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ANALYSIS OF THE LIME SOFTENING TREATMENT PROCESS OF INDUSTRIAL COOLING WATER USING THE MINTEQ GEOCHEMICAL MODEL

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

John James Melescue, Jr.

December, 1993

DEDICATION

This thesis is dedicated to my parents John and Florence Melescue for their support and love during this endeavor, and to my Lord and Savior Jesus Christ whom I give all glory and honor and praise. I give thanks to the Lord for He is good; His love endures forever (Psalm 107:1).

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ABSTRACT

This report investigated the economic feasibility of using lime softening treatment for the Saturn Corporation cooling tower in Spring Hill, Tennessee. The MINTEQ geochemical equilibrium model was used to simulate hydrated lime and soda ash addition to the make-up water in a clarifier. Model predictions of precipitates and clarifier effluent species concentrations were used to determine cycles of concentrations possible in the cooling tower without scale formation. The component costs for construction, operation, maintenance, labor and electricity were estimated for all systems required in the softening treatment process. Sludge and blowdown water disposal on-site and off-site were considered in the cost estimates. The results of the research determined that for on-site disposal of the blowdown water and sludge, the minimum total cost for make-up softening treatment only was $22,983/month at 18.8 cycles of concentration, as compared to $23,099/month at four cycles of concentration without softening. For off-site disposal, the minimum cost with make-up softening only would be $44,736/month at 15.1 cycles of concentration, as compared to $35,058/month at four cycles of concentration without softening. Using cost ratios found in the literature, the cost for a combination of make-up and sidestream softening is 30% of the cost for make-up softening only. It was concluded that it was not economically feasible to use softening treatment for make-up water only. It was economically feasible to use a combination of make-up and sidestream softening. For a well designed cooling tower operating at zero blowdown, the drift losses would limit the cycles of concentration to 11.0.

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NOMENCLATURE

a_{ij}	Stoichiometric Coefficient of Component J in Species i
B	Cooling Tower Blowdown Water, liters
b	Cooling Tower Blowdown Water Rate, l/hr
C	Cycles of Concentration
c_M	Concentration of a Conservative Species in the Make-up Water, mg/l
c_w	Concentration of a Conservative Species in the Cooling Water, mg/l
c_o	Initial Concentration of a Given Species Added to the System at Time t_o, mg/l
c_n	Number of Components
D	Cooling Tower Water Drift Losses, liters
d	Cooling Tower Water Drift Loss Rate, l/hr
E	Cooling Tower Water Evaporation Losses, liters
e	Cooling Tower Water Evaporation Rate, l/hr
f	Number of Degrees of Freedom
I	Ionic Strength
K_i	Equilibrium Constant for the Formation of Species i
LSI	Langlier Saturation Index
M	Cooling Tower Make-up Water, liters
m	Cooling Tower Make-up Water Rate, l/hr
p	Sum of the Number of Type III Species with Fixed Activity and Type IV Finite Solid Species
pH_s	Calculated Saturation pH of Water for Calcium Carbonate Scale
R	Cooling Tower Recirculating Water, liters
r	Cooling Tower Recirculating Water Rate, l/hr
TS_m	Total Solids in Make-up Water, mg/l
TS_r	Total Solids in Recirculating Water, mg/l
t_o	Initial Time at Which a Chemical is Added to the System
V	Cooling Tower Water Basin Volume, liters
V_{xz}	Stoichiometric Coefficients for Component x of Phase Z
V_{yz}	Stoichiometric Coefficients for Component y of Phase Z
X_j	Activity of Component j
x	Component x in an Aqueous Phase
y	Component y in an Aqueous Phase
z	Aqueous Phase Ion Complex or a Solid Phase
Δc	Change of Concentration of a Given Species Added to the System at Time t_o
ΔT	Temperature Change of Water from Top to Bottom of Cooling Tower
ΔW	Change of Total Weight of a Given Species, mg
$[S_i]$	Molarity of Species i
$\{S_i\}$	Activity of Species i
Π_j	Indicates the Product Over All Components in Species i
λ_i	Activity Coefficient of Species i

CHAPTER 1

INTRODUCTION

Industrial processes such as power generation, air conditioning, and heat exchangers require cooling water systems. Two common types of cooling systems include once-through and open recirculation systems. Once-through systems are becoming less popular because the volume of water which is discharged is much greater than the water discharged from open recirculating systems. This makes them less attractive as environmental standards for discharged water become stricter and as water costs increase. Open recirculation systems, also called recycled cooling water or recirculating water systems, recycle some of the water and discharge the rest of the water to a stream.

Due to water quality degradation in cooling water systems, several operational problems occur which include scaling, corrosion, and biological growth. These problems are intensified with recycled water systems due to evaporation losses which cause an increase in the concentration of dissolved solids in the cooling tower water. Since scaling decreases heat exchanger efficiency, the formation of scale has both an economic and environmental impact. Common scales include calcium carbonate, calcium sulfate, calcium phosphate, calcium silicate, and magnesium silicate.

Due to increased environmental regulations and costs of waste disposal for cooling water discharges, there is a strong incentive for industries to increase the amount of recycle in the cooling water system. Since the amount of recycle is limited by the concentration of scale forming species, chemical treatments can be used to precipitate out

these species from the cooling tower water. The amount of recycle is measured in terms of the cycles of concentration, which is defined as the multiple of the increase of concentration of a conserved species in the water. Several cooling water treatment processes have been used to increase the cycles of concentration which in turn decreases the blowdown rates of discharged water. In lime softening treatment, lime is added in a clarifier to increase the pH. This will cause calcium, magnesium, phosphate and some silica to precipitate. If there is not enough carbonate in the water to remove the desired amount of calcium, then soda ash (Na_2CO_3) is added in the same clarifier to provide more carbonate. Although the addition of soda ash decreases the calcium concentration in solution, it may increase the total dissolved solids due to the increase in sodium.

Three possible plant configurations can be used for the lime and soda ash additions. In make-up softening, lime and soda ash are mixed with the incoming flow upstream of the recirculating water (Fig. 1-1). In sidestream softening, some of the recirculating water is softened and mixed with the incoming water which dilutes the solids concentration of the recycled flow (Fig. 1-2). Softening can also be performed on both the sidestream and make-up flows (Fig. 1-3).

Conventional lime softening processes provide a limited increase in the cycles of concentrations in the cooling tower. However, conventional processes may remove only a limited amount of silica in the make-up water. Ultra-high lime softening does remove silica and possibly some sulfate from the cooling water, thereby increasing the allowable cycles of concentration. An analysis must be performed to determine if a treatment process is economically and environmentally advantageous.

The advantages of softening include a lower volume of water required for make-up

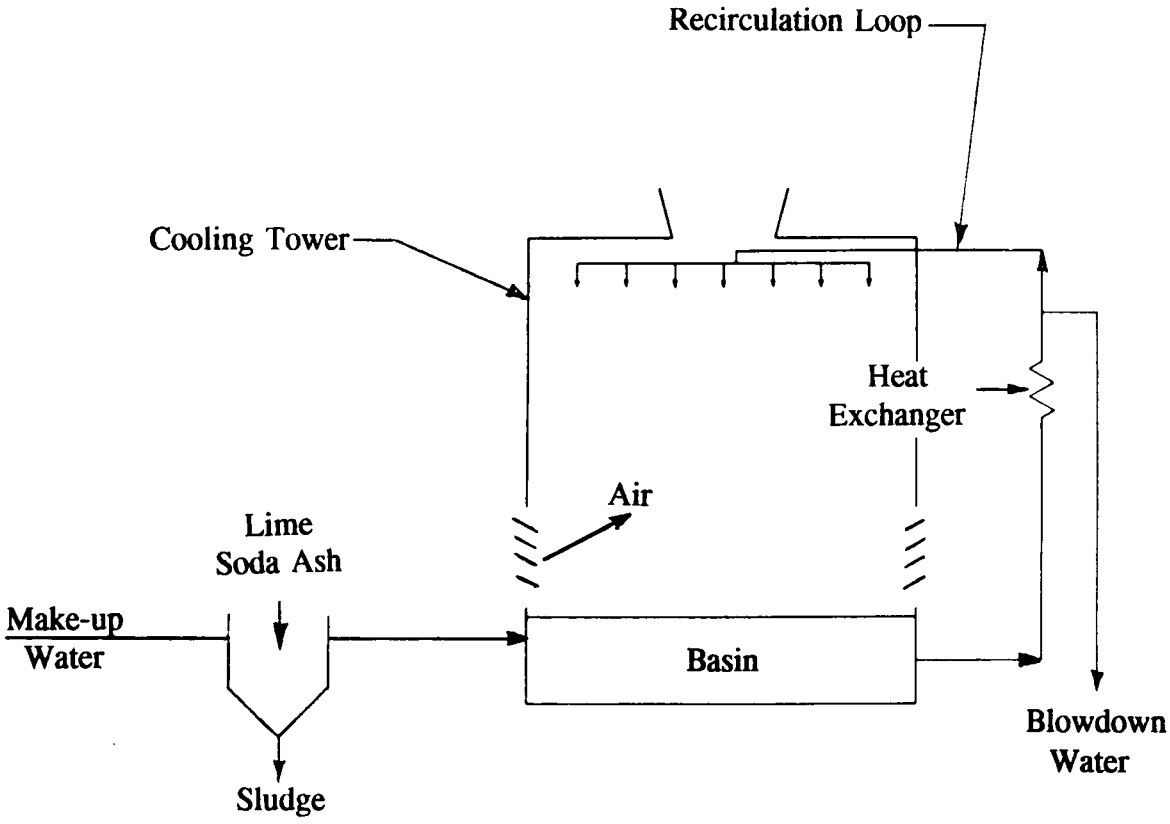


Fig. 1-1. Clarifiers Outside Recirculation Loop for Make-up Softening Only

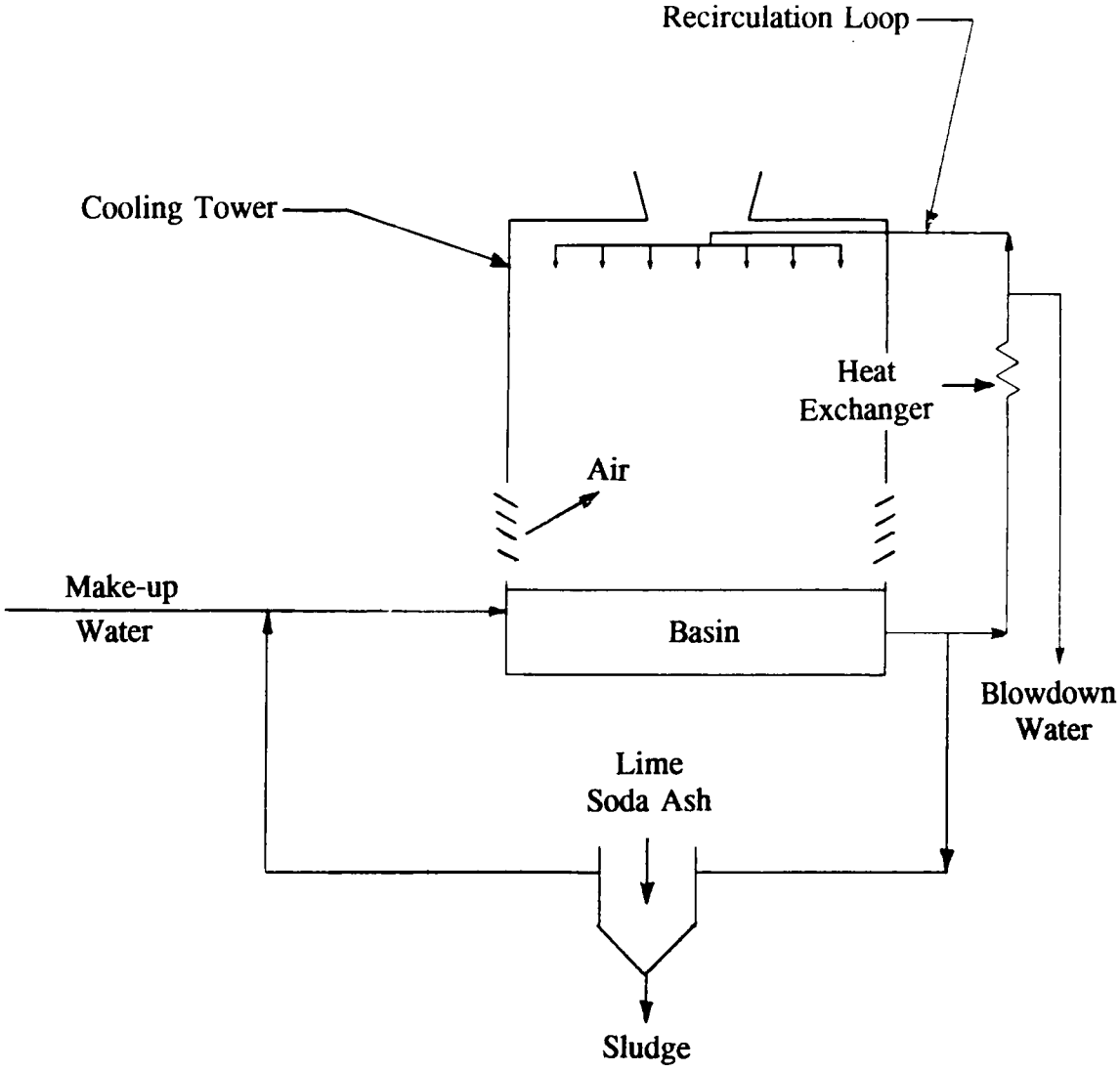


Fig. 1-2. Clarifiers Inside Recirculation Loop for Sidestream Softening Only

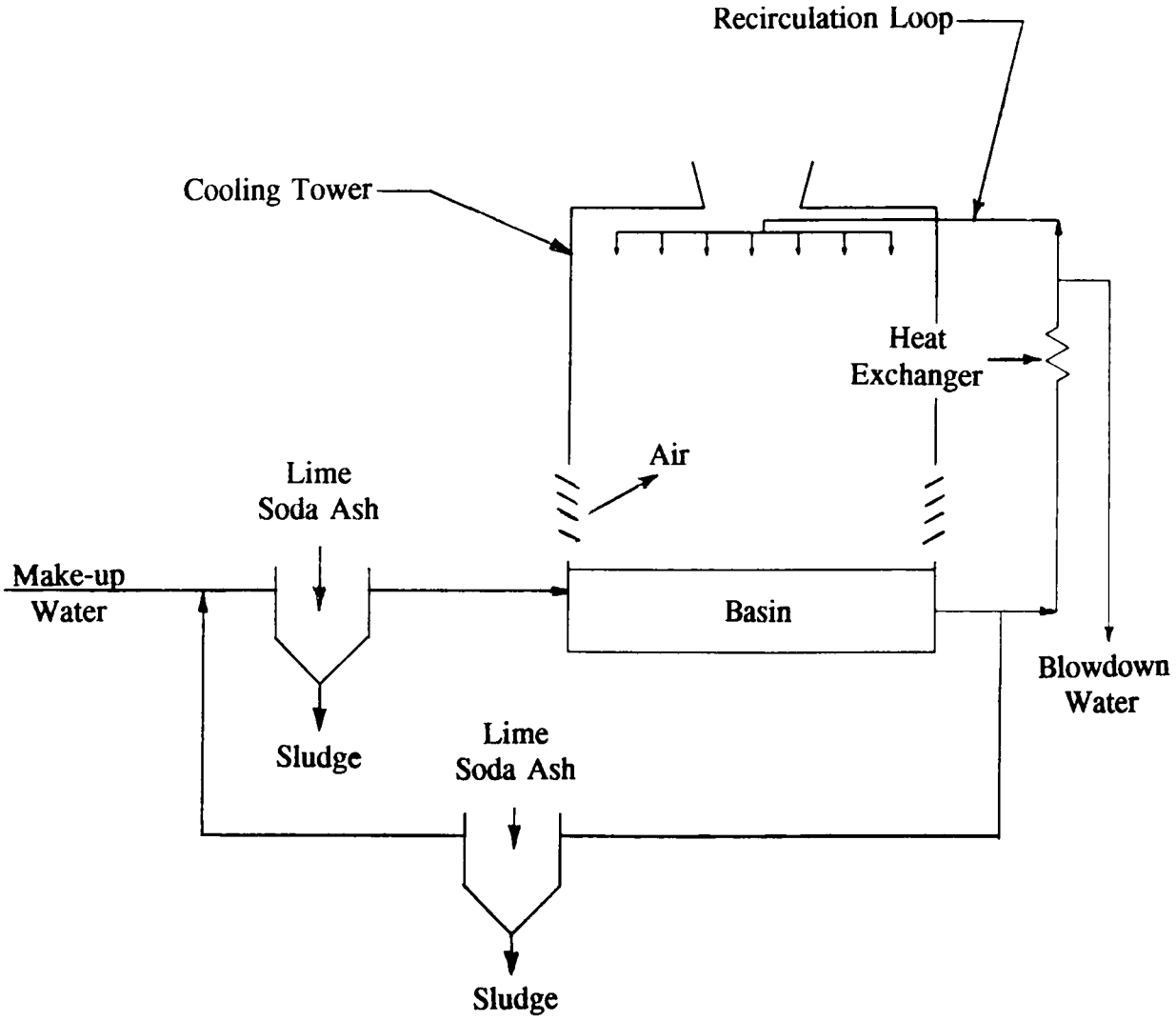


Fig. 1-3. Combination of Make-up and Sidestream Softening

and discharged as blowdown. Lime softening is attractive economically because lime is less expensive than other treatment chemicals. If the ultra-high lime process is found to be advantageous for a plant currently using conventional lime softening treatment, then the conversion to ultra-high lime operation can be made with minor modifications. In some arid regions of the country, the availability of water has, or may soon, become limited to such an extent that reuse will be the only alternative.

One disadvantage of lime softening is the drift losses from the cooling tower may cause aerosols to precipitate on nearby land. These aerosols will have much higher dissolved solids concentrations, including toxins, than those from conventional systems. The incremental detrimental effects on crops, vegetation, and wild-life has not been ascertained. A second problem is that the sludge from the softeners must be disposed of, which raises the cost. But the sludge usually has good dewatering characteristics, and recalcination of the sludge may be a viable option for minimizing the quantity for disposal.

CHAPTER 2

PURPOSE OF RESEARCH AND APPROACH

The purpose of this thesis was to use the chemical equilibrium model MINTEQ [1] to determine if the lime softening treatment process was economically and practically feasible for the General Motor's Saturn Automobile Manufacturing plant located in Columbia, TN. The Saturn cooling tower does not currently use any softening treatment. This study was to determine whether Saturn can significantly reduce the cost of operating its cooling tower by using the lime softening treatment process.

The geochemical computer model called MINTEQ can determine the precipitation of scale forming species by lime and soda ash addition. MINTEQ can compute the chemical equilibrium point of water for a given set of species concentrations. These species concentrations can be input in their dissolved or solid phase. The MINTEQ model in its present form can be used to simulate make-up softening only. This would also allow direct use of the equations which relates cycles of concentration to make-up and blowdown water rates as presented in Chapter 3. Using MINTEQ to simulate sidestream softening would require that at each step in the recirculation loop which involves a change in species concentration or flow rate, the mass balance of each species must be recalculated. A computer program would have to be written to perform the mass balance calculations at each step in the recirculation loop where a change of mass takes place. MINTEQ would have to be incorporated into this mass balance program, with MINTEQ automatically accepting inputs from and providing outputs to the mass balance program. An analysis using this approach is not currently available and is beyond the

scope of this thesis.

The methodology for cost determination used for make-up softening in this thesis also applies to the sidestream softening process which would be a natural progression of the current problem. Make-up softening costs as determined in this thesis were projected to predict sidestream softening costs based on cost relationships determined from work performed by others.

The approach for this study basically consisted of using MINTEQ to model the addition of lime and soda ash to the make-up water in a clarifier to decrease the concentration of scale forming species, then determining the maximum cycles of concentration possible in the cooling tower. Simulating the addition of sulfuric acid was also required for pH control. The maximum species concentrations allowed in the cooling tower without forming scale was determined using limits that the Saturn cooling tower operators currently allow, and investigating what other researchers and plants have determined to be practical operating limits for those species which are not currently monitored by Saturn. Finally, the costs of the chemicals required, make-up water used, blowdown water disposal, construction, operation, and maintenance of the clarifiers and subsystems required, and sludge disposal were determined. The chemical requirements and cost analysis were estimated for a range of lime and soda ash additions until the most economical design for the Saturn cooling tower was determined. The results of this analysis were then generalized to give guidelines on the applicability of the lime softening treatment process for other plant conditions.

Recommendations were made for the necessary MINTEQ model modifications for its applicability to a sidestream softening process, as well as other improvements which

were deemed necessary but were beyond the scope of this thesis.

CHAPTER 3

PRINCIPLES OF OPEN RECIRCULATING COOLING WATER SYSTEMS

3.1 Description of the Cooling Tower

A counterflow evaporative cooling tower schematic is presented in Fig. 3-1. The water basin at the bottom is filled with fresh water for system start-up, with the volume of this basin, V, being the cooling water system capacity. A supply of make-up water, M, is pumped from the basin through a heat exchanger, C, cooling some process, and being itself warmed. The warm water return, R, is pumped to the plenum at the top of the cooling tower, and distributed uniformly over the cross-sectional area through an assembly of nozzles.

The interior of the structure contains splash packing, or fill material, constructed of slats stacked in decks and spaced in staggered rows. For splash packing, water splashes from row to row, breaking into droplets, typically at the rate of 2-4 gpm/ft^2. This rate is called the "water loading" of the tower. For fill material, the water is exposed to air in thin films over the surface of the fill. The sheets can be made of wood, cellulose, molded polystyrene, or asbestos. It is essential that the sheets wets well, otherwise the water forms in rivulets instead of droplets.

A counterflow tower as depicted in Fig. 3-1 will draw air, A, from the bottom of the tower through louvers, and then the air will be drawn upward, counterflow to the water which is descending from the top of the tower. The air velocity is typically 300 to 700 fpm.

