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AN ANALYIS OF WATER FOR WATER-SIDE FOULING POTENTIAL INSIDE SMOOTH AND AUGMENTED COPPER ALLOY CONDENSER TUBES IN COOLING TOWER WATER APPLICATIONS

by

Ian Tubman

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AN ANALYIS OF WATER FOR WATER-SIDE FOULING POTENTIAL INSIDE SMOOTH AND AUGMENTED COPPER ALLOY CONDENSER TUBES IN COOLING TOWER WATER APPLICATIONS

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This thesis investigates the potential for fouling in plain and augmented tubes in cooling tower applications. Three primary factors that affect fouling potential are examined: inside tube geometry, water velocity, and water quality. This paper presents a literature survey for in general precipitation fouling, particulate fouling, cooling water fouling, and fouling in enhanced tubes. This thesis also attempts to determine water qualities that are typical of those found in actual cooling towers. The water quality was determined by taking water samples from cooling towers throughout the country and chemically analyzing the samples. From this analysis, three water qualities were determined: an average fouling potential, a low fouling potential, and a severe fouling potential. These water qualities will be used in experimental determinations of fouling resistances in augmented tubes.

ACKNOWLEDGMENTS

I would first like to thank my major professor, Dr. Louay Chamra, for his support and guidance during my time in graduate school. I would acknowledge my graduate committee members, Dr. B.K. Hodge and Dr. Carl James.

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NOMENCLATURE

A	Internal surface area
A_p	Internal surface area of a plain tube
B	Constant
b	Constant
C	Concentration of the foulant
C_b	Concentration of the foulant in the bulk of the solution
$c_{p,w}$	Specific heat at constant pressure of water
C_s	Concentration of the foulant near the surface
C_x	Constant
D	Diffusion coefficient
d_i	Inside diameter
d_o	Outside diameter
d_p	Diameter of particle
E	Activation energy
e	Fin height
f	Friction factor
K_1'	First dissociation constant of carbonic acid, based on concentration units and taking into account ionic strength factors
K_2'	Second dissociation constant of carbonic acid, based on concentration units and taking into account ionic strength factors

k_{BF}	Mass transfer coefficient for diffusion of Ca^{+2} ions, HCO_2^- ions or $Ca(HCO_3)_2$
k_D	Mass transfer of ions
k_E	Mass transfer coefficient for diffusion of dissolved CO_2
k_m	Mass transfer coefficient
k_r	First-order reaction rate constant
k_s	Thermal conductivity of the scale
K_s’	Solubility product of the calcite, based on concentration units and taking into account ionic strength factors
K_{sp}’	Solubility product of $CaCO_3$
LMTD	Log Mean Temperature Difference
L	Length
LSI	Langelier Saturation Index
$\dot{m}_w$	Mass flow rate of water
N	Mass flux normal to the surface
n_s	Number of starts
p	Fin pitch
P	Sticking probability
P_a	Probability of a value falling above a given value
P_b	Probability of a value falling below a given value
P_d	Probability function of velocity
$\dot{Q}$	Heat flow rate
R_f	Fouling resistance

R_f*	Asymptotic fouling resistance
R_g	Universal gas constant
Sc	Schmidt number
STI	Ryznor Index
t	Time
t_o	Initial time
T_s	Surface temperature
$T_{w,in}$	Water temperature at inlet
$T_{w,out}$	Water temperature at outlet
U_c	Over-all heat transfer coefficient of clean tubes
U_f	Over-all heat transfer coefficient of fouled tubes
U_i	Over-all heat transfer coefficient inside the tubes
u_m	Average fluid velocity
W	Weight of the fluid
w	Rate of growth of scale layer
x	Size of potential factor
x_c	Threshold value for fouling
x_f	Thickness of the deposit
Y	Probability distribution
z	Constant
z_c	Constant that corresponds to the threshold value of fouling potential

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Greek Symbols

α	Helix angle
β	Fraction of the heat transfer surface covered by bursts
μ	Dynamic viscosity
μ_m	Gausian mean
ξ	Deposit strength factor
ϕ_d	Deposition rate
ϕ_r	Removal rate
ψ	Characterizing function of the deposit structure
ρ_s	Density of the scale
τ	Fluid sheer stress
τ_s	Surface sheer stress
σ	Standard deviation
Ω	Water characterization factor

