

Deposition

Introduction

Water is one of the Earth's most unusual features. It is continually dissolving or depositing solids. The phrase "depositing solids" encompasses the scope of this chapter. These deposited solids are classified as scale or foulants. This chapter identifies the important types of scale and foulants, examines how the solids are deposited (mechanisms influencing deposition) and recommends treatment of these scaling/fouling waters.

Having read this chapter, you should know-

1. The difference between scaling and fouling
2. Mechanisms and factors involved in scaling and fouling
3. Types of scales and foulants commonly found in cooling water applications
4. How to predict the scaling tendency of a water sample
5. Methods used to control scale
6. Basic scale inhibitor and dispersant chemistries

Scale Deposition Overview

The causes of scale and other fouling deposits are many, varied and extremely complex. Investigators have studied scale and deposit mechanisms in an effort to understand them, quantify them, and develop remedial or preventative treatments. Deposits in cooling waters are generally classified either as scale or as foulants, even though these deposits commonly occur together. Scale is a hard, adherent mineral deposit that usually

precipitates from solution and grows in place. It is a crystalline form of deposit. Foulants, on the other hand, are usually high in organics. More often than not, they are formed from suspended solids at a point in the system other than where they deposit. Foulants tend to be amorphous or noncrystalline.

Cooling waters contain a large number of these potential scale- and deposit-causing constituents. These include soluble ions (such as calcium, magnesium, soluble silica, zinc and iron salts) that precipitate as insoluble deposits when they encounter changes in water temperature, pH, concentration or incompatible additives. Examples of deposits are calcium carbonate, calcium phosphate, silica, iron hydroxides, sulfides, calcium sulfate, magnesium salts, zinc phosphate and zinc hydroxide.

Fouling deposits can occur from natural or artificial causes. Although these deposits are generally less adherent than mineral scale, they cause similar problems. Examples of some of the more common natural foulants are sand, mud, silt, clay, natural organics, dust and debris. Corrosion by-products, process contaminants, pretreatment carryover and incompatible chemical treatments are a few examples of artificially induced foulants. Microbiological growth such as algae and bacteria are some of the most common organic foulants in cooling water systems.

Scale Deposition - Mechanisms and Influencing Factors

Scale deposition, unlike other types of deposition, is a complex

crystallization process. The time it takes for an initial scale layer to form and its subsequent rate of growth are determined by the interaction of several rate processes (e.g., supersaturation, nucleation, diffusion, chemical reaction and molecular arrangement of the scale crystal lattices).

Most, though not all, mineral scale-forming constituents are inversely soluble (i.e., their solubility decreases as water temperature increases). Therefore, when these supersaturated solutions contact heat transfer surfaces, they precipitate solids due to their lower equilibrium solubility.

Compounds carried by water as soluble constituents may precipitate and form scale as a result of pressure drop, temperature change, flow velocity alterations, pH or alkalinity change or other water conditions.

Studies have shown that crystallization from solution of a material is influenced by the following factors:

Supersaturation - A saturated solution is one that is in equilibrium with its solute. Supersaturated solutions are solutions that contain higher concentrations of dissolved solute than their equilibrium concentration. When the concentrations of the scaling ions exceed their solubility product, scaling begins. Solutions can become supersaturated by a change in temperature, a change in pH, addition of solid seeding material, evaporation or pressure change. Thus, if $(Ca^{2+}) \times (CO_3^{2-})$ is greater than the K_{sp} for

CACO₃, at a given temperature, calcium carbonate will precipitate

CONTROLLING PARAMETERS

- Time
- Temperature
- pH
- Pressure
- Velocity
- Particle Size
- Other Environmental Factors

Nucleation - Nucleation, the initial formation of a precipitate can occur for many reasons. Corrosion products, oxide films, surface imperfection, slime masses and bacterial growths can form as nucleation sites. The nucleation occurs rapidly at high degrees of supersaturation. These nuclei serve as the starting point for additional crystal growth leading to scale formation.

Contact Time - For scale to form after a solution has become supersaturated and nucleation has occurred, there must be sufficient contact time between the solution and the nucleating sites on the surface. Generally, the longer the contact time, the more likely the scale formation becomes.

Adherence - Corroding surfaces are more likely to promote scale deposition than noncorroding surfaces. Studies using polished surfaces indicate that microscopic roughness, whether natural or produced by corrosion; makes subsequent scale deposits more adherent.