Two kinds of heat transfer can occur between the warm water and air: latent heat

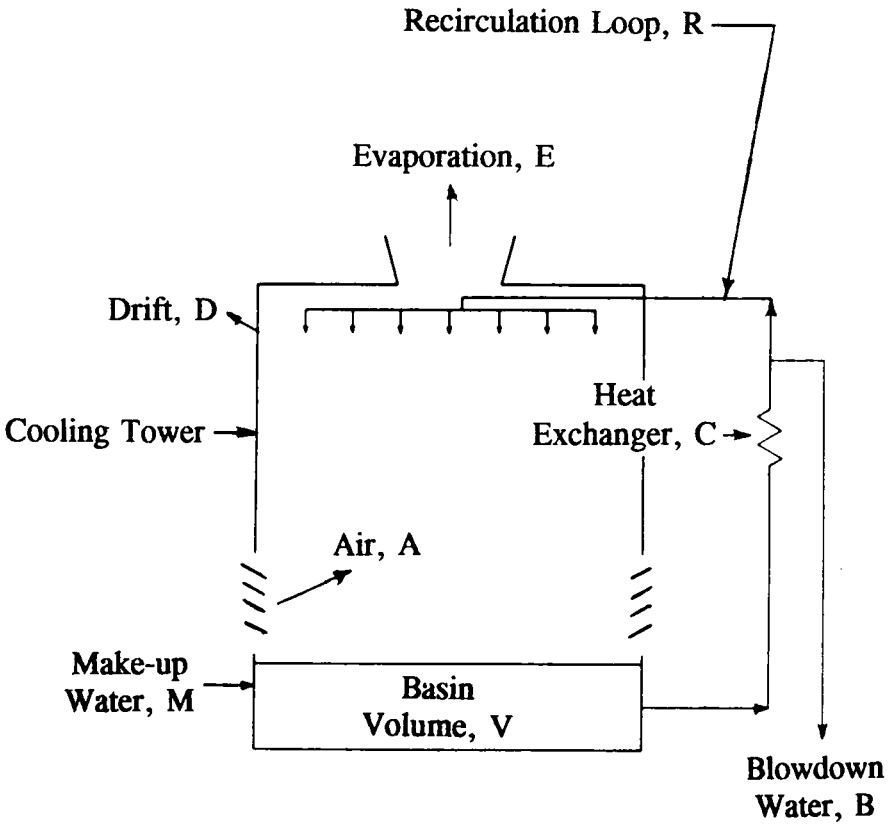


Fig. 3-1. Recirculating Cooling System with Cooling Tower (After Ref. [2])

of vaporization and sensible heat transfer. The latent heat of vaporization is the energy required to overcome the attractive forces between molecules in the liquid state when liquid water vaporizes. This heat is abstracted from the remaining liquid water and therefore lowers its temperature, transferring about 1000 Btu/lb of water which evaporates. Absorption of latent heat typically accounts for 75-80 percent of heat transferred in cooling towers [2]. Sensible heat transfer occurs due to the temperature difference between the water and air and accounts for the remaining 20-25 percent of heat transferred. The heat content of the atmospheric air, called the wet-bulb temperature, must be lower than the water temperature for heat transfer to take place, thereby raising the air temperature and lowering the water temperature. This is called sensible heat transfer, and it accounts for the remaining 20-25 percent of heat transferred.

The stream of air and water vapor which is traveling upward will entrain some water droplets. Therefore an arrangement of baffles is set up at the top of the tower, called a "drift eliminator", to cause a sudden change in the stream direction. This will result in inertial separation of the entrained water droplets so that they will fall with the bulk of the water into the basin, minimizing the water loss in the tower. Water vapor, E, and air pass out through the fan stack into the atmosphere. A small amount of liquid water, D, is lost due to being blown out by wind. This is called drift or windage loss and is typically 0.1 to 0.2 percent of the recirculation rate [2].

As the water in the system decreases due to water vaporization and drift losses, the species concentrations in the remaining water will increase. In order to prevent excessive scale buildup on the heat exchanger, the concentration of the scale-forming species must be kept below a certain level. This is accomplished by continuously withdrawing a

volume of water, B, from the system and adding a volume of fresh water, M, to the basin to maintain the total volume of water, V, at a constant level. The amount of fresh water that must be added is then equal to the sum of the evaporation and drift losses and the blowdown water.

3.2 Cooling Tower Efficiency

There are two different methods that are typically used for measuring the efficiency of the cooling tower. One measure is the approach of the cooling tower, which is the difference between the temperature of the cooled water in the basin of the tower and the wet-bulb temperature of the atmosphere. The cost of the tower will depend on the design approach desired. For example, a tower with a 5°F design approach will cost 60-70 percent more than a 10°F approach under the same heat load [2]. A 5°F approach would require a tower perhaps 35-40 feet high, whereas a 10°F approach could be obtained in a tower around 25 feet high [2]. The average design approach in industrial cooling towers is 8-15°F [2].

A second measure of performance is the cooling range, which is the difference between the temperature of the supply water, M, and the return water, R. The cooling range in a typical industrial tower is 15-30°F [2].

3.3 Heat Transfer within the Cooling System

The cooling system depicted in Fig. 3-1 allows a hot fluid to be cooled by water, which is itself heated without any loss of exchanged heat. Industrial heat exchangers

consist of a number of tubes enclosed in a shell. Usually the cooling water is circulated through the tubes with the hot fluid flowing in the shell. This is usually more efficient than when the water is circulated through the shell because the water velocity is higher in the tubes, minimizing fouling. Fouling and scale buildup on the surfaces of the tubes will decrease the amount of heat transfer obtained. Also, the tubes are much easier to clean than the shell, especially if the shell contains fixed internal baffles to produce turbulent flow.

3.4 Calculation of Make-up Water Required, Losses, and Concentration

Referring to Fig. 3-1, there is a quantity of water leaving the system continuously from evaporation, E, drift, D, and blowdown, B, depleting the total volume of water, V. These losses must be continuously replaced with additional make-up water, M. Since the evaporative losses do not carry the salts with them, the salts will increase in concentration in the recirculating water. A maximum value of this concentration cannot be surpassed in order to prevent precipitates from forming in the recirculating system. When this concentration is first reached, a valve in the return line is opened allowing a certain volume of water, B, to bleed off to the drain continuously. The ratio of the total solids in the make-up water with that in the recirculating water is termed the "cycles of concentration".

Equations relating the blowdown, evaporation and make-up water rates were presented by McCoy [2]. At any point in time,

$$M=E+B+D \tag{1}$$

where M is the make-up water, E is the evaporation losses, B is the blowdown losses, and D is the windage loss. The bleed-off valve is adjusted until the system reaches a preselected value of total solids in the make-up water. At steady-state, the weight of solids entering in the make-up water equals the weight of solids removed in B and D,

$$M(TS_m)=(D+B)(TS_r) \tag{2}$$

where TS_m is the total solids in the make-up water and TS_r is the total solids in the recirculating water.

The number of concentrations, C, is then

$$C=\frac{TS_r}{TS_m} \tag{3}$$

Therefore

$$M=(D+B)C \tag{4}$$

and

$$C=\frac{M}{B+D}=\frac{(E+B+D)}{B+D} \tag{5}$$

Solving for the blowdown water, B, gives

$$B=\frac{E-D(C-1)}{C-1} \tag{6}$$

This results in an expression for blowdown in terms of evaporation, drift, and cycles of concentration. Although there is uncertainty about E and D, it is usually

assumed that E is one percent of the recirculating rate per 10°F. The equation for estimating E then becomes

$$E=\frac{R\Delta T}{1000} \tag{7}$$

Eq. 6 can be written as

$$B+D=\frac{E}{C-1} \tag{8}$$

Substituting Eqs. 7 and 8 into Eq. 1 gives

$$M=\frac{R\Delta T}{1000}+\frac{E}{C-1} \tag{9}$$

or

$$M=\frac{R\Delta T}{1000}+\frac{R\Delta T}{C-1} \tag{10}$$

and finally

$$M=\frac{R\Delta T}{1000}\frac{C}{C-1} \tag{11}$$

The above equations are also applicable for continuous processes. Using small letters to denote flowrates, Eq. 1 can be written as

$$m=e+b+d \tag{12}$$

Eq. 7 can be written as

$$e = \frac{r\Delta T}{1000} \tag{13}$$

and Eq. 12 can be written as

$$m = \frac{r\Delta T}{1000}\frac{C}{C-1} \tag{14}$$

3.5 Determining a Treatment Program

A complete treatment process as presented by McCoy [2] would typically include:

1. An inhibitor to protect steel from corrosion.
2. An inhibitor added specifically to prevent the corrosion of copper and its alloys.
3. An acid (usually sulfuric acid) to regulate the pH of the recirculating water.
4. An antiscalant to prevent the precipitation of alkaline earth salts.
5. An antifoulant to retard the deposition of corrosion products.
6. A dispersant to prevent the accumulation of deposits of silt and other suspended material.
7. Biocides to control microbiological fouling.
8. A surfactant to improve the performance of the biocides.
9. Special chemicals to minimize the ill effects of adventitious contamination.

To prevent scaling, typical antiprecipitants include polyacrylates, phosphonates, diphosphonates, polyphosphates and phosphate esters.

CHAPTER 4

LITERATURE REVIEW

Comparisons have been made in previous studies between the conventional, high-lime, and ultra-high lime treatment processes. These studies were conducted to investigate the possible reduction of cooling water blowdown for economic and environmental reasons. Some of these studies have included a complete review of state-of-the-art technology, modeling approaches for the lime-softening process, assessing the success of plants which are currently achieving discharge reduction using lime softening, and environmental impact and cost analysis for such processes. Literature discussing current levels of understanding in the lime treatment process is presented below.

4.1 Introduction

It is generally accepted that lime softening is applicable to high-hardness waters. If water is recycled in the cooling tower, hardness levels may be concentrated to high levels such that sidestream softening is practical. Plants whose make-up water contains 100 ppm hardness should consider sidestream softening [3]. For sidestream softening systems, the essentials of design require minimizing the sidestream flow rate since it is used to size the equipment and chemical feed rates [3].

Typical cycles of concentrations obtained in conventional practice was reported by Spear and Matson [3] to be four to six, which they say can be increased to 15 cycles or more with sidestream softening.

4.2 Precipitation of Species

There is general agreement that conventional lime treatment removes calcium, magnesium and phosphate. Silicate removal will occur at higher pH, and therefore requires high or ultra-high lime treatment [4,5]. A description of the species which precipitate during the softening process follows.

As lime is added in the first clarifier to raise the pH, the carbonate ion (CO_3^{2-}) dissociates from the bicarbonate ion (HCO_3^-). The free carbonate then reacts with calcium to form calcium carbonate precipitate. Soda ash is added to provide additional carbonate if needed to react with calcium still in solution. If the pH is high, then carbon dioxide can be used instead of soda ash. In high sulfate cooling waters, ion pairing between the sulfate anion and divalent cations may cause the concentration of calcium remaining in solution after softening to be greater than predicted by the calcium carbonate solubility [6].

Magnesium is precipitated mainly as magnesium hydroxide.

Phosphate will precipitate mainly as calcium phosphate in the lime clarifier.

Silica is principally removed by adsorption onto magnesium hydroxide floc [4,6,7]. More efficient silica removal is possible if more magnesium is added, but this can be expensive [4]. Silica may also be removed by precipitation as calcium silicate if a high pH and calcium concentration is maintained [4]. The solubility product for calcium silicate may underestimate the amount of calcium removed due to adsorption of calcium ions onto calcium silicate solids [4]. Kinetic studies of silica removal by the ultra-high lime process found that silica removal was rapid enough to occur in clarifiers designed for conventional lime treatment [4].

Inadequate sulfate removal is a major problem with lime softening treatment of cooling water [4]. If the calcium and sulfate concentrations are sufficiently high, then some sulfate may precipitate as calcium sulfate [4,7]. Since most water systems operate at a pH between 7 and 9, calcium sulfate may form only after all the carbonate is precipitated as calcium carbonate [7]. If additional sulfate removal is required, it may be possible to add aluminum or iron salts to precipitate sulfate as calcium sulfoaluminate or calcium sulfoferrate [4].

Iron oxide and barium sulfate scales may form in the cooling tower, but they are probably not significant because the concentrations of these cations are low in the make-up water [6]. Other possible scales are zinc phosphate (if zinc is used as a corrosion inhibitor), calcium flouride, and iron carbonate [7]. Ions such as sodium, potassium, and chloride are not removed in the softening process [6].

4.3 Limits Established by Others

The following species concentration limits, found in the literature, were used as a guide for establishing limits for the cooling tower simulation in this study.

4.3.1 Calcium and Sulfate

High concentrations of sulfate in the cooling tower can cause the deterioration of concrete basins, and can also produce extremely insoluble scales of calcium sulfate [2]. A rule of thumb to predict the safe upper limit of the calcium and sulfate concentrations is given by Strauss and Puckorius [7]:

$$[Ca^{2+}]x[SO_4^{2-}]=500{,}000 \quad (15)$$

However, they claim that when there are high chloride levels, calcium sulfate solubility can be higher than expected. When chloride levels exceed 5000 ppm, an alternative is to limit calcium hardness to 280 mg/l regardless of sulfate levels.

Matson and Harris [6] cite Klen's [8] extensive pilot test work that demonstrate that if the calcium concentration in the cooling water is maintained below 280 mg/l, calcium sulfate hydrate and anhydrite scale does not form, even with sulfate concentrations as high as 50,000 mg/l.

Exxon [9] recommends a limit on the product of the calcium and sulfate concentrations of $5.77x10^5$ $(mg/l)^2$, and on the contribution of calcium to total hardness of 320 mg/l. This limit may be conservative based on data from power plant wastewater which had between 500 and 1000 mg/l calcium and 25,000 to 50,000 mg/l sulfate without scale formation [10]. For calcium, Exxon recommended that the Langlier Saturation Index (LSI) be limited to approximately one to prevent calcium carbonate scale. The LSI is defined as

$$LSI=pH-pH_s \quad (16)$$

where pH is the measured pH of the water and pH_s is the calculated saturation pH of the water [11]. To calculate pH_s, the calcium, bicarbonate, and TDS concentrations must be known, along with the water temperature. For a pH range between 6.5 and 9.5, the saturation pH is computed as

$$pH_s=pK_{a,2}-pK_{so}+p[Ca^{2+}]+p[HCO_3^-]-\log\lambda_{Ca^{2+}}-\log\lambda_{HCO_3^-} \quad (17)$$

These terms are defined as follows:

1) Benefield et. al. [12] have presented the following equations for computing $pK_{a,2}$ and pK_{so} to account for temperature corrections for the standard K values given at 25°C for $CaCO_3$. The equation for $pK_{a,2}$ is,

$$pK_{a,2}=\frac{2902.39}{T,°K}+0.02379(T,°K)-6.498 \quad (18)$$

and for pK_{so} is,

$$pK_{so}=0.01183(T,°C)+8.03 \quad (19)$$

2) To calculate the activity coefficients for Ca^{2+} and HCO_3^-, the ionic strength must first be determined. An equation was presented by Benefield et. al. [12] to calculate the ionic strength as,

$$I=(2.5x10^{-5})(TDS,mg/l) \quad (20)$$

3) The activity coefficient for Ca^{2+} can be found from either the Güntelberg or Davies approximations. Using the Davies relationship for divalent ions,

$$\log\lambda_D=-(1.82x10^6)[(78.3)(T,°K)]^{-3/2}(2)^2[\frac{I^{1/2}}{1+I^{1/2}}-0.3I] \quad (21)$$

4) Finally, the activity coefficient for $[HCO_3^-]$ was computed from the Davies equation for monovalent ions:

$$\log\lambda_m=-(1.82x10^6)[(78.3)(T,°K)]^{-3/2}(1)^2[\frac{I^{1/2}}{1+I^{1/2}}-0.3I] \quad (22)$$

If there are no scale inhibitors added to the water, a positive LSI means the water is oversaturated with respect to $CaCO_3$, and therefore calcium carbonate will precipitate.

Without scale inhibitors, a negative LSI means the water is undersaturated with respect to $CaCO_3$, and a zero LSI means the water is just saturated with respect to $CaCO_3$. It is possible to achieve some corrosion protection by allowing the LSI to be slightly greater than zero so that a thin film of calcium carbonate will line the pipe walls [11]. A slight supersaturation with $CaCO_{3(S)}$ and high alkalinity also provides the water with pH buffering capacity against CO_2 generated in the distribution systems, by slime growths for example, and prevents corrosion by preventing low pH values from occurring [11]. Shoeyink and Jenkins [11] point out Larson's [13] findings that waters that have a low calcium concentration and a low alkalinity, and thus a low buffer intensity, may require the use of LSI values as high as 1.0 to prevent corrosion. However, Shoeyink and Jenkins [11] cite Stumm's [14] findings that good protective films usually do not form under these conditions; when a high pH was necessary to create a positive LSI, scale formation was not uniform.

4.3.2 Magnesium and Silica

Exxon [9] recommends limiting the magnesium contribution to total hardness to 61 mg/l. Chen, Petrillo and Kaylor [10] indicates that the present day approach is to limit the product of the magnesium and silica concentrations to approximately 8,540 $(mg/l)^2$.

McCoy [2] states that silica should not exceed 150 to 175 ppm in cooling water to avoid forming troublesome silicate scales, which have exceedingly low thermal conductivity [2]. A silica scale 1/100-inch thick, for example, can reduce the overall heat-transfer coefficient of a heat exchanger by 80-90 percent [2]. Data indicate that

silica will not precipitate if its content in water is below 70 mg/l as Si at pH 7, with silica solubility increasing to 93.3 mg/l as Si at pH 8.5 [7]. Exxon recommended limits for silica of 82 mg/l as Si to prevent magnesium silicate scale [9]. A silica concentration limit of 70 mg/l was recommended by Chen, Petrillo and Kaylor [10] to prevent magnesium silicate scale and by Batchelor et. al. [5] to prevent calcium silicate scale.

Amorphous silica exists in the normal cooling water pH range of 6 to 8 units as the uncharged species $Si(OH)_4$. In this pH range, its solubility generally increases with temperature. Matson and Harris [6] cite Cowan and Weintritt [15] who presented a formula for silica solubility (mg/l as SiO_2):

$$SiO_2=(4.7)(T,^{\circ}C)+24 \qquad (23)$$

At 9.5°C, this gives a silica concentration of 69 mg/l as SiO_2 (32 mg/l as Si).

4.3.3 Phosphate

The total phosphorus limit recommended by Exxon was 0.15 mg/l as PO_4 to avoid heat exchanger scaling [9]. Calcium phosphate scale is likely when phosphate levels are above 5 mg/l as PO_4, calcium hardness levels are 500 mg/l as $CaCO_3$, and the pH is above 7 [7].

4.3.4 Chloride

Several authors cited Crits and Glover [16] who recommended that the chloride concentration be kept below 2000 and 3000 mg/l for non-stainless and stainless steel pipes, respectively [9,10].

4.3.5 Hydrogen

To achieve adequate silica removal during softening treatment, the pH should be raised to a value between 10.5 and 12.0 [4,5,6]. Acid addition is required to decrease the water pH prior to entering the cooling tower. The pH of the cooling tower water should be reduced below 8 for prevention of calcium carbonate scale [6,9]. Chromate corrosion inhibitors, if used, work best at pH 6.87 to 7.0 [9].

4.3.6 Total Dissolved Solids

High concentrations of dissolved solids increase the ionic strength of the recirculating water, and in some instances this interferes with the formation of protective films, particularly when using an organic treatment. Also, the increase in conductivity is favorable to corrosion. Finally, some microbiocides are rendered innocuous, or inefficient by high concentrations of dissolved solids, which may allow microbial growth in the cooling tower [2].

Exxon recommended a total dissolved solids limit of 3000 mg/l, or 4000 to 5000 mg/l if automatic control equipment is used for scale prevention [9].

A summary of the limits for species concentrations in cooling towers recommended by others is presented in Table 4-1.

4.4 Operational Experiences

Several plants in operation are presented to provide typical ranges for species concentrations and cycles of concentrations obtained in the cooling tower.

TABLE 4-1. Cooling Tower Species Concentration Limits Recommended by Others, mg/l

Species	STUDY 1	2	3	4	5	6
Calcium (as Ca)	320	280	280	280[1]	---[2]	360
Magnesium (as Mg)	61	---	---	---	---	---
Silica (as Si)	82	88[3]	70	70	70	70
Phosphate (as PO_4)	0.15	---	---	4.0	---	---
Sulfate (as SO_4)	1500	50,000	---	---	25,000	---
Chloride (as Cl)	2000[4]	---	---	---	2000[4]	---
HCO_3	50	---	---	---	---	---
Ca x SO_4	$5.77x10^5$	---	---	$5x10^{5}$[5]	$5.77x10^5$	---
Na + K	---	---	---	---	---	---
Total Hardness (as $CaCO_3$)	1050	---	---	---	---	---
TDS	4000	---	5000	---	---	---
Suspended Solids	300	---	---	---	400	---
pH	7.0	---	---	---	---	---

STUDY 1: Exxon Chemical Co., Baton Rouge, Louisiana, 1975
2: Matson and Harris
3: Spear and Matson, 1984
4: Strauss and Puckorius, 1984
5: Chen, Petrillo, and Kaylor, 1975
6: Batchelor, Lasala, McDevitt, and Peacock, 1991

Notes: (1) If Chloride concentration > 5000 mg/l
(2) LSI = 0 to 1
(3) At 35°C
(4) 2000 mg/l for non-stainless steel in the cooling tower, 3000 mg/l for stainless steel
(5) If Chloride concentration < 5000 mg/l

4.4.1 Full Scale Plants in Operation

Two industrial plants in the U.S. which are achieving zero discharge by the lime-soda ash process are the Gaseous Diffusion Plant in Oak Ridge, Tenn., and the Georgia Pacific Petrochemical Plant in Plaquemine, La. Both plants use sidestream softening of the blowdown water by recycling it through the make-up softeners to achieve zero blowdown. This design took advantage of the enhanced softening efficiency which occurs

at the higher recirculating water temperatures of the sidestream flow [6].

For the Gaseous Diffusion Plant, the pH is maintained between 6.4 and 6.5 to minimize calcium carbonate scale, with the potential for calcium sulfate scale closely monitored [6]. The raw water is obtained from the Clinch River with 200 mg/l total dissolved solids (TDS), and the cooling tower TDS was measured at approximately 4800 mg/l TDS [3]. Another plant using sidestream softening is the Cool Water Plant of Southern California Edison Co. in Daggart, California. The cooling tower water was expected to run at 15,000 mg/l TDS, but was actually running at 3000 mg/l TDS due to less evaporation than expected [6].

Maguire, Harpel, and Carter [17] presented some experiences that plants in operation had with reusing various waste streams of blowdown water as boiler and cooling system make-up water. The cases of two southwestern refineries were presented, each using three cooling towers. The highest concentrations obtained for several species were as follows: calcium levels were as high as 324 mg/l, magnesium levels reached 78 mg/l, silica concentrations reached 89 mg/l as Si, phosphate levels were as high as 17 mg/l as PO_4, sulfate levels reached 1845 mg/l as SO_4, chloride levels reached 1340 mg/l, and total hardness levels were as high as 1055 mg/l as $CaCO_3$. The cooling towers used a chromate/zinc/polyphosphate corrosion inhibitor and a phosphonate based deposit control agent as a scale inhibitor.

The operating concentrations of various species for the Gaseous Diffusion Plant, the Georgia Pacific Petrochemical Plant, the Cool Water Plant of Southern California Edison Co., and the Southwestern Refineries are summarized in Table 4-2.

TABLE 4-2. Summary of Cooling Tower Species Concentrations for Plants in Operation, mg/l

Species	PLANT 1	2	3	4	5	6	7	8
Calcium (as Ca)	384	141	146	158	324	106	132	160
Magnesium (as Mg)	126	31	28	29	60	35	56	78
Silica (as Si)	111	50	24	32	63	38	59	89
Phosphate (as PO_4)	---	---	---	---	---	17	14	13
Sulfate (as SO_4)	2345	4500	378	456	1052	1425	1500	1845
Chloride (as Cl)	647	750	510	678	1340	448	692	1050
HCO_3	---	56	---	---	---	---	---	---
Ca x SO_4	---	---	---	---	---	---	---	---
Na + K	---	2648	---	---	---	---	---	---
Total Hardness (as $CaCO_3$)	1478	480	480	516	1055	408	560	720
TDS	4869	8000	---	---	---	---	---	---
Suspended Solids	---	---	---	---	---	---	---	---
pH	6.4	6.5	6.7	6.7	6.7	6.6	6.5	6.7

PLANT 1: Gaseous Diffusion Plant, Oak Ridge, Tenn., 1974 [6]
2: Georgia Pacific Petrochemical Plant, Plaquemine, La., 1977 [6]
3: Southwestern Refinery #1, Tower #1 [17]*
4: Southwestern Refinery #1, Tower #2 [17]*
5: Southwestern Refinery #1, Main Tower [17]*
6: Southwestern Refinery #2, Tower #1 [17]*
7: Southwestern Refinery #2, Tower #2 [17]*
8: Southwestern Refinery #2, Tower #3 [17]*

* Chromate/Zinc/Polyphosphate used for corrosion inhibitor; Phosphate-based deposit control agent used for scale inhibitor.