CHAPTER I

INTRODUCTION

1.1 Introduction to Fouling

Fouling is defined as the formation of deposits on heat transfer surfaces that impede heat transfer and increase the resistance to the flow of fluids over the surface. Fouling causes an economic penalty in a heat exchanger by the need to oversize the heat exchanger, by the energy losses due to poor performance, by the loss of production for cleaning, and by the blockage of the heat exchanger in a severe cases. The following six types of fouling that have been defined for the interface of a fluid with a solid heat transfer surface:

1. Precipitation Fouling: The deposition of materials on a heat transfer surface when a substance comes out of solution due to a change in temperature or phase of the solvent.
2. Particulate Fouling: The deposition of a suspended solid in a fluid.
3. Chemical Reaction Fouling: The deposition left when the fluid flowing over the heat transfer surface chemically reacts with the surface.
4. Biological Fouling: The growth of macro or micro-organisms on the heat transfer surface.
5. Corrosion Fouling: The deposition of deposits, which are formed with the assistance of the surface material.

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6. Solidification Fouling: The freezing of a pure liquid onto a sub-cooled surface.

Fouling resistances will follow one of three major types of fouling curves. The first is a linear fouling curve, where the fouling resistance increases at a constant rate until the tube is completely blocked. Pure precipitation fouling follows a linear fouling curve. The second type of fouling curve is a falling rate curve, in which the rate curve the fouling resistance again rises until the tube is blocked, but the rate decreases as the resistance increases. The third type of fouling curve is asymptotic, where the rate increases sharply and then decreases as it approaches a constant fouling resistance. Pure particulate fouling and combined precipitation and particulate fouling follow this type of fouling curve. The three fouling curves can be seen in Figure 1.1.

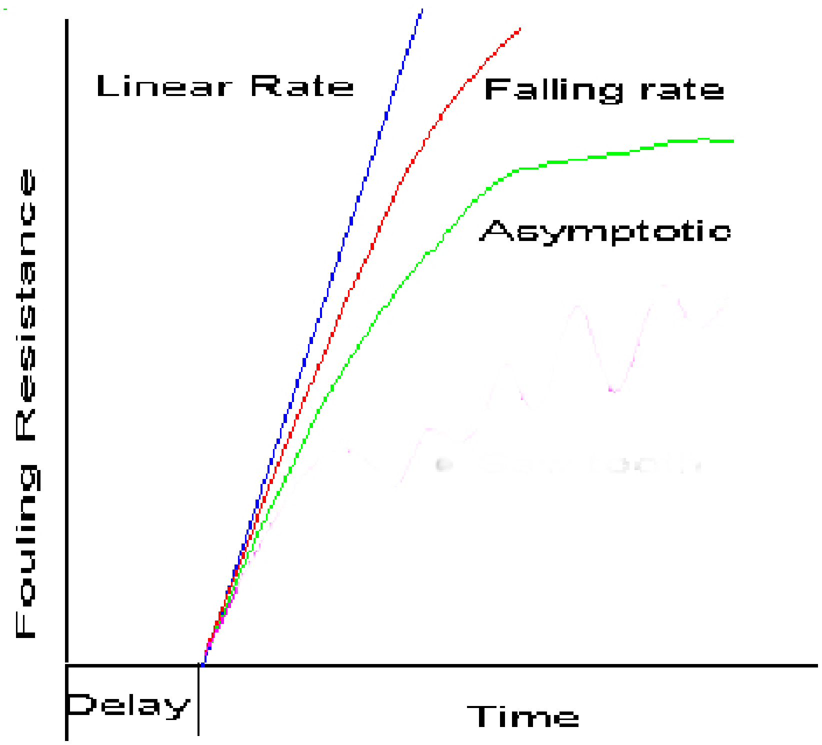

Figure 1.1: Fouling Curve Types

1.2 Introduction to Cooling Towers

Industrial chillers consist of two shell-and-tube heat exchangers, one a condenser and one an evaporator. Refrigerant is cycled through the shell sides of the heat exchangers. Water is the tube-side fluid in both of the heat exchangers. The evaporator is used to cool water that is then used as a chilled water supply in an air handler unit. The condenser is used to reject the heat in the refrigerant. The water to which the heat is rejected is pumped to a device to reject heat to the ambient air. In many cases, this heat rejection is accomplished by use of a convective cooling tower. In a cooling tower, water is sprayed into the air at the top of the cooling tower, while a fan blows air up the cooling tower. The water is then collected in a basin at the bottom of the cooling tower. Since some of the water is blown out of the cooling tower and some is evaporated, make-up water is added into the system. A float valve, or some other level indicator in the basin, normally controls the rate of make-up water added. A schematic of a typical chiller/cooling tower set-up can is presented in Figure 1.2. Because the water is exposed to open air, many foulants can be taken to the system through the cooling tower.

