Powell
Fabrication & Manufacturing, Inc.

Hypochlorite Production
General Information

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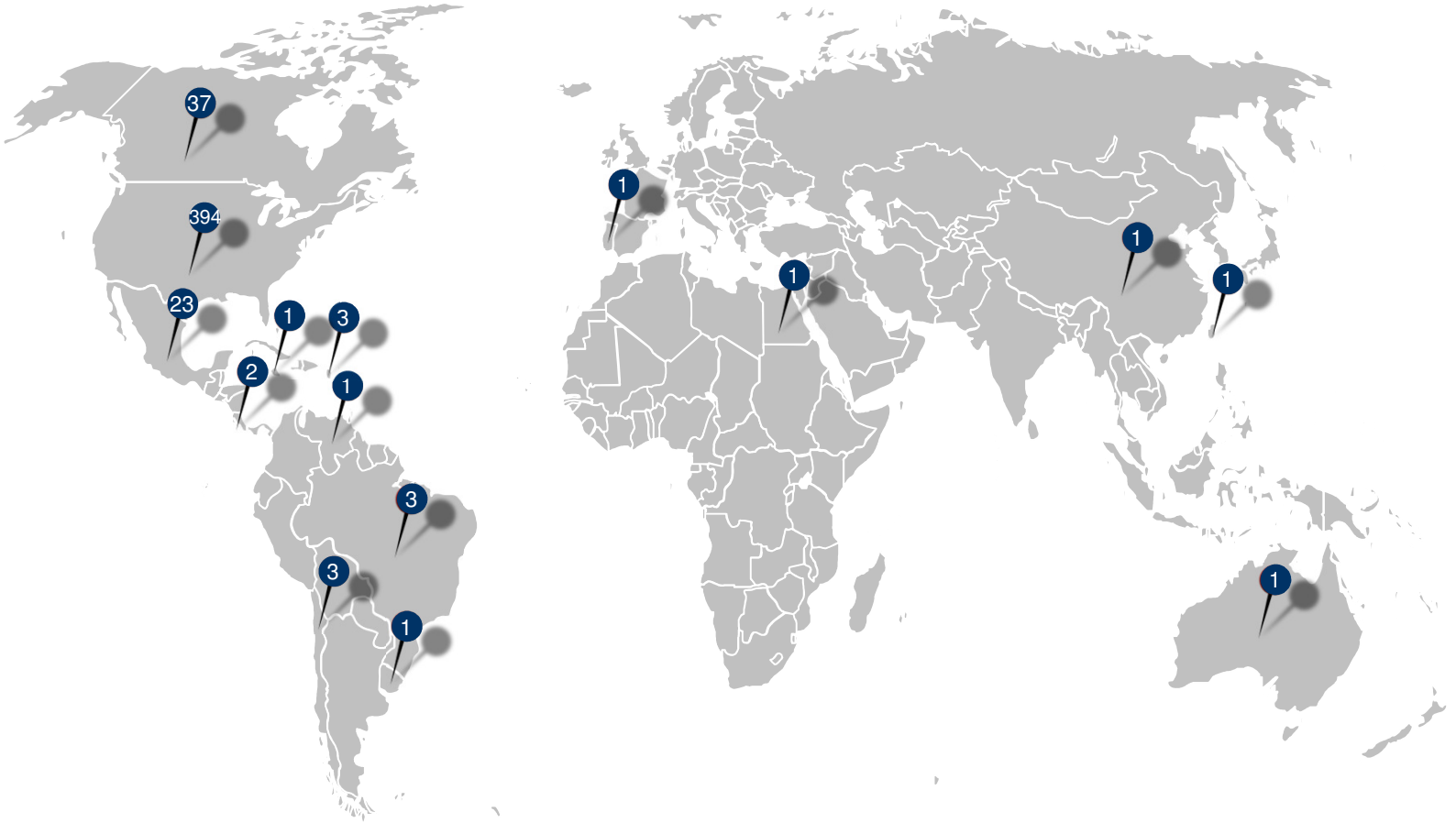
Cinderella

Powell Fabrication & Mfg.