4.4.2 Pilot Plant Scale Tests

Matson and Harris [6] presented a pilot plant scale test performed by Arco Polymers, Inc. in which they used carbon dioxide instead of sulfuric acid for pH control to minimize total dissolved solids in the system. Carbon dioxide must be added in excess because it is stripped out in the cooling tower. The economic tradeoffs between carbon dioxide and sulfuric acid appear to be higher chemical costs for the carbon dioxide versus potentially lower corrosion and scaling rates in the heat-transfer system because of the

lower dissolved solids level. The total dissolved solids level in the cooling water using carbon dioxide was 4300 mg/l compared to the calculated value of 8923 mg/l for pH control by sulfuric acid.

Nalco Chemical Co. also operated a test unit at very high dissolved solids levels [6]. A description of the pilot plant test was not available, but the average cooling water quality was included for comparison with other tests.

Kluesener, Heist, and Van Note [18] presented results from a pilot plant scale test for using Phoenix Wastewater Treatment Plant effluent for the Palo Verde Nuclear Generating Station cooling water. A lime/soda ash treatment system was used to treat the effluent. Based on the chemical reactions which take place in the water, they state that by adding a biological treatment step ahead of the lime-treatment plant, it is possible to reduce the ammonium concentration and, therefore, the alkalinity upstream of the lime clarifier. This reaction results in a substantial reduction in the lime demand, which in turn decreases the solids produced. Biological nitrification should reduce the total solids produced and the lime demand by approximately 50% each. Their lab tests showed that the magnesium removed to silica removed was approximately 90:13, which agreed with a Mg:Si ratio of 7:1 reported in the literature. They set the maximum calcium concentration in the cooling tower at 420 mg/l. The maximum magnesium concentration in the cooling tower was set at 36 mg/l, the silica limit was set at 150 mg/l as SiO_2 (70 mg/l as Si), and the phosphate limit was set at 0.5 mg/l as PO_4. The pH of the second stage was controlled between 9.8 to 10.3. An average of 138 mg/l of soda ash was added in the second stage to reduce the calcium concentration to 70 mg/l. However, calcium removal was sometimes inadequate despite high levels of soda ash addition.

They thought that this may have been caused by the complexation of calcium with dissolved organics or inorganics in the wastewater. Silica removal increased as the suspended solids concentration increased up to a suspended solids concentration of 10,000 mg/l. Above this value, the silica removal leveled off. The pH of the effluent from the lime-soda ash system was reduced to a value between 9.2 and 9.4. Sulfuric acid was used instead of carbon dioxide to minimize the bicarbonate alkalinity of the cooling tower water, with a filter downstream of the neutralization step. This pilot scale test plant demonstrated that 15 cycles of concentration can be achieved in the cooling tower with the concentration limits stated above using a two stage lime/soda ash treatment system.

A summary of the species concentrations achieved or limits used for the pilot plant scale tests performed by Arco Polymers, Inc., Nalco Chemical Co., and Pheonix Wastewater use for the Palo Verde Nuclear Generating Station are presented in Table 4-3.

4.5 Cost Comparisons of Lime Treatment Processes

Batchelor and McDevitt [4] performed a cost analysis comparing the high lime treatment to the ultra-high lime treatment. They used lime softening stoichiometry to calculate the lime doses required. They obtained the chemical costs from the Chemical Marketing Reporter [19]: Lime (CaO)=$0.044/kg, Soda Ash=$0.26/kg, and Magnesium=$1.32/kg. They determined that the ultra-high lime process was less expensive than the high lime process as shown in Table 4-4.

Spear and Matson [3] developed a computer model to compare the economics of sidestream softening with a conventional cooling water system with blowdown. The program logic involved determining the softener flow rates from make-up water quality

TABLE 4-3. Summary of Cooling Tower Species Concentrations for Pilot Plant Scale Tests, mg/l

Species	STUDY 1	2	3
Calcium (as Ca)	420	200	116
Magnesium (as Mg)	36	61	12
Silica (as Si)	70	---	20
Phosphate (as PO_4)	0.5	---	---
Sulfate (as SO_4)	---	33,800	1239
Chloride (as Cl)	---	12,136	1498
HCO_3	---	61	299
Ca x SO_4	---	---	---
Na + K	---	23,690	1342
Total Hardness (as $CaCO_3$)	---	1000	341
TDS	---	70,000	4300
Suspended Solids	---	---	---
pH	---	6.0	7.1

STUDY 1: Limits used during Pilot plant scale test for using Phoenix Wastewater Treatment Plant Effluent for the Palo Verde Nuclear Generating Station cooling water [18]
2: Nalco Chemical Co., 1976 [6]
3: Arco Polymers, Inc., 1974 [6]

and cooling-tower parameters. Removal of calcium and magnesium hardness was assumed to be 80-90% complete in the softening loop. Chemical dosages were then determined based on stoichiometric requirements. Water quality was then determined from mass balance equations. The total cost for the sidestream system comprised of chemical expenses, labor, maintenance, power, capital depreciation (20-year straightline), sludge disposal, make-up water, and make-up treatment costs. The labor, maintenance, power, and depreciation were considered as simple functions of the capital cost, which itself was projected by a "six-tenths-factor" formula. The cost of the system with blowdown was simply the sum of the chemical, make-up water, make-up treatment,

TABLE 4-4. Summary of Preliminary Cost Estimates

System	Cost ($/yr)
Low quality make-up water (high concentrations)	
Ultra-high lime	1.15×10^6
High lime	
with soluble Mg	2.07×10^6
with MgO	1.40×10^6
High quality make-up water (low concentrations)	
Ultra-high lime	2.09×10^5
High lime	
with soluble Mg	3.13×10^5
with MgO	2.32×10^5

and effluent treatment costs. For the sidestream system, Spear and Matson [3] limited the recirculating water quality to 5000 mg/l TDS, with maximum calcium concentrations of 280 mg/l and silica limits of 70 mg/l as Si. Without softening, they note that the TDS limit would have been 2000 mg/l due to the higher concentration of calcium in solution. Spear and Matson [3] hypothetically increased the raw water cost, calcium, and silica concentrations separately. The sidestream to blowdown costs were then compared. They found that when the make-up water cost exceeded $0.65/1000 gal, sidestream treatment became economically viable. As make-up water calcium concentrations rose above 110-125 ppm as $CaCO_3$ and silica exceeded 40-50 ppm as SiO_2, sidestream softening became favorable.

Batchelor et. al. [5] conducted a set of experiments to evaluate the technical and economic feasibility of the ultra-high lime process for treating recycled cooling water.

These experiments used a bench-scale, continuous flow reactor system with automatic control of pH and flow. Results showed that approximately 75% of the costs for the optimum treatment technique were lime costs. The cost of the ultra-high lime treatment was found to be approximately $0.5 million per year using a combined make-up/sidestream softening configuration and an average make-up water quality as shown in Fig. 4-1. This compares with $2.7 million per year for make-up softening only. They also found that the ratio of estimated costs for the ultra-high lime treatment to high lime treatment was approximately 0.3 for average make-up water quality with make-up softening only as shown in Fig. 4-2.

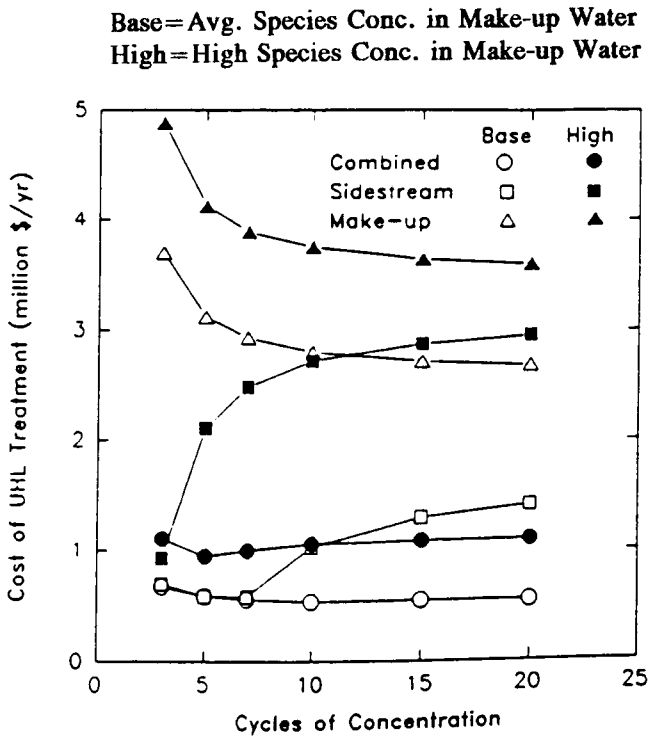


Fig. 4-1. Estimated Cost of Ultra-High Lime Process in Various Configurations as Functions of Cycles of Concentration (After Ref. [5])

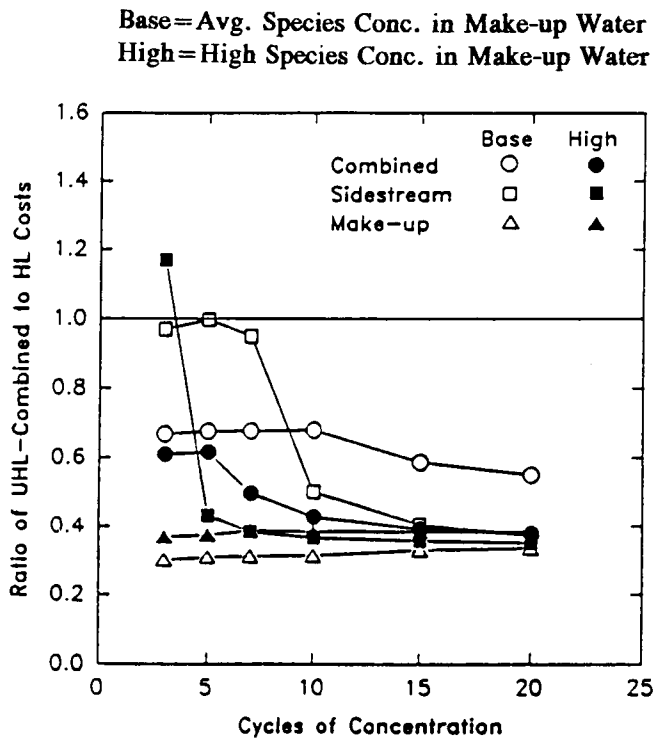


Fig. 4-2. Ratio of Estimated Costs of Ultra-High Lime Process in Combined Configuration to Cost of High Lime Process in Various Configurations as Functions of Cycles of Concentration (After Ref. [5])

CHAPTER 5

MINTEQ COMPUTER CODE

5.1 MINTEQ Geochemical Model Description

The MINTEQ computer code [1] is a geochemical model which can simulate the contact of aqueous solutions with solid phases or it can perform simple ion speciation/solubility, adsorption, oxidation-reduction, gas phase equilibria, and precipitation/dissolution of solid phases. The thermodynamic data base for the MINTEQ code was taken from the WATEQ3 code which was developed by the United States Geological Survey (USGS) [20-22], and it was expanded to include many more aqueous species and solids. The MINTEQ code can also recompute the pH and pe (negative log of electron activity) as the solution composition changes in response to aqueous speciation, precipitation, and dissolution of solid phases. A modified form of the electroneutrality condition (proton condition) is used to calculate the pH, and the pe is calculated by initializing the mass totals for each oxidation state of an element and including a redox reaction between the components of each oxidation state. Adsorption reactions can also be modeled using one of several adsorption algorithms available in the MINTEQ model.

There are basically four submodels which make up the MINTEQ code. The first submodel simulates speciation, the second one simulates solubility, the third one simulates mass transfer, and the fourth one simulates adsorption. The submodels for speciation and solubility are interrelated and will be discussed together in the next section.

5.2 Ion Speciation/Solubility Calculations

In the speciation submodel the activities of complexed and uncomplexed cationic and anionic species, neutral ion pairs, and cationic and anionic redox species are calculated. These activities are then used in the solubility submodel to perform solubility calculations to determine the ion activity products of solids and minerals. A saturation or disequilibrium index is computed by comparing the ion activity product with the solubility product (K) in MINTEQ's data base (log (activity product/solubility product)). Oversaturated conditions occur, with respect to a particular solid phase, if the saturation index is less than zero. The oversaturated condition is usually explained by precipitation kinetics and/or mineralogical factors that prevent the solid from precipitating at a rate sufficient to control the concentrations of its dissolved components. For undersaturated conditions, the saturation index will be less than zero. Undersaturation could result if one of three circumstances exists: 1) a less soluble solid is controlling the dissolved constituents' concentrations, 2) another mechanism, such as adsorption, is controlling the concentrations of the component species below their solubility products, or 3) the constituents' concentrations in the source are lower than that at which the solid phase would control. The activity coefficient corrections used in calculating the activity products are based on either the extended Debye-Huckel equation with two adjustable parameters [20] or, alternatively, the Davies equation [23].

5.3 Mass Transfer Calculations

The results from the solubility submodel are fed into the mass transfer submodel to determine the mass of solids which precipitates or dissolves. If the solubility submodel

indicates that a solution is oversaturated with respect to a solid phase, then the mass transfer model will precipitate the solid phase until the saturation index equals zero, which indicates that the solution is at equilibrium with the solid. For an undersaturated solution, the mass transfer model will dissolve the solid until the solution and the solid are in equilibrium or the mass of the solid completely dissolves. This equilibrium state is computed in MINTEQ as a single step, not as a reaction path where the solid is slowly "titrated" in small incremental steps until equilibrium is reached. Although reaction path codes such as EQ6 [24] can provide information on what stage in the progress of a reaction these solids precipitated or dissolved and under what conditions, it is sufficient in most cases that the final equilibrium state is given in a "single-step" code like MINTEQ.

5.4 Geochemistry Used in the MINTEQ Computer Model

The fundamental principles of thermodynamics is used in MINTEQ to solve the geochemical equilibria equations. The MINTEQ model can simulate systems which can exchange both energy and material (open systems) or just energy (closed systems) with the surrounding environment. Distinct chemical entities form various components which exist in either the solid, liquid, or gaseous form. A particular set of components are defined in the MINTEQ data base and are usually defined in their simplest form of cations or anions (e.g., Ca^{2+}, Na^{+}, Cl^{-}, CO_3^{2-}, SO_4^{2-}), unless the bare ion is not the dominant aqueous species over the normal pH range of the water (e.g., H_4SiO_4 is used in place of SiO_4^{4-}).

The number of system variables which can be independently varied (i.e.,

temperature, pressure, and the masses of each of the components) will determine the number of degrees of freedom of the system. In the MINTEQ code, the temperature and pressure is fixed, so the number of degrees of freedom is:

$$f=c_n-p \tag{24}$$

where f is the number of degrees of freedom, c_n is the number of components, and p is the sum of the number of Type III species with fixed activity and Type IV finite solid species. Each solid phase present removes one degree of freedom from the system (i.e., the concentration of one component), thus simplifying the computation of multicomponent equilibria.

To compute the geochemical equilibria in MINTEQ, the total mass of each component must be distributed among the various solid phases, surface sites, and aqueous ion-complexes using equilibrium thermodynamic relationships. A typical reaction is

$$v_{xz}x+v_{yz}y=z \tag{25}$$

where x and y are components in the aqueous phase and z is either an aqueous-phase ion complex or a solid phase, and v_{xz} and v_{yz} are stoichiometric coefficients for components x and y of phase z, respectively. The reaction has the corresponding equilibrium relationship

$$[S_i]=\frac{K_i}{\lambda P_i X_j^{a_{ij}}} \tag{26}$$

where:

$[S_i]$ = molarity of species i

K_i = equilibrium constant for the formation of species i

λ_i = activity coefficient of species i

P_i = indicates the product over all components in species i

X_j = activity of component j

a_{ij} = stoichiometric coefficient of component j in species i

The product (symbolized by P_i) is taken over all components. The thermodynamic activity of a component is based on the difference in chemical potential between the component in solution and the component in its standard state. The standard state in MINTEQ is an infinitely dilute solution of the component in water. The thermodynamic activity of each component, which is a measure of the chemical driving force of a particular component in reaction, is related to the concentration by an activity coefficient. The activity coefficients for solute components in MINTEQ are calculated either from the Davies equation or the extended Debye-Huckel equation, and the activity of water is calculated using an approximation to Raoult's law.

If the component is distributed among various ion-complexes, then an additional correction to the thermodynamic activity must be computed according to the equilibrium relationships. This calculation forms the speciation portion of MINTEQ.

The equilibrium constants in the thermodynamic data base of MINTEQ is given for a temperature of 25°C. The temperature dependence of the equilibrium constant for each reaction is also given, generally through the integration of the heat capacity difference function from 25°C to the temperature of interest. For some reactions, the heat capacity difference is assumed to be constant and the Van't Hoff equation is used to

temperature correct the equilibrium constant. If no thermodynamic data exists to allow for a temperature correction, the equilibrium constant is assumed to be temperature independent.

Water, hydrogen, and electrons are treated somewhat differently than the other components in an aqueous solution. Since water has at least 104 times more moles in solution than any of the major dissolved constituents, the mass of the water is considered a constant for the system. Thus, no mass balance equation for water is used even though it is involved in reactions.

If the equilibrium pH is known, the mass balance can be ignored since the hydrogen is measured in terms of its activity ,i.e. pH, instead of its mass. In this case, the activity of hydrogen is assumed to be fixed at the known equilibrium pH. If the equilibrium pH is not known, such as when lime is added to water, then the total mass of the ionized hydrogen can be computed using charge balance and using the mass total for hydrogen. The final pH can then be calculated based on the free hydrogen ion concentration.

CHAPTER 6

DESCRIPTION OF GENERAL MOTOR'S SATURN COOLING TOWER

The General Motors Saturn Automobile manufacturing plant, located in Spring Hill, TN, was used as a basis for studying the economic feasibility of the lime softening treatment process for industrial cooling water systems. The following is a description of Saturn's cooling tower, the source of the make-up water, current treatment processes, cooling tower design and operation, blowdown water disposal, and cooling tower control parameters for scale prevention.

6.1 Make-up Water Supply and Treatment

Saturn's current process uses make-up water supplied by the city water treatment plant. A water analysis report of the Saturn cooling tower make-up water quality was performed by the Dexter Corporation and was presented by Barnett [25]. This water quality analysis was the most comprehensive one available and therefore it was also used for this study. It is presented in Table 6-1, along with the corresponding species identification numbers used for the MINTEQ inputs.

Saturn is not currently softening its make-up water [26]. Scale inhibitors are added to the water upstream of the cooling tower. The scale inhibitors used include digestive and organic phosphates, called phosphonates. The digestive phosphate level is maintained at 2.0 to 3.5 ppm, and the organic phosphate level is maintained at 3.5 to 4.5 ppm [27]. These phosphonates are not equivalent to phosphates and cannot be modeled in MINTEQ. However, their effect of inhibiting scale formation for LSI's will be taken into account

Table 6-1. Saturn Cooling Tower Make-up Water Quality Analysis

Species	Make-up Water Species Concentrations (mg/l)	MINTEQ ID Number
Silica	0.4	770[1]
Total Organic Carbon	15.4	---[2]
Total Dissolved Solids	223.2	---
Sulfate	58.0	732
Chloride	10	180
Carbonate	1.0	---[3]
Bicarbonate	142.4	---[3]
Nitrogen-Nitrate	0.8	492
Fluoride	1.0	270
Phosphates, Total	0.4	580
Hardness (as $CaCO_3$)	118.0	---
Alkalinity (as $CaCO_3$)	144.0	140
Calcium	64.0	150
Magnesium	5.6	460
Iron	0.006	281[4]
Manganese	<0.005	470[4]
Beryllium	<0.001	110[4]
Copper	0.14	231
Nickel	<0.005	540[4]
Aluminum	0.32	030
Sodium	12.8	500
Potassium	1.3	410
Antimony	<0.005	740[4]
Cadmium	<0.005	160[4]
Chromium, Total	<0.005	210[4]
Lead	0.008	600[4]
Mercury	<0.0002	360[4]
Selenium	<0.001	762[4]
Silver	<0.005	020[4]
Thallium	<0.005	870[4]
Zinc	<0.005	950[4]
Arsenic	<0.001	060[4]
pH	7.8	---

Notes: (1) Input as 38.4 mg/l H_4SiO_4
(2) Total Organic Carbon was not input in MINTEQ because it would have been interpreted as inorganic carbon.
(3) Carbonate and Bicarbonate input as Alkalinity
(4) Not input due to negligible concentrations

in this study.

6.2 Cooling Tower Design and Operation

The cooling tower was designed to cool 110,000 gpm of water from 96°F to 85°F at a wetbulb temperature of 79°F [27]. During normal operation, the cooling tower is not run at 100% capacity. The maximum amount of cooling during normal operation is approximately 24,000 tons, which requires a recirculation rate of 75,000 gpm [26]. The average recirculation rate in the cooling tower is approximately 55,000 gpm in the summer and 27,000 gpm in the winter [26,27], with a typical ΔT of 10°F [26]. The evaporation rate is a function of the recirculation rate and the water temperature change which occurs in the cooling tower. For this study, the cost comparisons will be based on a recirculation rate of 55,000 gpm at a tower ΔT of 10°F.

The cooling tower basin water level is maintained at 140 inches. Make-up water is intermittently pumped into the basin to maintain this level [28].

6.3 Blowdown Water Disposal

Saturn currently disposes the blowdown water directly into the city sewage system [26]. On-site disposal onto Saturn owned wetlands will also be evaluated in this study.

6.4 Cooling Tower Control Parameters for Scale Prevention

To prevent the formation of calcium carbonate scale, the Langlier Saturation Index (LSI) is used as a control parameter. For the scale inhibitors which Saturn is currently adding to the make-up water, it is possible for the LSI to reach a level as high as

approximately 3.5 without undesirable scale formation occurring in the cooling system. To allow for a margin of safety, the LSI is controlled in the Saturn cooling tower to a value between 2.0 and 3.0 [26].

The magnesium concentration limit which Saturn currently allows is a function of the calcium concentration, where the magnesium carbonate-to-calcium carbonate ratio is not allowed to exceed 20/80 [26].

The cooling water currently operates at a pH value of 8.3 to 8.5. The city water has a typical pH of 6.9 to 7.2, and increases to a pH of 8.4 in the cooling tower due to the 3 to 4 recycles which take place. A pH of 8.3 to 8.5 allows for corrosion protection by the formation of a thin film of calcium carbonate on the surfaces [26]. Saturn does not let the pH decrease below 8.3 to avoid the need of adding chromate as a corrosion inhibitor to prevent pitting. Adding chromate would require removing it from the blowdown water prior to discharge into the sewage system. Sulfuric acid addition is currently used in the cooling tower for pH control.

The M-alkalinity level is controlled between 140 to 240 ppm as $CaCO_3$, and the p-alkalinity is controlled between 10 to 40 ppm as $CaCO_3$ [27]. However, these limits are not exceeded under normal operating conditions.

