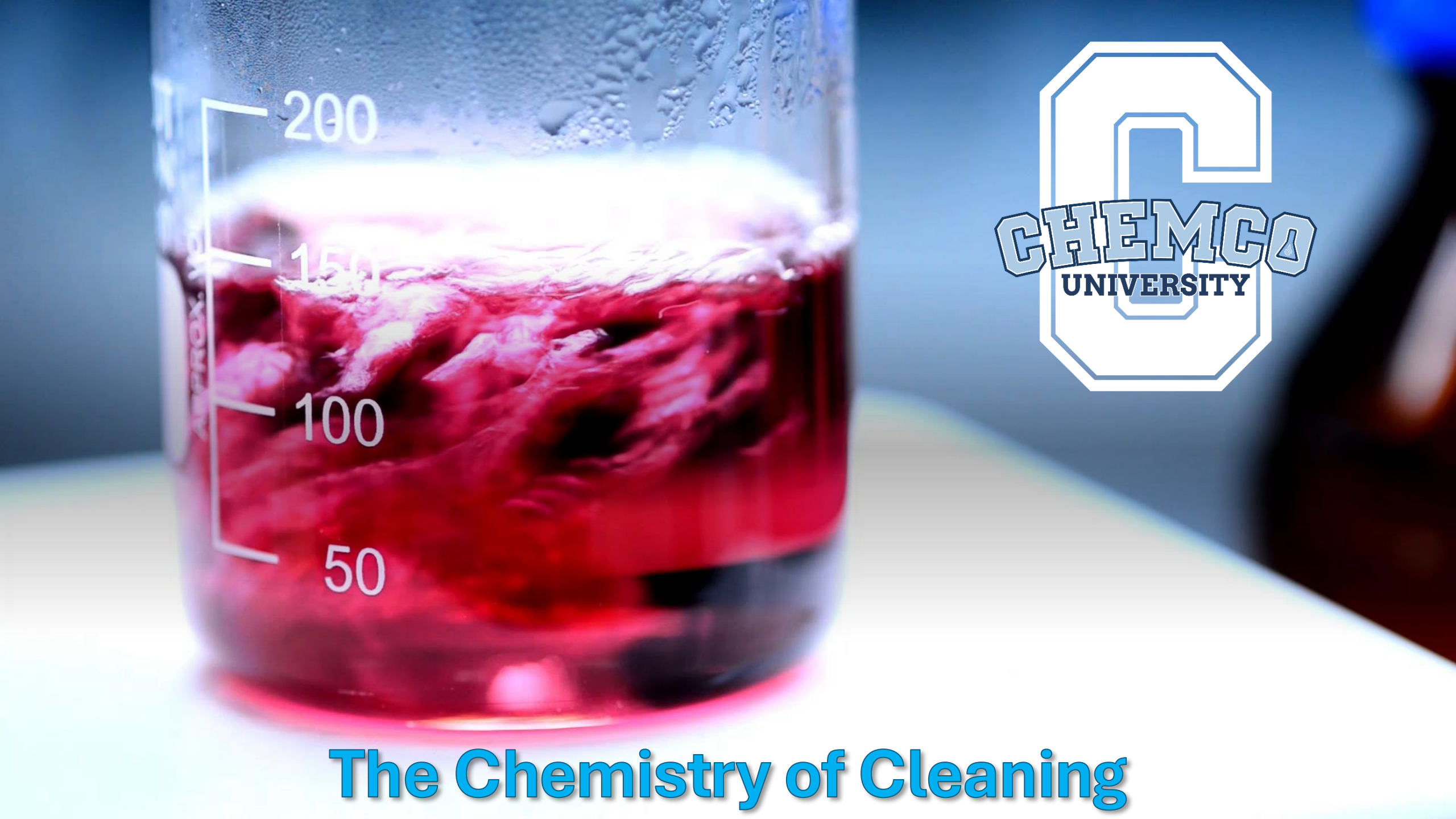


The Chemistry of Cleaning

What is Cleaning?

Definition: Removing contaminants (soils) from surfaces.

Importance: Food Safety, Product Quality, Shelf Life

Soil Identification

Soils can be categorized a couple of different ways. The easiest way to remember the different types of soil is:

Alive	Never Lived
Organic	Inorganic

OR

Organic Soils

- CARBOHYDRATE
- FATS
- OILS
- PROTEINS

Carbohydrates

Simple Carbohydrates

Sugars, syrups, and some organic salts only require ***HOT water*** to remove them. Example: Sugars like Lactose are easily dissolved in water.

Complex Carbohydrates

Starchy soils are removed by a detergent as these are typically a more difficult film to dissolve. A ***COLD water*** pre-rinse is best for starchy soils. A hot rinse can cause the soil to stick to the surface and make it more difficult to remove.

Fats & Oils

FATS & OILS - (animal and vegetable) require an ***ALKALINE*** cleaning solution.

- Fats are typically removed by rinsing with water 5 degrees above the melting point of the fat or oil.
- The residual is removed by detergents through saponification or emulsification.

Saponification = Chemical Reaction

Caustic + Fat ⟶ Soap

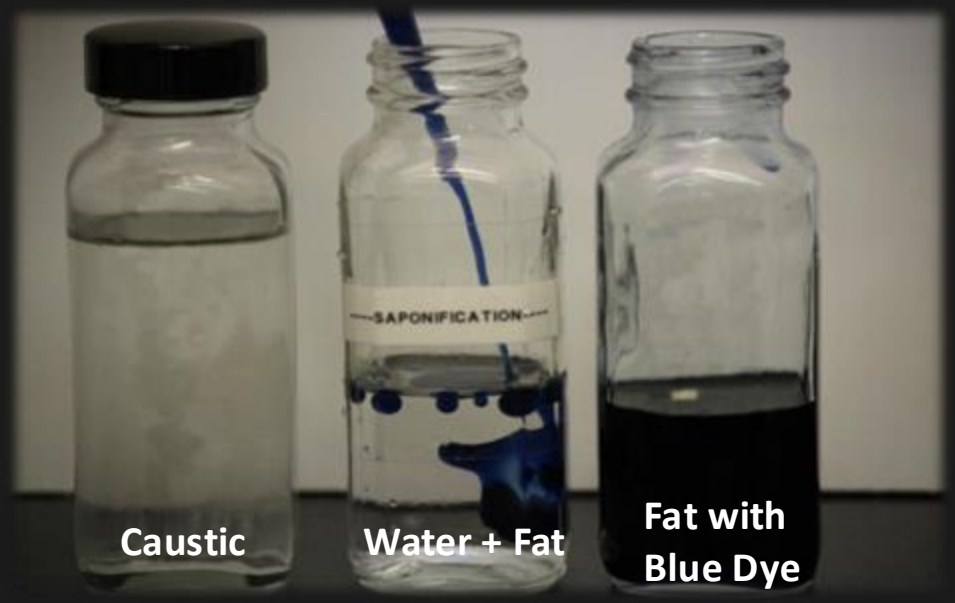
Emulsification = Physical Action

The breaking up of the fat or oil into small droplets by surfactants so that it can be suspended in the wash solution for removal.

Saponification

Fat added to water don't mix! Fat floats on the surface.