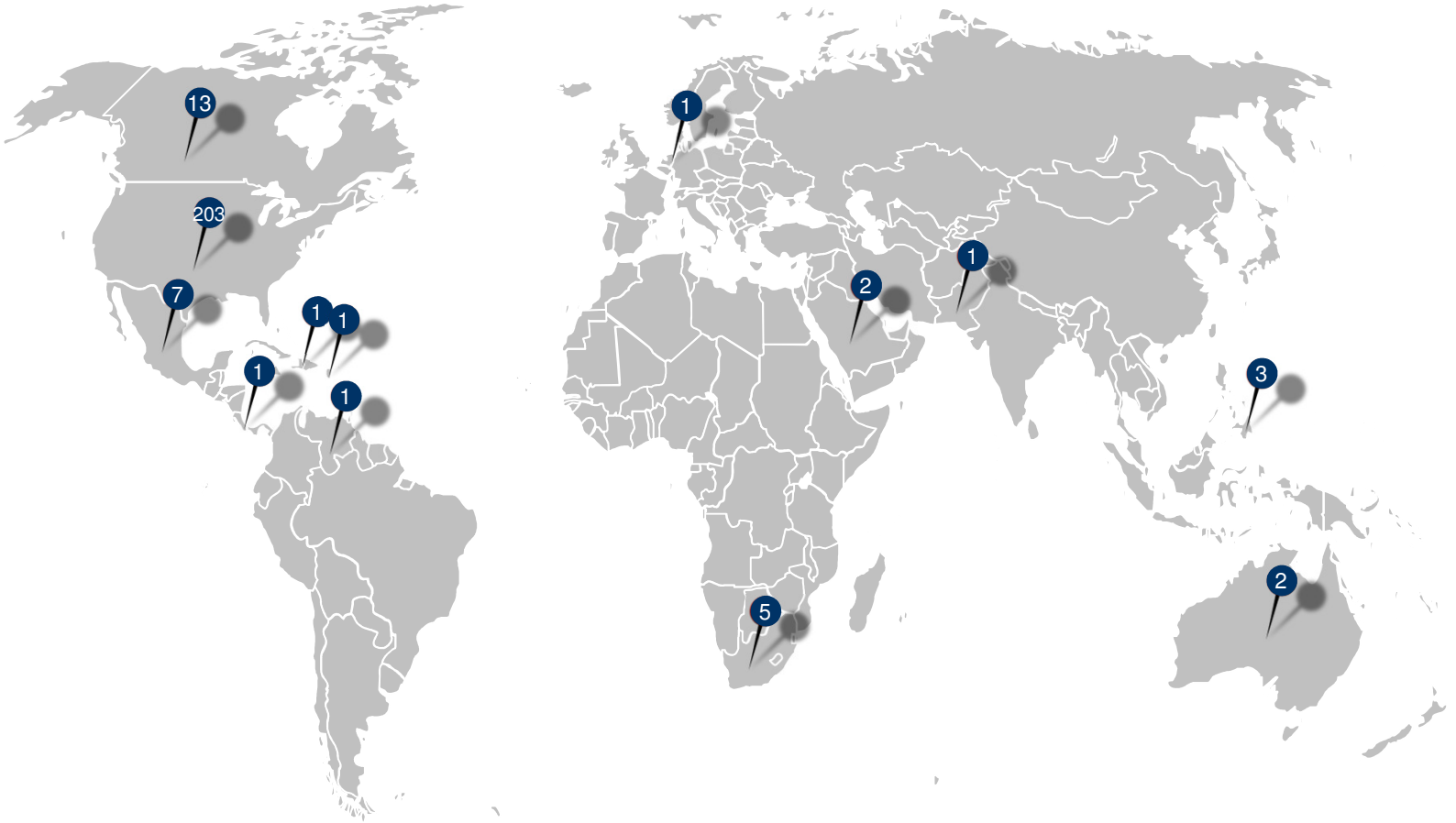
- Sodium hypochlorite production equipment starting in 1964 with filtration since 1983
- 75% of NaOCl in US made on Powell equipment
- 90% in Canada
- Significant production in other countries – Brazil, 80% Mexico, 80% Chile, Taiwan, Philippines, 65% Costa Rica, Saudi Arabia and others
- Chlorine scrubbing and chlorine valve emergency shutoff systems
- Chemical Blending Systems: NaOCl, Caustic, HCl, sulfuric, methanol, ammonia, etc.
- One Shop Point: Engineering, Procurement, Fabrication, Startup, Field Services

Bleach Plant Owners

Valve Closure Owners



Scrubber Owners



Powell Equipment Owners

Discussion Topics

- Sodium Hypochlorite Chemistry
- Packed Tower Chemistry
- Oxidation Reduction Potential (ORP/Redox)
- Batch to Continuous Chlorine Scrubbing
- Batch to Continuous Sodium Hypochlorite Production
- Filtration & Hypo Dilution Systems

Terms of Hypochlorite Strength

- Grams per Liter of Available Chlorine
- Grams per Liter of Sodium Hypochlorite
- Trade Percent of Available Chlorine
- Weight Percent of Available Chlorine
- Weight Percent of Sodium Hypochlorite

Production of Sodium Hypochlorite

- $Cl_2 + 2\ NaOH = NaOCl + NaCl + H_2O$
- Exothermic reaction
- 526 BTU/Pound of chlorine if Cl_2 liquid
- 626 BTU/Pound of chlorine if Cl_2 vapor
- Slight amount of excess NaOH always remains in solution (typically 3-5 GPL or 0.25% to 0.35% by weight)
- pH for commercial NaOCl (typically greater than 13)

Basis of Production

- 32% or 50% sodium hydroxide is diluted to 17% NaOH for typical commercial strength NaOCl
- Heat of solution removed
- Cl_2 added into solution until excess caustic is reduced to the 3-5 GPL excess caustic range – approximately 13 pH
- Cl_2 addition should always be controlled by ORP (oxidation reduction potential)
- Process can be either batch or continuous

Sodium Hypochlorite Decomposition

- Parameters That Influence Decomposition
  - Concentration
  - Temperature
  - Ionic Strength
  - Transition Metal Ions

- 2nd Order — Rate = $k_2 [OCl^-]^2$
- Primary Pathway — $OCl^- + OCl^- \rightarrow ClO_2^- + Cl^-$
  $OCl^- + ClO_2^- \rightarrow ClO_3^- + Cl^-$
- Stoichiometry — $3OCl^- \rightarrow ClO_3^- + 2Cl^-$
- Secondary Pathway — $OCl^- + OCl^- \rightarrow O_2 + 2Cl^-$
  "uncatalyzed" and "catalyzed"