CHAPTER 7

METHODOLOGY FOR COST DETERMINATION

7.1 Determining Chemical Feed Rates and Cycles of Concentrations

Chemical feed rates for lime and soda ash were systematically increased, with the chemical feed rate for sulfuric acid and the cycles of concentrations for each lime/soda ash combination being determined. The process for determining the sulfuric acid addition required and cycles of concentration obtainable involved several iterations using the MINTEQ model. First, lime was added to the make-up water. If further reduction in the calcium concentration was required, soda ash was also added to the clarifier with the lime. The possibility of using carbon dioxide instead of soda ash was also evaluated. However, a closed system was desired to simulate clarifier operation such that the CO_2 gas added would not equilibrate with the atmosphere. Since MINTEQ does not accommodate the addition of a gas in a closed system, a special procedure was used. The carbon dioxide added would combine with oxygen from a water molecule to form carbonate, freeing the two protons from the water molecule. Therefore, to simulate carbon dioxide addition in a closed system, one mole of carbonate and two moles of hydrogen were added to solution for each mole of carbon dioxide addition desired. A first guess of the maximum cycles of concentration was made and the effluent of the clarifier was multiplied by this cycles of concentration to simulate the species concentration in the cooling tower. An open system was used to simulate the cooling tower, allowing CO_2 in solution to equilibrate with the atmosphere based on its partial pressure. Also, no solids were allowed to form in the cooling tower simulation since the

limits presented in Section 7.3 were used to determine acceptable species concentrations in the cooling tower. The results of the cooling tower simulation provided the cooling tower water pH. The process of adding sulfuric acid to the effluent of the clarifier and simulating the same cycles of concentration was repeated until the cooling tower water pH was 8.4. Then, a new cycles of concentration was guessed and the process was repeated until a species concentration limit was reached. This provided the cycles of concentration obtainable for this lime/soda ash combination and the amount of sulfuric acid required.

Sulfuric acid was used instead of hydrochloric acid for pH control since it is cheaper than hydrochloric acid and it is easier to store. Hydrochloric acid gives off fumes which makes storage difficult and potentially hazardous. Sulfuric acid is usually used in industry because it is safer, even though it may increase the sulfate concentration in the cooling tower water to the point where calcium sulfate scale will form, limiting the cycles of concentration attainable.

7.2 Costs Associated with the Softening Process

7.2.1 Make-up Water Costs

The make-up water for the Saturn cooling tower is being supplied by the city of Columbia public water supply. The Columbia Power and Water Company [29] provided the water cost rates for industrial usage for companies outside the city limits, which is applicable to the Saturn plant, and are given in Table 7-1. Saturn is currently averaging a water cost rate of approximately $0.92/1000 gallons [26].

Table 7-1. Columbia Water System Water Rate Schedule

Gallons/Month[1]	Rate ($/1000 Gallons)[2]
0-50,000 Gallons	1.32
50,001-500,000 Gallons	1.21
500,001-1,000,000 Gallons	1.03
1,000,001-45,000,000 Gallons	0.66
Over 45,000,000 Gallons	0.53

Notes: (1) A customer charge of $25.00/month is also required for all customers.
(2) A charge of five cents per 1,000 gallons of water used is included in the above rates to defray the City of Columbia's share of the Dam System on the Duck River.

7.2.2 Blowdown Water Disposal Costs

The cost paid by Saturn for disposing the blowdown water into the city sewage system is currently $1.51/1000 gallons [26], which is the rate that was used in this thesis. This is lower than the standard industrial rate of $2.50/1000 gallons charged by the city for industries in general [29]. Total costs were also estimated using on-site disposal of the blowdown water onto wetlands owned by Saturn. On-site disposal costs were assumed to be negligible for this study. Both disposal methods were considered since on-site disposal will be less expensive but under worst case conditions, the blowdown water may not meet the irrigation water quality standards for wetlands disposal.

7.2.3 Sludge Disposal Costs

For sludge disposal into a landfill, the sludge produced in the lime and soda ash clarifiers can be disposed of by the Browning-Ferris Industries (BFI) at a cost of $225/truck load, where each truck has a capacity of 20 yd^3 (15.29 m^3) [30]. This cost

includes both shipping and disposal of the sludge into a non-hazardous landfill by BFI, and was used for the cost analysis in this study. No free liquids are allowed when disposing of this sludge, so a filter press is required for dewatering the sludge prior to disposal. As with the blowdown water, the total costs were also estimated for on-site disposal of the sludge onto wetlands owned by Saturn. On-site disposal costs of the sludge were assumed to be negligible for this study.

7.2.4 Chemical Costs

The chemical costs for the lime, soda ash and sulfuric acid when purchased in bulk are given in Table 7-2 [31].

Table 7-2. Chemical Costs

Chemical	Cost[1]	Cost[2]
Lime, hydrated, $Ca(OH)_2$	$56.50/ton	$0.0623/kg
Sodium Carbonate, monohydrated bags, Na_2CO_3[3]	542.00/ton	0.7045/kg
Sulfuric Acid, H_2SO_4, virgin, 100% tanks, East Coast	75.00/ton	0.0827/kg

Notes: (1) This is the average cost as shipped and was calculated based on the price range given in the *Chemical Marketing Reporter*. This cost may not be the pure chemical cost since the chemical is sold in diluted form.
(2) Pure chemical cost.
(3) 84.8% Na_2CO_3 by weight.

7.2.5 Construction, Operation and Maintenance Costs

The construction, operation and maintenance costs for the treatment system was calculated using the EPA cost estimating approach [32]. The EPA estimated the cost of treatment plants ranging in size from 1 to 200 mgd in October 1978 dollars. The

construction and maintenance material costs in May 1993 dollars were calculated by assuming that the costs increased in proportion to the consumer price index. The consumer price index rose from 67.1 in October, 1978 to 144.2 in May, 1993, or an increase of 114.9% [33]. Therefore, the construction and maintenance material costs for May 1993 was also assumed to increase 114.9% over the EPA's October 1978 figures.

The possible hardware requirements for the chemical treatments included clarifiers for the hydrated lime and soda ash additions, the chemical feed systems, a rapid mix unit for each clarifier, the flocculation systems, and the filter press for sludge dewatering. Rectangular clarifiers were arbitrarily chosen over circular clarifiers for this thesis. The construction costs for rectangular clarifiers are more expensive than for circular clarifiers, but the flocculator systems are less expensive. A description of the hardware and operation requirements for each subsystem and the EPA cost estimating approach can be found in Ref. 44.

7.2.6 Power and Labor Rates

The Saturn plant purchases its electricity directly from TVA at the approximate rate of 3.8 cents/kw-hr for firm power and approximately 2.4 cents/kw-hr for interruptible power [34]. The firm power rate will be used for the cost analysis in this study.

The average labor costs used in the EPA study in October 1978 dollars was $10.00/hr. Based on the increase in the consumer price index of 114.9%, the labor rate in May 1993 dollars was calculated to be $21.49/hr.

7.3 Establishing the Maximum Concentration Limits in the Cooling Tower

Limits for the cooling tower water species concentrations for this study were established according to current limits used by Saturn if available. For those species for which Saturn has not established limits, the limits were set based on plants in operation, pilot plant scale tests, and limits recommended by others as was summarized in Tables 4-1 through 4-3.

The calcium concentration in the cooling tower was controlled by limiting the LSI to 3.0, which is consistent with Saturn's current operation.

The magnesium concentration in the cooling tower was controlled by limiting the magnesium carbonate-to-calcium carbonate ratio to 20/80, which is consistent with Saturn's current operation.

Strauss and Puckorious [7] suggested that if the calcium concentration is over 500 mg/l as $CaCO_3$, a phosphate concentration as low as 5 mg/l may cause scale. Although this is less than operating experiences which range from 6.5 mg/l (Table 4.10-1) to 17 mg/l (Table 4.10-2), a conservative limit of 4.0 mg/l will be set. The phosphate limits recommended by the Exxon Chemical Co. of 0.15 mg/l as PO_4 [9] and the limits used in the study of the Palo Verde Nuclear Generating Station cooling water of 0.5 mg/l as PO_4 [18] were so much lower than the levels being obtained in operating plants, these limits were deemed too low. Therefore, a level of 4.0 seems reasonable for this study.

A silica concentration limit of 70 mg/l as Si was chosen since it was recommended by many sources which include Spear and Matson [3], Strauss and Puckorius [7], Chen, Petrillo and Kaylor [10], Batchelor et. al. [5], and the study performed for the Palo

Verde Nuclear Generating Station [18]. It is also only slightly less than the limits recommended by Exxon of 82 mg/l [9] and Matson and Harris of 88 mg/l [6]. It is within the range observed in operating plants whose silica concentrations ranged from 24 to 111 mg/l (Table 4-2).

The sulfate limit used was based on the limit recommended by the Exxon Chemical Company [9] and by Chen, Petrillo and Kaylor [10], in which the product of the calcium and sulfate concentrations should not exceed 5.77×10^5 $(mg/l)^2$. This limit is also in close agreement to that proposed by Strauss and Puckorius [7] of 5×10^5 $(mg/l)^2$. It was also much less than the recommended sulfate limits of Matson and Harris of 50,000 mg/l [6] and Chen, Petrillo and Kaylor of 25,000 mg/l [10].

The chloride limit was based on Crits and Glover [16] who recommended a chloride concentration of 2000 mg/l for non-stainless steel pipes in the cooling tower. This was the same limit recommended by Exxon [9] and Chen, Petrillo and Kaylor [10].

The pH was set at 8.4 based upon Saturn's current operation [26]. This provides for corrosion protection without the need for a corrosion inhibitor being added, and it also provides for a highly undersaturated condition in the cooling tower prior to recycling.

The limit for the sum of the sodium and potassium ions was set at 2648 mg/l, since this level was achieved during operation of the Georgia Pacific Petrochemical Plant [6]. This may not reflect an upper limit, but due to the lack of definition and concern in the literature, this limit was deemed sufficient for this study. Since the sodium and potassium concentrations in the cooling tower were low, this limit was not a factor in the cycles of concentration obtainable.

A total dissolved solids limit of 4000 mg/l was chosen based on Exxon's [9] recommendations. It is also similar to Spear and Matson's [3] recommendation of 5,000 mg/l, and is conservative compared to the levels being obtained in plants in operation which range from 4300 to 8000 mg/l (Table 4-2). The Nalco pilot plant [6] was not considered because its TDS level of 70,000 mg/l was not consistent with the other data.

The concentration limits which were used for the cooling tower water are summarized in Table 7-3.

Table 7-3. Species Concentration Limits in the Cooling Tower Chosen for this Study

Species	Limit	Source
Ca, CO_3	LSI=3.0	Saturn [26]
$MgCO_3/CaCO_3$	0.25	Saturn [26]
Silica (mg/l as Si)	70*	Spear and Matson [3], others
Phosphate (mg/l as PO_4)	4	Strauss and Puckorius [7]
Chloride (mg/l as Cl)	2000	Crits and Glover [16]
Ca x SO_4	5.77×10^5	Exxon Chem. Co. [9]
Na + K	2648	Georgia Pacific Petrochemical Plant [6]
TDS (mg/l)	4000	Exxon Chem. Co. [9]
pH	8.4	Saturn [26]

* Corresponds to 239 mg/l H_4SiO_4

CHAPTER 8

RESULTS AND DISCUSSION

8.1 Evaluation of the Saturn Cooling Tower Make-up Water Analysis

Prior to the cost analysis which was performed, the make-up water analysis supplied by Saturn was first evaluated by simulating these species concentrations in MINTEQ. The model should have predicted no precipitates since all the species in the water analysis were dissolved. This was not the case, for the model determined that several precipitates formed as shown by Table 8-1.

Table 8-1. Precipitates Predicted by MINTEQ from Saturn's Make-up Water Analysis

Component Species	Solid Formed*	Percent Precipitated in MINTEQ	Precipitated Amount in MINTEQ, mg/l	Dissolved Amount in MINTEQ, mg/l
H_4SiO_4	Quartz, Leonhardite	86.1	33.1	5.3
Ca^{2+}	Leonhardite, Hydrapatite, Calcite	1.9	1.2	62.8
Al^{3+}	Leonhardite	100.0	0.32	0.0
PO_4^{3-}	Hydrapatite	98.2	0.39	0.01
CO_3^{2-}	Calcite	0.6	0.5	85.8

*Chemical Formulas: Quartz = SiO_2
Leonhardite = $Ca_2Al_4H_{14}Si_8O_{31}$
Hydrapatite = $Ca_5(PO_4)_3OH$
Calcite = $CaCO_3$

There may be several reasons why the MINTEQ model predicted these precipitates to form. One reason may be the reaction was thermodynamically stable, and therefore MINTEQ predicted that the solid will form, even though the kinetics of the reaction may

be too slow to allow its formation in the actual water. For example, the kinetics for Quartz formation is so slow, the reaction time is not presented in the chemical properties by Snoeyink [11]-only amorphous silica dioxide is given. Another reason for precipitates forming in MINTEQ but not in the actual water may be that the solubility products in the MINTEQ model may be too low since they represent typical average values.

To best simulate the actual water, the solids which were predicted to form in MINTEQ (Table 8-1) were excluded from possible solids in the MINTEQ model since they did not form in the actual water. The model was rerun with these solids being excluded, and the results showed that additional solids were predicted to form. The process of excluding the solids which formed in MINTEQ and rerunning the simulated make-up water was continued until no solids precipitated. A summary of all the species which were excluded from precipitating are presented in Table 8-2.

Not included in the excluded solids were calcite ($CaCO_3$) and hydrapatite ($Ca_5(PO_4)_3OH$), even though they were predicted to precipitate. These solids were not excluded because they would precipitate readily in the actual lime softening process. Since only two percent of the calcium was predicted to precipitate in forming these solids, and the phosphate concentrations in the actual water were low, the impact of these solids forming prior to the softening process was considered negligible. By including these species as possible solids, their effect on chemical equilibrium after precipitation in the clarifier could be maintained.

After excluding the solids presented in Table 8-2, there still remained a sufficient number of solids in the MINTEQ data base to simulate the softening process. The remaining solids in the MINTEQ data base included six aluminum silicate species, two

Table 8-2. Solids not Allowed to Precipitate in the MINTEQ Model

Excluded Solids	Chemical Formula
Quartz	SiO_2
Leonhardite	$Ca_2Al_4H_{14}Si_8O_{31}$
FCO3apatite	$Ca_{9.496}Na_{0.36}Mg_{0.144}(PO4)_{4.8}(CO3)_{1.2}F_{2.48}$
Diaspore	AlOOH
Pyrophyllite	$Al_2H_2Si_4O_{12}$
Kaolinite	$Al_2H_4Si_2O_9$
Cristobalite	SiO_2
Chalcedony	SiO_2
Muscovite	$Al_3KSi_3O_{12}H_2$
Microcline	$AlKSi_3O_8$
Halloysite	$Al_2H_4Si_2O_9$
Laumontite	Al_2CaSiO_4
H Sanidine	$AlKSi_3O_8$
Low Albite	$AlNaSi_3O_8$
Gibbsite	$Al(OH)_3$
Boehmite	$AlHO_2$
Analcime	$AlNaH_2Si_2O_7$
Analbite	$AlNaSi_3O_8$
Al4(OH)10SO4	$Al_4(OH)_{10}SO_4$
Alunite	$AlK(SO_4)_2(OH)_6$
Leucite	$AlKSi_2O_6$

aluminum sulfate species, eleven calcium silicate species, two calcium sulfate species, seven magnesium silicate species, and one magnesium sulfate species.

8.2 Temperature Effects on Species Solubility

The solubility of many species is a function of the water temperature. When the water in the cooling tower enters the heat exchanger, the water increases in temperature. This may cause some species which were dissolved in solution upstream of the heat exchanger to form precipitates in the heat exchanger pipes. The recirculation water

temperature was reported to be 9.5°C for a Saturn water analysis taken in November, and was considered near the lower range of water temperatures encountered. The water temperature in the heat exchanger is typically 35°C during the summer [26], so this was assumed to be an upper temperature range for the make-up water. This range of temperatures was used to investigate the effect of temperature on the solubility of the species in the Saturn cooling water.

As can be seen from Table 8-3, the precipitates formed were hydrapatite, calcite, anorthite and tenorite.

Table 8-3. MINTEQ Model Predictions of Species Solubilities as a Function of Temperature[1]

Species	Temperature, °C					
	9.5	15	20	25	30	35
Precipitates Formed[2]	A,B	A,B,C	A,B,C	A,B,C,D	A,B,C,D	A,B,C,D
Silica (as H_4SiO_4)	0	0.2	1.2	1.5	1.3	1.0
Phosphate (as PO_4)	98.2	97.9	97.5	97.1	96.6	96.1
Calcium (as Ca)	2.2	3.6	4.9	6.5	8.1	9.8
Copper (as Cu)	0	0	0	15.4	37.6	53.2
Aluminum (as Al)	0	7.0	41.5	49.9	45.2	34.4
Carbonate (as CO_3)	0.9	1.7	2.4	3.2	4.1	5.0
pH	7.66	7.59	7.53	7.48	7.42	7.36

Notes: (1) Values in the Table are the Percent Precipitated for those Species which Formed a Solid

(2) Precipitates Formed: A = Hydrapatite, $Ca_5(PO_4)_3OH$
B = Calcite, $CaCO_3$
C = Anorthite, $Al_2CaSi_2O_8$
D = Tenorite, CuO

The species which make up these solids included silica, phosphate, calcium, copper, aluminum and carbonate. The temperature effects on species solubility are also presented

in Fig. 8-1. The amount of silica which formed precipitates increased from 0% at 9.5°C to a maximum of 1.5% at 25°C. Silica solubility was expected to increase as the temperature increased based on the results presented by Cowan and Weintritt [15], but the change in silica concentration was considered to have a negligible impact on this study. Calcium solubility was effected to a greater extent, where an additional 7.6% of calcium formed precipitates for the temperature increase. For each mole of calcium which precipitated, one mole of carbonate precipitated, forming calcite. This resulted in the carbonate precipitation to increase from 0.9% at 9.5°C to 5.0% at 35°C. Since there was only a small amount of phosphate, copper and aluminum in the make-up water (0.016 mg/l phosphate, 0.14 mg/l copper, 0.32 mg/l aluminum), the effects of the temperature change on these species solubilities did not significantly effect the make-up water composition. The pH of the water decreased from 7.66 for 9.5°C to 7.36 for 35°C. At the 9.5°C temperature, the species concentrations in the make-up water were generally highest, and therefore this temperature was used to simulate a worst case condition. This required more chemical additions to achieve the desired effluent concentrations and therefore resulted in a more conservative cost estimate for a given cycles of concentration.

8.3 Effects of Hydrated Lime Addition on Make-up Water Quality

The effects of adding hydrated lime to the make-up water resulted in lower species concentrations in the effluent as can be seen in Fig. 8-2. The dissolved calcium concentration in solution decreased as hydrated lime was added due to the formation of calcite ($CaCO_3$). Although the hydrated lime added calcium to the water, the increase in