1.3 The Use of Enhanced Tube Geometries

The use of enhanced tube surfaces first started being used in industry in the 1970s. Since then many new enhancement types have been developed as manufacturing techniques have become more sophisticated. In industrial chillers, the use of enhanced tubes, both on the tube side and the annulus side, has become a standard practice.

Webb (1994) states that there are three objectives of using enhanced surfaces:

1. Size reduction

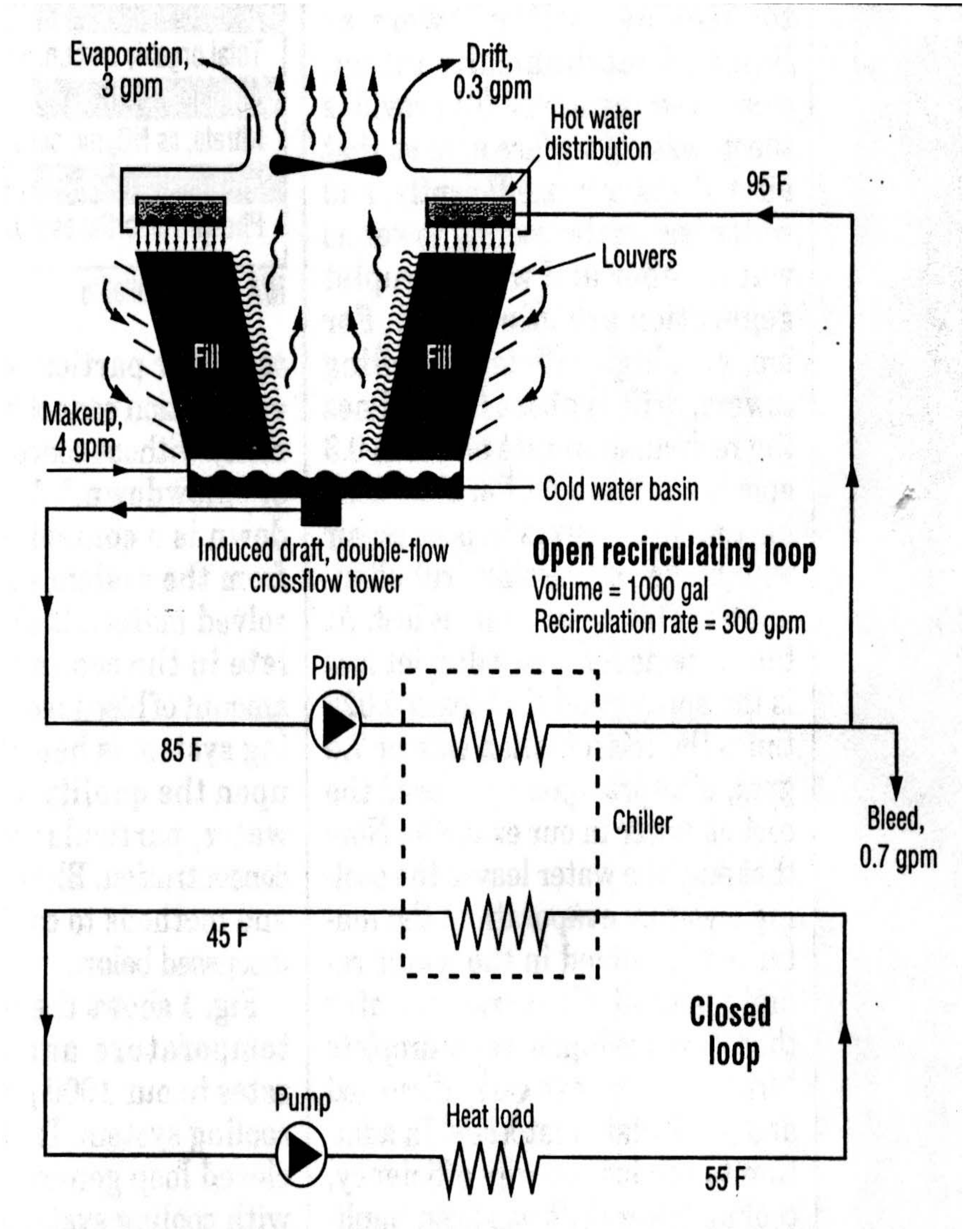

Figure 1.2: Typical Cooling Tower Set-up (Meitz 1999)