Crystal Growth - Although the solubility limit must be exceeded for

scale to form, the rate of scale formation is controlled by the presence or absence of scale inhibitors and other factors. The rate of crystal growth and the rate of inhibition of crystal growth can be studied by monitoring the amount of inhibitor required to keep the calcium level constant during periods when solubility limits are exceeded (i.e., during scale formation),

CONTROLLING PARAMETERS

- Flow Velocity
- Surface Temperatures
- Bulk Temperatures
- Water Composition
- Molecular & Atomic Ordering
- Diffusion
- Other Factors

Exposure to Localized High Temperature - Because the solubility of most calcium and magnesium salts decreases with an increase in temperature, these salts tend to form scale on heat transfer surfaces where the metal skin temperature is greater than the bulk water temperature.

Changes in pH or Alkalinity - Changes in the pH or alkalinity of the cooling water may also have a major effect on the solubility of scaling ions. An increase in alkalinity decreases the solubility of calcium carbonate and also affects the solubility of calcium and iron phosphates. An increase in pH also decreases the solubility of most calcium salts, with the exception of calcium sulfate.

Addition of Sulfuric Acid for pH Control - Using sulfuric acid

for pH control can cause high sulfate levels and increases the probability of calcium sulfate scaling. Hydrochloric acid should be used if calcium sulfate is a potential problem.

Addition of Corrosion Inhibitors and/or Scale Inhibitors -

High concentrations of some corrosion inhibitors and scale inhibitors may cause deposits. Polyphosphate inhibitors, for example, may hydrolyze and revert to orthophosphate, leading to deposition of calcium or iron phosphate. The overfeed of some phosphonates may lead to the formation of calcium phosphate, because phosphonates can revert to orthophosphate.

Uncommon Ion Effect - The solubility of most slightly soluble salts

can be increased by the addition of sodium chloride and nitrate ions.

This increase in solubility is known as the uncommon ion effect.

Common Types of Scale

The following is a discussion of the common types of scale. Although they will be dealt with individually, deposits that form in cooling water systems are rarely homogenous. Invariably, deposits consist of a mixture of water-formed scale deposits that can act as a cement to incorporate silt and other foulants into the overall deposit

Calcium Carbonate (CaCO₃) Scale

Calcium carbonate forms a dense, extremely adherent deposit. It is by far the most common scale problem in cooling systems. Most natural waters contain bicarbonate alkalinity and are at a pH < 8.2. At a pH > 8.2, free carbon dioxide ceases to exist. While calcium bicarbonate is soluble in most natural waters, calcium bicarbonate will be converted to calcium carbonate if the pH and/or the water temperature is raised. On heating, the following reaction occurs:



The tendency to form calcium carbonate can be predicted qualitatively by the Langelier Index, the Ryznar Index, or the Stiff and Davis Index, all discussed below.

Calcium Sulfate (CaSO₄) Scale

The most common form of calcium sulfate is gypsum (CaSO₄ · 2H₂O), which is approximately 50 times more soluble than calcium carbonate at 100 F (37.78 C). Above 100 F, the solubility of calcium sulfate decreases as the water temperature increases.

Calcium sulfate should not present a scale problem in a cooling system using proper blowdown procedures. The higher solubility of calcium sulfate is the basis for scale control by pH adjustment with sulfuric acid.

Without exceeding the solubility limits of CaCO_3 , sulfuric acid feed allows the cooling tower to operate at higher cycles of concentration. This method of scale control can lead to calcium sulfate deposition if excessive amounts of sulfuric acid are used for pH control, or if the makeup water is high in sulfates. The solubility product for calcium sulfate is 1.95×10^{-4} .

To prevent calcium sulfate scale, the sum of the calcium concentration (as CaCO_3) and the sulfate concentration (as CaCO_3) must be less than 1,500 and their product should be kept below 500,000. With chemical treatment by a phosphonate, the sum of calcium (as CaCO_3) and the sulfate (as CaCO_3) can be as high as 2,500, and their product should be less than 1,500,000.

Calcium Phosphate Scale

If polyphosphate is being used alone, or in combination with zinc or zinc/chromate for corrosion protection, the polyphosphate ions may hydrolyze and revert to orthophosphate ions. Orthophosphate levels can also be contributed to by reversion of phosphonates or naturally from the makeup water.

