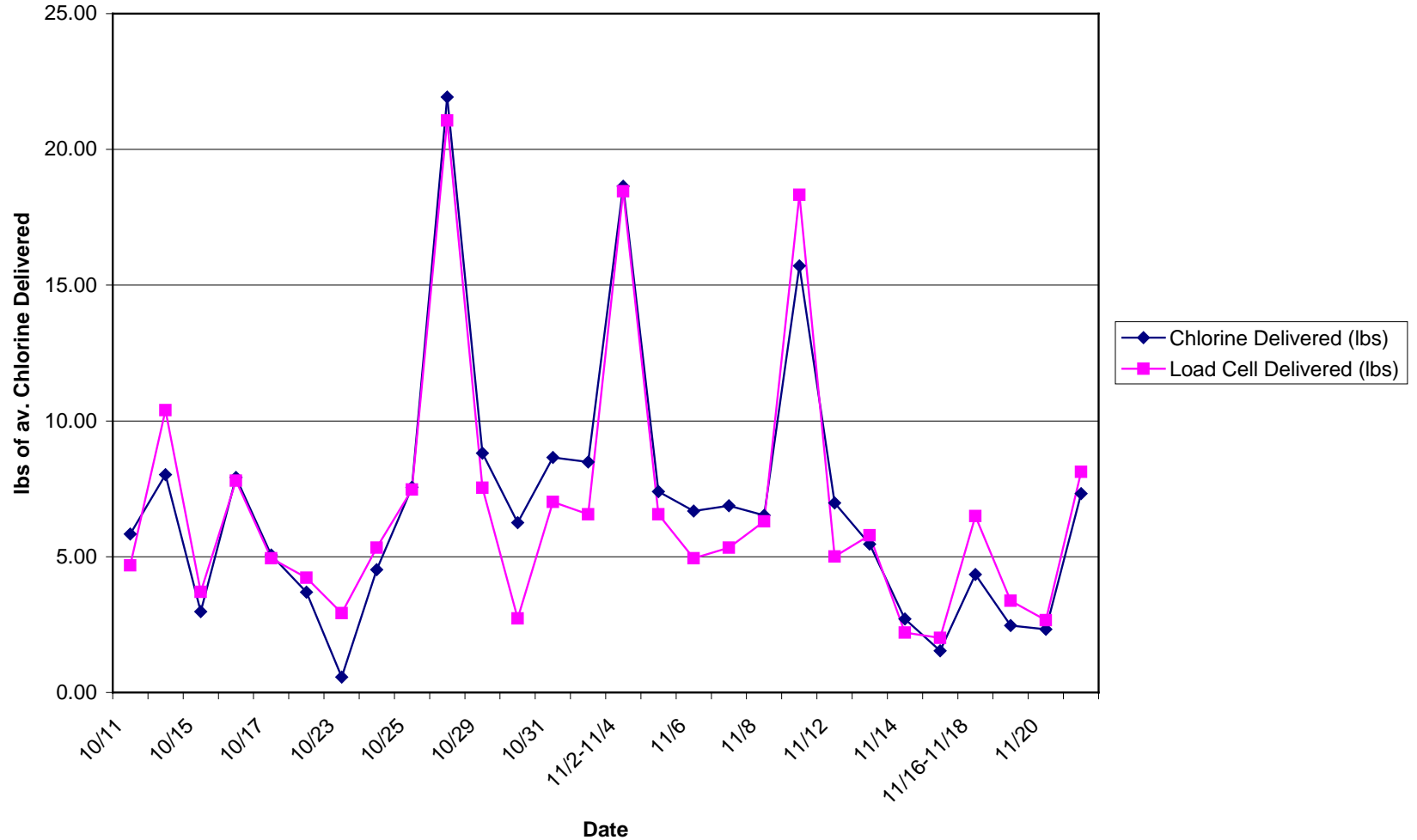
	Amount fed	Residual	Chlorine Demand
Ave TC ppm	5.31	1.66	3.65
StDev	1.50	0.72	1.35
Max	11.19	2.50	9.41
Min	3.57	0.80	1.92