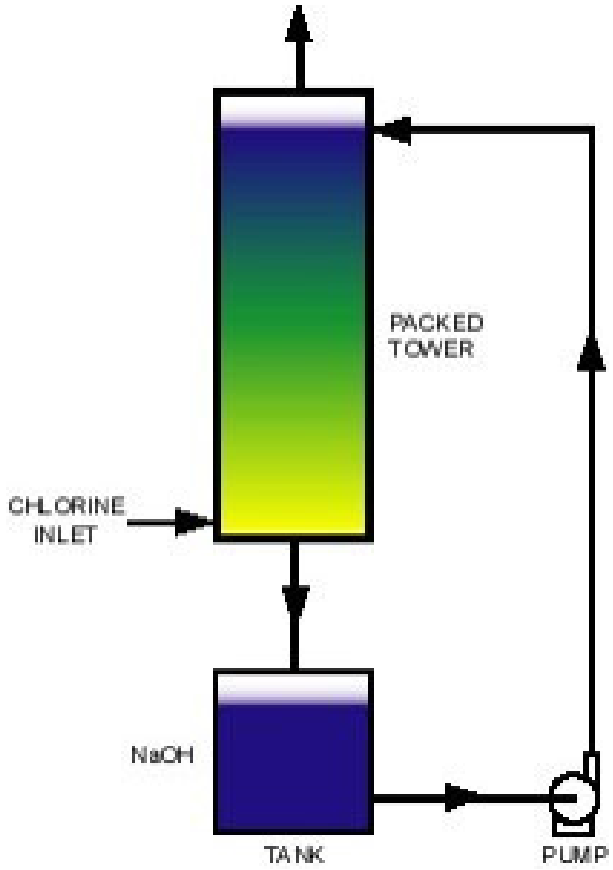
Unwanted By-Products

- Bromate $(BrO_3)^-$
  - Bromide ion in salt used to make Cl_2
  - Forms Br_2 (Impurity in caustic)
  - Reacts with caustic to form $(BrO_3)^-$
- Chlorate $(ClO_3)^-$
  - Inefficiency of chlorine/caustic reaction
  - $3\ OCl^- \rightarrow ClO_3^- + 2\ Cl^-$
- Perchlorate $(ClO_4)^-$
  - Decomposition of Chlorate Ion
  - $OCl^- + ClO_3^- \rightarrow ClO_4^- + Cl^-$

Hypochlorite Production

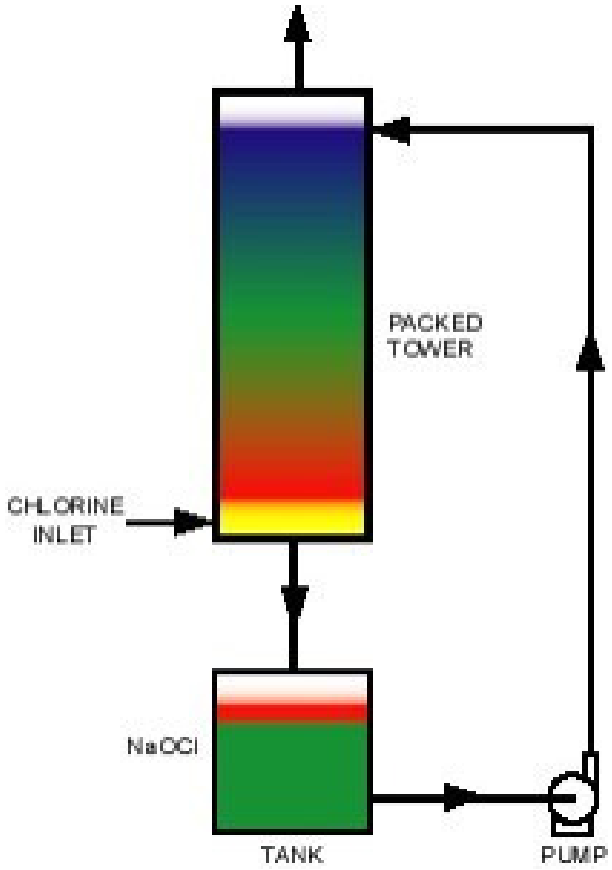
- Hypochlorite Productions
  - Tower System
    - Batch vs. Continuous
  - ORP Control

Initial Tower Cl2 & NaOH Reaction



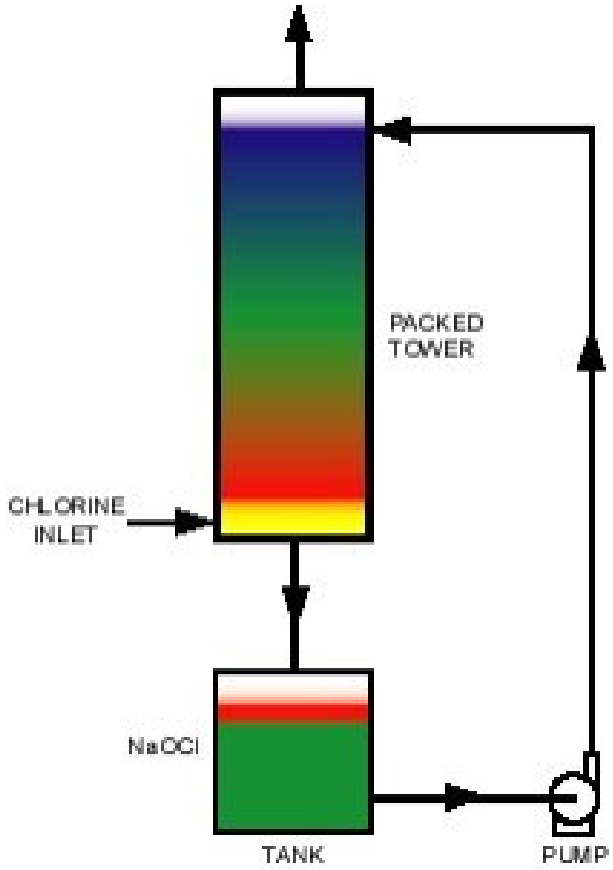
- Cl2 + 2NaOH = NaOCl + NaCl + H20
- 17 - 20% NaOH typical scrubbing solution strength
- High pH reaction >11

Tower Reaction Zones End of Batch



- Top of tower – High pH (NaOH – NaOCl – NaCl)
- Center of tower – pH > 11 (NaOH – NaOCl - NaCl- Cl2)
- Bottom of Tower-Low pH (NaOCl – NaClO3 – NaCl – Cl2)