2. Increased heat exchange or a smaller operating temperature difference
3. Reduced pumping power for a fixed-heat duty.

To achieve the third goal an increase in the frontal area of the heat exchanger is needed; therefore, although reduced pumping power is possible it is not practical in the real world. The benefit that is of the most interest to the heating/cooling industry is the reduction in size of the heat exchanger and the subsequent initial cost savings. In cooling water condensers, the most commonly used enhancements are helical ribs on the water-side and integral fins on the outside surface.

The current practice to account for fouling in design is to include a fouling resistance in calculations and to oversize the heat exchanger based on this value. However, the recommended values are based upon smooth tubes or were set by experience (Somerscales, 1990), years before enhanced tubes were used. Recent research (Webb and Kim, 1989, and Chamra and Webb, 1993) suggests that fouling increases in augmented tubes, and may negate the benefits of the enhancements. The increased heat transfer gained by using the enhancements is lost because a thermal resistive layer is formed and the area between the enhancements is filled in, thus smoothing the pipe.

1.4 Project Purpose and Need

Because of the complexity of fouling mechanisms, they have been primarily studied as individual mechanisms. But, in actual conditions multiple mechanisms may be present. Little is understood about individual fouling mechanisms, and almost nothing is understood about how different mechanisms interact. In cooling tower applications, water is treated with corrosion inhibitors and biocides to eliminate biological and

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corrosion fouling mechanisms. Therefore, the fouling in cooling towers is typically a combination of precipitation and particulate fouling.

A study by Haider et al. (1991, 1992) was conducted on evaporator loops in industrial chillers. The current study will perform a similar analysis as that of Haider et al., except on the condenser loop instead of the evaporator loop. The stated objectives of this project are

1. Develop a water quality database for cooling water applications
2. Correlate fouling data with water quality
3. Experimentally determine the fouling on smooth and augmented tubes by directly using or simulating cooling tower water.

These objectives are to be accomplished in three phases:

Phase I: Literature Survey
Phase II: Water Quality Sampling Program
Phase III: Precipitation and Particulate Fouling Experimental Program

This thesis covers the first two phases of the project and lays the groundwork for the work to be done in Phase III.

In Phase I, a comprehensive literature survey was conducted. In Phase II sites around the country were contacted and asked to send water samples. The goal was to collect at least 60 samples. Unfortunately of the 220 sites contacted, only 19 responded. The samples that were collected were analyzed by the Mississippi State Chemical Laboratory for several parameters related to water quality. The samples were then statistically analyzed for fouling potential. The results of this analysis is discussed in Chapter III.

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CHAPTER II

LITERATURE SURVEY

2.1 Introduction

Somerscales (1990) presents the history of fouling research from its first appearance in the literature in 1756 to the International Conference On the Fouling of Heat Transfer Equipment in 1979. He discusses the origins of the fouling factor as a means of accounting for the fouling while designing heat exchangers. TEMA first published a table of fouling factors for different fluids in a multitude of applications in 1941. The current TEMA standards (Chenoweth, 1990) recommend a minimum design fouling factor for treated cooling tower water of 0.001.

This study focuses on fouling in cooling tower loops. Four of the possible fouling mechanisms can be found in cooling tower loops: precipitation, particulate, biological and corrosion. Cooling water, whether in a cooling tower loop or a once through system, is a very complex mixture that changes from location to location. Knusden (1981) provides a list of some of the possible constituents of cooling water. The constituents may fall into three categories: Salts, which may precipitate out of solution, suspended particles, typically from rivers, ponds, wells, etc., and residual water treatment components or substances added to the system after intake.