New Berlin, WI Trial



New Berlin, WI Trial

Daily Chlorine Delivery (lbs)



New Berlin, WI Trial

- Data Gathered Every Day for 30+ days
 - Well pump total gpd
 - TC residuals in reservoir (4x/day)
 - Solution strength in CCF (1x/day)
 - GPD pumped by chemical dosing pump
 - Water fed into CCF
 - Daily load cell readings

New Berlin, WI Trial

- Results:
 - Ave TC in reservoir = 0.14 ppm (target is 0.15 ppm)
 - Load cell on average was within 3% of analytical calculation of chlorine delivery
 - The chemical dosing pump was turned slightly up 1 time during the test with no automated analyzer on site = accurate dosing
 - Equipment approved by WI DNR for use

El Paso, TX Trial

- Worked with state engineering firm in TX along with City of El Paso
- Protocol approved by TCEQ
 - Gas chlorine baseline
 - Turbidity
 - Total chlorine (manual and analyzer)
 - Temperature
 - Solution strengths
 - Report submitted

Spray Technology – Units in Field

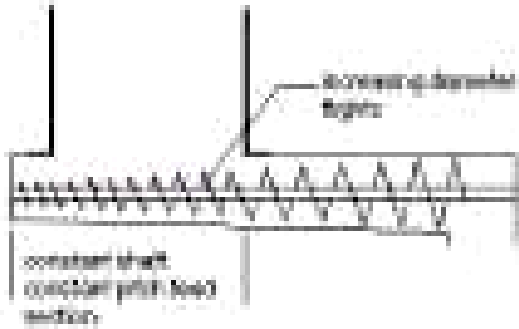


Arch Briquettes

Chemical Properties	Minimum	Maximum
Available Chlorine	65	—
(% by weight)		
Water (% by weight)	4.0	8.5
Iron (% by weight)	—	0.05
Oxides, heavy metals & Al		0.5
(% by weight)	—	
Scale inhibitors	0.4	0.6
(% by weight)		
Weight (grams)	6.5	7.5
Dimension (mm)	Approx. 32 x 19 x 13	

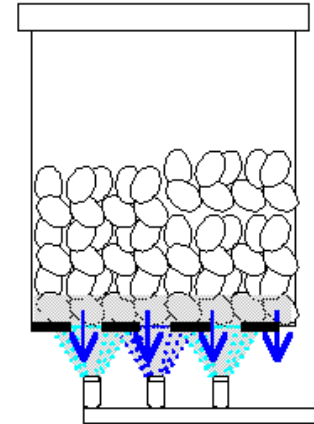
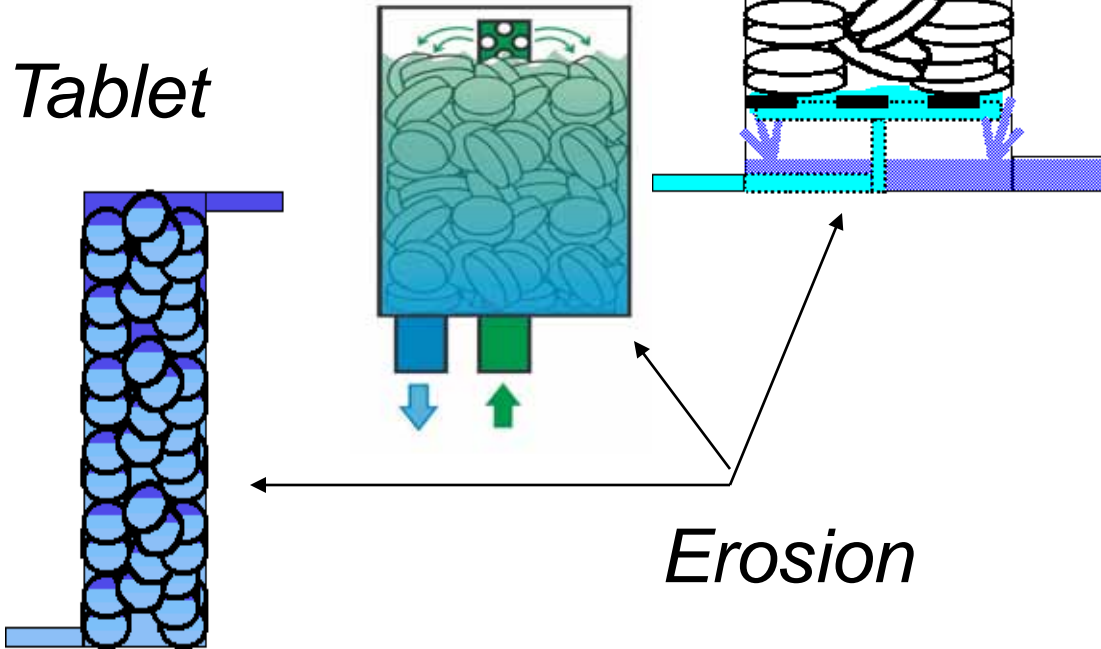
Feeder System Design Options