However, phosphate scales can occur if conditions are favorable for tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$) since the solubility product for calcium phosphate is very small. Temperature, pH, calcium and orthophosphate concentrations affect the formation of calcium phosphate. Calcium orthophosphate scale is more insulating than calcium carbonate, and thus causes rapid heat transfer loss.

Silica Scale

The solubility of silica in water is high, so pure silica scale (SiO_2) is rare in cooling systems. The maximum amount that can be maintained in solution in cooling systems is approximately 200 ppm. The higher the pH, the more silica will stay in solution (see Table below). Silica may coprecipitate with iron, manganese, aluminum and magnesium hydroxides.

TABLE

Solubility of SiO_2 at Various pH Levels

pH	Wt% SiO_2 in sat. solution	pH	Wt% SiO_2 in sat. solution
1	0.015	7	0.011
2	0.016	8	0.012
3	0.015	9	0.015

4	0.014	10	0.035
5	0.011	11	0.33

Magnesium Silicate Scale

Soluble silica reacts readily with cations to form various complex silicates.

If magnesium is present in high enough concentrations, magnesium silicate scaling will occur at pH of 8.5. Deposition of magnesium silicate can be prevented by keeping

1. $(\text{Mg ppm as CaCO}_3) \times (\text{SiO}_2 \text{ ppm}) < 35,000 \text{ ppm @ pH} < 7.5$
2. $(\text{Mg ppm as CaCO}_3) + (\text{SiO}_2 \text{ ppm}) < 17,000 \text{ ppm @ pH} > 7.5$

or more generally by keeping silica levels <200 ppm in the recirculating water. Magnesium silicates form by a two-step process: First, magnesium hydroxide precipitates, then reacts with dissolved and colloidal silica to form scale. Magnesium silicate scale occurs when the pH level is higher than 7.8. Magnesium silicate does not occur if the pH of the circulating water is lower than the pH of saturation of magnesium hydroxide. This pH of saturation can be determined using the Table below, which is also helpful in predicting the deposition of magnesium silicate.

TABLE

Prediction of Magnesium Silicate Scale Deposition

	Magnesium Factor		Temperature Factor		Concentration Factor
mg Hardness of Makeup, ppm CaCO3	MG	Exchanger Temperature, deg F (deg C)	T	Cycles of Concentration of Cooling Water	C
10	2.01	70(21.11)	8.85	2	0.13
15	1.92	80(26.67)	8.64	3	0.20
20	1.85	90(32.22)	8.44	4	0.24
30	1.76	100(37.78)	8.25	5	0.28
40	1.70	110(43.33)	8.16	6	0.31
50	1.65	120(48.89)	7.88	7	0.33
60	1.61	130(54.44)	7.71	8	0.36
70	1.58	140(60.00)	7.55	9	0.38
80	1.59	150(65.56)	7.39	10	0.39
90	1.52	160(71.11)	7.29		
100	1.51	170(76.67)	7.09		
		180(82.22)	6.95		
		190(87.78)	6.81		
		200(93.33)	6.67		
		212(100.00)	6.50		

$$\text{pHs} = \text{MG} + \text{T} - \text{C}$$

Example: MgH of makeup = 20 ppm, Cycles of concentration = 10 and pH of circulating water = 8.7

Calculation of pHs at temperatures of 130, 150, 170, and 190 deg F:

	130 deg F	150 deg F	170 deg F	190 deg F
MG	1.85	1.85	1.85	1.85
T	7.71	7.39	7.09	6.81
C	-0.39	-0.39	-0.39	-0.39
pHs	9.17	8.95	8.65	8.27

This water would deposit magnesium silicate in coolers whose temperature exceeds 170 deg F.

Iron-Based Scales

Iron exists in two states, Fe^{+2} and Fe^{+3} . The chemistry of iron compounds is considerably more complex than alkaline earth carbonate and sulfate scale-forming materials. When these two oxidation states (Fe^{+2} and Fe^{+3}) of iron join with the same anion, the result is usually the formation of compounds with significant differences in solubilities. Iron deposits typically are in the form of Fe_2O_3 , FeO , FeS , iron silicate, etc. Often manganese is also detected in these deposits.