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Table 2.1: Possible Cooling Water Constituents

Cooling Water Constituents	Salts	Suspended Particles	Water Treatment Residuals
Calcium Carbonate	X		
Calcium Sulfate	X		
Calcium Phosphate	X		
Magnesium Salts	X		
Silica	X		
Iorn Oxide	X		
Silt		X	
Clay		X	
Mud		X	
Natural Organics		X	
Dissolved Iron		X	
Sand		X	
Debris		X	
Corrosive Products			X
Phosphates			X
Organic Dispersants			X
Trivalent Chromium			X
Microorganisms			X

As can be seen above the use of cooling towers causes many water quality issues which relate to fouling. The fact that the cooling tower is open to the air, introduces two fouling considerations. First having the cooling tower open promotes microbiological growth, and second allows particulate matter to enter the cooling water circuit. The source of the make-up water will contribute to its fouling potential. For example city water may contain chlorine or river water may have a higher concentration of suspended particles. The third factor that affects the quality of the water, and thus its potential for fouling, is the water treatment method used. Some of the chemicals used to prevent one

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fouling mode can contribute to another. For example, sulfuric acid, added to control pH, adds sulfate ions to the water that may precipitate out as calcium sulfate.

Heavy emphasis has been placed on the treatment of cooling tower water. Most municipal sources add chlorine to the water as a biocide, but chlorine has been implicated as a carcinogen when it reacts with dissolved organic compounds. Other biocides are also typically part of a treatment program, along with corrosion inhibitors. Through the use of these biocides and corrosion inhibitors, biological and corrosion fouling can be fairly-well controlled. This project focuses only on particulate and precipitation fouling.

2.2 Particulate Fouling

Particulate Fouling Models

The first significant attempt to derive of general fouling model was by Kern and Seaton (1959). They defined the net fouling rate as the difference between the deposition and the removal rate:

$$\frac{dR_f}{dt} = \phi_d - \phi_r \tag{2.1}$$

A commonly observed type of fouling is asymptotic fouling. In asymptotic fouling, the thermal resistance increases rapidly when fouling first begins and then reaches a constant value. Particulate fouling follows an asymptotic fouling curve. Kern and Seaton (1959) showed that if the rate of deposition were constant, and if the rate of

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removal were taken to be directly proportional to the mass of the fouling deposit on a unit area of the heat transfer surface, then

$$R_f = R_f^*(1-e^{-Bt}) \tag{2.2}$$

Kern and Seaton proposed that the deposition rate be a function of the concentration of the fouling and the constant weight of the fluid flow and takes the form

$$\phi_d = k_1 CW \tag{2.3}$$

For the removal rate, they proposed the following relationship between the thickness of the deposit and the sheer stress

$$\phi_r = k_2 \tau_s x_f \tag{2.4}$$

Kern and Seaton also found that the asymptotic fouling resistance was inversely proportional to the mass flow rate, and that the initial fouling rate was directly proportional to the mass flow rate.

Watkinson and Epstein (1970) expanded the Kern and Seaton model by suggesting that the deposition process was caused by the transfer of suspended particles to the wall region, followed by adhesion of particles to the wall or to previously-deposited film. The deposition rate was taken as proportional to mass flux normal to the

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surface, N. The Watkinson and Epstein model took into account the sticking probability, P. The mass flux normal to the surface was given by

$$N = K_m P(C_b - C_s) \tag{2.5}$$

where C_b is the bulk particle concentration and C_s is the particle concentration near the surface. The sticking probability was found from

$$P = \frac{C_x e^{-H}}{f \cdot u_m^2} \tag{2.6}$$

where $H = E/(R_g T_s)$ and f is the surface friction factor. Watkinson and Epstein compared experimental data as fouling-time curves against the Kern and Seaton model. Watkinson and Epstein found the asymptotic fouling resistance to be inversely proportional to the square of the mass flow rate, instead of to the first power as in the Kern and Seaton model. Watkinson and Epstein also found the initial fouling rate was inversely proportional to the mass flow rate and depended exponentially on the initial fouling rate. In both models, the shear stress plays an important role in the removal rate. The shear stress is a direct function of the fluid velocity. This suggests that as the fluid velocity increases, the overall fouling should go down. A study conducted on particulate fouling in plate heat exchangers by Thonon et al. (1999) demonstrated this fact. They found that the asymptotic fouling resistance was inversely proportional to the velocity squared.