Figure 2. Increasing Diameter Screw Feeder



Granular

Tablet



Spray Technology

Designed for Calcium Hypochlorite Briquettes



General Design Recommendations

- Polyethylene tanks are recommended.
- Diaphragm pumps provide excellent dosing accuracy.
- Pump should be magnetically or motor driven.
- Pumps should have variable stroke length and speed control.
- Tanks should be equipped with a stirrer and bottom drain valve.
- Wetted parts should be:
PE, PP, PVC, PTFE, Hypalon, or Viton.

Design Considerations

- Proper hopper capacity sizing
 - Cal-hypo is hygroscopic and absorbs water
 - If cal-hypo sits exposed for long durations, it can off-gas and degrade
- Solution Mixing
 - A cal-hypo solution has around 6% insoluble material that must be suspended prior to injection
- Pre-Treatment
 - High alkaline and silica source water can cause plugging and solution delivery problems

Solution Mixing

- Constant solution mixing in a reservoir is critical
- This solution reservoir did not have sufficient homogenous mixing



Solution Mixing

- Proper tank-mixing eductors can prevent solid build-up
- Solids need to be suspended in solution at all times



Source Water Chemistry

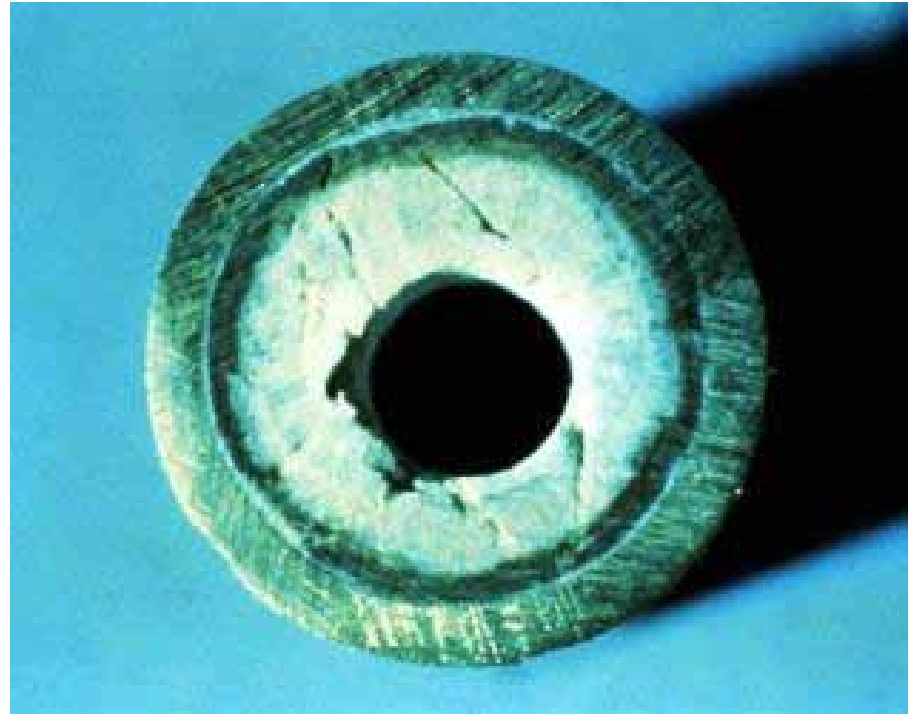
- Very important to understand how source water can effect a cal-hypo feed system
- Typical parameters to consider:
 - Carbonate (CO_3^{2-}) , also referred to as Total Alkalinity, Hardness, etc
 - Silica level
- These chemical species can react inside cal-hypo feed equipment to form insoluble material