Ending Batch Reactions



- $Cl_2 + NaOCl + H_2O = 2HOCL + NaCl$
- $2HOCl + NaOCl = NaClO_3 + 2HCl$
- End reaction is:
  $3\ NaOCl = NaClO_3 + 2\ NaCl$
- Occurs in low pH regions at bottom of tower

Packed Tower Advantages

- Very good chlorine reactor
- Low gas pressure drop
- High inert gas loading
- Predictable results
- Low PPM chlorine outlet concentrations

Packed Tower Disadvantages

- Packed towers - Poor NaOCl production units.
- Low excess caustic less than 2% - 3% by weight produces high NaClO3
- NaOCl side reaction to NaClO3 creates more salt, potentially plugging the tower packing.
- Each 1 gpl of NaClO3 loses 2.1 GPL of NaOCl
- Packed towers are limited in strength of NaOCl due to NaClO3 side reactions creating NaCl and high excess caustic

Production Losses

- Typical packed towers produce 135-155 gpl NaOCl with 12-15 gpl excess NaOH and 8-10 gpl $NaClO_3$
- High quality hypo is 135 -155 gpl NaOCl, 3 gpl excess NaOH and 1.0 gpl $NaClO_3$
- 25,000 MT of hypo per year of high quality hypo versus packed tower hypo equals a savings of 305 tons of Cl_2 and 532 tons of NaOH @ 135 gpl

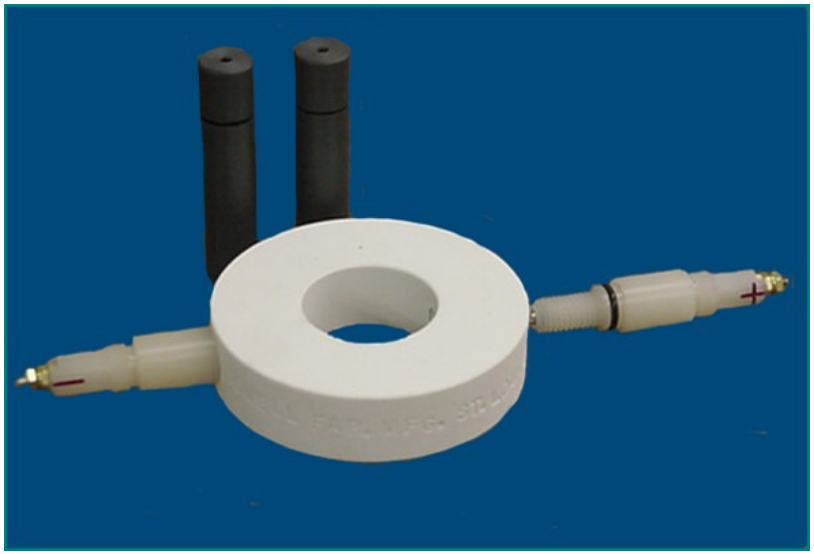
Production Improvements

- Convert batch towers to continuous
- Operate towers at higher excess caustic such as 3-4% excess NaOH or greater
- Move hypo production downstream of chlorine towers
- Allows use of cooling tower water in lieu of chilled water for towers and hypo production

Production Improvements

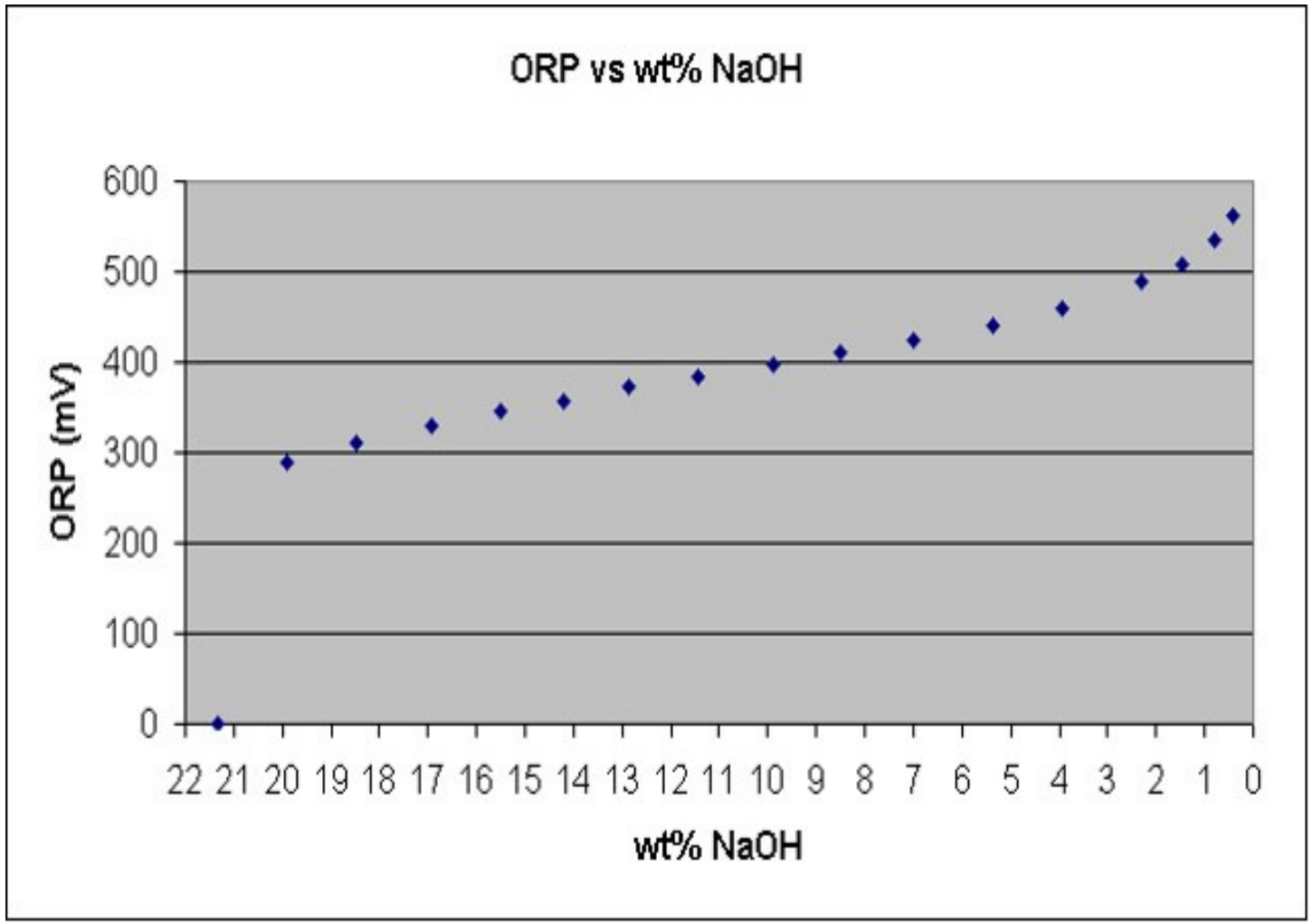
- Allows production of up to 16.5% by weight (200 gpl available chlorine)
- Reduce Excess NaOH to as low as 2-3 gpl
- Reduce $NaClO_3$ to as low as 1 gpl
- Reduce Operator Labor (elimination of 1 or more operators per shift)
- Reduce Shipping Cost