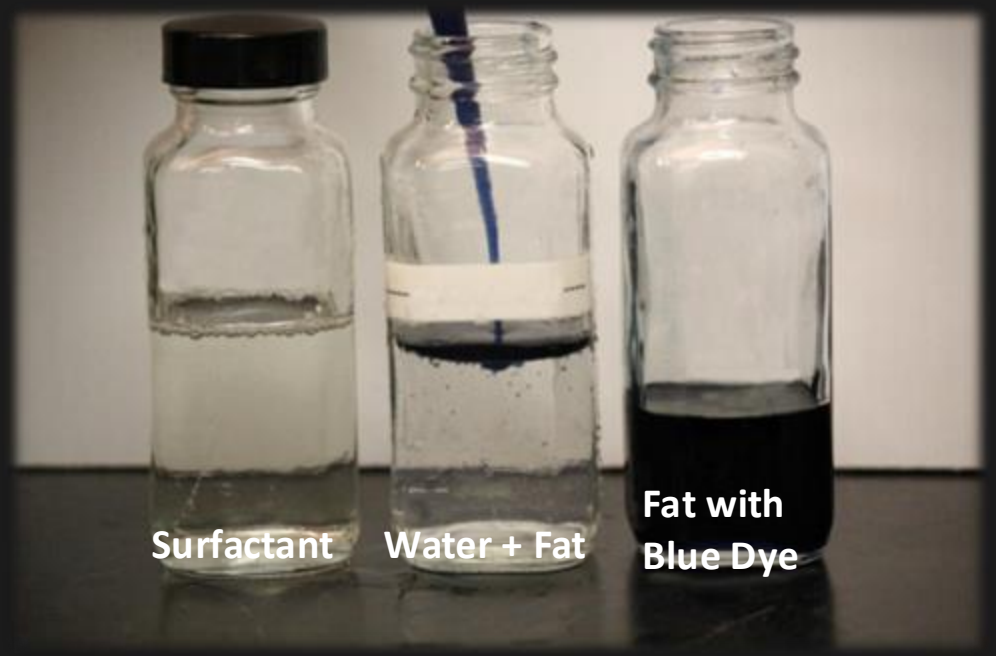
Chemical Reaction: Alkaline + Fat → Soap

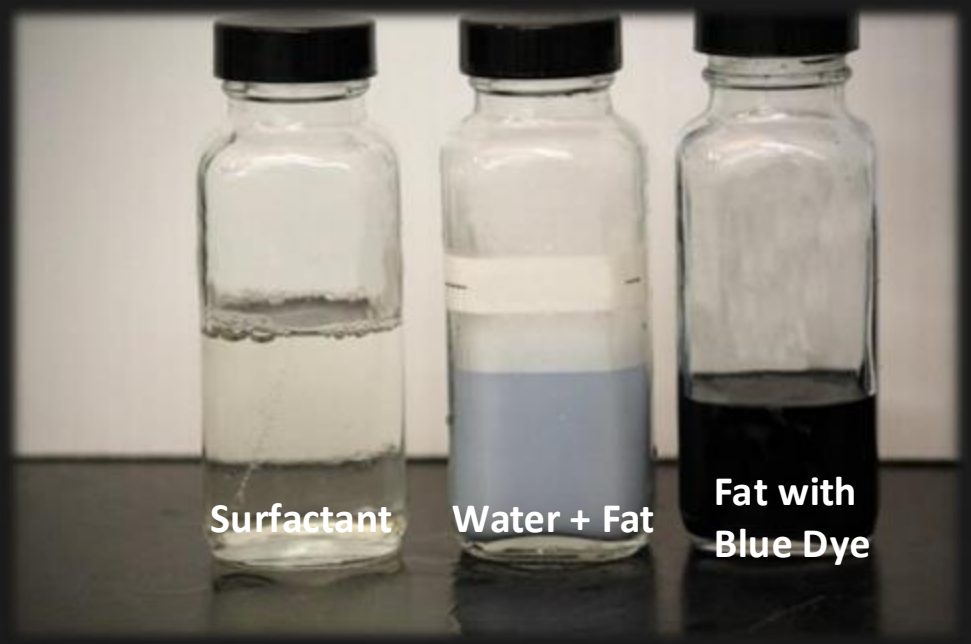


Emulsification

Surfactant + Fat = Reduced Surface Tension

Fat physically breaks down surface tension making tiny fat globules to wash away. Fat will separate out after a period of time.





Proteins

Removed by two methods:

- ✓ Adding ***Bleach*** to an alkaline solution w/ min of 40 ppm active
- ✓ Adding caustic at a min. of 0.75% - 1% active alkalinity.
  - Example – HTST, Cook Vats, Evaporators, Cheese Cookers, etc.

Protein is usually the most difficult soil to remove.

- ➢ Cold residues are easier to remove.
- ➢ Cooked on deposits are more difficult (***denatured***).
- ➢ Chlorine peptizes the protein into smaller amino acids.
- ➢ Enzymes can be used to do this as well.
  - ➢ **Proper p**H, temperature, and extended contact time.

Inorganic – Mineral Deposits

Mineral Deposits - are removed by ***ACIDS***.

- Source can come from both food and process water.
- Milkstone, beerstone, beetstone, waterstone can all be problematic. Typically, a ***complex mixture*** of mineral, fat, and protein.
- Mineral deposits or films –can usually be prevented using alkaline detergents containing sequestering or chelating agents to keep the minerals in solution.