Source Water Chemistry

- Cal-Hypo solutions are around pH ~11
 - With high alkalinity, and high pH, calcium carbonate scale can form
 - High silicates can react with calcium to form calcium silicate complexes that are hard and insoluble
 - Plugging of pump and discharge lines can result

Calcium Scale Formation

- High alkalinity (>150 ppm) can lead to line plugging in the discharge line of a cal-hypo feed system
- Optimal TA is between 60-90 ppm.
- Minimal cleaning of solution tank and discharge lines



Calcium Silicate Formation

- Calcium silicate can start forming inside cal-hypo feed systems when silica levels $>5\text{ppm}$
- Very harsh scale, difficult to remove (porcelain)
- Once crystal deposition is formed, scale can build rapidly



Water Chemistry - Solubility

Formation of scale requires two factors, calcium and carbonate. By itself high calcium hardness cannot cause scale to form. In fact some calcium salts are quite soluble, e.g. calcium chloride and calcium bicarbonate.

Maximum Concentration

calcium chloride	42.9%	429,000 ppm
calcium hypochlorite	21.8%	218,000 ppm
calcium bicarbonate	14.4%	144,000 ppm
calcium carbonate	0.0015%	15 ppm

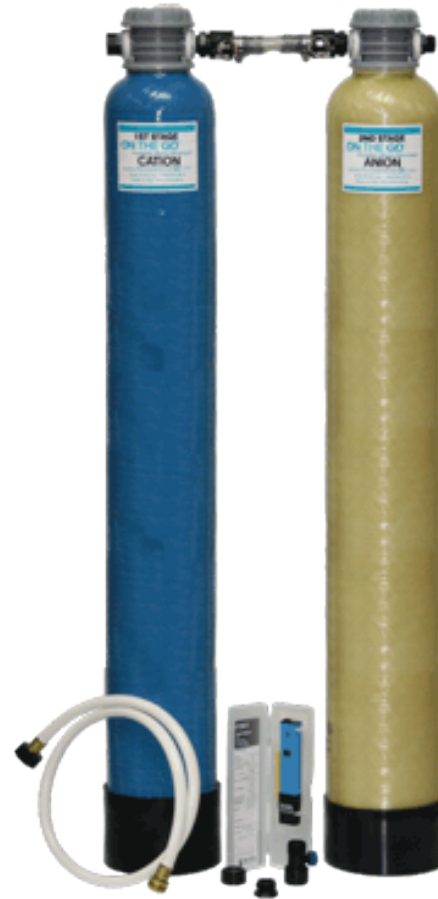
On the other hand bicarbonates are the major component of the total alkalinity (TA), and they are converted to carbonates as the pH increases. This is a direct cause of scale formation.