ORP Instrumentation



- ORP for chlorine scrubbers and hypo production
- Successful patented electrodes developed by Dow in 1960's
- Originally sold under license by Powell since 1963
- Voltage increases as sodium hydroxide decreases

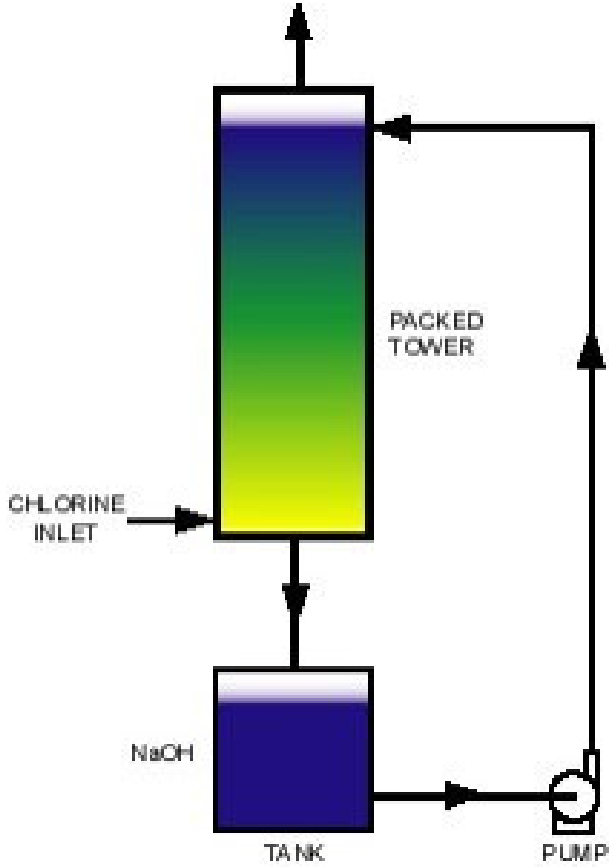
ORP Control


ORP vs wt% NaOH
ORP (mV)
600
500
400
300
200
100
0
22 21 20 19 18 17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
wt% NaOH

Tower Design Changes

- Add ORP electrodes, indication and alarms
- Location of electrodes depend on process design
- Convert from batch towers to continuous system
- Requires level control and ORP control for automatic caustic addition

Hypochlorite Prod. Downstream of Towers



- Towers are continuous
- Towers operate at high excess NaOH levels
- Towers have low NaClO3
- No chilled water
- Safer operation

Advantages

- Continuous Equipment to chlorinate tower hypo
- Uses scrubber solution from 3-4% excess NaOH and higher to maximum of 21% caustic
- Liquid and/or gas (wet or dry) chlorine for final chlorination
- Cooling Tower Water during production
- Chilled water used for some storage applications

Additional Advantages

- Hypo production during cell room maintenance if liquid chlorine is used
- Reduced shipping costs due to higher strength
- High turn down of production such as 250 ton/day down to 25 ton per day
- Totally automatic with extremely good repeatability of bleach strength and excess caustic