Iron fouling occurs as a result of corrosion processes throughout the system. Thus, it is very important to implement a good corrosion control program. Iron fouling sometimes occurs in cooling waters as a result of carryover from clarifiers, where iron salts may be used as coagulants or where raw water (such as well water) may be high in iron. Iron levels of 2 ppm or greater in the recirculating water can be controlled through the use of iron dispersants or deposit control agents. Use of an iron dispersant is strongly recommended to avoid major equipment failure problems. In cooling waters, Fe_2O_3 (hematite) and FeO are the most common iron deposits. Magnetite (Fe_3O_4) is rarely found in cooling systems. Magnetite needs high temperatures and/or anaerobic conditions. Most magnetite found in cooling systems arrives via airborne or waterborne solids. If iron levels exceed 4-5 mg/l, mechanical or other means to remove iron should be strongly considered, such as oxidation, aeration, coagulation, etc.

Zinc Phosphate and Zinc Hydroxide

Zinc hydroxide scale is normally found when pH exceeds 7.6 or when over-feed of a zinc product occurs. Zinc hydroxide is a grayish-white precipitate. With increasing pH, precipitate amounts increase. As pH is lowered below 7.0, zinc hydroxide will resolubilize. Above 140 deg F (60 deg C) it has an inverse temperature solubility.. The most common methods to prevent scale in cooling water systems are:

- using scale inhibitors.
- adjusting pH.
- softening makeup water.

Estimating the Scale-Forming Tendency of Water

Scale forming and/or corrosive tendencies of water can be predicted qualitatively by using the Langelier Index, Ryznar Solubility Index, or the Stiff and Davis Index.

The Langelier Index: For any given temperature and water composition, one can calculate the tendency of the water to form calcium carbonate scale by using the Langelier Index.

$$\text{LSI} = \text{pH} - \text{pHs}$$

where

$$\text{pHs} = \text{pCa} + \text{palk} + \text{C}$$

where

pHs = saturated pH

pCa = calcium hardness factor (expressed as ppm CaCO_3),

palk = M alkalinity factor (expressed as ppm CaCO_3),

C = total solids (expressed as ppm at the temperature of the water)

The Langelier Saturation Index (LSI) is defined as the difference between the actual pH and the calculated saturated pH (pH_s),

$$\text{LSI} = \text{pH (actual)} - \text{pH (calculated)}$$

$$\text{LSI} = \text{pH} - \text{pH}_s$$

When the actual pH is equal to the saturated pH, the Langelier Saturation Index is zero (LSI = 0 when pH = pH_s). A saturation equilibrium exists. There is no scale formation and corrosive attack is minimized.

When the actual pH is greater than the saturated pH, the Langelier Saturation Index is positive (LSI when pH > pH_s). Supersaturation of CaCO₃, exists with respect to alkalinity and total solids at that temperature. There is a tendency to form scale on heat transfer surfaces-

When the actual pH is less than the saturated pH, the Langelier Saturation Index is negative (LSI = - when pH < pH_s). Any scale previously formed will be dissolved. Corrosion of unprotected or bare metal will occur.

The Langelier Index does not tell whether scale will actually form, nor how rapidly it will form.

The prediction of water characteristics by LSI appears in the Table below:

TABLE

Prediction of Water Characteristics by the Langelier Index

LSI	Tendency of Water
+2-0	Scale-forming and for practical purposes noncorrosive
+0.5	Slightly scaling and noncorrosive
0.0	Balanced but pitting corrosion possible
-0.5	Slightly corrosive and nonscale-forming
-2.0	Highly corrosive

Ryznar Stability Index (RSI) - It is possible for a

low-hardness water and a high-hardness water to have the same LSI value.

Using operational data and experience with scale and corrosion in a large

number of systems, Ryznar refined the Langelier Index to allow for a

distinction between two waters having the same Langelier Index. The

Ryznar equation is:

Ryznar Stability Index (RSI) = $2pH_s - pH$

The predictive nature of the Ryznar Index is shown in the Table below:

TABLE

Prediction of Water Characteristics by the Ryznar Index

Ryznar Stability Index	Tendency of Water
4.0 - 5.0	Heavy Scale
5.0 - 6.0	Light Scale
6.0 - 7.0	Little Scale or Corrosion
7.0 - 7.5	Corrosion Significant
7.5 - 9.0	Heavy Corrosion
9.0 and Higher	Corrosion Intolerable