Pre-Treatment Options

- For sites that have hard water, and high silicates, pre-treatment can be installed on some cal-hypo systems
- Requirement for pre-treatment equipment is low inlet flow
- Species such as silica and carbonate alkalinity can be produce maintenance issues inside feeder and injection point

Pre-Treatment Options - Deionizers

- Deionizers (2 or 3 bed) can remove all ions in the water, producing completely deionized water
- Optimal for harsh water conditions
- Tanks must be serviced periodically



Pre-Treatment Options – Water Softening

- Water softeners can remove iron, manganese, silicates
- The media is regenerated depending on “grains per gallon”, or raw water quality
- Requires periodic addition salt into brine tank
- Generates a brine waste stream



Pre-Treatment Options – Reverse Osmosis

- RO systems generate ultra pure water, with no alkalinity
- Good option if there is no iron or silica present, as these compounds can blind the membrane
- Generates a waste stream of brine



Maintenance

- Briquettes have scale-control in formulation
- The amount of scaling also depends on the total alkalinity of the water.
- Above 90 ppm, the majority of maintenance for the Cal-Hypo feeders is keeping it clean of calcium carbonate scale.
- Periodic cleaning will prevent scale from hindering operation of feeder
- Areas with high alkalinity source water may want to invest in a reverse osmosis or a de-ionizer unit to lower alkalinity and silicates in the water

Estimated Maintenance

	Parts to be Inspected and Cleaned	Alkalinity (ppm)	Frequency	Estimated Time
<p style="text-align: center;">MC-2S and MC-3S</p>	<p style="text-align: center;">1. Support Grid 2. Spray Nozzle 3. Supply and Discharge Lines and Pump Head of Chemical Dosing Pump 4. Chemical Injector</p>	50	Annual	1 hour
		100	Quarterly	
		150	Bi-monthly	
		200+	Monthly	

	Parts to be Inspected and Cleaned	Alkalinity (ppm)	Frequency	Estimated Time
<p style="text-align: center;">MM-1S</p>	<p style="text-align: center;">1. Support Grid 2. Spray Nozzle 3. Supply and Discharge Lines and Pump Head of Chemical Dosing Pump 4. Chemical Injector 5. Plastic Eductor on Circulation Line 6. Supply and Discharge Line and Pump Head of Circulation Pump</p>	50	Annual	1-1.5 Hour
		100	Quarterly	
		150	Bi-monthly	
		200+	Monthly	

Constant Chlor[®] System

Integrated Chemical and Equipment System



to provide benefits needed for
Public Water

- Oxidizer
- Disinfectant
- Residual for Distribution



- **Fresh Solutions:**
 - On-site
 - On Demand
- **Less Corrosion Damage**
- **No Pump Failures**
- **Higher Labor Efficiency**
- **No Bulky Storage**

Constant Chlor® System

Overview

- Automatically prepares dry calcium hypochlorite briquettes into an available chlorine solution for disinfection purposes
- 2 feeders: 50lb/day delivery and 250lb/day delivery

Chemical

- 68% 7 gram briquettes of calcium hypochlorite NSF 60 certified

Feeder

- Can prepare solutions of available chlorine of 1.8% (1.5% for smaller equipment). Solutions are consistent
- Feeder can produce 0.9% av Cl solutions for areas that have secondary containment restraints (dilution nozzle)
- NSF 61 certified (smaller feeder pending)