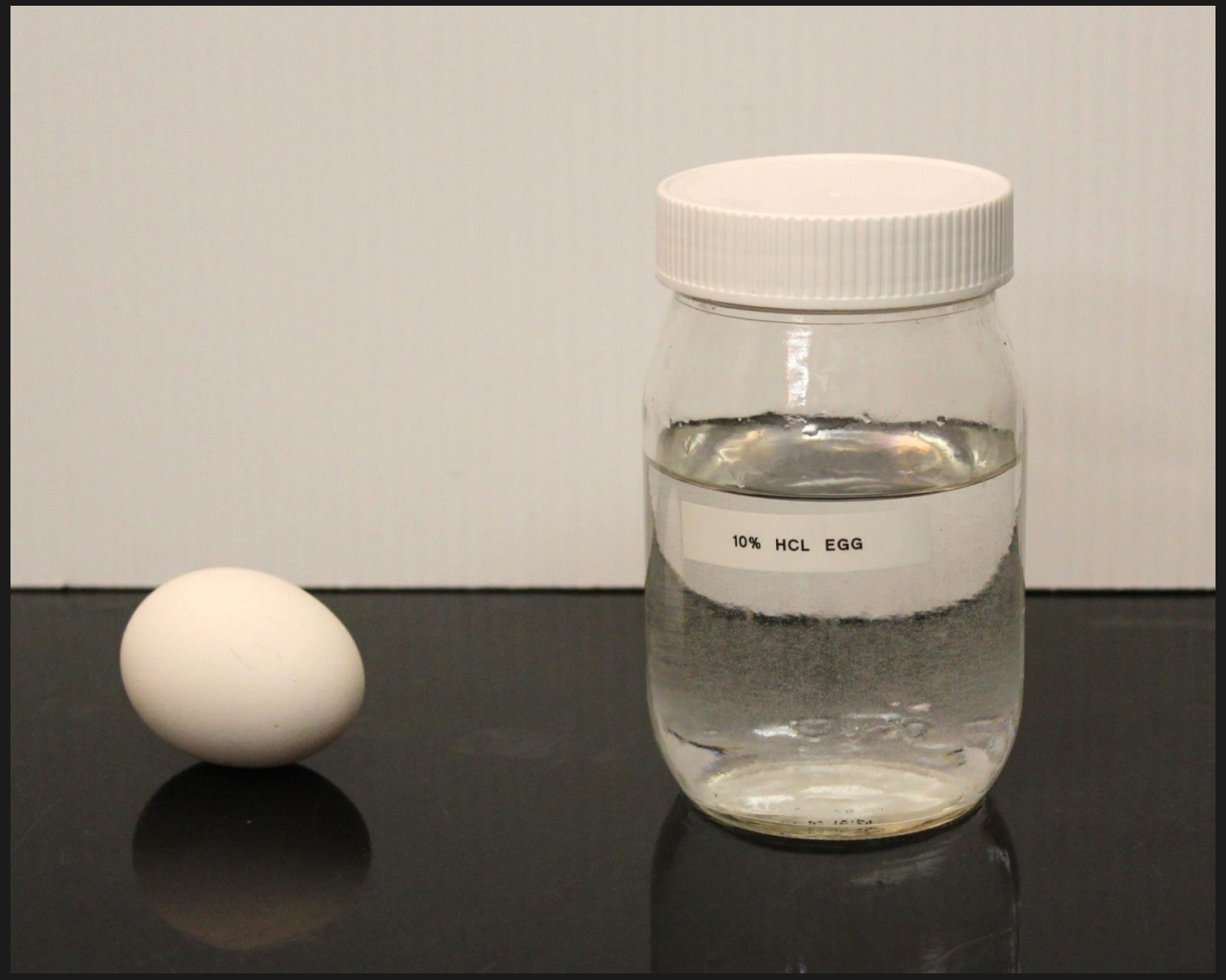
Complex Soil - Egg

Egg Composition

Shell – Calcium
Liquid – Protein
Yolk – Fat

Effect of Acid

Mineral – Dissolves
Protein – Denatures
Fat – Some effect



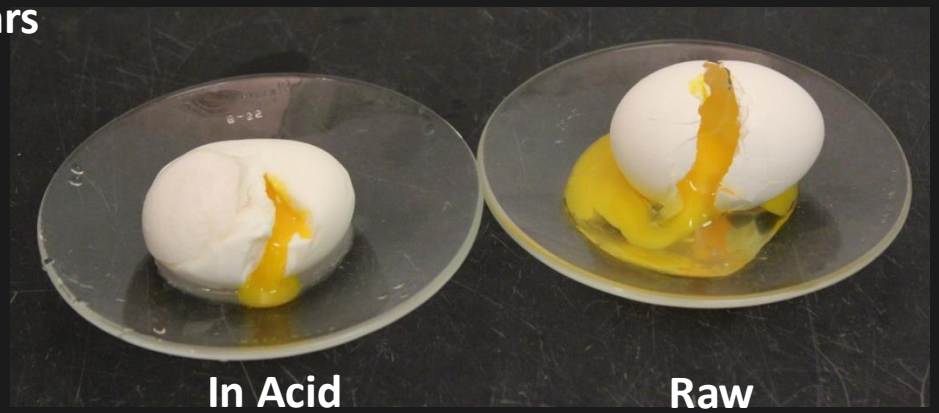
Complex Soil - Egg

30 Sec

1 min

3 min

4 hrs



Shell dissolved
Protein firm

Carbonaceous Soils

- They are inert to acid and alkaline wash solutions.
- This type of soil is generally found on a heat transfer surface, such as fryers or ovens.
- These deposits are held on to the surface by other soils. When we remove the other soils, we can suspend the carbonaceous soils and wash them away.
- We can use ***special solvents*** **or** ***surfactant packages*** along with ***chelating agents*** to assist in cleaning with a strong alkaline solution.

Building a Detergent

Types of Soils

Component on Surface	Solubility Characteristics	Ease of Removal	Changes Induced by Heating Soiled Surface
Sugar	Water soluble	Easy	Caramelization, more difficult to clean
Fat	Water insoluble, alkali soluble	May be difficult	More difficult to clean after heating.
Protein	Water insoluble, alkali soluble especially with chlorine, slightly acid soluble	Can be very difficult	Much more difficult to clean
Salts	Water soluble, acid soluble	Easy	----
Minerals	Water insoluble, acid soluble	Difficult	Interactions with other constituents, more difficult to clean

Types of Cleaners

- ACIDS
- NEUTRAL
- BASIC or ALKALINE
- ADDITIVES
- SANITIZERS

Mineral Acids

Really Strong Acids

Sulfuric Acid	H_2SO_4
Hydrochloric Acid	HCl
Nitric Acid	HNO_3

Strong Acids

Phosphoric Acid	H_3PO_4

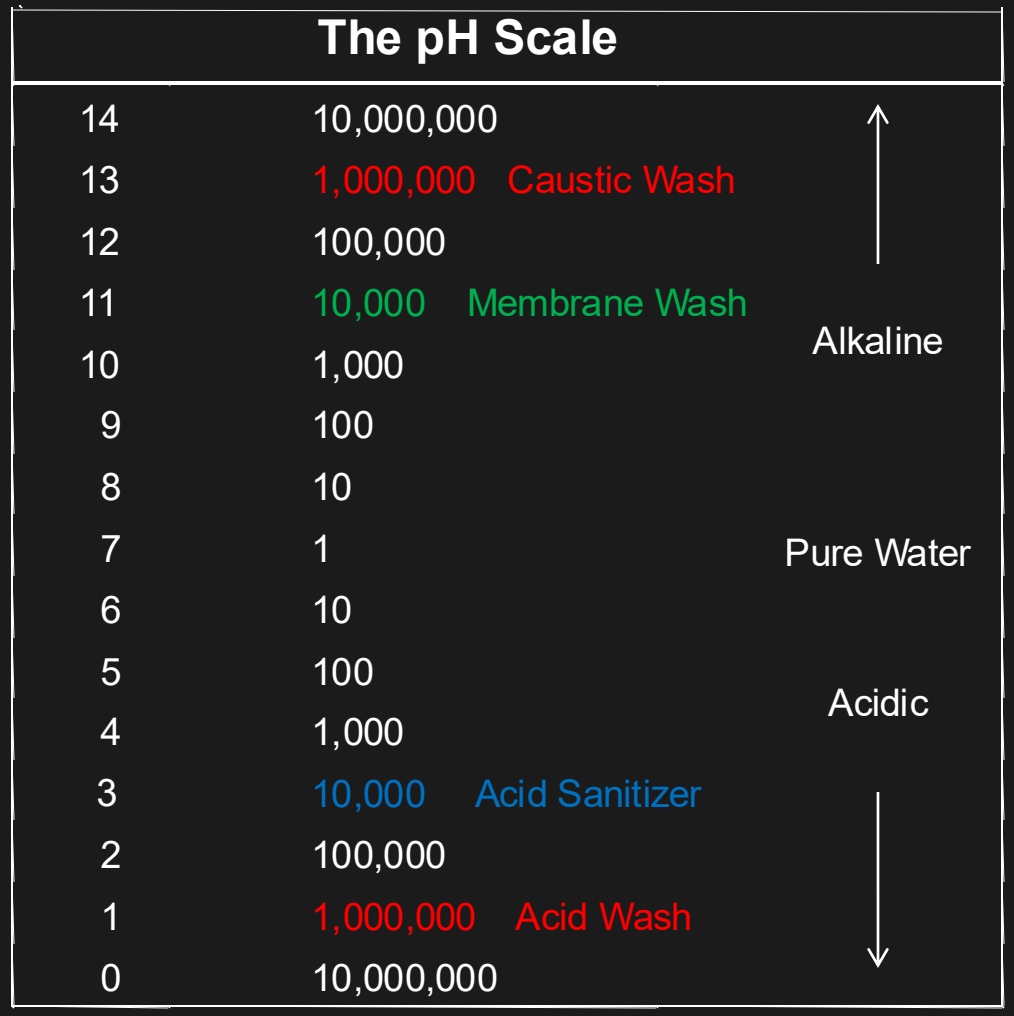
Strong Bases

Sodium Hydroxide (Caustic Soda)	$NaOH$
Potassium Hydroxide (Caustic Potash)	KOH
Ammonium Hydroxide (Aqua Ammonia)	NH_4OH
Magnesium Hydroxide	$Mg(OH)_2$