Cleaver and Yates (1975,1976) show that particles are subjected to “turbulent

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bursts" near the heat transfer surface. These upsweeps, or small tornado-like vortices, and downsweeps affect the removal and deposition of the particles to the wall. By continuity, the fluid bursts are compensated for by gentler downsweeps. Downsweeps cause the deposition. Cleaver and Yates (1975) developed a sublayer model for the deposition of particles. They state that once a particle is caught in a downsweep, it will continue within the downsweep with little interruption. The position that the particle enters the downsweep and its inertia will determine whether it contacts the surface. Only those particles between the turbulent bursts will have the possibility of approaching the surface; the others will be within the influence of the burst and will be swept away from the wall back into the outer regions of the boundary layer. To deduce the particle trajectory equations, Cleaver and Yates (1975) considered a two-dimensional stagnation point flow pattern within the viscous sublayer, in which the only force acting on the particle was the Stokes viscous drag. The agreement between the predictions and available data for large and small particles was good. The removal process is caused by the turbulent bursts, which act like small tornadoes lifting the particles from the surface. Cleaver and Yates (1976) show that these turbulent bursts would provide a much higher particle removal rate then the classical picture of turbulent flow. Epstein (1979) reviewed the work of Cleaver and Yates and derived an expression for the time constant of the asymptotic fouling curve based on the turbulent burst flow. Based on that expression, the removal rate has the form

$$\phi_r = C\frac{\tau_s \beta}{\mu \xi} \tag{2.7}$$

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where β is the fraction of the heat transfer surface covered by bursts at any instant, μ is the absolute viscosity of the liquid, and ξ is the deposit strength factor.

Particulate Fouling Experiments on Enhanced Tubes

In the literature there have been several studies done on particulate fouling in enhanced tubes. Webb and Kim (1989) measured accelerated particulate fouling in water for three helically-ribbed tubes (GEWA-SC tube, GEWA-TWX tube, and GEWA-Spin tube all made by Weiland-Werke AG.) and one plain tube. Pictures of the three tubes can be found in Figure 2.1. The purpose of the study was to compare the fouling resistance of the enhanced tubes with the plain tube and to see how well on-line brushes cleaned these deposits. Ferric oxide powder and 3μm diameter aluminum oxide particles were used separately as foulants. The results were similar for both foulants. The tests were run at a concentration of 2000 ppm and a water velocity of 1.7 m/s. At this velocity, only the SC tube showed significant fouling. At the lower water velocity, 1.2 m/s, all of the tubes showed significant fouling. These conditions are much more severe then those expected in the field and, therefore, cannot be used to predict the long term fouling rates in actual heat exchanger units.

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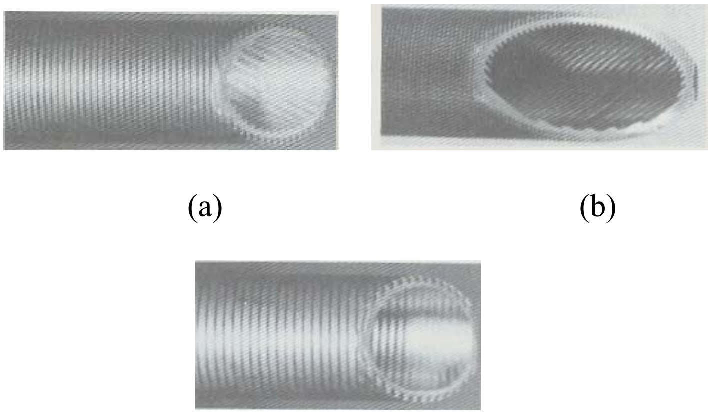

(a) (b)

(c)

Figure 2.1: a) GEWA-SC, b) GEWA-SPIN, c) GEWA-TWX Tubes

Webb and Chamra (1991) performed particulate fouling tests on two commercially available enhanced tubes (GEWA-NW tube by Weiland-Werke AG. and Korodense tube by Wolverine Tube Inc.) and a plain tube, using 0.3μm diameter aluminum oxide particles. The tests were performed at a water velocity of 1.8 m/s and a concentration of 1500 ppm. All of the runs reached a asymptotic fouling resistance within 32 hours. Both of the enhanced tubes fouled significantly faster than the plain tube, which showed negligible fouling. The NW tube was also tested with a particle size of 3μm. As the particle size increased, the fouling rate decreased. This is because in the diffusion regime, the particle deposition velocity becomes proportional to $Sc^{-2/3}$, as shown by Webb and Kim (1989), and Sc is proportional to $1/d_p$.