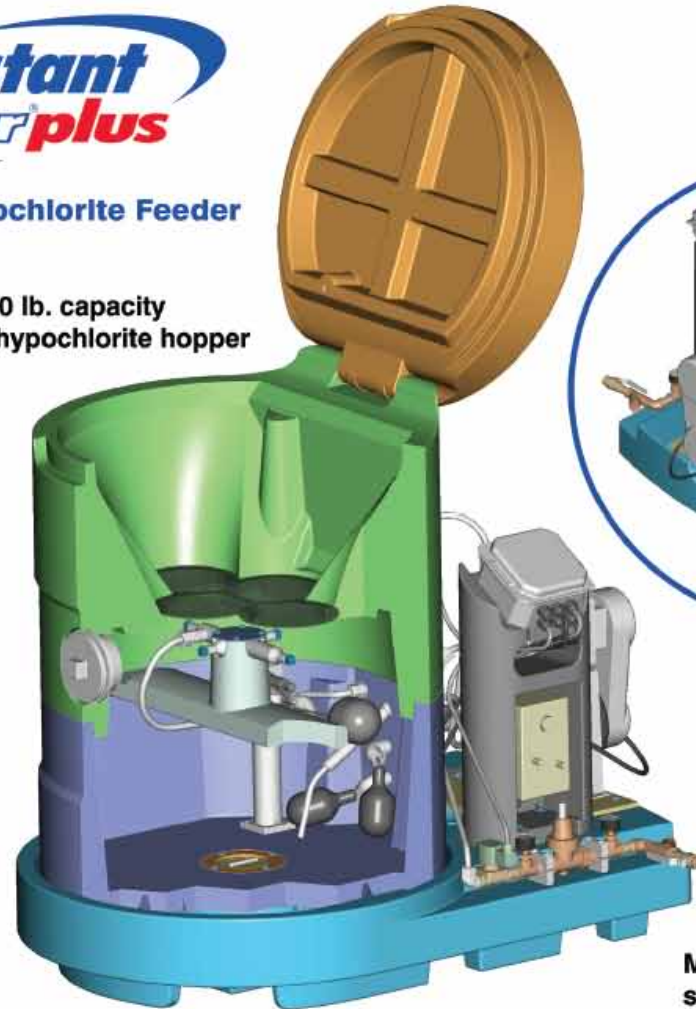
**No more liquid bleach
or chlorine gas!**



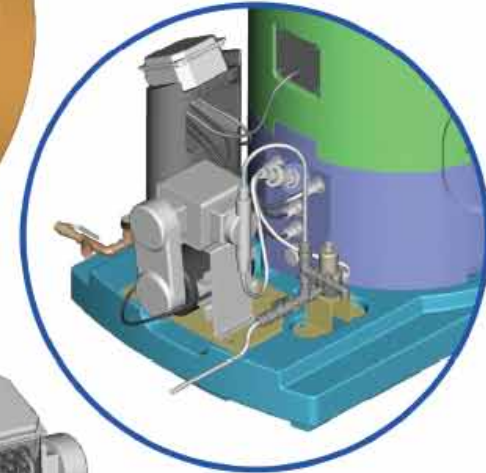
Dry Calcium Hypochlorite Feeder



**Large 220 lb. capacity
calcium hypochlorite hopper**



Rear View



**SCADA and modem
compatible for
use with manually
controlled pumps
or speed/stroke
controlled pumps.**

- ➔ **Delivers up to 250 lbs AVCl per day**
- ➔ **Adjustable, consistent and reliable**
- ➔ **Easy installation and maintenance**

**Motor-driven magnetic
stir bar keeps insolubles
in suspension.**



Arch Chemicals, Inc.

Features

- Solution is pumped out by a metering pump based on demand in the water and injected into the stream
- System is capable of injecting chlorinated solutions into flows from 200 gpm to 7000 gpm. Most dosing pumps provide 0-150 psig.
- Typical dosages range from 0.5 ppm to 10 ppm @ +/- 0.2 ppm
- Electronic float arms keep a working chlorine solution in the tank at all times

Control

- Large feeder utilizes an “e-box” to control device
- E-box circuitry:
 - **Constant Chlor® pump**
 - Interlocks Constant Chlor® pump to the main water pump
 - Prevents chemical feed when main water pump is off
 - **Mixer**
 - Keeps any insoluble material suspended in solution
 - **Sensors**
 - Lid Open
 - Add Briquettes (Optional)
 - Electronic Float Arms
 - Water Solenoid

Arch's New Spray Chlorinators for 2010

- Still in beta testing
- Customized, engineered skid units
- Fully programmable PLC control panel
- Load cells, Low/hi solution alarms, other diagnostics
- Full FMEA being performed
- “F1” Feeder – 50lbs avCl/day
- “F2” Feeder – 150 lbs avCl/day
- “F3” Feeder – 400 lbs avCl/day
- “F4” Feeder – 1000 lbs avCl/day