Weak Bases & Buffering Agents

Sodium Carbonate (Soda Ash)	Na_2CO_3
Sodium Bicarbonate (Baking Soda)	$NaHCO_3$
Amines	MEA, TEA, DEEA

pH Scale



Examples:

- A *p*H of 2 is 100,000 times more acidic (H^+) than a *p*H of 7.
- A *p*H of 13 is 1,000,000 times more active in alkalinity (OH^-) than a *p*H of 7.

Alkalinity vs pH

- **Alkalinity is the name given to the capacity of an aqueous solution to neutralize an acid.**
  - **Can be measured by titration with an acid of *known* concentration**
  - **Alkalinity is a linear measure of concentration.**

- **pH is the negative log of the hydrogen ion concentration in solution.**
  - **Measured by electrical potential difference.**
  - **Logarithmic scale, each unit is a 10-fold difference from the last.**

Questions we should ask?

- Type of soil? Organic or Inorganic
- How was it deposited? Cold or Hot Surfaces
- Material substrate? Stainless Steel or Soft Metals
- Method of application? Manual or CIP

Building Detergents

A detergent is an agent which aids in the removal of unwanted or extraneous material from a surface.

Detergents contain one or more of the following properties:

- Conditioning Agents
    - Polymers
    - Chelants
- Wetting Agents (Surfactants)
- Alkalinity Source
- Bleach (to Peptize)
- Suspension and Rinse Agents

Chelants & Water Conditioning Agents

Bind metal ions in solution to prevent the precipitation of mineral salts and soaps.

- Gluconate & Glucoheptonate
- EDTA
- Phosphates
- Phosphonates

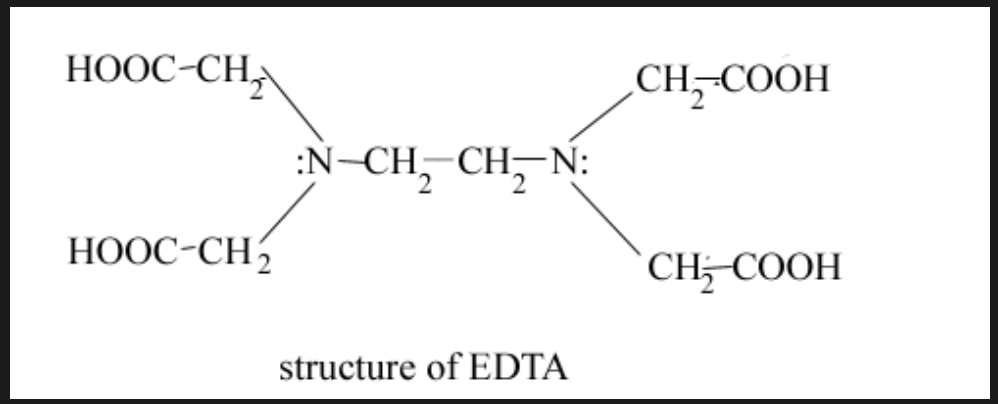
Associate with metal ions in solution to modify the crystallization of metal salt and soaps to keep them suspended in solution.

- Phosphonates
- Polyacrylates

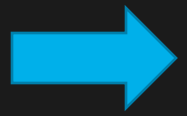
Example of Chelation

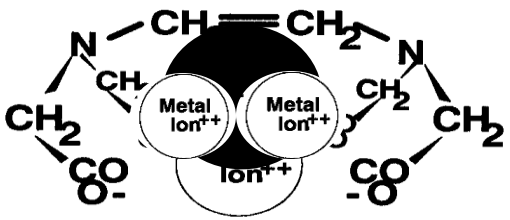
Ethylene Diamine Tetra Acetic Acid (EDTA)

- Strong chelator of calcium and magnesium ions in alkaline solutions
- Key ingredient in single phase cleaning
- Poor chelator of iron in extremely alkaline solutions (pH 12.5-13)



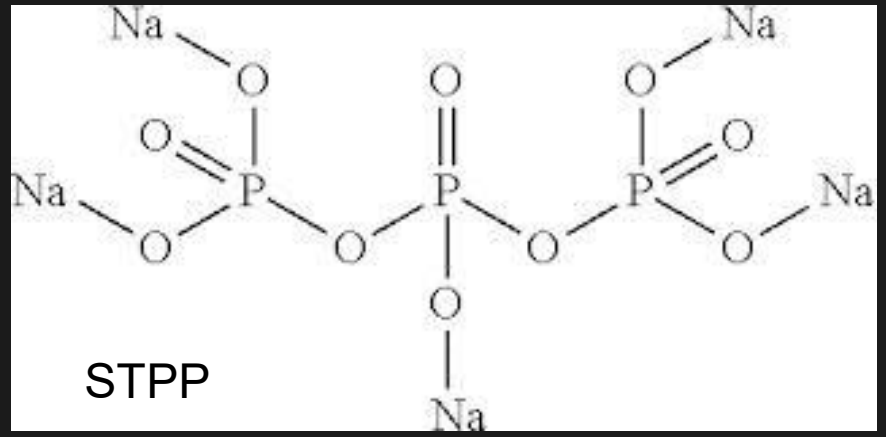
structure of EDTA





Ethylenediaminetetraacetic acid (EDTA) chelates a metal ion

Examples



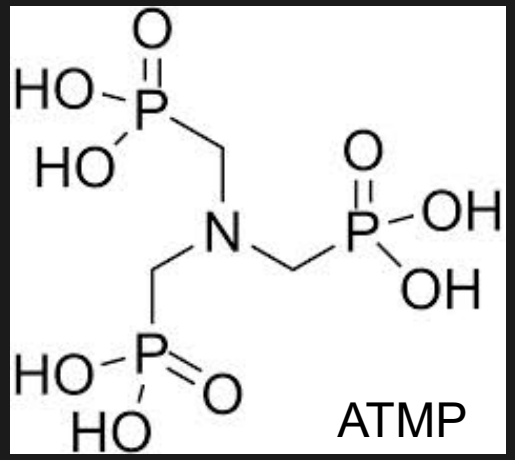
STPP

What is the target pH of the cleaning solution?

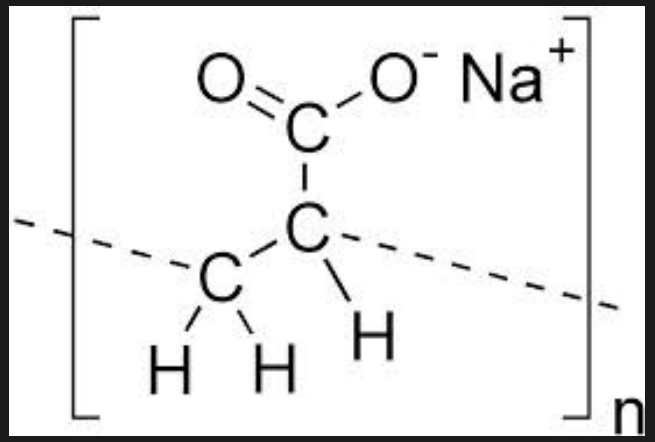
What inorganic cation (+) am I trying to chelate or suspend?