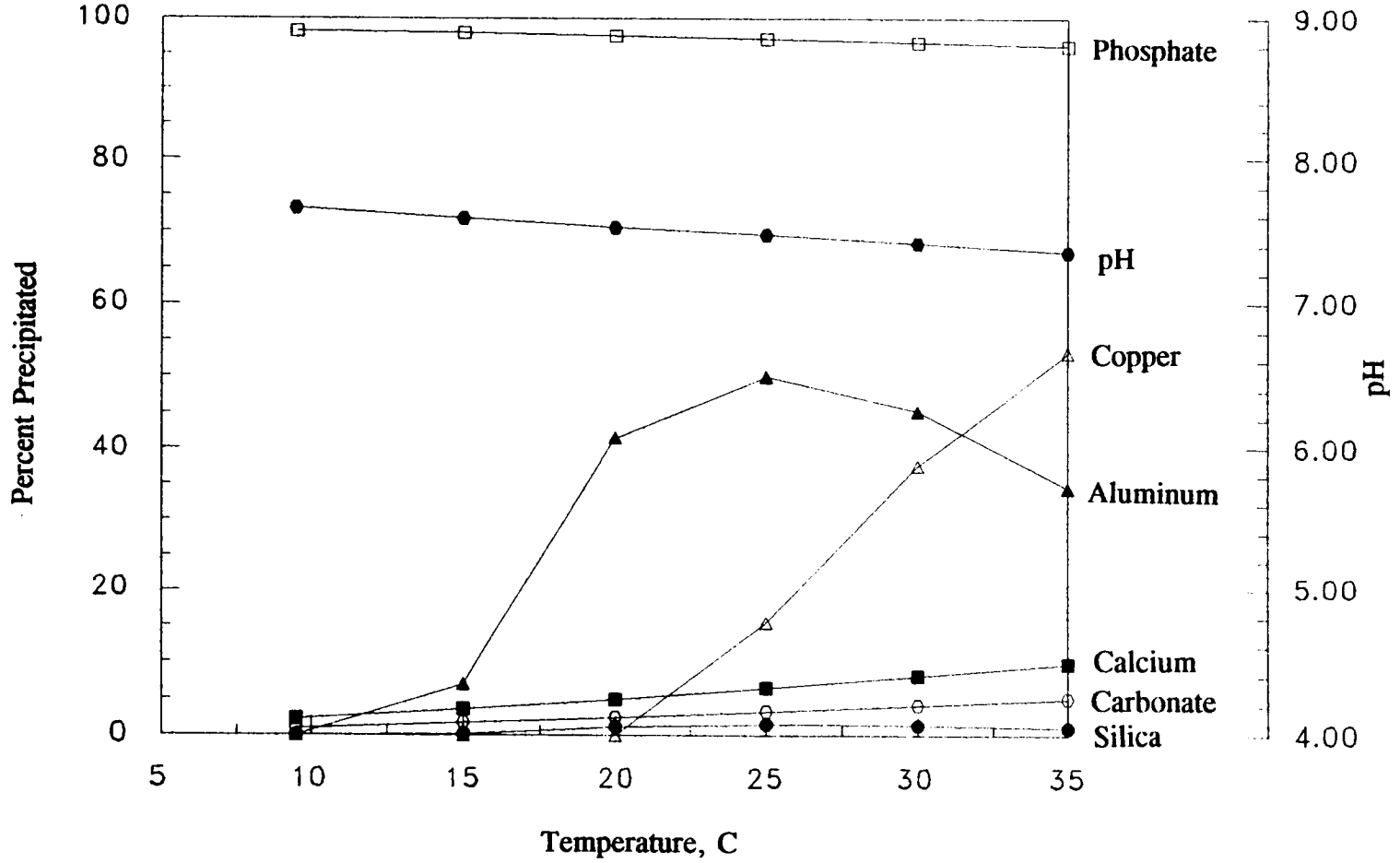


Fig. 8-1. Temperature Effects on Species Solubility

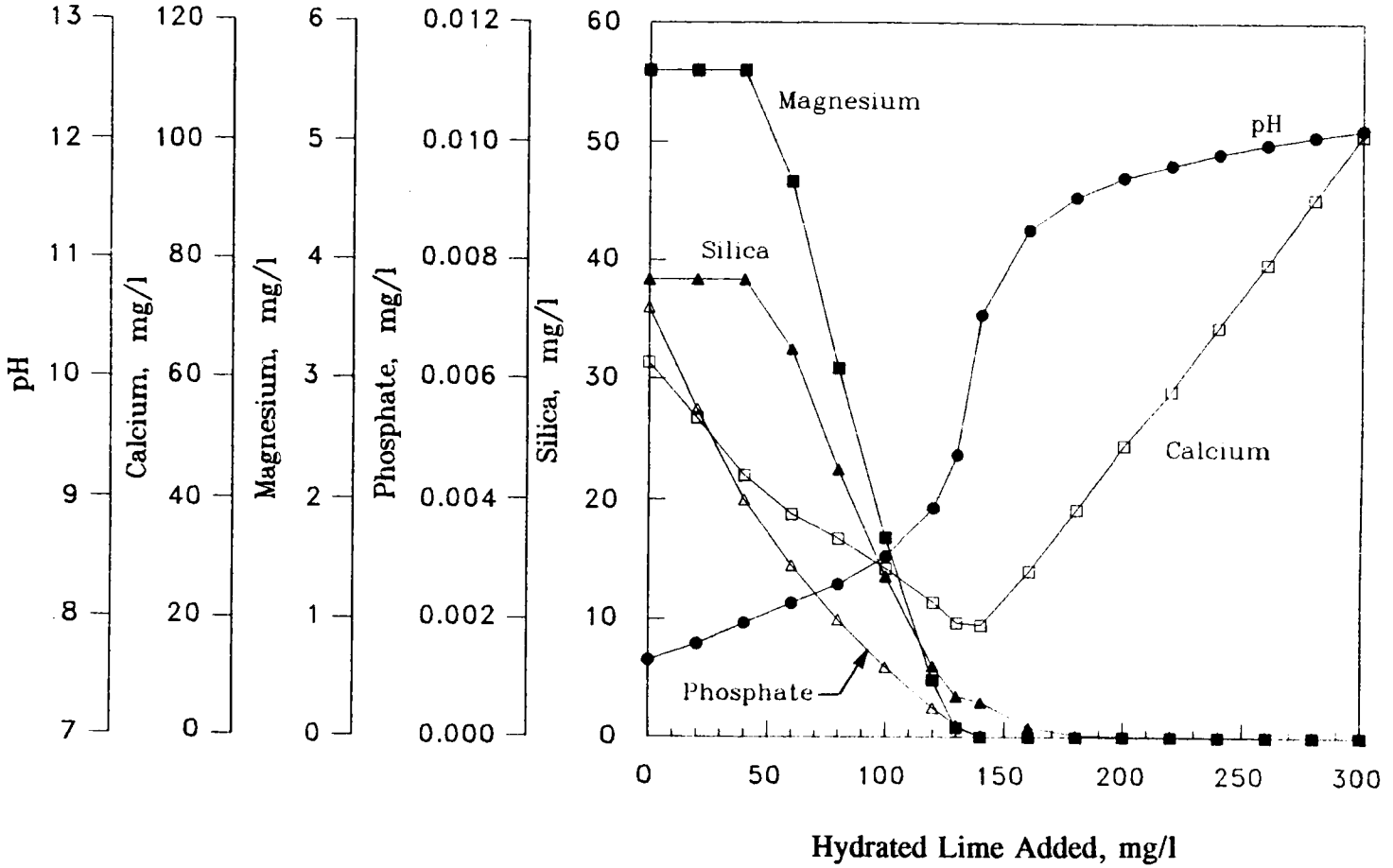


Fig. 8-2. Effects of Hydrated Lime Addition on Species Solubility

pH freed up enough moles of carbonate for the formation of the calcite solid to cause a net decrease in the calcium concentration in solution. The minimum calcium concentration in solution was obtained at 140 mg/l hydrated lime addition. Phosphate and magnesium precipitated readily in the lime clarifier as was predicted by Matson and Harris [3] and Batchelor and McDevitt [4]. Magnesium and silica started precipitating at 40 mg/l hydrated lime addition, which corresponded to a pH of 8.05, with sharp decreases in the amount of magnesium and silica remaining in solution at higher levels of hydrated lime addition. Based on the literature, significant silica precipitation was not expected until pH levels reached between 10.5 to 12. Most of the magnesium and silica was removed from solution at a pH of 9.4.

The sharp increase in the pH at 130 mg/l lime was due to the decrease in the buffering effects of bicarbonate, which combined with the hydroxide in the hydrated lime to form magnesium carbonate. When there was little bicarbonate remaining in solution, the pH rose sharply for small increases in hydrated lime addition.

8.4 Cycles of Concentration Obtained

Using the methodology described in Chapter 7, a range of cycles of concentrations were obtained for the various lime and soda ash combinations evaluated. The results show that the silica and the product of the calcium and sulfate concentrations were the limiting factors. The results are presented in Fig. 8-3, where the LSI value, silica and TDS concentrations, and the Ca x SO_4 concentration product are given for the lime and soda ash combinations evaluated and the cycles of concentrations obtained. If a limit was reached, this point was circled on the graph. To increase the cycles of concentrations

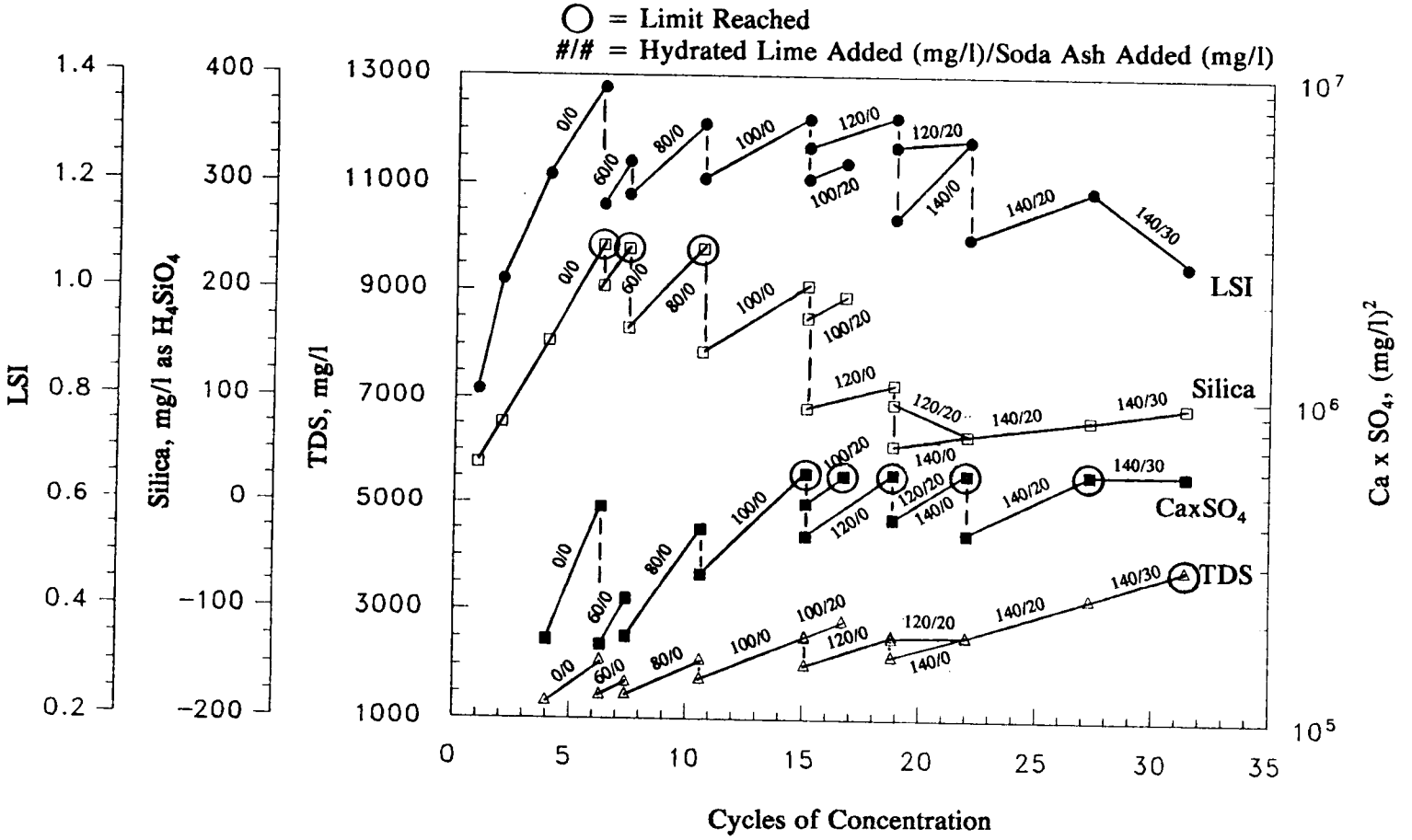


Fig. 8-3. Limits Reached and Cycles of Concentrations Obtained for the Lime/Soda Ash Combinations Evaluated

further, the amount of lime or soda ash added had to be increased, lowering the variables as shown by the dotted lines on the graph. As shown in Fig. 8-3, the silica limit was reached at 6.3 cycles of concentration without using any softening treatment. Current Saturn operations use approximately four cycles of concentration, but they are limited by the Langlier Saturation Index rather than silica. MINTEQ predicted that the silica concentration, calcium and sulfate concentration product, or TDS concentration reached their limits, resulting in the Langlier Saturation Index never exceeding 1.38, and therefore the LSI was not a limiting factor in this analysis. This was possible since the make-up water used for this analysis was a typical sample and not a worst case sample, which explained why the LSI was significantly below 3.0 at four cycles of concentration. Hydrated lime addition was required to decrease the silica concentration such that higher cycles of concentrations could be obtained. Adding 20 and 40 mg/l hydrated lime did not increase the pH sufficiently to reduce the silica concentration as was shown in Fig. 8-2. At 60 mg/l hydrated lime addition, the precipitation of some silica allowed the cycles of concentration to be increased to 7.35, again limited by the silica concentration. At 80 mg/l hydrated lime addition, more silica was removed from solution, allowing the cycles of concentration to increase to 10.6, again being limited by silica. When 100 mg/l hydrated lime was added, 15.1 cycles of concentration was obtained before reaching the limit on the product of the calcium and sulfate concentrations. The silica limit was no longer a factor for all hydrated lime additions above 80 mg/l (which corresponds to cycles of concentrations above 10.6). Further increases in the cycles of concentration above 15.1 required reducing the calcium concentration by adding more hydrated lime or soda ash. Adding 20 mg/l soda ash in the clarifier allowed the cycles of concentration to be

increased from 15.1 to 16.7. Increasing the hydrated lime addition from 100 to 120 mg/l (without using soda ash) allowed the cycles of concentration to be increased to 18.8. Obviously, it would be cheaper to add an additional 20 mg/l of hydrated lime than adding 20 mg/l soda ash and supporting systems, so no further soda ash additions were evaluated at the 100 mg/l hydrated lime addition level. Increasing the hydrated lime addition from 120 to 140 mg/l (without using soda ash) allowed the cycles of concentration to be increased to 22.0. Coincidentally, this was the same cycles of concentration obtained by adding 20 mg/l soda ash with 120 mg/l hydrated lime. Therefore, using 140 mg/l hydrated lime and no soda ash would give the lowest treatment cost for 22.0 cycles of concentration, and no further soda ash additions were evaluated for the 120 mg/l hydrated lime addition level. Increasing the hydrated lime addition from 140 to 160 mg/l caused the product of the calcium and sulfate concentrations to increase to 1.13×10^6 at 22.0 cycles of concentration, which was greater than the 5.77×10^5 $(mg/l)^2$ limit. This was expected since hydrated lime additions above 140 mg/l caused an increase in the calcium concentration in solution as was shown in Fig. 8-2. Therefore, further increases in the cycles of concentration above 22.0 required the addition of soda ash in the clarifier to remove more calcium from solution.

Adding 20 mg/l of soda ash with the 140 mg/l hydrated lime removed enough calcium to allow the cycles of concentration to be increased from 22.0 to 27.3, again reaching the limit of the product of the calcium and sulfate concentrations. Increasing the soda ash addition from 20 to 30 mg/l allowed the cycles of concentration to increase to 31.4. This resulted in a total dissolved solids concentration of 3,816 mg/l, which was slightly lower than the 4,000 mg/l limit. It was not deemed feasible to perform a cost

analysis for cycles of concentration of 31.4 or higher due to drift loss considerations as explained in the following section. The cycles of concentrations obtained and the limits reached for each lime/soda ash combination are summarized in Table 8-4.

Table 8-4. Cycles of Concentrations Obtained for the Chemical Feed Rates Used

Hydrated Lime Added, mg/l	Soda Ash Added, mg/l	Sulfuric Acid Added, mg/l	Limit Reached	C.O.C. Obtained
0	0	123.6	Silica	6.3
20	0	---	Silica	6.3
40	0	---	Silica	6.3
60	0	57.9	Silica	7.4
80	0	45.6	Silica	10.6
100	0	31.6	Ca x SO_4	15.1
100	20	34.3	Ca x SO_4	16.7
120	0	14.1	Ca x SO_4	18.8
120	20	16.0	Ca x SO_4	22.0
140	0	4.4	Ca x SO_4	22.0
140	20	6.3	Ca x SO_4	27.3
140	30	8.3	TDS	31.4

The possibility of using carbon dioxide instead of soda ash was evaluated at 27.3 cycles of concentrations by adding the same number of moles of CO_2 as was added for soda ash. The carbon dioxide addition caused the pH to decrease from 10.54 to 9.16 due to the increase in the free hydrogen concentration. The lower pH resulted in only 85.1% of the calcium being removed from solution, compared with 86.3% with no CO_2, despite the higher carbonate concentration from the CO_2 addition. Therefore, carbon dioxide was not considered as a treatment option.

8.5 Drift Loss Considerations

Drift losses for a well designed cooling tower is typically between 0.1 and 0.2% of the recirculation rate [2]. At 0.1%, the drift losses are 55 gpm for the Saturn cooling tower recirculation rate of 55,000 gpm. For zero blowdown, 550 gpm evaporation and 55 gpm drift losses, the corresponding cycles of concentration can be calculated from Eq. 12,

$$b+d=m-e \tag{27}$$

and Eq. 14,

$$m=\frac{r\Delta T}{1000}\frac{C}{C-1} \tag{28}$$

Solving for C.O.C.,

$$0+55gpm=\frac{(55{,}000gpm)(10)}{1000}\frac{C.O.C.}{C.O.C.-1}-550gpm \tag{29}$$

$$\frac{C.O.C.}{C.O.C.-1}=1.1 \tag{30}$$

$$C.O.C.=11.0 \tag{31}$$

Therefore, for cycles of concentration of 11.0 or greater, the blowdown rate was zero. The blowdown rates and drift losses for the cycles of concentrations analyzed in this study are presented in Table 8-5. At 27.3 cycles of concentration, the drift losses are 0.038% of the recirculation rate, which is well below the 0.1% rate for a well designed cooling tower. It was not considered necessary to determine costs for higher cycles of concentration. Drift losses less than 0.1% of the recirculation rate may not be currently

Table 8-5. Blowdown Rates and Drift Losses for the Cycles of Concentrations Evaluated

Cycles of Concentration	Make-up Rate, gpm	Evaporation Rate, gpm	Blowdown Rate, gpm	Drift Loss Rate, gpm	Drift Loss % of Recirc. Rate
4.0	733.3	550	128.3	55.0	0.1
6.3	654.0	550	49.0	55.0	0.1
7.4	636.6	550	31.6	55.0	0.1
10.6	607.4	550	2.4	55.0	0.1
15.1	589.0	550	0	39.0	0.071
16.7	585.0	550	0	35.0	0.064
18.8	580.9	550	0	30.9	0.056
22.0	576.2	550	0	26.2	0.048
27.3	570.9	550	0	20.9	0.038

achievable with conventional cooling tower designs, and therefore cost savings determined from this analysis for cycles of concentration higher than 11.0 may be theoretical in nature, but may provide direction for future research.

8.6 Cost Determinations

The costs associated with the cycles of concentrations obtained for the range of hydrated lime and soda ash additions analyzed are presented in Fig. 8-4 and Table 8-6. A sample calculation of the total cost estimate for 27.3 cycles of concentration is presented in Appendix A. The possibility of disposing the blowdown water on-site was evaluated by Barnett [25] and is presented in Appendix B. Due to varying make-up water quality, environmental regulations and the possiblility of exceptions for specific cases, both on-site and off-site disposal costs were estimated. From Fig. 8-4, it can be seen that with on-site disposal, the total cost for no softening at four cycles of concentration was

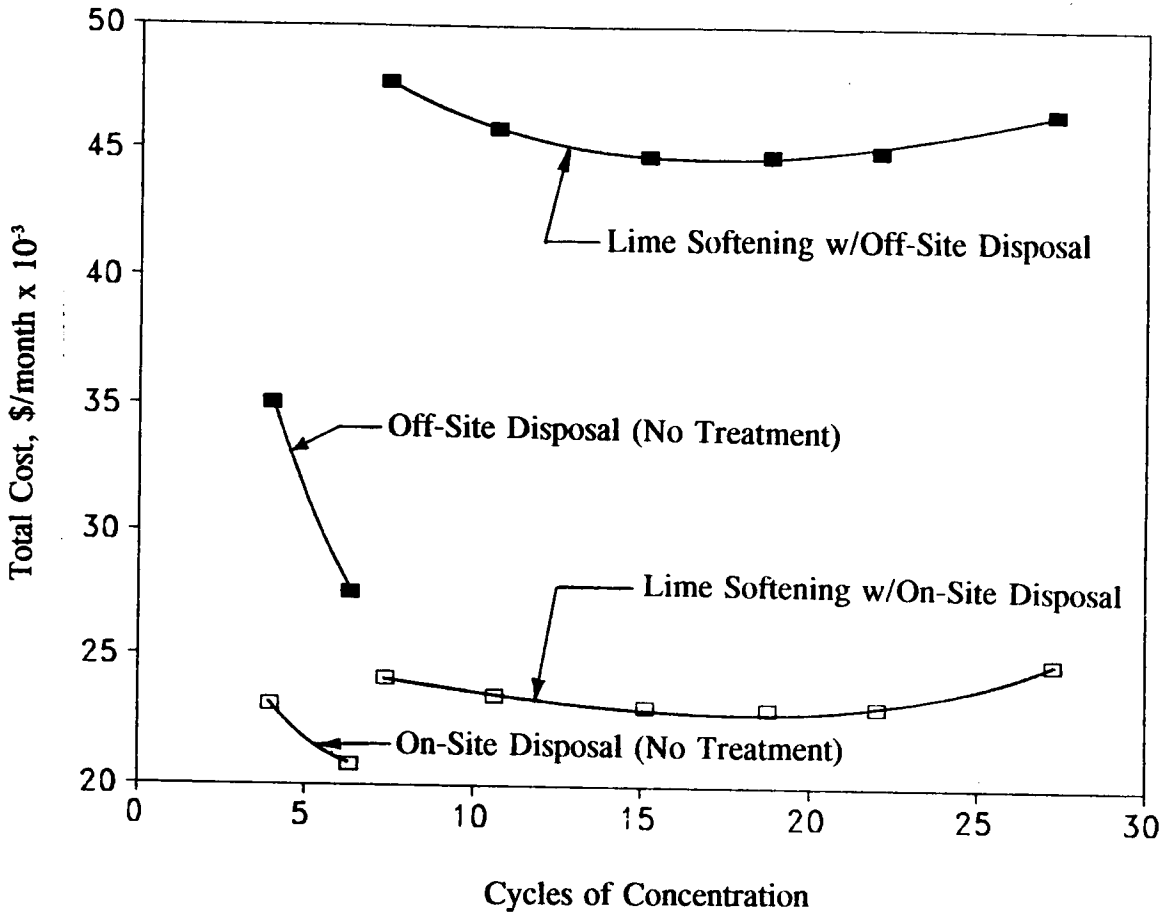


Fig. 8-4. Total Costs for the Cycles of Concentrations Obtained

nearly the same as using 120 mg/l hydrated lime (without soda ash). The cost for four cycles of concentration was used as a baseline for no softening treatment since it corresponds with Saturn's current operation, which is limited by the LSI. For this study using MINTEQ predictions, four cycles of concentration also maintains a margin of safety on the silica limit to allow for fluctuating make-up water quality. The cost for four cycles of concentration was $23,099/month. With softening treatment, the lowest cost used 120 mg/l hydrated lime and no soda ash, which allowed 18.8 cycles of concentration and cost $22,983/month.

If on-site disposal is not possible, then the cost for lime softening treatment increases significantly due to the requirement of a filter press for sludge dewatering. The lowest cost using lime softening with off-site disposal occurred using 100 mg/l hydrated lime and no soda ash, which allowed 15.1 cycles of concentration and cost approximately $44,736/month. This cost was approximately $9,000/month higher than using four cycles of concentration without softening treatment. It was interesting to note that the total costs did not decrease substantially as the cycles of concentration was increased. This was due to the higher concentrations of hydrated lime required and therefore higher costs for the hydrated lime feed systems, which offset cost savings in other areas.

8.7 Cost Adjustments for Sidestream Softening Cost Estimation

Softening treatment inside the recirculation loop should be more cost effective than make-up softening only since species concentrations within the recirculation loop are much higher and should precipitate more readily. An adjustment to the costs of make-up softening was made based on cost ratios derived from the study performed by Batchelor

et. al. [5]. Their study determined that the cost of using a combined make-up/sidestream softening combination was between 0.3 (Fig. 4-1) to 0.6 (Fig. 4-2) of the costs of make-up softening only. Using the cost ratio of 0.3, and assuming it to be applicable throughout the range of cycles of concentrations evaluated in this study, the costs for 18.8 cycles of concentration for a combination of make-up/sidestream softening would be $6,895/month for on-site disposal of sludge and blowdown water, and $13,432/month for off-site disposal. Based on these estimates, a softening treatment system could result in substantial savings of approximately $9600/month for on-site disposal, or $21,600/month for off-site disposal as compared to using four cycles of concentration without any softening treatment.