Typical Real Case

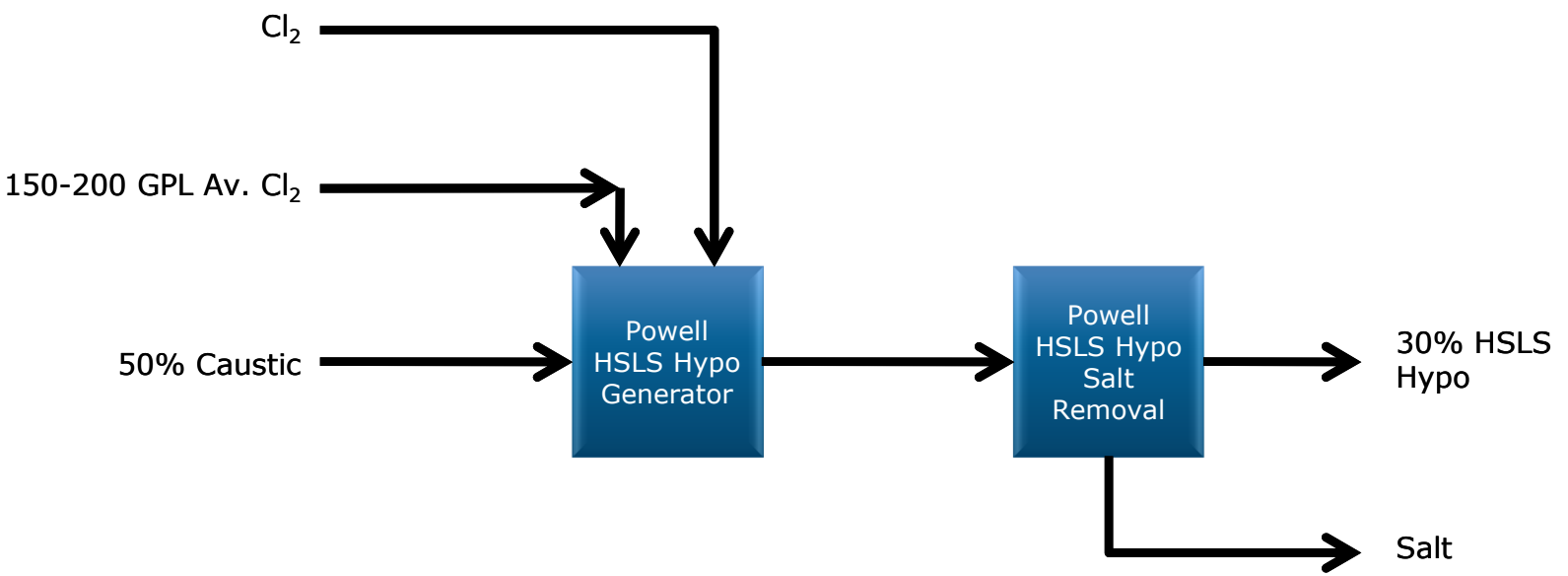
100 Ton per day Bleach Unit

	Junio 27/03 al Oct 10/03	Oct 08/03 al Dic 9/03
Número de Datos	201	189
NaOCl	146.031	146.241
NaCl	145.649	128.729
NaCl Teórico	114.640	114.810
Sobrante NaCl	31.01	13.92

Typical Real Case

- Difference 16,92 gr Salt/lt bleach
- Equivalent to 32.33 gr bleach/lt
- 100 ton per day bleach production means over consumption 2.57 ton chlorine and 2.9 ton dry caustic

Next Generation Hypochlorite Production



Powell HSLS Hypo Process Diagram

HSLS Hypo Solution

Traditional Hypo vs. HSLS Hypo

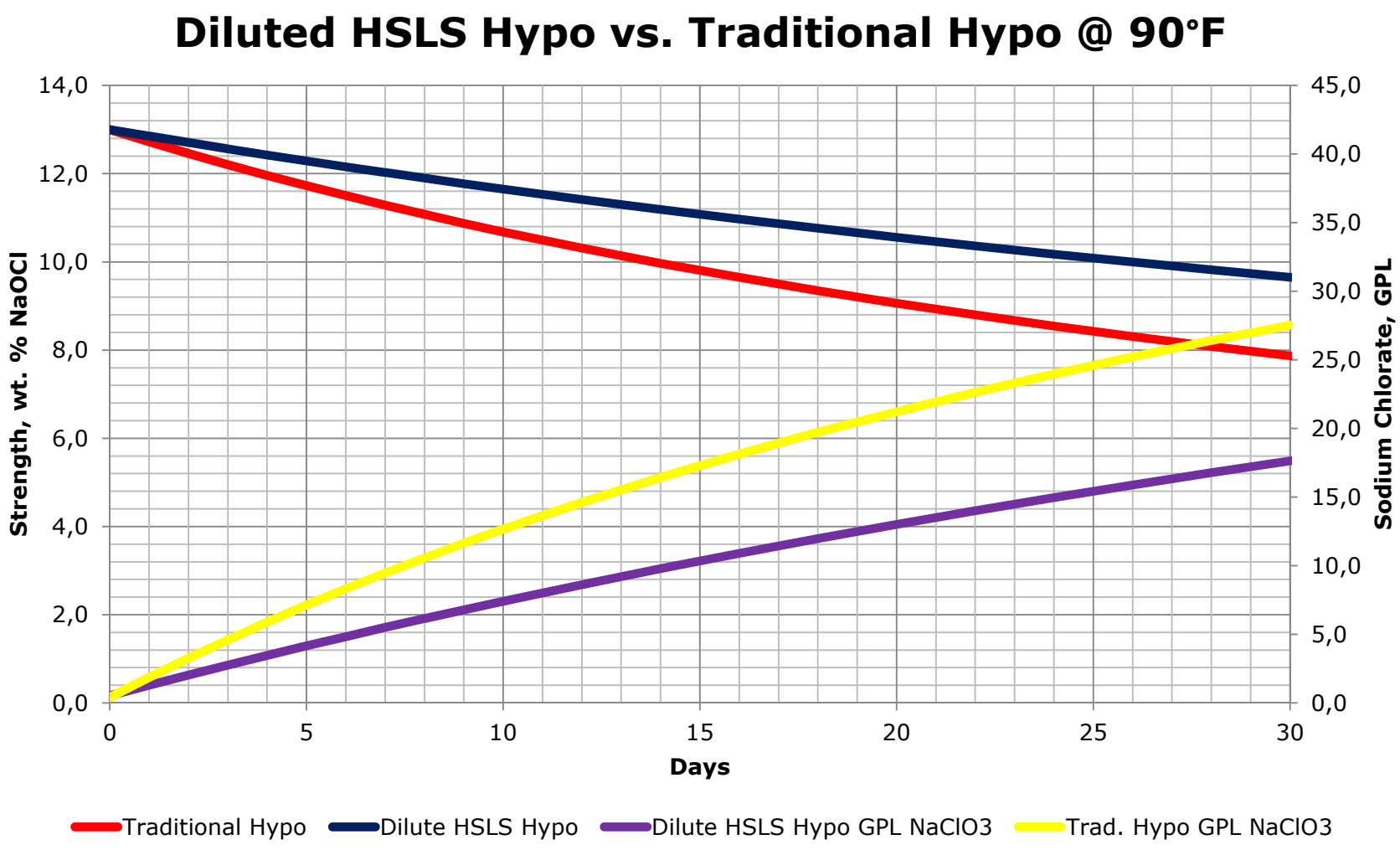
Tradition Hypo		
NaOCl	NaCl	SG
Wt. %	Wt. %	
30.0%	X	X
25.0%	X	X
20.0%	X	X
16.5%	13.0%	1.2622
15.0%	11.9%	1.2382
13.0%	10.4%	1.2052
10.5%	8.3%	1.1610
8.0%	6.3%	1.1210
6.0%	4.7%	1.0920
3.0%	2.4%	1.0490