Are there discharge limitation?

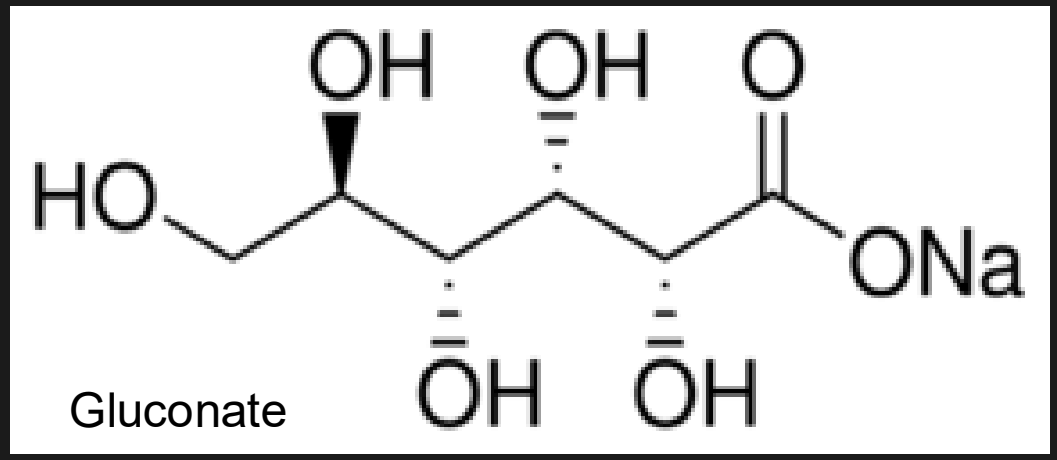
Prohibited by the customer?



ATMP



Polyacrylate



Gluconate

Surfactants

Surfactants perform many functions in a cleaning formulation.

- ✓ Wetting
- ✓ Emulsification
- ✓ Soil Dispersion
- ✓ Foaming
- ✓ Defoaming
- ✓ Improved Rinsing

Surfactant Properties

Wetting

- The reduction of surface tension of the cleaning solution to wet and penetrate all surfaces being cleaned. Water = 72 dynes. Addition of a good surfactant = 32 dynes.

Emulsification

- The encapsulation and suspension of fats and oils in a water solution.
- Emulsification is also responsible for soil dispersion and anti-redeposition.

Surfactant Types

Anionic

- Sodium Dodecyl Benzene Sulfonate (DDBSA)
- Sulfonates, Phosphate Esters, etc.

Nonionic

- Alkyl Poly Glucosides
- Alcohol Ethoxylates
- Block Copolymers

Amphoteric

- Amine Oxides
- Betaines

Effects of Surfactant

Carbon floats on water
No surfactant
No water penetration

Add surfactant
Reduces surface tension

Time (30 seconds)

Oxidizers

Sodium Hypochlorite

- Bleach - NaOCl
- Peptizes protein, very effective protein removal
- Oxidizes organic soils

Hydrogen Peroxide

- Weaker oxidizer that hypochlorite
- Under alkaline conditions, activated to provide improve oxidation of organic soils
- Not stable in alkaline formulations

Building A Detergent

RELATIVE CLEANING VALUES OF VARIOUS DETERGENT INGREDIENTS

Key to Chart

A High Value
B Medium Value
C Low Value
D Negative Value

MANUAL FOR MILK PLANT OPERATORS Third Ed.
MILK INDUSTRY FOUNDATION

	INGREDIENTS	Comparative Ability											
		Emulsification	Saponification	Wetting	Dispersion	Suspension	Peptizing	*Water* Softening	*Mineral* Deposit *Control*	Rinsability	*Suds* Formation	Non-Corrosive	Non-Irritating
Basic Alkalis	Caustic Soda	C	A	C	C	C	C	C	D	D	C	D	D
	Soda Ash	C	B	C	C	C	C	C	D	C	C	C	D
	Sodium Metasilicate	B	B	C	B	C	C	C	C	B	C	B	D
	Tri-Sodium Phosphate	B	B	C	B	B	B	A	D	B	C	C+	C-
Complex Phosphates	Sodium Tri-Polyphosphate	A	C	C	A	A	A	A	B	A	C	AA	B
	Sodium Hexametaphosphate	A	C	C	A	A	A	B	B	A	C	AA	A
	Tetrasodium Pyrophosphate	B	B	C	B	B	B	A	B	A	C	AA	B
	Sodium Tetra-Phosphate	A	C	C	A	A	A	B	B	A	C	AA	A
Organic Compounds	Chelating Agents	C	C	C	C	C	A	AA	A	A	C	AA	A
	Surfactants	AA	C	AA	A	B	B	C	C	AA	AAA	A	A
	Organic Acids	C	C	C	C	C	B	A	AA	B	C	A	A
	Mineral Acids	C	C	C	C	C	C	A	AA	C	C	D	D

Factors Affecting Formulation

- Time Available for Cleaning
- Cleaning Temperature
- Cleaning Concentration
- Raw Material Costs
- Type of Soil
- Water Chemistry
- Cleaning Method
- Dispensing & Application Equipment
- Surface to be Cleaned
- Government Regulations
- Environmental Factors (i.e. wastewater limits)

Membrane Uses in the Food and Dairy Industries

Pre-concentration

- Removal of water prior to evaporation.

Fractionation

- Removal of specific solids from the feed stream.

Solids Recovery

- Retention of product for re-introduction to the process.

Clarification

- Removing soils from a re-used liquid.

Water re-use

- Recovery of condensate for re-use as cleaning water.

Chemical Recovery

- Recovery of spent caustic from CIP streams.

Types of Membranes

The most commonly used membranes in the dairy industry are Spiral Wound.

- Other types include:
  - Tubular
  - Hollow fiber
  - Ceramic
  - Flat Sheet / Plate & Frame
  - Stainless Steel

Dairy Applications

Microfiltration (MF)

- Fat removal
- Reduce and remove bacteria
- Cheese brine clarification
- Cook water clarification

Ultrafiltration (UF)

- Whole and skim milk fractionation (MPC)
- Whey protein fractionation (WPC/WPI)
- Cheese brine clarification

Nanofiltration (NF)

- Demineralization of salt whey
- Concentration of UF permeate
- Clarification of cheese brine
- Acid whey concentration

Reverse Osmosis (RO)

- Concentration of whole and skim milk
- Concentration of whey
- Concentration of UF permeate
- Reduce BOD/Polish Permeate and Condensate

Filtration Terminology

Feed

- Material supplied to the membrane system.

Concentrate (Retentate)

- The portion of the feed that does not pass through the membrane surface.

Permeate

- The portion of the feed that passes through the membrane.

Flux

- A measurement of permeate flow through the membrane.

Fouling

- The term fouling is used to describe the soiling of the membrane. Fouling is normally related to a reduction in the system capacity or flux.