Table 8-6. Component Costs, $/month

Component	Cycles of Concentration 4	6.3	7.4	10.6	15.1	18.8	22.0	27.3
Make-up Water Cost	21,375	19,112	18,617	17,785	17,260	17,029	16,894	16,744
Hydrated Lime and Soda Ash Clarifiers								
Construction	0	0	567	558	552	550	548	547
Maintenance Mat.	0	0	49	49	49	49	49	48
Energy	0	0	10	10	10	10	10	10
Labor	0	0	300	299	298	298	297	297
Subtotal	0	0	926	916	909	907	904	902
Hydrated Lime Feed Systems								
Construction	0	0	461	527	592	659	728	724
Maintenance Mat.	0	0	113	126	140	154	168	167
Energy	0	0	84	84	85	85	85	85
Labor	0	0	537	704	869	1042	1218	1205
Subtotal	0	0	1195	1441	1686	1940	2199	2181
Hydrated Lime	0	0	389	495	600	710	822	814
Soda Ash Feed Systems								
Construction	0	0	0	0	0	0	0	293
Maintenance Mat.	0	0	0	0	0	0	0	78
Energy	0	0	0	0	0	0	0	83
Labor	0	0	0	0	0	0	0	108
Subtotal	0	0	0	0	0	0	0	562
Soda Ash	0	0	0	0	0	0	0	1315
Rapid Mix Systems								
Construction	0	0	234	233	233	233	233	233
Maintenance Mat.	0	0	3	3	3	3	3	3
Energy	0	0	21	20	19	19	19	18
Labor	0	0	842	842	842	842	842	842
Subtotal	0	0	1100	1098	1097	1097	1097	1096
Flocculator Systems								
Construction	0	0	683	660	646	639	636	632
Maintenance Mat.	0	0	62	61	60	60	60	60
Energy	0	0	15	14	13	13	13	12
Labor	0	0	196	193	191	190	190	189
Subtotal	0	0	956	928	910	902	898	893

Table 8-6. Component Costs, $/month (continued)

Component	Cycles of Concentration 4	6.3	7.4	10.6	15.1	18.8	22.0	27.3
Sulfuric Acid Feed Systems								
Construction	300	292	199	180	161	138	126	129
Maintenance Mat.	16	16	13	12	11	10	10	10
Energy	17	17	22	23	24	25	25	25
Labor	253	249	193	177	148	114	96	100
Subtotal	586	574	427	392	344	287	257	264
Sulfuric Acid	1138	1084	498	375	252	111	34	48
TOTAL COST with On-Site Disposal*	23,099	20,770	24,108	23,430	23,058	22,983	23,105	24,819
Blowdown Water Disposal	11,959	6782	5650	3745	2545	2016	1708	1364
Filter Press Systems								
Construction	0	0	3733	4028	4278	4588	4661	4867
Maintenance Mat.	0	0	215	232	248	267	281	287
Energy	0	0	656	747	757	801	836	846
Labor	0	0	13,145	13,378	13,557	13,772	13,915	13,951
Subtotal	0	0	17,749	18,385	18,840	19,428	19,811	19,951
Sludge Hauling and Disposal	0	0	195	244	293	346	389	405
TOTAL COST with Off-Site Disposal	35,058	27,552	47,702	45,804	44,736	44,773	45,013	46,539

* Assumes on-site disposal costs of blowdown water and sludge are negligible, and no filter press is needed

CHAPTER 10

CONCLUSIONS AND RECOMMENDATIONS

The results of the research show that it was not economically feasible for Saturn Corporation to apply make-up softening treatment to the cooling tower make-up water, even if on-site disposal of the sludge and blowdown water was possible. The costs for lime softening treatment using on-site disposal ranged from $22,983/month to $24,819/month for cycles of concentrations up to 27.3. For off-site disposal, the costs were much higher, ranging from $44,736/month to $47,702/month. The only advantage of make-up softening would be the environmental benefits of lower water usage since the lowest lime treatment costs were approximately the same as no treatment. Although the cost estimates for a system using a combination of make-up and sidestream softening were crude, they indicate that such a system may be economically feasible. However, on-site disposal of sludge may be critical for consideration of a lime softening treatment system. Based on the irrigation water quality standards, on-site disposal of the blowdown water and sludge does not appear possible. Also, with the plentiful supply of water in Spring Hill, TN, and the problems which may occur due to the sludge disposal and drift loss deposition effects on the environment, the installation of a lime softening treatment plant does not appear to be environmentally advantageous. In addition to the environmental considerations, to run cycles of concentrations above 11.0 would require decreasing the drift losses below 0.1% of the recirculation rate, which may not be physically possible with current technology.

There were several factors unique to Saturn that cause the lime softening treatment

process to be less cost effective than it would be at other locations. One was the low cost of water due to the plentiful supply in Spring Hill, Tennessee. Another was the relatively low hardness levels in the make-up water. For other cooling towers where the make-up water costs and/or hardness levels are higher than those at Saturn, lime softening treatment may be much more cost effective.

For further investigations of the lime softening process for Saturn or other cooling towers, it is recommended that a computer model be developed to simulate cooling tower operation. The MINTEQ program would be incorporated into such a model to perform the chemical equilibrium calculations. The model could initially be written for make-up softening only to determine the cycles of concentrations obtainable and sulfuric acid required for various lime and soda ash combinations as was manually done in this study. This study could be used to validate this phase of the model development. The relevant EPA cost curves should be updated and curve fitted for incorporation into the model. Once this is done, further development would involve programming the model to determine the optimum configuration for the lowest treatment cost. More accurate limits on species concentrations and drift losses should be determined for the specific cooling tower being investigated. The final phase of model development would involve modifications to simulate the clarifiers being inside the cooling tower recirculation loop. This would involve performing mass balances on all species at each point in the recirculation loop where changes in mass occur.

Improvements in model predictions of a cooling tower simulation may be possible if MINTEQ would not predict the formation of solids in the make-up water. Laboratory work may be required to determine the cause of this model deficiency. Improvements

in solubility product values may also result from the laboratory experiments. This may also determine why MINTEQ predicted most of the silica to precipitate at a pH of 9.4 when the literature indicated that a pH of 10.5 to 12.0 is needed.

Another MINTEQ model deficiency was the prediction of precipitates for species such as quartz (SiO_2) when the kinetics for this mineral to form is much slower than would occur in a cooling tower simulation. A provision for reaction kinetics would improve model performance, but this may be too difficult to determine and may change with various cooling tower simulations.

Ion exchange should also be investigated as a possible treatment technique for comparison with lime softening treatment costs.

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APPENDICES

APPENDIX A

COST DETERMINATION FOR 27.3 CYCLES OF CONCENTRATION

The following is a cost determination and the model output for 27.3 cycles of concentration. For a hydrated lime addition of 140 mg/l and a soda ash addition of 20 mg/l, the product of the calcium and sulfate concentrations in the cooling tower reached its limit of 5.77×10^5 $(mg/l)^2$ at 27.3 cycles of concentration. The sulfuric acid addition required to control the pH to 8.4 was 6.4×10^{-5} mole/l, or 6.28 mg/l. A sample output is also included in this appendix. All other species concentrations were below their limits as presented in Table A-1.

Table A-1. Species Concentrations in the Cooling Tower for 27.3 Cycles of Concentration

Species	Limit	Cooling Tower Concentration
Ca, CO_3	LSI=3.0	LSI=1.19
Mg/Ca	0.152	0
Silica (mg/l as Si)	70	60
Phosphate (mg/l as PO_4)	4	0
Chloride (mg/l as Cl)	2000	273
Ca x SO_4	5.77×10^5	5.79×10^5
Na + K (mg/l)	2648	622
TDS (mg/l)	4000	3256
pH	8.4	8.4

A.1 Make-up, Blowdown and Evaporation Water Rates and Costs

The make-up water rate was calculated based on an average recirculation rate of 55,000 gpm and a tower cooling range of 10°F. Using Eq. 14, with 27.3 cycles of

concentration, the make-up water rate was

$$m(gpm)=\frac{(55{,}000gpm)(10)}{1000}\frac{27.3}{27.3-1}=570.9\ gpm \tag{32}$$

Based on a cooling tower operation of 24 hours per day and a 30 day month, the make-up rate was 24,663,422 gal/month. Using the water rate schedule in Table 7-1, the cost of the water up to 1,000,000 gallons was

$$(\frac{\$1.32}{1kgal})(\frac{50kgal}{month})+(\frac{\$1.21}{1kgal})(\frac{450kgal}{month})+(\frac{\$1.03}{1kgal})(\frac{500kgal}{month})=\frac{\$1{,}126}{month} \tag{33}$$

and the cost for the water over 1,000,000 gallons was

$$(\frac{\$0.66}{1kgal})(\frac{24{,}663kgal-1{,}000kgal}{month})=\frac{\$15{,}618}{month} \tag{34}$$

for a total cost of $16,744/month.

Determining the blowdown water rate required calculating the evaporation rate first. The evaporation rate was given in Eq. 13 and was equal to

$$e(gpm)=\frac{(55{,}000gpm)(10)}{1000}=550\ gpm \tag{35}$$

The sum of the blowdown and drift water rates were then obtained from Eq. 12 and was equal to

$$b+d\ (gpm)=m-e=570.9-550=20.9\ gpm \tag{36}$$

Since this was less than 0.1% of the recirculation rate, or 55 gpm, a zero blowdown condition existed and all losses were assumed due to drift.

A.2 Chemical Rates and Costs

To determine the cost for the hydrated lime, the feed rate was calculated as

$$(570.9\frac{gal}{\min})(3.7854\frac{l}{gal})(60\frac{\min}{hr})(140\frac{mg_{lime}}{l})(\frac{kg}{10^6\ mg})=18.153\frac{kg}{hr} \quad (37)$$

The cost for the hydrated lime was then

$$(18.153\frac{kg}{hr})(24\frac{hr}{day})(30\frac{day}{month})(\frac{\$0.0623}{kg})=\frac{\$814}{month} \quad (38)$$

For the soda ash, the feed rate was

$$(570.9\frac{gal}{\min})(3.7854\frac{l}{gal})(60\frac{\min}{hr})(20\frac{mg_{soda\ ash}}{l})(\frac{kg}{10^6\ mg})=2.593\frac{kg}{hr} \quad (39)$$

The cost for the soda ash was then

$$(2.593\frac{kg}{hr})(24\frac{hr}{day})(30\frac{day}{month})(\frac{\$0.7045}{kg})=\frac{\$1{,}315}{month} \quad (40)$$

The sulfuric acid feed rate was

$$(6.4x10^{-5}\frac{mole}{L_{acid}})(98.08\frac{g}{mole})(\frac{L_{acid}}{1831g})(570.9\frac{gal}{\min})(1440\frac{hr}{day})=2.818\frac{gal}{day} \quad (41)$$

The cost for the sulfuric acid was then

$$(2.818\frac{gal}{day})(3.7854\frac{L}{gal})(30\frac{day}{month})(1.831\frac{kg_{acid}}{L})(\frac{\$0.0827}{kg_{acid}})=\frac{\$48}{month} \quad (42)$$

A.3 Construction, Operation and Maintenance Costs

A.3.1 Rectangular Clarifiers for Hydrated Lime and Soda Ash

The costs for the hydrated lime and soda ash clarifiers were the same since both must be sized for the same make-up water rate and detention time. The cost estimates were based on the clarifier basin area. Using a side wall height of 12 feet as recommended by the EPA, the basin area was calculated as

$$(570.9\frac{gal}{\min})(30\min)(\frac{ft^3}{7.48052gal})(\frac{1}{12ft})=190.8\ ft^2 \qquad (43)$$

Using the EPA cost estimates, this gave a construction cost of $35,654 in October 1978 dollars. For a CPI adjustment of 2.149, the cost in May 1993 dollars was $76,620. Using 20 year amortization at 6% per year, the cost was $547/month for each clarifier system.

The EPA estimates for maintenance material costs were $270/yr in October 1978 dollars. Adjusting for the increase in the CPI of 2.149, the cost was $48/month in May 1993 dollars.

The process and building energy requirements as estimated by the EPA were 3211 kw-hr/yr. Using an electrical rate of $0.038/kw-hr, the cost was $10/month.

The labor requirements as estimated by the EPA were 165.9 hr/yr. For a labor rate of $21.49/hr, the cost was $297/month.

The total cost for each clarifier system was then $902/month, or $1,804/month for both clarifier systems.

A.3.2 Hydrated Lime Feed Systems

The hydrated lime feed systems were determined based on the feed capacity calculated in Eq. 41, which was equal to 18.15 kg/hr or 40.02 lb/hr. Using EPA estimates for lime feed systems, the construction cost was $47,684 in October 1978 dollars, or $102,473 in May 1993 dollars after applying the CPI adjustment. Using 20 year amortization at 6%, the cost was $724/month.

The EPA estimate for the maintenance material cost was $934/yr in October 1978 dollars, or $167/month in May 1993 dollars.

EPA estimates for energy requirements were 26,904 kw-hr/yr, or $85/month.

Labor requirements were estimated by the EPA to be 673 hr/yr, or $1,205/month.

The total cost for the hydrated lime feed system was then $2,181/month.

A.3.3 Soda Ash Feed Systems

Since the EPA did not have cost estimates for soda ash feed systems, the cost estimates for the lime feed systems were used. The soda ash feed rate was calculated in Eq. 43 as 2.593 kg/hr, or 5.717 lb/hr. The construction cost was estimated by the EPA to be $7,280 in October 1978 dollars, or $15,645 in May 1993 dollars. After 20 year amortization at 6%, the construction cost was $129/month.

Maintenance material costs were $55/yr in October 1978 dollars, or $10/month in May 1993 dollars.

Energy requirements were 25,282 kw-hr/yr, or $25/month.

Labor requirements were 56 hr/yr, or $100/month.

The total cost for the sulfuric acid feed systems was then $264/month.

A.3.4 Rapid Mix Units for Hydrated Lime and Soda Ash Clarifiers

The make-up water was assumed by the EPA to be in the rapid mix unit for 45 seconds, and this assumption was also used for this analysis. For a make-up water rate of 570.9 gpm, the volume of the rapid mix unit was

$$(570.9\frac{gal}{\min})(\frac{\min}{60\sec})(45\sec)(\frac{ft^3}{7.48052gal})=57.24\ ft^3 \quad (44)$$

Three G values and their respective cost curves were provided by the EPA. Using the mid-range G value of 600, the construction cost was approximately $14,340 in October 1978 dollars, or $30,817 in May 1993 dollars after the CPI adjustment. This cost was then amortized over 20 years at 6% to arrive at a cost of $233/month.

The maintenance material cost was estimated by the EPA to be $18/yr, or after the CPI adjustment was $3/month.

The energy requirements were approximately 5,827 kw-hr/yr, or $18/month.

The labor needed was approximately 470 hr/yr, or $842/month.

The total cost for the rapid mix unit for each of two clarifiers was then $1,097/month, or $2,194/month for two systems.

A.3.5 Flocculation Systems for Hydrated Lime and Soda Ash Clarifiers

The cost estimates were based on the total basin volume of the clarifiers. For a make-up water rate of 570.9 gpm and assuming a detention time of 30 minutes, the total basin volume was calculated as

$$(570.9\frac{gal}{\min})(30\min)(\frac{ft^3}{7.48052gal})=2{,}290\ ft^3 \quad (45)$$

Costs for three G values were estimated by the EPA. The construction cost for the horizontal paddle flocculators, assuming the mid-range G value of 50, was $41,436 in October 1978 dollars, or $89,046 after correcting for the increase in the CPI. After amortizing for 20 years at 6%, the cost was $632/month.

The maintenance material cost was $333/yr, or $60/month after accounting for the CPI increase.

The energy required was estimated by the EPA to be 3859 kw-hr/yr, which cost $12/month.

The labor requirements were estimated to be 106 hr/yr, which cost $189/month.

The total cost for the flocculation systems for each clarifier system was then $893/month, or $1786/month for both systems.

A.3.6 Filter Press

The costs for the filter press was calculated for off-site disposal of sludge. To determine the filter press costs, the volume of the filter had to be determined. For 27.3 cycles of concentration, the concentration of the species which formed precipitates in the lime and soda ash clarifiers was 336.9 and 17.6 mg/l, respectively, resulting in a total of 354.5 mg of precipitates formed for each liter of make-up water. For a make-up water rate of 570.9 gpm, the sludge production rate was calculated as

$$(354.5\frac{mg}{l})(570.9\frac{gal}{\min})(3.78541\frac{l}{gal})(\frac{kg}{10^6 mg})(60\frac{\min}{hr})(2.20462\frac{lb}{kg})=101.3\frac{lb}{hr} \quad (46)$$

Using the EPA assumption for the filter loading of 5.3 lb dry solids/ft³/hr, the filter press volume was then calculated as

$$\frac{101.3\ lb/hr}{5.3\ lb/ft^3 \cdot hr}=19.1\ ft^3 \quad (47)$$

Based on the EPA cost estimates, the construction cost was approximately $329,000 in October 1978 dollars, or $707,021 after the CPI adjustment. This cost was then amortized over 20 years at 6% to arrive at a cost of $4,867/month.

The maintenance material cost was approximately $1,602/yr, or after the CPI adjustment was $287/month.

The energy required was estimated to be 267,000 kw-hr/yr, or $846/month. The labor needed was approximately 7,790 hr/yr, or $13,951/month.

A.4 Sludge Disposal Costs

For the sludge production rate of 101.3 lb/hr as calculated in Eq. 48, and using the EPA assumption that the dry solids density is approximately 75 lb/ft³, the volume of the dry sludge was calculated as

$$(101.3\frac{lb}{hr})(24\frac{hr}{day})(\frac{30day}{month})(\frac{yd^3}{27ft^3})(\frac{ft^3}{75\ lb})=36\frac{yd^3}{month} \quad (48)$$

For the hauling and disposal rate of $225/20 yd³, the sludge disposal cost was $405/month.

A.5 Total Cost for Lime Softening Treatment for 27.3 Cycles of Concentration

If Saturn can dispose the sludge and blowdown water on-site, and assuming these costs are negligible, the total cost for the hydrated lime and soda ash clarifier systems, hydrated lime, soda ash, sulfuric acid, the chemical feed systems, two rapid mix units and two flocculation systems was $27,710/month. If on-site disposal is not possible, then off-site disposal costs would also include the filter press systems, and the sludge and blowdown disposal costs for a total cost of $49,430/month.

A.6 Input and Output Files for 140 mg/l Hydrated Lime and 20 mg/l Soda Ash Addition

The model output for 140 mg/l hydrated lime and 20 mg/l soda ash addition to the make-up water follows. The output file includes the inputs, iteration steps showing the component most out of balance during the iteration process, the precipitation and dissolution of species during the iteration process, the final species concentrations dissolved in solution and precipitated, and a summary of the saturation indices and stoichiometry of all minerals.

A.6.1 Input File

```
SATURN MAKE-UP WATER QUALITY, 6/8/93
jj2000.dat
 9.50 MOLAL  0.000  0.00000E-01
0 0 1 1 3 0 0 0 1 1 0 0 0
0   0   0
    330  2.967E-03   -7.00 y                    /H+1
    770  3.996E-04   -3.40 y                    /H4SiO4
    732  6.040E-04   -3.22 y                    /SO4-2
    180  2.821E-04   -3.55 y                    /Cl-1
    492  1.291E-05   -4.89 y                    /NO3-1
    270  5.265E-05   -4.28 y                    /F-1
    580  4.213E-06   -5.38 y                    /PO4-3
    150  1.597E-03   -2.80 y                    /Ca+2
    460  2.304E-04   -3.64 y                    /Mg+2
    231  2.204E-06   -5.66 y                    /Cu+2
     30  1.186E-05   -4.93 y                    /Al+3
    500  5.569E-04   -3.25 y                    /Na+1
    410  3.326E-05   -4.48 y                    /K+1
    140  2.941E-03   -5.95 y                    /TOTAL CARBON, CO3

  4   2
2015001   -22.6750    30.6900   1.892E-03      /PORTLANDITE
5050001    -0.1250     2.8020   1.887E-04      /THERMONATR
  6  21
7015002   114.4000   -39.3900                  /FCO3APATITE
2077002     4.0060    -6.2200                  /QUARTZ
8415000   -16.4900    85.3600                  /LEONHARDITE
8603002     1.5980     0.0000                  /PYROPHYLLITE
2077001     3.5870    -5.5000                  /CRISTOBALITE
8603001    -5.7260    35.2800                  /KAOLINITE
2077000     3.5230    -4.6150                  /CHALCEDONY
8641000   -12.9900    59.3400                  /MUSCOVITE
2003002    -6.8730    24.6300                  /DIASPORE
8441002    -0.6160    12.3090                  /MICROCLINE
8603000    -8.9940    39.7300                  /HALLOYSITE
8415002   -14.4600    50.4500                  /LAUMONTITE
8441003    -1.0620    14.2520                  /H SANIDINE
8450002    -2.5920    17.4000                  /LOW ALBITE
2003003    -8.7700    22.8000                  /GIBBSITE (C)
2003001    -8.5780    28.1300                  /BOEHMITE
8450001    -6.7190    22.8400                  /ANALCIME
8450003    -3.5060    20.0000                  /ANALBITE
6003001   -22.7000     0.0000                  /AL4(OH)10SO4
6041001     1.3460    -3.9180                  /ALUNITE
8441001    -6.4230    22.0850                  /LEUCITE
```

A.6.2 Output File

```
                                PART 1 of OUTPUT FILE
  PC MINTEQA2 v3.10    DATE OF CALCULATIONS: 30-OCT-93  TIME: 18: 0: 7

SATURN MAKE-UP WATER QUALITY, 6/8/93
jj2000.dat

--------------------------------------------------------------------------------
 Temperature (Celsius):   9.50
 Units of concentration: MOLAL
 Ionic strength to be computed.
 If specified, carbonate concentration represents total inorganic carbon.
 Do not automatically terminate if charge imbalance exceeds 30%
 Precipitation is allowed for all solids in the thermodynamic database and
   the print option for solids is set to: 1
 The maximum number of iterations is: 200
 The method used to compute activity coefficients is: Davies equation
 Intermediate output file

--------------------------------------------------------------------------------
    330  2.967E-03   -7.00 y
    770  3.996E-04   -3.40 y
    732  6.040E-04   -3.22 y
    180  2.821E-04   -3.55 y
    492  1.291E-05   -4.89 y
    270  5.265E-05   -4.28 y
    580  4.213E-06   -5.38 y
    150  1.597E-03   -2.80 y
    460  2.304E-04   -3.64 y
    231  2.204E-06   -5.66 y
     30  1.186E-05   -4.93 y
    500  5.569E-04   -3.25 y
    410  3.326E-05   -4.48 y
    140  2.941E-03   -5.95 y

 H2O has been inserted as a COMPONENT
  4   2
2015001   -22.6750    30.6900   1.892E-03
5050001    -0.1250     2.8020   1.887E-04
  6  21
7015002   114.4000   -39.3900
2077002     4.0060    -6.2200
8415000   -16.4900    85.3600
8603002     1.5980     0.0000
2077001     3.5870    -5.5000
8603001    -5.7260    35.2800
2077000     3.5230    -4.6150
8641000   -12.9900    59.3400
2003002    -6.8730    24.6300
8441002    -0.6160    12.3090
8603000    -8.9940    39.7300
8415002   -14.4600    50.4500
8441003    -1.0620    14.2520
8450002    -2.5920    17.4000
2003003    -8.7700    22.8000
2003001    -8.5780    28.1300
```

8450001	-6.7190	22.8400
8450003	-3.5060	20.0000
6003001	-22.7000	0.0000
6041001	1.3460	-3.9180
8441001	-6.4230	22.0850

INPUT DATA BEFORE TYPE MODIFICATIONS

ID	NAME	ACTIVITY GUESS	LOG GUESS	ANAL TOTAL
330	H+1	1.000E-07	-7.000	2.967E-03
770	H4SiO4	3.981E-04	-3.400	3.996E-04
732	SO4-2	6.026E-04	-3.220	6.040E-04
180	Cl-1	2.818E-04	-3.550	2.821E-04
492	NO3-1	1.288E-05	-4.890	1.291E-05
270	F-1	5.248E-05	-4.280	5.265E-05
580	PO4-3	4.169E-06	-5.380	4.213E-06
150	Ca+2	1.585E-03	-2.800	1.597E-03
460	Mg+2	2.291E-04	-3.640	2.304E-04
231	Cu+2	2.188E-06	-5.660	2.204E-06
30	Al+3	1.175E-05	-4.930	1.186E-05
500	Na+1	5.623E-04	-3.250	5.569E-04
410	K+1	3.311E-05	-4.480	3.326E-05
140	CO3-2	1.122E-06	-5.950	2.941E-03
2	H2O	1.000E+00	0.000	0.000E-01

Charge Balance: UNSPECIATED

Sum of CATIONS= 7.252E-03 Sum of ANIONS = 7.450E-03

PERCENT DIFFERENCE = 1.349E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

IMPROVED ACTIVITY GUESSES PRIOR TO FIRST ITERATION:

H4SiO4	Log activity guess:	-3.40
SO4-2	Log activity guess:	-3.22
PO4-3	Log activity guess:	-11.31
Cu+2	Log activity guess:	-5.70
Al+3	Log activity guess:	-9.97
CO3-2	Log activity guess:	-6.10