The Stiff and Davis Index (SDI): The Langelier Index has been further modified by Stiff and Davis. Their index takes into account the influence of high levels of dissolved solids on the solubility of calcium carbonate. The SDI Index was developed for use in the oil field, where highly saline waters or brines are produced. Where fresh water is being used as makeup water for a cooling system, there is no need for the refinements of the Stiff and Davis Index. However, as zero blowdown systems become more common, as more and more reuse of water becomes necessary, and as recovered wastewater is used in larger quantities as a makeup source, it may become necessary to use the Stiff and Davis Index. The index is defined as:

$$\text{SDI} = \text{pH} - \text{pCa} - \text{pAlk} - \text{K}$$

K = a constant based on the total ionic strength and temperature.

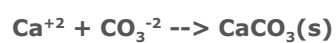
Methods of Scale Inhibition

Lime or Lime/Soda Softening

For cooling water applications, only partial lime or lime/soda softening is economical. Often, sidestream lime softening is used as a supplement or replacement for softening during external pretreatment prior to cooling water applications. Occasionally, hot process lime or lime/soda softening is used for silica removal in cooling water applications. In boiler applications, however, hot or cold lime-soda softening is commonly used for external treatment. This reaction is as follows:

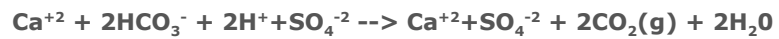


(M alkalinity)



Acid Treatment

The traditional method of calcium carbonate scale control is to reduce the water's alkalinity sufficiently with sulfuric acid to create non-scaling conditions.



The calcium bicarbonate is converted to volatile carbon dioxide and calcium sulfate. Calcium sulfate is more soluble than calcium carbonate. The cycles of concentration are limited by the solubility of calcium sulfate.

If the makeup water is high in sulfates, hydrochloric acid may be used to reduce the alkalinity-, but chloride ions may cause problems because they can penetrate oxide films, setting up local anodic cells and causing corrosion.

Scale Inhibitors and Dispersants

The answer to the question of how scale inhibitors work is fraught with complexities. One of the more logical explanations is that sub-stoichiometric amounts of certain types of chemical additives can have

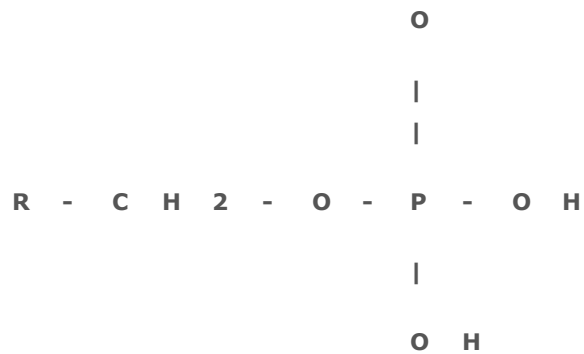
very marked effects on the growth rate of crystals deposited in a scaling environment. These threshold inhibitors function by adsorbing onto the growing crystals and distorting the lattice, which disrupts the crystal growth process. The most commonly used threshold scale inhibitors are inorganic polyphosphates, organophosphorous compounds, synthetic organic dispersants and natural organic dispersants. Threshold treatment is the term that describes the effective use of a scale inhibitor at concentrations below the level required to sequester, or donate electrons to the metal ions forming a water-soluble metal ion complex. The dispersant products are also used to prevent scale formation by modifying the crystal structure of the deposit-forming substance. This crystal distortion prevents deposition, and the highly irregular stressed crystals tend to slough off as crystal growth occurs.

Conventionally, scale inhibitors are classified as inorganic scale inhibitors (such as sodium hexametaphosphate, sodium polyphosphate, sodium pyrophosphate) or organic phosphorus compounds (such as the phosphate esters and phosphonates). The inorganic phosphates used to treat scale contain repeating oxygen/phosphorus bonds (-O-P-O-PO-P-). These bonds are highly unstable in aqueous solutions, and as a result, they hydrolyze, or react with water, and end up as ineffective orthophosphate. The hydrolysis of such products is also referred to as reversion. Organic phosphorus products are also subject to hydrolysis. The main factors that effect the rate of reversion are pH and temperature. It is also influenced by complexing cations, concentrations, holding time index, ionic environment

in the solution, and other factors. Environmental restrictions imposed upon the industry have made organic treatments almost a necessity. The following discussion about organic scale inhibitors and dispersants will be useful in understanding the types of products.