Rejection

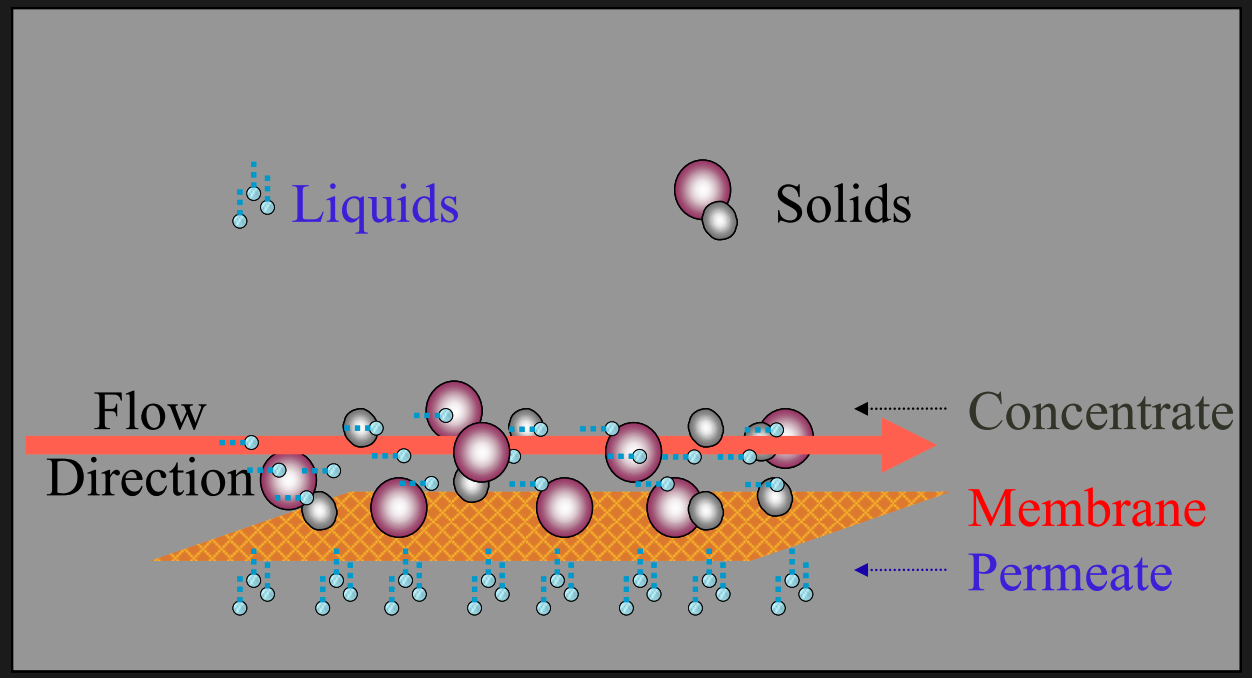
- The membrane's ability to permeate or reject particles.

Water Flux Readings

- Clean water flow through the membrane at given pressure and temperature.

Cross Flow Filtration

The flow of the feed stream is tangential to the membrane surface.

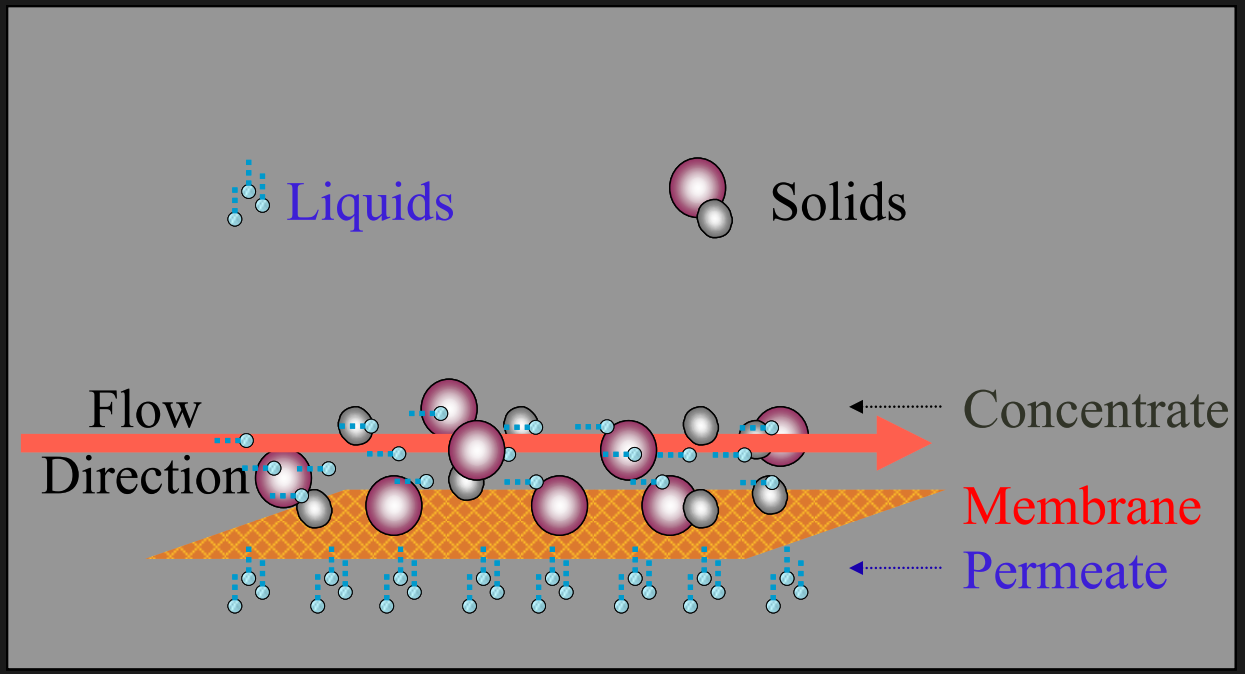


A boundary (fouling) layer is formed on the membrane surface.

- Cross-flow reduces the development of this layer.
- Increases time before permeation is impeded.
- After increased fouling, the system can be cleaned to remove the soil layer.

Flow Dynamics

If the flow rate over the membrane surface is too low, the soil layer will build up quickly and impede permeate flow and increase pressures.



Hydraulics required for membrane cleaning.

- High velocity turbulent flow is created by the recirculation pumps.
- Membrane Spacers Size - 31, 48, 63, 80 mil.
- Membrane Size - 3.8”, 6.2”, 8” diameter.
- Number of membranes per vessel.
- Number of vessels per stage.

High velocity turbulent flow will help to keep the membrane surface free of the fouling layer over the production run.

Balancing Act

- Production Throughput
- Time
  - CIP
  - PM
  - Emergency Repairs
- Detergent Costs
- Membrane Performance
  - Recovery %
  - Flux & Pressures
  - Leakers & Life Span
- Waste Water Effluent
- Water

Five Factors to Cleaning

Time
- Time is the duration allotted to a cleaning task. Time allows the chemistry to break up soils and being more effective.