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
0	Na+1	-5.325E-03	-1.883E+21	-3.25000	1.882E+21
1	Na+1	-5.325E-03	-8.366E+20	-3.07391	8.365E+20
2	Na+1	-5.325E-03	-4.141E+20	-2.89782	4.140E+20
3	Na+1	-5.325E-03	-1.840E+20	-2.72173	1.840E+20
4	Na+1	-5.325E-03	-8.177E+19	-2.54563	8.176E+19
5	Na+1	-5.325E-03	-3.634E+19	-2.36954	3.634E+19
6	Na+1	-5.325E-03	-1.615E+19	-2.19345	1.615E+19
7	Na+1	-5.325E-03	-7.177E+18	-2.01736	7.177E+18
8	Na+1	-5.325E-03	-3.190E+18	-1.84127	3.189E+18
9	Na+1	-5.325E-03	-1.418E+18	-1.66518	1.417E+18
10	Na+1	-5.325E-03	-6.300E+17	-1.48909	6.299E+17
11	Na+1	-5.325E-03	-2.800E+17	-1.31300	2.800E+17
12	Na+1	-5.325E-03	-1.244E+17	-1.13691	1.244E+17
13	Na+1	-5.325E-03	-5.530E+16	-0.96082	5.530E+16
14	Na+1	-5.325E-03	-2.458E+16	-0.78474	2.457E+16
15	Na+1	-5.325E-03	-1.092E+16	-0.60867	1.092E+16
16	Na+1	-5.325E-03	-4.854E+15	-0.43262	4.853E+15
17	Na+1	-5.325E-03	-2.157E+15	-0.25663	2.156E+15
18	Na+1	-5.325E-03	-9.580E+14	-0.08077	9.579E+14
19	Na+1	-5.325E-03	-4.253E+14	0.09481	4.252E+14
20	Na+1	-5.325E-03	-1.885E+14	0.26974	1.885E+14
21	Na+1	-5.325E-03	-8.328E+13	0.44326	8.328E+13
22	Na+1	-5.325E-03	-3.654E+13	0.61370	3.653E+13
23	Na+1	-5.325E-03	-1.579E+13	0.77769	1.579E+13
24	Na+1	-5.325E-03	-6.632E+12	0.92917	6.631E+12
25	Na+1	-5.325E-03	-2.654E+12	1.05969	2.654E+12
26	Na+1	-5.325E-03	-9.953E+11	1.16205	9.952E+11
27	Na+1	-5.325E-03	-3.492E+11	1.23550	3.492E+11
28	Na+1	-5.325E-03	-1.160E+11	1.28538	1.160E+11
29	Na+1	-5.325E-03	-3.707E+10	1.31844	3.707E+10
30	Na+1	-5.325E-03	-1.153E+10	1.34017	1.153E+10
31	Na+1	-5.325E-03	-3.520E+09	1.35445	3.520E+09
32	Na+1	-5.325E-03	-1.059E+09	1.36382	1.059E+09
33	Na+1	-5.325E-03	-3.141E+08	1.36995	3.140E+08
34	Na+1	-5.325E-03	-9.163E+07	1.37392	9.162E+07
35	Na+1	-5.325E-03	-2.616E+07	1.37644	2.616E+07
36	Na+1	-5.325E-03	-7.266E+06	1.37798	7.266E+06
37	Na+1	-5.325E-03	-1.959E+06	1.37888	1.959E+06
38	Na+1	-5.325E-03	-5.141E+05	1.37938	5.141E+05
39	Na+1	-5.325E-03	-1.322E+05	1.37961	1.322E+05
40	Na+1	-5.325E-03	-3.354E+04	1.37960	3.354E+04
41	Na+1	-5.325E-03	-8.427E+03	1.37911	8.426E+03
42	Na+1	-5.325E-03	-2.088E+03	1.37700	2.088E+03
43	Na+1	-5.325E-03	-4.967E+02	1.36865	4.967E+02
44	Na+1	-5.325E-03	-9.955E+01	1.33590	9.953E+01
45	Na+1	-5.325E-03	-5.233E+00	1.21085	5.230E+00
46	Na+1	-5.325E-03	2.334E+00	0.77913	2.333E+00
47	Na+1	-5.325E-03	-8.438E-01	0.55532	8.433E-01
48	Na+1	-5.325E-03	-4.873E-02	0.59507	4.829E-02

49	Na+1	-5.325E-03	-5.781E-04	0.59806	1.343E-04
50	Al-3	1.186E-05	7.142E-01	-29.77329	7.141E-01
51	Al+3	1.186E-05	2.141E-05	-34.10504	2.141E-05

ITERATIONS= 53: SOLID THERMONATR DISSOLVES

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
53	CO3-2	3.130E-03	3.716E+00	-0.95851	3.716E+00
54	CO3-2	3.130E-03	6.155E-01	-0.99661	6.155E-01
55	CO3-2	3.130E-03	5.445E-02	-1.94741	5.444E-02
56	CO3-2	3.130E-03	2.984E-03	-2.94741	2.984E-03
57	CO3-2	3.130E-03	-2.127E-03	-3.94741	2.126E-03
58	CO3-2	3.130E-03	3.145E-04	-3.47370	3.142E-04
59	CO3-2	3.130E-03	2.637E-06	-3.51267	2.324E-06
60	Cu+2	2.204E-06	3.479E-10	-18.70836	1.275E-10

ITERATIONS= 61: SOLID PORTLANDITE DISSOLVES

PART 3 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 30-OCT-93 TIME: 18: 1:55

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
61	Ca+2	3.489E-03	1.152E-02	-2.13746	1.152E-02
62	Ca+2	3.489E-03	4.860E-03	-2.50896	4.860E-03
63	Ca+2	3.489E-03	3.050E-04	-2.85925	3.047E-04
64	Ca+2	3.489E-03	4.625E-05	-2.90171	4.590E-05
65	Ca+2	3.489E-03	1.285E-05	-2.89480	1.250E-05
66	Ca+2	3.489E-03	4.637E-07	-2.88797	1.148E-07
67	Ca+2	3.489E-03	-3.744E-06	-2.88208	3.395E-06
68	Ca+2	3.489E-03	-3.679E-06	-2.87797	3.331E-06
69	Ca+2	3.489E-03	-1.329E-06	-2.87653	9.799E-07
70	Al+3	1.186E-05	-4.207E-08	-25.13893	4.088E-08

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 30-OCT-93 TIME: 18: 2:16

ITERATIONS= 71: SOLID HYDRAPATITE PRECIPITATES

PART 3 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 30-OCT-93 TIME: 18: 2:19

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
71	CO3-2	3.130E-03	-1.900E-03	-3.01230	1.900E-03
72	CO3-2	3.130E-03	-8.538E-04	-2.90858	8.535E-04
73	CO3-2	3.130E-03	-1.570E-03	-3.03752	1.569E-03
74	CO3-2	3.130E-03	-1.293E-03	-2.98405	1.292E-03
75	CO3-2	3.130E-03	-1.004E-03	-3.01190	1.003E-03
76	CO3-2	3.130E-03	6.554E-04	-3.00296	6.551E-04
77	CO3-2	3.130E-03	1.500E-04	-3.01323	1.497E-04
78	CO3-2	3.130E-03	4.697E-06	-3.01334	4.384E-06
79	CO3-2	3.130E-03	-2.263E-06	-3.01235	1.950E-06
80	SO4-2	6.040E-04	-7.488E-08	-3.45978	1.448E-08

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 30-OCT-93 TIME: 18: 2:40

ITERATIONS= 81: SOLID CALCITE PRECIPITATES

PART 3 of OUTPUT FILE

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 30-OCT-93 TIME: 18: 2:43

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
81	Na+1	9.343E-04	-9.468E-05	-3.07661	9.459E-05
82	Na+1	9.343E-04	6.643E-05	-3.03053	6.633E-05
83	Na+1	9.343E-04	-8.981E-07	-3.06019	8.046E-07
84	Na+1	9.343E-04	-3.272E-06	-3.05978	3.178E-06
85	Na+1	9.343E-04	-1.546E-06	-3.05828	1.452E-06
86	Na+1	9.343E-04	-4.459E-07	-3.05757	3.525E-07
87	Mg+2	2.304E-04	-3.854E-08	-3.78898	1.550E-08

PC MINTEQA2 v3.10 DATE OF CALCULATIONS: 30-OCT-93 TIME: 18: 3: 0

ITERATIONS= 88: SOLID TREMOLITE PRECIPITATES

PARAMETERS OF THE COMPONENT MOST OUT OF BALANCE:

ITER	NAME	TOTAL MOL	DIFF FXN	LOG ACTVTY	RESIDUAL
88	Al+3	1.186E-05	-7.092E-07	-24.59080	7.081E-07
89	Al+3	1.186E-05	-5.956E-06	-24.03179	5.955E-06
90	Al+3	1.186E-05	-7.169E-06	-23.42933	7.167E-06
91	Al+3	1.186E-05	-5.485E-06	-22.86719	5.484E-06
92	Al+3	1.186E-05	-1.716E-06	-22.52558	1.715E-06
93	Al+3	1.186E-05	-5.084E-08	-22.44726	4.965E-08

ID	NAME	ANAL MOL	CALC MOL	LOG ACTVTY	GAMMA	DIFF FXN
330	H+1	-8.170E-04	2.873E-11	-10.56515	0.947412	5.421E-11
770	H4SiO4	3.996E-04	1.047E-05	-4.97989	1.000577	7.249E-12
732	SO4-2	6.040E-04	5.832E-04	-3.32802	0.805666	7.964E-10
180	Cl-1	2.821E-04	2.821E-04	-3.57306	0.947412	9.624E-11
492	NO3-1	1.291E-05	1.291E-05	-4.91253	0.947412	4.404E-12
270	F-1	5.265E-05	5.257E-05	-4.30272	0.947412	1.796E-11
580	PO4-3	4.213E-06	1.092E-12	-12.17274	0.614964	-2.069E-10
410	K+1	3.326E-05	3.318E-05	-4.50262	0.947412	1.135E-11
500	Na+1	9.343E-04	9.322E-04	-3.05396	0.947412	3.187E-10
231	Cu+2	2.204E-06	9.685E-14	-13.10774	0.805666	-1.022E-13
30	Al+3	1.186E-05	5.832E-23	-22.44531	0.614964	-6.637E-12
460	Mg+2	2.304E-04	1.058E-08	-8.06917	0.805666	-8.386E-20
140	CO3-2	3.130E-03	2.177E-05	-4.75595	0.805666	-1.588E-22
2	H2O	3.973E-03	4.174E-03	-0.00007	1.000000	0.000E-01
150	Ca+2	3.489E-03	2.784E-04	-3.64917	0.805666	0.000E-01

Type I - COMPONENTS AS SPECIES IN SOLUTION

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK
330	H+1	2.873E-11	2.722E-11	-10.56515	0.94741	0.023
770	H4SiO4	1.047E-05	1.047E-05	-4.97989	1.00058	0.000
732	SO4-2	5.832E-04	4.699E-04	-3.32802	0.80567	0.094
180	Cl-1	2.821E-04	2.673E-04	-3.57306	0.94741	0.023
492	NO3-1	1.291E-05	1.223E-05	-4.91253	0.94741	0.023
270	F-1	5.257E-05	4.981E-05	-4.30272	0.94741	0.023
580	PO4-3	1.092E-12	6.718E-13	-12.17274	0.61496	0.211
150	Ca+2	2.784E-04	2.243E-04	-3.64917	0.80567	0.094
460	Mg+2	1.058E-08	8.528E-09	-8.06917	0.80567	0.094
231	Cu+2	9.685E-14	7.803E-14	-13.10774	0.80567	0.094
30	Al+3	5.832E-23	3.587E-23	-22.44531	0.61496	0.211
500	Na+1	9.322E-04	8.832E-04	-3.05396	0.94741	0.023
410	K+1	3.318E-05	3.143E-05	-4.50262	0.94741	0.023
140	CO3-2	2.177E-05	1.754E-05	-4.75595	0.80567	0.094

Type II - OTHER SPECIES IN SOLUTION OR ADSORBED

ID	NAME	CALC MOL	ACTIVITY	LOG ACTVTY	GAMMA	NEW LOGK

3305802	H3PO4	6.785E-23	6.789E-23	-22.16820	1.00058	21.700
3300020	OH-	1.133E-04	1.073E-04	-3.96931	0.94741	-14.511
3307700	H3SiO4 -	2.027E-05	1.921E-05	-4.71656	0.94741	-10.278
3307701	H2SiO4 -2	2.384E-07	1.920E-07	-6.71662	0.80567	-22.773
7702700	SiF6 -2	7.428E-43	5.984E-43	-42.22298	0.80567	30.927
4603300	MgOH +	1.316E-10	1.247E-10	-9.90422	0.94741	-12.377
4602700	MgF +	1.922E-11	1.821E-11	-10.73976	0.94741	1.656
4601400	MgCO3 AQ	1.125E-10	1.125E-10	-9.94878	1.00058	2.876
4601401	MgHCO3 +	1.438E-12	1.363E-12	-11.86564	0.94741	11.548
4607320	MgSO4 AQ	6.256E-10	6.260E-10	-9.20342	1.00058	2.194
4605800	MgPO4 -	1.762E-14	1.669E-14	-13.77752	0.94741	6.488
4605801	MgH2PO4 +	5.784E-21	5.480E-21	-20.26121	0.94741	21.134
4605802	MgHPO4 AQ	2.642E-16	2.643E-16	-15.57782	1.00058	15.229
1503300	CaOH +	5.717E-07	5.416E-07	-6.26631	0.94741	-13.159
1501400	CaHCO3 +	2.276E-08	2.156E-08	-7.66629	0.94741	11.327
1501401	CaCO3 AQ	4.298E-06	4.300E-06	-5.36652	1.00058	3.038
1507320	CaSO4 AQ	1.873E-05	1.874E-05	-4.72728	1.00058	2.250
1505800	CaHPO4 AQ	5.092E-12	5.095E-12	-11.29282	1.00058	15.094
1505801	CaPO4 -	3.435E-10	3.255E-10	-9.48751	0.94741	6.358
1505802	CaH2PO4 +	1.192E-16	1.129E-16	-15.94720	0.94741	21.028
1502700	CaF +	7.226E-08	6.846E-08	-7.16455	0.94741	0.811
5001400	NaCO3 -	1.329E-07	1.259E-07	-6.90008	0.94741	0.933
5001401	NaHCO3 AQ	5.066E-09	5.069E-09	-8.29507	1.00058	10.080
5007320	NaSO4 -	1.979E-06	1.875E-06	-5.72700	0.94741	0.678
5005800	NaHPO4 -	7.372E-14	6.985E-14	-13.15586	0.94741	12.659
5002700	NaF AQ	7.130E-09	7.134E-09	-8.14668	1.00058	-0.790
4107320	KSO4 -	8.237E-08	7.804E-08	-7.10771	0.94741	0.746
4105800	KHPO4 -	2.648E-15	2.509E-15	-14.60051	0.94741	12.663
303300	AlOH +2	5.563E-18	4.482E-18	-17.34850	0.80567	-5.374
303301	Al(OH)2 +	4.058E-12	3.845E-12	-11.41514	0.94741	-10.077
303302	Al(OH)4 -	1.168E-05	1.107E-05	-4.95593	0.94741	-24.747
302700	AlF +2	2.269E-20	1.828E-20	-19.73803	0.80567	7.104
302701	AlF2 +	8.295E-20	7.859E-20	-19.10463	0.94741	11.970
302702	AlF3 AQ	3.680E-19	3.682E-19	-18.43395	1.00058	16.919
302703	AlF4 -	1.223E-20	1.158E-20	-19.93618	0.94741	19.743
307320	AlSO4 +	1.527E-23	1.446E-23	-22.83975	0.94741	2.957
307321	Al(SO4)2 -	5.345E-25	5.064E-25	-24.29550	0.94741	4.829
303303	Al(OH)3 AQ	1.777E-07	1.778E-07	-6.75006	1.00058	-16.000
2311400	CuCO3 AQ	7.346E-12	7.350E-12	-11.13369	1.00058	6.730
2311401	Cu(CO3)2-2	2.015E-13	1.623E-13	-12.78964	0.80567	9.924
2311800	CuCl +	2.661E-17	2.521E-17	-16.59847	0.94741	0.106
2311801	CuCl2 AQ	3.030E-21	3.032E-21	-20.51830	1.00058	-0.265
2311802	CuCl3 -	2.271E-27	2.152E-27	-26.66717	0.94741	-2.817
2311803	CuCl4 -2 1	6.183E-33	4.981E-33	-32.30268	0.80567	-4.809
2312700	CuF +	6.425E-17	6.087E-17	-16.21557	0.94741	1.218
2313300	CuOH +	3.026E-11	2.866E-11	-10.54265	0.94741	-7.977
2313301	Cu(OH)2 AQ	2.199E-06	2.200E-06	-5.65757	1.00058	-13.680
2313302	Cu(OH)3 -	5.152E-09	4.881E-09	-8.31149	0.94741	-26.876
2313303	Cu(OH)4 -2	4.430E-11	3.569E-11	-10.44741	0.80567	-39.506
2313304	Cu2(OH)2+2	8.812E-17	7.100E-17	-16.14877	0.80567	-10.970
2317320	CuSO4 AQ	6.683E-15	6.687E-15	-14.17479	1.00058	2.261
2311402	CuHCO3 +	3.932E-16	3.725E-16	-15.42884	0.94741	13.023
3301400	HCO3 -	1.574E-05	1.491E-05	-4.82649	0.94741	10.518
3301401	H2CO3 AQ	7.670E-10	7.675E-10	-9.11494	1.00058	16.771
3307320	HSO4 -	8.621E-13	8.167E-13	-12.08791	0.94741	1.829
3302700	HF AQ	1.451E-12	1.452E-12	-11.83794	1.00058	3.030
3302701	HF2 -	2.624E-16	2.486E-16	-15.60447	0.94741	3.590
3302702	H2F2 AQ	1.076E-23	1.077E-23	-22.96774	1.00058	6.768
3305800	HPO4 -2	6.980E-11	5.623E-11	-10.25001	0.80567	12.582
3305801	H2PO4 -	2.852E-14	2.702E-14	-13.56837	0.94741	19.758

Type III - SPECIES WITH FIXED ACTIVITY

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
2	H2O	4.174E-03	-2.379	0.000	0.000

Type IV - FINITE SOLIDS (present at equilibrium)

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
7015003	HYDRAPATITE	1.404E-06	-5.853	44.199	0.000
5015001	CALCITE	3.088E-03	-2.510	8.405	2.585
8215001	TREMOLITE	4.608E-05	-4.337	-60.429	96.615

Type V - UNDERSATURATED SOLIDS (not present at equilibrium)

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
6041000	ALUM K	7.168E-29	-28.145	5.460	-7.220
5023102	AZURITE	1.818E-12	-11.740	15.965	23.770
6015000	ANHYDRITE	3.223E-03	-2.492	4.486	3.769
5015000	ARAGONITE	6.336E-01	-0.198	8.207	2.615
5046000	ARTINITE	3.023E-11	-10.520	-10.755	28.742
3046000	SPINEL	4.439E-09	-8.353	-39.914	89.089
2046000	BRUCITE	1.700E-05	-4.770	-17.831	25.840
5050001	THERMONATR	7.915E-12	-11.102	-0.238	2.802
8015004	MERWINITE	4.972E-18	-17.303	-72.848	107.111
8646000	CHRYSOTILE	8.432E-06	-5.074	-34.298	52.485
8246000	CLINOENSTITE	8.686E-05	-4.061	-12.142	20.015
5023101	MALACHITE	5.144E-06	-5.289	4.553	15.610
8015003	MONTICELLITE	2.013E-07	-6.696	-32.258	49.421
8215000	DIOPSIDE	2.507E-01	-0.601	-21.183	32.280
5015002	DOLOMITE	2.732E-05	-4.563	16.667	8.290
6046000	EPSOMITE	7.172E-10	-9.144	2.253	-2.820
8646003	SEPIOLITE(C)	1.491E-06	-5.826	-17.009	27.268
2015001	PORTLANDITE	3.736E-07	-6.428	-23.909	30.690
8015006	GEHLENITE	9.838E-14	-13.007	-61.490	116.125
4215000	FLUORITE	7.922E-02	-1.101	11.153	-4.710
8046000	FORSTERITE	7.844E-10	-9.105	-30.248	48.510
4250000	CRYOLITE	3.197E-26	-25.495	31.928	-10.904
3003000	A12O3	3.312E-05	-4.480	-22.980	0.000
6015001	GYPSUM	7.606E-03	-2.119	4.858	-0.261
4150000	HALITE	6.728E-09	-8.172	-1.545	-0.918
5015003	HUNTITE	1.127E-18	-17.948	28.933	25.760
5046001	HYDRMAGNESIT	2.677E-32	-31.572	6.667	52.210
8450000	MAGADIITE	8.966E-14	-13.047	14.300	0.000
5046002	MAGNESITE	9.035E-06	-5.044	7.781	6.169
6050001	MIRABILITE	2.757E-08	-7.559	1.877	-18.987
3050000	NATRON	1.200E-09	-8.921	1.944	-15.745
5046003	NESQUEHONITE	3.656E-08	-7.437	5.388	5.789
8646001	PHLOGOPITE	6.099E-31	-30.215	-69.771	86.360
8450004	NEPHELINE	1.694E-04	-3.771	-15.553	33.204
8646004	SEPIOLITE(A)	2.527E-08	-7.597	-18.780	0.000
2077003	SIO2(A,GL)	1.647E-02	-1.783	3.196	-4.440
2077004	SIO2(A,PT)	7.716E-03	-2.113	2.867	-3.910
8646002	TALC	6.340E-06	-5.198	-24.462	35.005

6050002	THENARDITE	5.249E-10	-9.280	0.156	0.572
6003000	ALOHSO4	1.051E-12	-11.978	3.230	0.000
2015000	LIME	6.675E-18	-17.176	-34.657	46.265
4123100	MELANOTHALLI	3.319E-25	-24.479	-4.225	12.320
5023100	CUCO3	5.839E-09	-8.234	9.630	0.000
4223100	CUF2	2.352E-22	-21.629	0.085	13.320
4223101	CUF2, 2H2O	4.898E-18	-17.310	4.403	3.650
2023100	CU(OH)2	5.881E-02	-1.231	-9.253	15.250
4123101	ATACAMITE	6.539E-07	-6.185	-8.091	18.690
5123100	CU2(OH)3NO3	4.265E-10	-9.370	-9.937	17.350
6023100	ANTLERITE	2.085E-09	-8.681	-8.290	0.000
6023101	BROCHANTITE	1.957E-08	-7.708	-15.340	0.000
6023102	LANGITE	1.776E-11	-10.751	-18.382	39.610
2023101	TENORITE	6.165E-01	-0.210	-8.233	15.240
6023103	CUOCUSO4	4.235E-22	-21.373	-12.960	35.575
7023100	CU3(PO4)2	1.518E-27	-26.819	36.850	0.000
7023101	CU3(PO4)2,3W	2.826E-29	-28.549	35.120	0.000
6023104	CUSO4	6.685E-21	-20.175	-3.739	18.140
6023105	CHALCANTHITE	1.827E-14	-13.738	2.698	-1.440
2023102	DIOPTASE	1.522E-04	-3.817	-6.860	8.960
2046001	PERICLASE	1.255E-10	-9.901	-22.962	36.135
8015002	LARNITE	3.473E-12	-11.459	-41.442	57.238
8441000	KALSILITE	2.150E-04	-3.668	-14.000	28.919
8215003	P-WOLLSTANIT	6.434E-03	-2.191	-14.693	21.068
8215002	WOLLASTONITE	5.268E-02	-1.278	-13.780	19.498
2003000	ALOH3(A)	6.066E-03	-2.217	-11.467	27.045
8015005	AKERMINITE	3.304E-13	-12.481	-50.545	76.445
8415001	ANORTHITE	5.643E-03	-2.248	-28.270	70.660
8015007	CA3SIO5	2.101E-31	-30.678	-78.141	106.335
8015001	CA-OLIVINE	1.364E-10	-9.865	-39.847	54.695
8415003	WAIRAKITE	4.506E-06	-5.346	-21.408	63.150