HSLS Hypo		
NaOCl	NaCl	SG
Wt. %	Wt. %	
30.0%	8.5%	1.3459
25.0%	7.1%	1.2936
20.0%	5.7%	1.2391
16.5%	4.7%	1.1997
15.0%	4.3%	1.1824
13.0%	3.7%	1.1592
10.5%	3.0%	1.1296
8.0%	2.3%	1.0994
6.0%	1.7%	1.0750
3.0%	0.9%	1.0376

Chemistry Advantages

- Reduction in Ionic strength of the solution:
  - Slower decomposition resulting in a longer half-life
  - Less chlorate ion formation
  - Less perchlorate ion formation
  - Less oxygen formation

Chlorate Formation



What are the Production Advantages?

- Reduced chlorine and caustic consumption per liter produced
- Recovery of salt for raw material savings
- Improved stability and reduced weight allow more flexibility of logistics
  - Lower specific gravity will reduced the overall weight load for shipment of same volume
  - Increased volume per shipment for same load weight

Salt Savings for HSLS Hypo

- Approximately 1,650-1,815 kg. of NaCl consumed to produce 1,000 kg. of chlorine
- 1,000 kgs. of chlorine reacted to 30% NaOCl = 615 kg. of NaCl savings by reclaiming salt
- 615 kg of reclaimed salt = 34-37% needed for original electrolysis
- Reclaimed salt is very pure; if returned back to chlor-alkali plant only requires secondary brine treatment