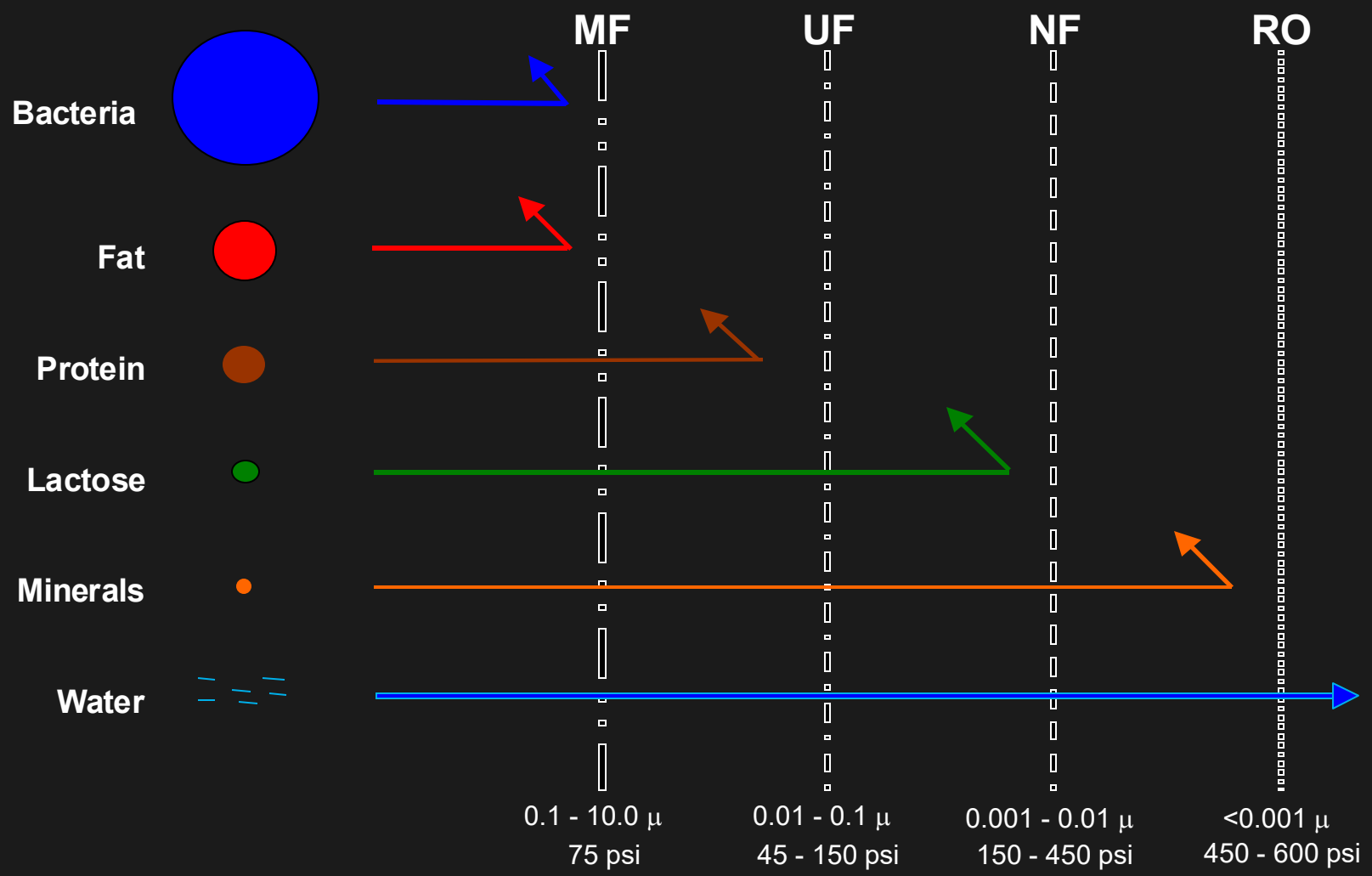
Temperature
- Higher temperatures aid in chemical productivity. To put it simply, the cleaning process becomes faster and easier as temperature increases. Higher temperatures also decrease the viscosity in soils, allowing for easier removal.

Mechanical Action
- Desired results occur when optimal chemical reaction and mechanical action takes place. Agitation can help break up soils, increase wash efficiency and reduce wash time.

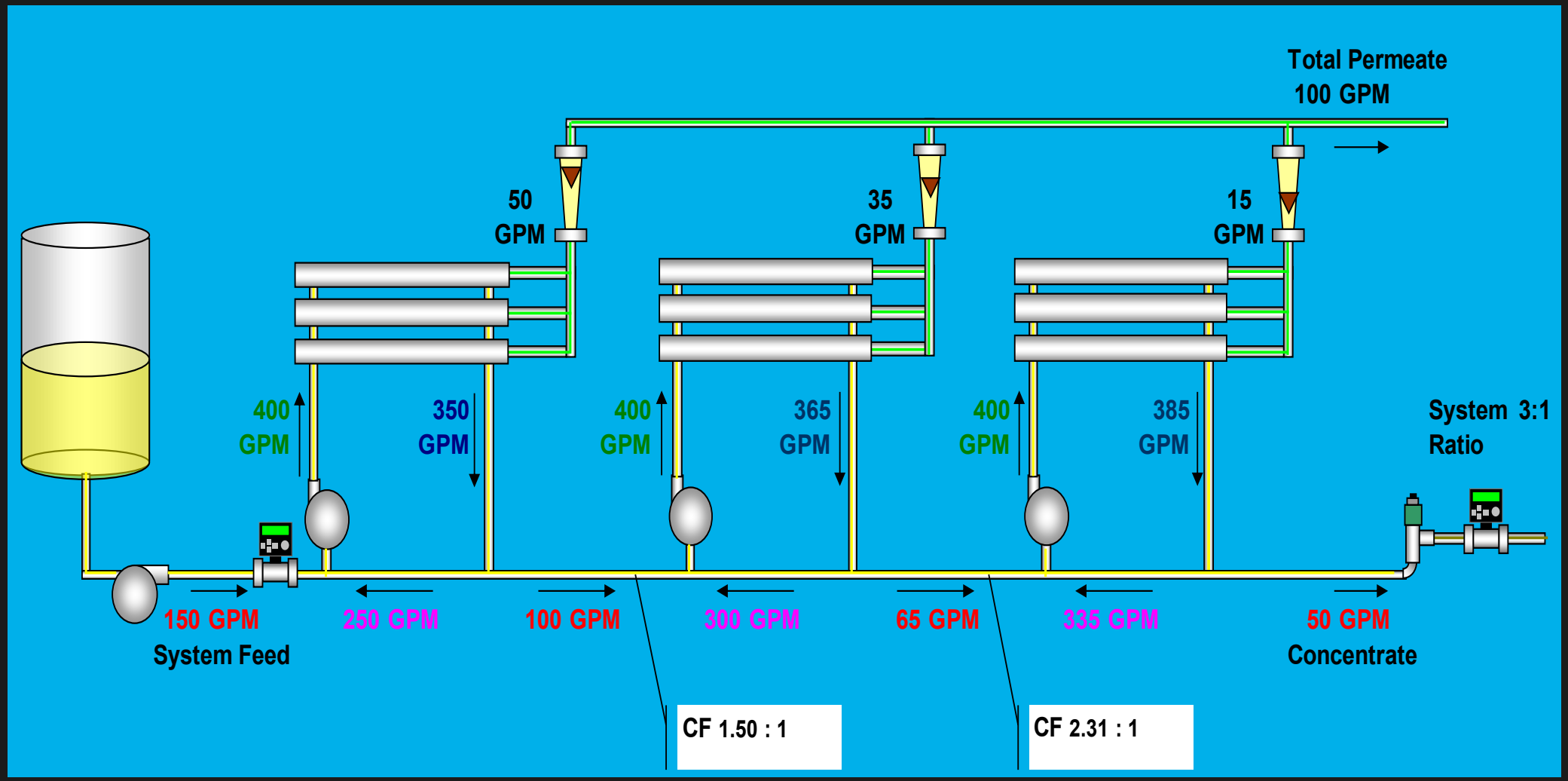
Chemical
- The type of chemical being applied will affect how the soil is removed from the surface.