Arch Chemicals Storage and Handling Guide

- Product Stewardship
- General Product Information
- Product Hazards
- PPE
- First Aid and Emergency Procedures
- Transportation
- Storage and Handling Guidelines

Chemical Safety Awareness and Storage

- **Anyone** who handles cal-hypo must be fully aware of handling and storage requirements as well as emergency and first aid procedures used in case of an accident.
- **Anyone** who ships cal-hypo must also be knowledgeable with and follow current laws including: Department of Transportation (DOT) regulations, Environmental Protection Agency (EPA) regulations, Occupational Safety and Health Administration (OSHA) regulations, and locally adopted building and fire codes.

Chemical Safety Awareness and Storage

- **Emergency Telephone Numbers**

- ACEAN
 - 24 hours **1-800-654-6911**
- Arch Advice Line - for Damaged Products
 - 8 am to 10 pm EST **1-800-253-9140**
- CHEMTREC - Report emergency incidents
 - 24 hours **1-800-424-9300**
- NATIONAL RESPONSE CENTER - Report spills. >10 lbs
 - 24 hours **1-800-424-8802**
- MSDS **1-800-511-MSDS**

Chemical Safety Awareness and Storage

- **DO NOT:**
 - **MIX** chemicals together or with other materials.
 - **STORE** chemicals where average daily temperatures exceed **95°F (35°C)**.
 - **PUT** spilled material back in the original container.
 - **ALLOW** un-neutralized or chlorinated materials into the sewer.
 - **ALLOW** children to handle cal-hypo
 - **DISPOSE** of spilled material without complying with safety instructions

Chemical Safety Awareness and Storage

- **DO:**

- Read and follow the guidance contained on the product label and MSDS.
- Have an established emergency response plan in place.
- Maintain good housekeeping standards.
- Wear or carry appropriate personal protective equipment.
- Know how to handle all spills promptly and correctly.
- Rotate inventory on a **First In-First Out (FIFO)** basis.
- Use water **ONLY** as an extinguishing media for small fires.
- Call **1-800-253-9140** for advice about disposing of damaged products.

PERSONAL PROTECTIVE EQUIPMENT

- **At all times:**
 - Goggles and or safety glasses
- **When exposure to chemicals is probable:**
 - Rubber, neoprene or PVC gloves
 - Rubber, neoprene or PVC boots
 - Coveralls/apron
 - Face shield
 - Appropriate respiratory protection
- **When in dusty areas:**
 - NIOSH-approved* chlorine gas/dust cartridge respirator
- **When fighting a fire:**
 - NIOSH-approved* positive pressure self-contained breathing apparatus
 - Wash all equipment after use.

* If a NIOSH-approved respirator is used, personnel must comply with the requirements for use of respirators detailed in US DOL OSHA Respiratory Protection Standard, 29CFR1910.134

GENERAL FIRST AID

FIRST AID PROCEDURES FOR OXIDIZERS

IN EYES:

- Immediately flush eyes with water for 15 minutes.
- Call a poison control center immediately for treatment advice.

ON SKIN:

- Immediately flush the skin with water for 15 minutes. If irritation persists, get medical attention.
- Call a poison control center immediately for treatment advice.

GENERAL FIRST AID

- **IF SWALLOWED:**

- Immediately drink large quantities of water.
- Call a poison control center immediately for treatment advice.
- **DO NOT** induce vomiting

- **IF INHALED**

- Remove victim to fresh air.
- If not breathing, call 911 and administer CPR
- Call a poison control center immediately for treatment advice.
- Any clothing which has come in contact with chemicals should be washed before reuse.