Type VI - EXCLUDED SPECIES (not included in mole balance)

ID	NAME	CALC MOL	LOG MOL	NEW LOGK	DH
8441001	LEUCITE	1.102E-02	-1.958	-7.311	22.085
6041001	ALUNITE	2.508E-14	-13.601	1.503	-3.918
6003001	AL4(OH)10SO4	6.943E-11	-10.158	-22.700	0.000
8450003	ANALBITE	3.251E-03	-2.488	-4.310	20.000
8450001	ANALCIME	1.461E-01	-0.835	-7.637	22.840
2003001	BOEHMITE	3.478E-01	-0.459	-9.709	28.130
2003003	GIBBSITE (C)	3.660E-01	-0.436	-9.686	22.800
8450002	LOW ALBITE	3.393E-02	-1.469	-3.291	17.400
8441003	H SANIDINE	5.476E-02	-1.262	-1.635	14.252
8415002	LAUMONTITE	3.750E-01	-0.426	-16.488	50.450
8603000	HALLOYSITE	8.903E-03	-2.050	-10.591	39.730
8441002	MICROCLINE	1.830E-01	-0.737	-1.111	12.309
2003002	DIASPORE	2.438E+01	1.387	-7.863	24.630
8641000	MUSCOVITE	3.149E+03	3.498	-15.375	59.340
2077000	CHALCEDONY	5.355E-02	-1.271	3.708	-4.615
8603001	KAOLINITE	2.491E+01	1.396	-7.144	35.280
2077001	CRISTOBALITE	6.735E-02	-1.172	3.808	-5.500
8603002	PYROPHYLLITE	1.510E+00	0.179	1.598	0.000
8415000	LEONHARDITE	1.595E+12	12.203	-19.921	85.360
2077002	QUARTZ	1.889E-01	-0.724	4.256	-6.220
7015002	FCO3APATITE	1.829E+04	4.262	115.983	-39.390
3301403	CO2 (g)	1.973E-08	-7.705	18.181	-0.530

PERCENTAGE DISTRIBUTION OF COMPONENTS AMONG
TYPE I and TYPE II (dissolved and adsorbed) species

H+1	66.4	PERCENT BOUND IN SPECIES #3300020	OH-
	11.9	PERCENT BOUND IN SPECIES #3307700	H3SiO4 -
	27.4	PERCENT BOUND IN SPECIES # 303302	Al(OH)4 -
	2.6	PERCENT BOUND IN SPECIES #2313301	Cu(OH)2 AQ
H4SiO4	33.8	PERCENT BOUND IN SPECIES # 770	H4SiO4
	65.4	PERCENT BOUND IN SPECIES #3307700	H3SiO4 -
SO4-2	96.6	PERCENT BOUND IN SPECIES # 732	SO4-2
	3.1	PERCENT BOUND IN SPECIES #1507320	CaSO4 AQ
Cl-1	100.0	PERCENT BOUND IN SPECIES # 180	Cl-1
NO3-1	100.0	PERCENT BOUND IN SPECIES # 492	NO3-1
F-1	99.8	PERCENT BOUND IN SPECIES # 270	F-1
PO4-3	1.2	PERCENT BOUND IN SPECIES #1505800	CaHPO4 AQ
	81.9	PERCENT BOUND IN SPECIES #1505801	CaPO4 -
	16.6	PERCENT BOUND IN SPECIES #3305800	HPO4 -2
K+1	99.8	PERCENT BOUND IN SPECIES # 410	K+1
Na+1	99.8	PERCENT BOUND IN SPECIES # 500	Na+1
Cu+2	99.8	PERCENT BOUND IN SPECIES #2313301	Cu(OH)2 AQ
Al+3	98.5	PERCENT BOUND IN SPECIES # 303302	Al(OH)4 -
	1.5	PERCENT BOUND IN SPECIES # 303303	Al(OH)3 AQ
Mg+2	92.2	PERCENT BOUND IN SPECIES # 460	Mg+2
	1.1	PERCENT BOUND IN SPECIES #4603300	MgOH +
	5.5	PERCENT BOUND IN SPECIES #4607320	MgSO4 AQ
CO3-2	51.9	PERCENT BOUND IN SPECIES # 140	CO3-2
	10.2	PERCENT BOUND IN SPECIES #1501401	CaCO3 AQ
	37.5	PERCENT BOUND IN SPECIES #3301400	HCO3 -
H2O	68.4	PERCENT BOUND IN SPECIES #3300020	OH-
	28.2	PERCENT BOUND IN SPECIES # 303302	Al(OH)4 -
	2.7	PERCENT BOUND IN SPECIES #2313301	Cu(OH)2 AQ
Ca+2	92.2	PERCENT BOUND IN SPECIES # 150	Ca+2
	1.4	PERCENT BOUND IN SPECIES #1501401	CaCO3 AQ
	6.2	PERCENT BOUND IN SPECIES #1507320	CaSO4 AQ

---------- EQUILIBRATED MASS DISTRIBUTION ----------

IDX	NAME	DISSOLVED		SORBED		PRECIPITATED	
		MOL/KG	PERCENT	MOL/KG	PERCENT	MOL/KG	PERCENT
330	H+1	-1.705E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
770	H4SiO4	3.098E-05	7.8	0.000E-01	0.0	3.686E-04	92.2
732	SO4-2	6.040E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
180	Cl-1	2.821E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
492	NO3-1	1.291E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
270	F-1	5.265E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
580	PO4-3	4.196E-10	0.0	0.000E-01	0.0	4.212E-06	100.0
410	K+1	3.326E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
500	Na+1	9.343E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
231	Cu+2	2.204E-06	100.0	0.000E-01	0.0	0.000E-01	0.0
30	Al+3	1.186E-05	100.0	0.000E-01	0.0	0.000E-01	0.0
460	Mg+2	1.147E-08	0.0	0.000E-01	0.0	2.304E-04	100.0
140	CO3-2	4.197E-05	1.3	0.000E-01	0.0	3.088E-03	98.7
2	H2O	1.655E-04	100.0	0.000E-01	0.0	0.000E-01	0.0
150	Ca+2	3.021E-04	8.7	0.000E-01	0.0	3.187E-03	91.3

Charge Balance: SPECIATED

Sum of CATIONS = 1.523E-03 Sum of ANIONS 1.721E-03

PERCENT DIFFERENCE = 6.114E+00 (ANIONS - CATIONS)/(ANIONS + CATIONS)

EQUILIBRIUM IONIC STRENGTH (m) = 2.506E-03

EQUILIBRIUM pH = 10.565

DATE ID NUMBER: 931030
TIME ID NUMBER: 18032838

Saturation indices and stoichiometry of all minerals

ID #	NAME	Sat. Index	Stoichiometry in [brackets]
2003000	ALOH3(A)	-2.217	[1.000] 30 [3.000] 2 [-3.000] 330
6003000	ALOHSO4	-11.978	[-1.000] 330 [1.000] 30 [1.000] 732
			[1.000] 2
6003001	AL4(OH)10SO4	-10.158	[-10.000] 330 [4.000] 30 [1.000] 732
			[10.000] 2
6041000	ALUM K	-28.145	[1.000] 410 [1.000] 30 [2.000] 732
			[12.000] 2
6041001	ALUNITE	-13.601	[1.000] 410 [3.000] 30 [2.000] 732
			[6.000] 2 [-6.000] 330
6015000	ANHYDRITE	-2.492	[1.000] 150 [1.000] 732
5015000	ARAGONITE	-0.198	[1.000] 150 [1.000] 140
5046000	ARTINITE	-10.520	[-2.000] 330 [2.000] 460 [1.000] 140
			[5.000] 2
2003001	BOEHMITE	-0.459	[-3.000] 330 [1.000] 30 [2.000] 2
2046000	BRUCITE	-4.770	[1.000] 460 [2.000] 2 [-2.000] 330
5015001	CALCITE	0.000	[1.000] 150 [1.000] 140
2077000	CHALCEDONY	-1.271	[-2.000] 2 [1.000] 770
8646000	CHRYSOTILE	-5.074	[-6.000] 330 [3.000] 460 [2.000] 770
			[1.000] 2
8246000	CLINOENSTITE	-4.061	[-1.000] 2 [1.000] 460 [1.000] 770
			[-2.000] 330
2077001	CRISTOBALITE	-1.172	[-2.000] 2 [1.000] 770
2003002	DIASPORE	1.387	[-3.000] 330 [1.000] 30 [2.000] 2
8215000	DIOPSIDE	-0.601	[-2.000] 2 [1.000] 150 [1.000] 460
			[2.000] 770 [-4.000] 330
5015002	DOLOMITE	-4.563	[1.000] 150 [1.000] 460 [2.000] 140
6046000	EPSOMITE	-9.144	[1.000] 460 [1.000] 732 [7.000] 2
8646003	SEPIOLITE(C)	-5.826	[-0.500] 2 [2.000] 460 [3.000] 770
			[-4.000] 330
7015003	HYDRAPATITE	0.000	[5.000] 150 [3.000] 580 [1.000] 2
			[-1.000] 330
7015002	FCO3APATITE	4.262	[9.496] 150 [0.360] 500 [0.144] 460
			[4.800] 580 [1.200] 140 [2.480] 270
4215000	FLUORITE	-1.101	[1.000] 150 [2.000] 270
8046000	FORSTERITE	-9.105	[-4.000] 330 [2.000] 460 [1.000] 770
2003003	GIBBSITE (C)	-0.436	[-3.000] 330 [1.000] 30 [3.000] 2
3003000	Al2O3	-4.480	[2.000] 30 [3.000] 2 [-6.000] 330
6015001	GYPSUM	-2.119	[1.000] 150 [1.000] 732 [2.000] 2
4150000	HALITE	-8.172	[1.000] 500 [1.000] 180
5015003	HUNTITE	-17.948	[3.000] 460 [1.000] 150 [4.000] 140
5046001	HYDRMAGNESIT	-31.572	[5.000] 460 [4.000] 140 [-2.000] 330
			[6.000] 2
8450000	MAGADIITE	-13.047	[-1.000] 330 [-9.000] 2 [1.000] 500
			[7.000] 770

ID #	NAME	Sat. Index	Stoichiometry in [brackets]							
5046002	MAGNESITE	-5.044	[1.000]	460	[1.000]	140				
6050001	MIRABILITE	-7.559	[2.000]	500	[1.000]	732	[10.000]	2		
3050000	NATRON	-8.921	[2.000]	500	[1.000]	140	[10.000]	2		
5046003	NESQUEHONITE	-7.437	[1.000]	460	[1.000]	140	[3.000]	2		
8646001	PHLOGOPITE	-30.215	[-10.000]	330	[1.000]	410	[3.000]	460		
			[1.000]	30	[3.000]	770				
2077002	QUARTZ	-0.724	[-2.000]	2	[1.000]	770				
8646004	SEPIOLITE(A)	-7.597	[-0.500]	2	[2.000]	460	[3.000]	770		
			[-4.000]	330						
2077003	SIO2(A,GL)	-1.783	[-2.000]	2	[1.000]	770				
2077004	SIO2(A,PT)	-2.113	[-2.000]	2	[1.000]	770				
8646002	TALC	-5.198	[-4.000]	2	[3.000]	460	[4.000]	770		
			[-6.000]	330						
6050002	THENARDITE	-9.280	[2.000]	500	[1.000]	732				
5050001	THERMONATR	-11.102	[2.000]	500	[1.000]	140	[1.000]	2		
8215001	TREMOLITE	0.000	[-8.000]	2	[2.000]	150	[5.000]	460		
			[8.000]	770	[-14.000]	330				
4123100	MELANOTHALLI	-24.479	[1.000]	231	[2.000]	180				
5023100	CUCO3	-8.234	[1.000]	231	[1.000]	140				
4223100	CUF2	-21.629	[1.000]	231	[2.000]	270				
4223101	CUF2, 2H2O	-17.310	[1.000]	231	[2.000]	270	[2.000]	2		
2023100	CU(OH)2	-1.231	[-2.000]	330	[1.000]	231	[2.000]	2		
4123101	ATACAMITE	-6.185	[-3.000]	330	[2.000]	231	[3.000]	2		
			[1.000]	180						
5123100	CU2(OH)3NO3	-9.370	[-3.000]	330	[2.000]	231	[3.000]	2		
			[1.000]	492						
6023100	ANTLERITE	-8.681	[-4.000]	330	[3.000]	231	[4.000]	2		
			[1.000]	732						
6023101	BROCHANTITE	-7.708	[-6.000]	330	[4.000]	231	[6.000]	2		
			[1.000]	732						
6023102	LANGITE	-10.751	[-6.000]	330	[4.000]	231	[7.000]	2		
			[1.000]	732						
2023101	TENORITE	-0.210	[-2.000]	330	[1.000]	231	[1.000]	2		
6023103	CUOCUSO4	-21.373	[-2.000]	330	[2.000]	231	[1.000]	2		
			[1.000]	732						
7023100	CU3(PO4)2	-26.819	[3.000]	231	[2.000]	580				
7023101	CU3(PO4)2,3W	-28.549	[3.000]	231	[2.000]	580	[3.000]	2		
6023104	CUSO4	-20.175	[1.000]	231	[1.000]	732				
6023105	CHALCANTHITE	-13.738	[1.000]	231	[1.000]	732	[5.000]	2		
2023102	DIOPTASE	-3.817	[-2.000]	330	[1.000]	231	[1.000]	770		
8450001	ANALCIME	-0.835	[1.000]	500	[1.000]	30	[2.000]	770		
			[-1.000]	2	[-4.000]	330				
8603000	HALLOYSITE	-2.050	[2.000]	30	[2.000]	770	[1.000]	2		
			[-6.000]	330						
8603001	KAOLINITE	1.396	[2.000]	30	[2.000]	770	[1.000]	2		
			[-6.000]	330						
8415000	LEONHARDITE	12.203	[-1.000]	2	[-16.000]	330	[2.000]	150		
			[8.000]	770	[4.000]	30				
8450002	LOW ALBITE	-1.469	[1.000]	500	[1.000]	30	[3.000]	770		
			[-4.000]	330	[-4.000]	2				
8450003	ANALBITE	-2.488	[1.000]	500	[1.000]	30	[3.000]	770		
			[-4.000]	330	[-4.000]	2				

ID #	NAME	Sat. Index	Stoichiometry in [brackets]
8641000	MUSCOVITE	3.498	[1.000] 410 [3.000] 30 [3.000] 770
			[-10.000] 330
8415001	ANORTHITE	-2.248	[1.000] 150 [2.000] 30 [2.000] 770
			[-8.000] 330
8603002	PYROPHYLLITE	0.179	[2.000] 30 [4.000] 770 [-4.000] 2
			[-6.000] 330
8415002	LAUMONTITE	-0.426	[1.000] 150 [2.000] 30 [4.000] 770
			[-8.000] 330
8415003	WAIRAKITE	-5.346	[1.000] 150 [2.000] 30 [4.000] 770
			[-8.000] 330 [-2.000] 2
5023101	MALACHITE	-5.289	[2.000] 231 [2.000] 2 [1.000] 140
			[-2.000] 330
5023102	AZURITE	-11.740	[3.000] 231 [2.000] 2 [2.000] 140
			[-2.000] 330
2015000	LIME	-17.176	[-2.000] 330 [1.000] 150 [1.000] 2
2015001	PORTLANDITE	-6.428	[-2.000] 330 [1.000] 150 [2.000] 2
2046001	PERICLASE	-9.901	[-2.000] 330 [1.000] 460 [1.000] 2
3046000	SPINEL	-8.353	[-8.000] 330 [1.000] 460 [2.000] 30
			[4.000] 2
4250000	CRYOLITE	-25.495	[1.000] 30 [3.000] 500 [6.000] 270
8215002	WOLLASTONITE	-1.278	[-1.000] 2 [-2.000] 330 [1.000] 770
			[1.000] 150
8215003	P-WOLLSTANIT	-2.191	[-1.000] 2 [-2.000] 330 [1.000] 770
			[1.000] 150
8015001	CA-OLIVINE	-9.865	[-4.000] 330 [1.000] 770 [2.000] 150
8015002	LARNITE	-11.459	[-4.000] 330 [1.000] 770 [2.000] 150
8015007	CA3SIO5	-30.678	[-6.000] 330 [1.000] 770 [3.000] 150
			[1.000] 2
8015003	MONTICELLITE	-6.696	[-4.000] 330 [1.000] 770 [1.000] 150
			[1.000] 460
8015005	AKERMINITE	-12.481	[-1.000] 2 [-6.000] 330 [2.000] 770
			[2.000] 150 [1.000] 460
8015004	MERWINITE	-17.303	[-8.000] 330 [2.000] 770 [1.000] 460
			[3.000] 150
8441000	KALSILITE	-3.668	[-4.000] 330 [1.000] 770 [1.000] 30
			[1.000] 410
8441001	LEUCITE	-1.958	[-2.000] 2 [-4.000] 330 [2.000] 770
			[1.000] 30 [1.000] 410
8441002	MICROCLINE	-0.737	[-4.000] 2 [-4.000] 330 [3.000] 770
			[1.000] 30 [1.000] 410
8441003	H SANIDINE	-1.262	[-4.000] 2 [-4.000] 330 [3.000] 770
			[1.000] 30 [1.000] 410
8450004	NEPHELINE	-3.771	[-4.000] 330 [1.000] 770 [1.000] 30
			[1.000] 500
8015006	GEHLENITE	-13.007	[-10.000] 330 [2.000] 30 [1.000] 770
			[2.000] 150 [3.000] 2

APPENDIX B

EVALUATION OF ON-SITE DISPOSAL OF BLOWDOWN WATER AND SLUDGE

B.1 On-site Disposal of Blowdown Water

The possibility of using the Saturn Cooling Tower blowdown water for irrigation water has been researched by Barnett [25]. He stated that irrigation water quality standards have been developed by the Tennessee Department of Health and Environment (TDHE) and by other independent sources. Assessing the impact of specific pollutants on crops, soils and the food chain is complex. Each pollutant may be of concern for a variety of reasons. Pollutants may be directly toxic to the crops, may accumulate to unacceptable levels in the soil, or the plants may absorb and concentrate the pollutants to such an extent that introduction into the food chain is unsafe. Complicating the situation is the fact that different crops have widely varying tolerances and uptakes of individual pollutants. Differences in soil characteristics may also influence the effect of individual pollutants. These standards issued by TDHE and others are based on the most likely damaging effect of a pollutant on the most sensitive plant species. In some cases, soil characteristics were considered in establishing limits for pollutant buildup in soils. In most instances, the limiting pollutant concentration is based on introduction of pollutants into the food chain. The irrigation water quality standards presented herein are considered safe for long-term irrigation of all plant species under normal conditions. Since many of the limits are based on pollutant concentration buildup in the soil, it may not be hazardous to exceed the limits on a short-term basis, and exceptions to the limits may be warranted for individual cases.

The species concentrations in the blowdown water was dependent upon the make-up water species concentrations and the cycles of concentration which the simulated cooling tower is operated at. The make-up water concentrations (which corresponds to blowdown water concentrations for a cycles of concentration of 1.0) and blowdown water concentrations for 27.3 cycles of concentration is presented in Table B-1, along with the irrigation water quality limits determined by TDHE and Wescot et. al. as presented by Barnett [25]. From Table B-1, it can be seen that for one cycle of concentration, the flouride concentrations in the make-up water is at the disposal concentration limit. Also, the bicarbonate may cause some slight restrictions on disposal since it is between the 90-500 mg/l range. Three cycles of concentrations without softening treatment would result in the TDS and copper concentration limits being surpassed. At six cycles of concentration without softening, the sodium limit would be surpassed, and the bicarbonate concentration would pose severe restrictions on disposal. Softening treatment would not decrease the flouride, copper, or sodium concentrations, and would increase the TDS concentration. Therefore, unless soil characteristics allow exceedence of the irrigation water quality limits established by TDHE or Wescot et. al., on-site disposal of the blowdown water is not considered a viable option.

B.2 On-site Disposal of Sludge

On-site disposal of sludge requires approval from the State of Tennessee-Department of Environment and Conservation [35]. Analysis of the settling basin and sand filter which includes the percent solids of 26 chemical species are required. Disposal site information is required which includes a soil sample, the location of the

Table B-1. Make-up and Blowdown Water Quality and Irrigation Water Quality Standards

Species	Make-up Water Quality (mg/l)	Blowdown Water Quality (mg/l)	Irrigation Limit (mg/l)[1]	TDHE Limit (mg/l)[2]
Silica	0.4	0.85	Not established	Not established
TDS	223	3256	500[3]	Not established
Sulfate	58	1752	Not established	Not established
Chloride	10	273	100	100
Bicarbonate	142	129	90[4]	91[5]
Nitrogen-Nitrate	0.8	21.9	5	Not established
Fluoride	1.0	27.3	1	1.8
Phosphates, Total	0.4	0	Not established	Not established
Calcium	64	331	Not established	Not established
Magnesium	5.6	0	Not established	Not established
Copper	0.14	3.82	0.2	0.4
Aluminum	0.32	8.74	5	10
Sodium	12.8	587	70	70
Potassium	1.3	36	Not established	Not established
pH	7.8	8.4	6.5-8.4	6.5-8.4

Notes: (1) Irrigation Limit from Wescot, D.W. and R.S. Ayers. "Irrigation Water Quality Criteria", Irrigation with Reclaimed Municipal Wastewater, Lewis Publishers, Chelsea, MI. 1985

(2) TDHE Limit from Tennessee Department of Health and Environment, Chapter 16, Slow Rate Land Treatment in Design Criteria of Sewage Treatment Works

(3) Limit is defined as <500 no restrictions, 500-2000 slight restrictions, >2000 severe restrictions

(4) Limit is defined as <90 no restrictions, 90-500 slight restrictions, >500 severe restrictions

(5) Limit is defined as <91 no problem, 91-519 increasing problems, >519 severe problems

nearest stream or tributary, public water supply, well and spring. The intended land usage while the site is receiving land applications must be stipulated. Other information required is the method of application and application rate of the sludge. Obtaining this information for sludge disposal is beyond the scope of this thesis and therefore approval

for on-site disposal of the sludge could not be ascertained.

VITA

John J. Melescue, Jr. was born in Portsmouth, Va in 1958. His family moved to District Heights, Maryland when he was 5 years old, where he attended elementary school. His family then moved to Burke, Va. when he was 14 where he attended Lake Braddock Secondary School, graduating in the class of '77. He received a B.S. degree in Aeronautical Engineering at Embry-Riddle Aeronautical University in Daytona Beach, Fl. in 1981. He went to work for Sverdrup Technology, Inc. in Tullahoma, Tennessee. for 10 years testing turbine engines for the Air Force at Arnold Engineering Development Center (AEDC). While working full time at AEDC, he attended the University of Tennessee Space Institute as a part time student, receiving a M.S. degree in Aeronautical Engineering in 1987. One June 1, 1991, he received Jesus Christ as his Lord and Savior. In August, 1991 he left Sverdrup to attend the University of Tennessee full time to get his M.S. degree in Environmental Engineering. He now works for Oak Ridge National Laboratory in Oak Ridge Tennessee.