Procedures
- Proper procedures ensure the same level of clean each and every time.

Membranes – What Soils Are Present?



Membrane Cleaning



Membrane Cleaning

CIP Step	Soil Removal
Pre-Rinse / Flush	80-90%
Detergent Steps	99.9%
Anti-Microbial / Sanitize	100%

Sanitation Factor – Water

Approximately 99.5% of the cleaning solution is water.

- It is critical that this water meets the standards set forth by the membrane manufacturers, equipment suppliers, and chemical supplier.

High levels of contaminants

- Can lead to reduced chemical efficiency.
- Can damage or foul the membrane surface.
  - Iron < 0.05 ppm
  - Manganese < 0.02 ppm
  - Silicate < 15ppm
  - SPC < 1000/mL
  - E. Coli 0/100mL
  - Average Chlorine 0 ppm
  - Suspended Solids 0 mg/L
  - Hardness < 50 ppm

Sanitation Factor – Product Quality

Product Feed

- pH
- Temperature (can impact pore size)
- Fat Content (premature fouling)
- Cheese Fines (<60 ppm)

pH can impact the membranes in two ways

- Membrane pores will close slightly in an acidic pH environment.
  - We try to end each cleaning procedure with an alkaline step to help open the membrane surface prior to production.
- A drop in feed pH for dairy systems indicates that bacteria are turning lactose into lactic acid.
  - Proteins in the feed may also become denatured as the pH drops. Denatured proteins tend to be more complex and difficult to clean.
  - Can damage or foul the membrane surface.

Sanitation Factor – Bacteria

Bacteria levels need to be controlled

- Silo rotation (every 4 hours)
- Temperature (lowering temperature to slow down growth).
- Pre-treatment – Pasteurization
- Suitable microbial reduction step at the end of CIP.
  - Contingent on CIP window and length of downtime prior to production start up

Sanitation Factor – Membrane Limitations

UF & MF Membranes

- Temperature 120 - 125 F
- pH 1.8 - 11.2
- 150 - 180 ppm Chlorine (Max. 200 ppm)
- Absolutely No defoamers
  - Irreversible fouling and loss of warranty

NF & RO Membranes

- Temperature 113 - 118 F
- pH 2 - 11
- Absolutely No Chlorine
  - This includes process water
- Absolutely No defoamers
  - Irreversible fouling and loss of warranty

Daily Operations

Record

- Chemical name and amount on each step
- Temperature during each step
- pH and concentrations on each step
- Baseline pressure on each step
- Daily clean water flux reading
- Microbial reduction and/or soak step as required

Observe

- Flow rates during each step
- Loop pressures during each step
- Loop temperatures during each step

Example UF Wash Program

Date:	3/5/2025	Written By:	Devin Woodill
Customer:		Location:	
Application:	Milk UF	Account Mgr:	
Membrane Type:	Ultrafiltration	Limitations:	
Membrane Material:	PES	pH:	1.8-11.50
Module Type:	Spiral	Temperature:	125°F
Internal Volume:	2310 gallons	Cl_2:	200 PPM
Foulants:	Milk	Peracetic:	90-195 PPM
CC:			

Example UF Wash Program

Procedure	Products	Initial Dose	Temperature	pH / ppm	Time	Note	Description
Pre Rinse						1	
Enzyme Wash	Excel 890k CMC 102 CMC 167	0.5 Gallons 2.0 Gallons 7.5 Gallons	120-125°F	9.0 - 10.0 Target 9.50	45-60 Minutes	2	Alkaline Cleaner Detergent Cleaner Enzyme Cleaner
Rinse						3	
Acid Wash	Hurricane Special	8 - 10 Gallons	120-125°F	1.80 - 2.0	30 Minutes	2	Phos/Nitric blend Acid Cleaner
Rinse						3	
Alkaline Wash	Excel 890k CMC 102 FloKlor	1.5 Gallons 2.0 Gallons 15-20 Gallons	120-125°F	10.8 -11.5 100-180 ppm	30 Minutes	2,4	Alkaline Cleaner Detergent Cleaner Chlorine
Rinse						3	
Clean Water Flux Reading							
Soak	CMC CMP	5 Gallons	<75°F No Heat	3.0- 4.0	Min 15 Minutes Recirc. Daily	5,6	Acid soak
Rinse						3	
Weekly Antimicrobial Treatment							
Sanitize	Chemco PAA	2.5 Gallons 1- 2 oz./5 gal.	<75°F	105 - 195 ppm peracetic	15 Minutes	7	Peracetic / Hyd. Per.
Rinse						3	

Notes:

1. Flush until discharge runs clear
2. Achieve and maintain pH throughout the wash with initial dose plus additional chemical boosts
3. Flush until pH is near neutral.
4. Maintain chlorine levels near 180 PPM throughout wash with initial dose plus additional chemical boosts
5. Recirculate for 15 minutes, shut down and soak until next production. Flush until pH is >6
6. Soak step is not required if duration between production and CIP will be under 3 hours.
7. Recirculate and flush until pH is >6 prior to production start up. Do NOT soak in PAA

Example RO Program

Date:	3/5/2025	Written By:	Devin Woodill
Customer:		Location:	
Application:	Milk Permeate	Account Mgr:	
Membrane Type:	Reverse Osmosis	Limitations:	
Membrane Material:	PES	pH:	1.8-11.0
Module Type:	Spiral	Temperature:	122°F
Internal Volume:	560 Gallons	Cl_2:	0 PPM (Never use chlorine)
Foulants:	Lactose, minerals, protein	Peracetic:	90-195 PPM
CC:			

Example RO Program

Procedure	Products	Initial Dose	Temperature	pH / ppm	Time	Note	Description
Pre Rinse						1	
Enzyme Wash	Excel 890k CMC 167 CMC 102	0.25 Gallons 3.0 Gallons 1.0 Gallon	118-122°F	9.0 - 10.0 Target 9.50	45-60 Minutes	2	Alkaline Cleaner Enzyme Cleaner Detergent Cleaner
Rinse						3	
Acid Wash	Hurricane Special	4.0 Gallons	118-122°F	1.80 - 2.0	30 Minutes	2	Phos/Nitric blend Acid Cleaner
Rinse						3	
Alkaline Wash	Excel 890k CMC 102	0.5 Gallons 1.0 Gallon	118-122°F	10.0 -11.0 Target 10.50	30 Minutes	2	Alkaline Cleaner Detergent Cleaner
Rinse						3	
Clean Water Flux Reading							
Soak	CMC CMP	2.0 Gallons	<75°F No Heat	3.0- 4.0	Min 15 Minutes Recirc. Daily	4,5	Acid soak
Rinse						3	
Weekly Antimicrobial Treatment							
Anti-Microbial	Chemco PAA	0.5 Gallons 1- 2 oz./5 gal.	<75°F	105 - 195 ppm peracetic	15 Minutes	6	Peracetic / Hyd. Per.
Rinse						3	

Notes:

1. Flush until discharge runs clear
2. Achieve and maintain pH throughout the wash with the additon of chemical
3. Flush until pH is near neutral.
4. Recirculate for 15 minutes, shut down and soak until next production.
5. Soak step is not required if duration between production and CIP will be under 3 hours.
6. Recirculate and flush until pH is >6 prior to production start up. Do NOT soak in PAA