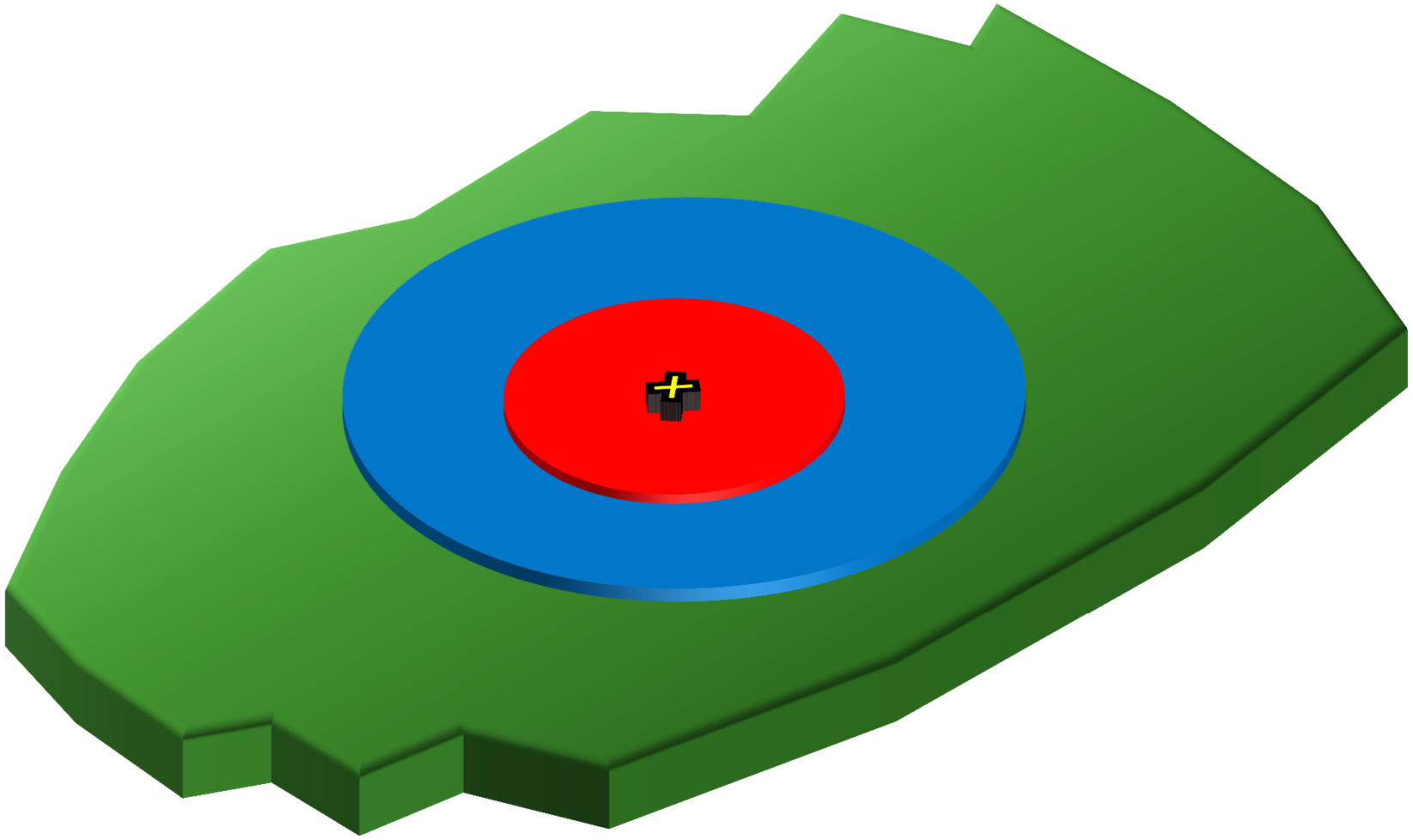
Salt Purity

Element / Compound	mg/kg
NaCl	99.85%
Moisture	3.85%
Insolubles	<0.005%
Al	<1.6
Ba	<0.17
Ca	0.39
Mg	<0.3
Sr	<1.6
Fe	<0.03
SiO_2	0.67
Na_2SO_4	N/D

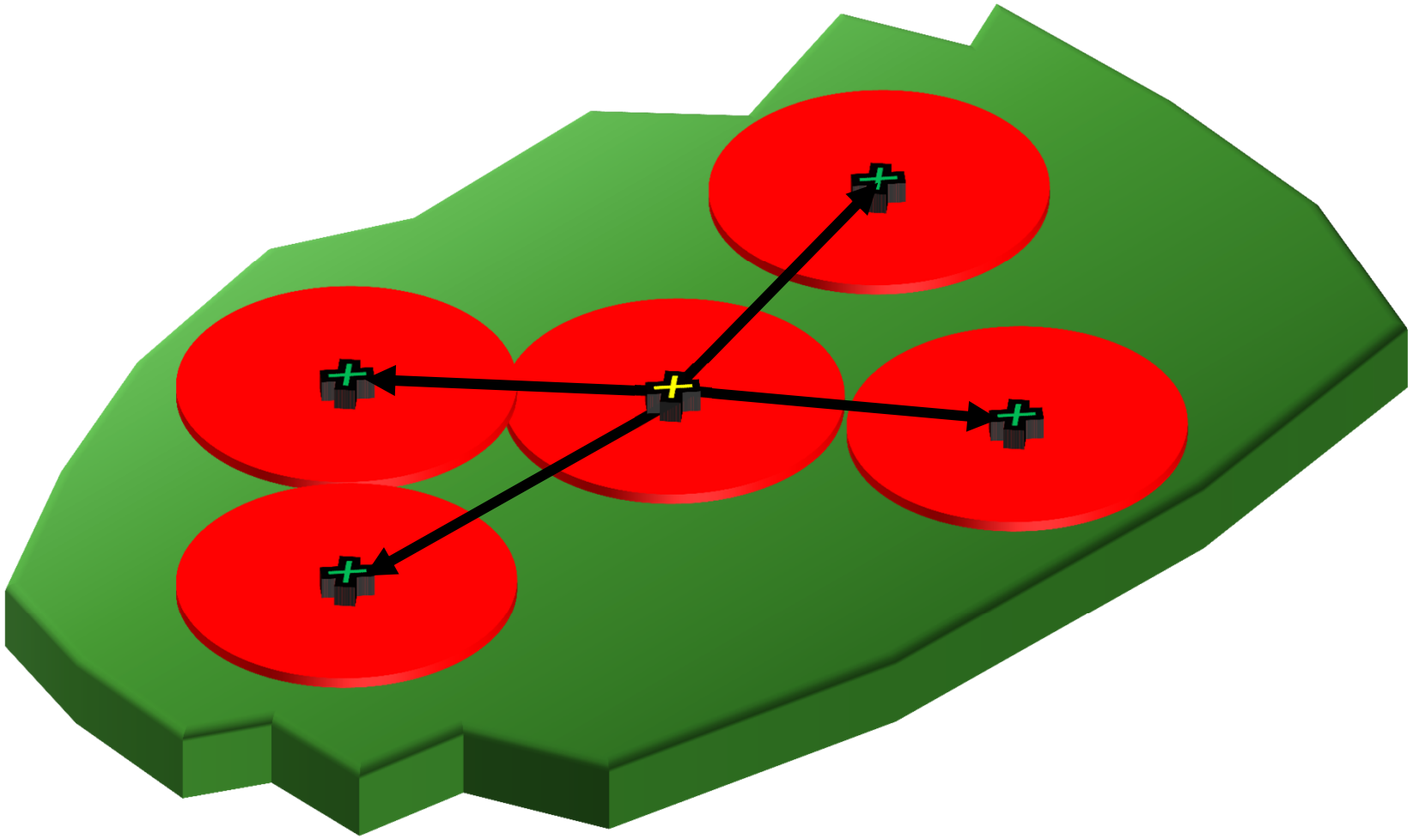
HSLS Hypo Shipping Advantages

- HSLS Hypo is stored on producers site at 10°C.
- 19 M3. tank truck load of 30% wt. equals 52 M3 of 13% wt.
- High dilution ratio allows for shipment flexibility.
  - Shipment of 30% wt.
    - Economically ship 2.75 time farther
    - Increase total delivered volume by 2.75, diluted at distribution center or customer site
  - Shipment of diluted product
    - Increased stability allows for decreased shipping strength
- One tank truck load (10 M3) of 13.0% diluted HSLS Hypo contains 1,800 kg. less salt than tradition hypo.

HSLS Hypo Shipping



HSLS Hypo Shipping



HSLS Hypo Summary

- HSLS Hypo with lower salt concentration offers a product that is more stable and lighter.
  - Greater stability means less sodium chlorate and perchlorate formation during decomposition.
- Reclaim salt to improve chlor-alkali plant efficiencies.
- HSLS Hypo can improve the shipment economics by:
  - Increasing shipping radius from the plant
  - Lighter product therefore more hypo per load

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