Phosphate Esters

A typical phosphate ester functional group may be represented as follows:



Phosphate esters are less likely to hydrolyze than inorganic polyphosphates and more likely to hydrolyze than phosphonates. They exhibit varying degrees of threshold scale inhibitor properties. In fact, some phosphate esters are ineffective as scale inhibitors.

Phosphonates

A typical phosphonate has the following structure:

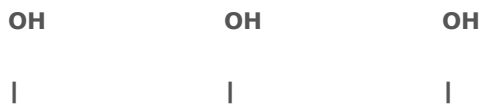




This structure with C-P-O bonding is more stable to hydrolysis than the phosphate ester.

A variety of amino methylene phosphonic acids and their salts are available commercially as scale inhibitors. They are effective inhibitors for both calcium sulfate and calcium carbonate scale at very low threshold concentrations. Non-nitrogen-containing phosphonic acids are widely used because they are more compatible with chlorine than the aminomethylene phosphonic acids. Phosphonates are believed to inhibit scale formation by being adsorbed on active crystal growth sites, where they decrease the crystal growth rate and decrease the nucleation rate. A number of blends or combination products that incorporate low molecular weight dispersant polymers with phosphonates are available. Phosphonates containing nitrogen are good for iron control because the close proximity of the nitrogens allows for formation of strong five-membered ring metal complexes with iron. The structure of a typical phosphonate is as follows:

HEDPA



Lignosulfonate derivatives come from pulping operations where wood is sulfonated at high temperatures to remove the lignin binder from the cellulose by forming a water-soluble polymer. This polymer is a highly complex natural derivative and its structure is not well defined.

Lignosulfonates are classified as anionic polyelectrolytes. Those used as dispersants usually have a molecular weight between 1,000 and 10,000.

Lignosulfonates are usually poor scale inhibitors. However, these organic polymers are reported to be good dispersants for calcium phosphate, suspended matter and iron oxides. Lignosulfonates function as dispersants by limiting attractive forces between particles, thereby reducing sedimentation.

Inorganic Polyphosphates

Polyphosphates are commonly used in once-through and municipal applications to minimize scaling and corrosion at dosages of 1 to 5 mg/l of polyphosphate as PO_4 . Thus, polyphosphates function as threshold treatments because they are effective at dosages much less than those stoichiometrically required to react with calcium, magnesium or iron. The repeating (P-O-P) structure is characteristic of inorganic polyphosphates.

Although the advantages of low cost and threshold activity are attractive for the use of polyphosphates, they are ineffective as scale inhibitors at

high levels of calcium. High iron and manganese levels can restrict the effectiveness of polyphosphates by forming stoichiometric iron-polyphosphate complexes that hinder the performance of polyphosphates as inhibitors for calcium and magnesium deposits. In addition, polyphosphates act as nutrients for bacteria. As a result, higher biocide dosages may be required if polyphosphates are used for scale or corrosion control.

Surfactants

Surfactants are used in cooling systems either to emulsify or disperse hydrocarbons, or to penetrate biomasses. Their primary purpose is to prevent hydrocarbon and microbial deposition on heat transfer surfaces. Surfactants also aid in de-oiling surfaces and keeping suspended solids, including biomass, dispersed. Surfactant types are generally classified as anionic, cationic, nonionic and amphoteric.

Surfactants work in one of two ways. If they are nonionic or amphoteric, they reduce surface tension or interfacial tension at liquid-solid, liquid-air, liquid-liquid and solid-air interfaces. This changes the wetting characteristics of solids, making them either water-wet or oil-wet. If the surfactants are anionic or cationic, they work by charge enhancing the solids, either oil or biomass, and forcing those solids to repel one another. This keeps the solids dispersed in the system water for later removal. Reduction of interfacial tension is also achieved through the

use of anionic and cationic surfactants.

Problems Caused by Scale or Fouling Deposits in

Cooling Systems

- Reduced or uneven heat transfer
- Unexpected equipment shutdown - loss of production
- Shortened equipment life
- Increased pumping costs
- Equipment corrosion
- Product loss due to ineffective cooling
- Increased product cost due to above factors
- Profit Loss