CALCIUM HYPOCHLORITE

EMERGENCY PROCEDURES – SMALL SPILLS

Spill Clean-Up Kit

- Two clean dry containers
- One clean dry broom
- One clean mop and bucket
- One clean dry dust pan
- A minimum of four clear sturdy plastic bags
- Compatible absorbent material – spill clean-up socks or pads, vermiculite, etc.
- Labels

CALCIUM HYPOCHLORITE

EMERGENCY PROCEDURES – SMALL SPILLS

Clean, dry product:

- Put on appropriate protective gear
- Sweep up with clean utensils.
- Place in clean dry container
- Do not return to original container

Wet and/or contaminated product

- Put on appropriate protective gear
- Fill 55 gal drum with water (to at least $\frac{3}{4}$ full).
- Slowly add not more than 10 lb. cal-hypo product
- Allow the solution of chlorine to dissolve and stand until the available chlorine is within acceptable discharge levels – according to local, state and federal regulations



CALCIUM HYPOCHLORITE

EMERGENCY PROCEDURES - FIRES

- NFPA Class 3 Oxidizers severely increase the burning rate of combustibles - **DO NOT USE DRY POWDER EXTINGUISHERS.**
- FIRE DEPARTMENT MUST BE CALLED IMMEDIATELY.
- USE LARGE AMOUNTS OF WATER.
 - “Drown, Cool, and Dilute”





Storage Recommendations

National Fire Protection Association

NFPA 1: Uniform Fire Code, 2006 ed.

NFPA 430: Code for the Storage of Liquid and
Solid Oxidizers, 2004 ed.

CALCIUM HYPOCHLORITE STORAGE

- SEGREGATE FROM INCOMPATIBLE MATERIALS:
 - FLAMMABLE LIQUIDS
 - COMBUSTIBLES
 - OTHER OXIDIZERS
- SPRINKLERS ARE RECOMMENDED

CALCIUM HYPOCHLORITE

STORAGE*

Permits Required:

- According to NFPA 1, for class 3 Oxidizers, any amount stored that is greater than 10 lbs/1 gallon requires fire code permit

Permits

- For un-sprinklered buildings, 1150 lbs of class 3 Oxidizers is allowed for (M) or (S) occupancy
- (H) Hazardous storage is required for amounts that exceed 1150 lbs
 - Technical assistance may be necessary for construction
- Allowable amount of product may be increased 100% if building is equipped with automated sprinklers

SEGREGATED STORAGE

STORAGE IN SAME ROOM AS INCOMPATIBLES.

MAXIMUM PILE HEIGHT

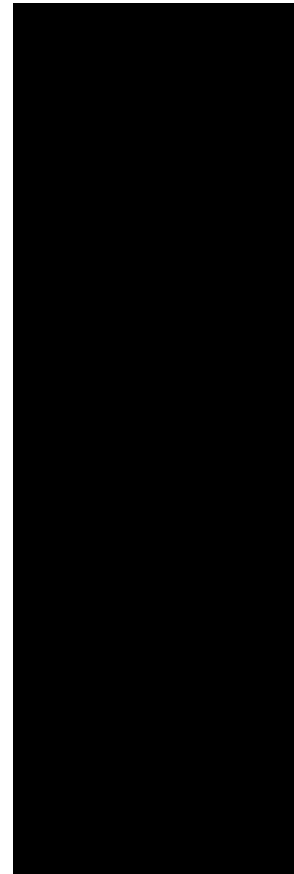
MAXIMUM PILE WIDTH

MINIMUM PILE SEPARATION

MAXIMUM QUANTITY/ PILE

MAXIMUM QUANTITY/ BUILDING

* Density 14 l/min/m²; area 465 m²



Transportation

- DOT 5.1 Oxidizer
- Material of Trade (MOT)
 - Maximum amount of material in one package is 66 lbs or 8 gal.
 - Maximum amount of hazardous material in one vehicle is limited to 440 lbs
 - MOT's do not require:
 - Shipping papers, emergency response information, placarding, formal training, or record keeping
- Placarding
 - Less than 20 pails (less than 1001 lbs.)
No Oxidizer placard required