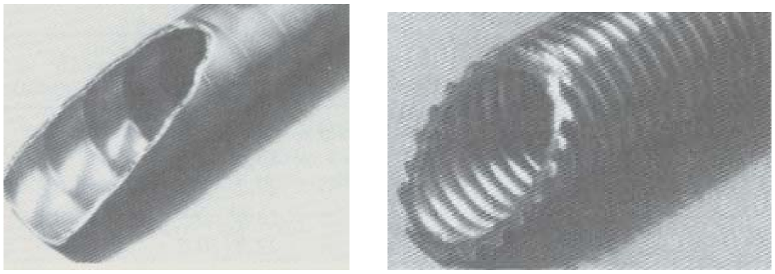

Figure 2.2: Korodense Tube and GEWA-NW Tubes

Somerscales et al. (1991) ran tests on five enhanced tubes and one plain tube. The tubes tested were the Wolverine Turbo-Chil, the Turbo-B, the Korodense, and two internally-finned tubes. The first finned tube had an ID of 12.3mm and 10 axial fins 1.57 mm in height. The second finned tube had an ID of 16.2mm with 38 helical fins 0.64mm high and with a 27-degree helix angle. Examples of a axial finned tube and a helically-finned tube is illustrated in Figure 2.3. The Somerscales et al. tests were run at a concentration of 2500 ppm of 3μm diameter aluminum oxide particles at two fluid velocities, 1.0 m/s and 1.5 m/s. Contrary to the Webb and Chamra (1991) study, Somerscales et al. found that the Korodense tube had a lower fouling rate than the plain tube. The Turbo-Chil tube tested by Somerscales et al. has the same inside geometry as the GEWA-SPIN tube tested by Webb and Kim (1989). Somerscales et al. found smaller fouling rates than Webb and Kim (1989). Webb (1994) suggests that the shorter test section used by Somerscales et al. may explain the difference in these results. Also the test sections in Somerscales et al. were mounted vertically, and this may account for some of the difference.

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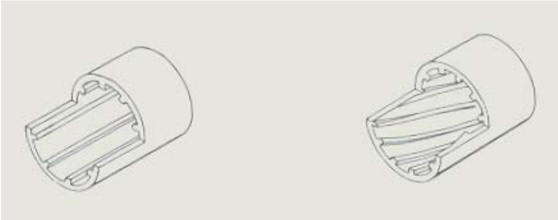

Figure 2.3: Axial Finned Tube and Helically Finned Tube

Chamra and Webb (1993) conducted tests using simulated river water with clay and silt as foulants and with a variety of particle diameters and concentrations. The tests were conducted at concentrations between 800 and 2000 ppm and diameters of 2, 4 and 16 μm. The fluid Reynolds numbers were varied between 24000 and 65000 for a fixed concentration of 1500 ppm. The fouling resistances of the Korodense and GEWA-NW tubes were compared against a plain tube. Fouling resistance was shown to be strongly dependent on the particle diameter, Reynolds number, and concentration. The asymptotic fouling resistance decreased as the Reynolds number and particle diameter increased. However, the asymptotic fouling resistance increased as particle concentration increased.

Chamra and Webb (1994) used the experimental results in the 1993 study and developed a semi-empirical model for the fouling in enhanced tubes. The model took into account the particle size distribution in the foulant. The model was used to compare the performance of the two enhanced geometries test with the performance of a plain tube with a given concentration, velocity, and particle size. By curve fitting the data to find R_f* and B it was found that sticking probability and deposit strength for the enhanced tube as compared to the plain tubes are

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$$\frac{P_{enh}}{P_{ref}} \propto \tau_s^{-0.721} d_p^{-0.319} C_b^{1.02} (\frac{e}{D})^{-0.307} \qquad (2.8)$$

$$\frac{\xi_{enh}}{\xi_{ref}} = \propto \tau_s^{-0.435} d_p^{-0.0769} C_b^{0.421} (\frac{e}{d_i})^{-0.396} \qquad (2.9)$$

All of the experiments by Webb and his colleagues were conducted on the same apparatus. It consists of four double-tube heat exchangers connected in parallel with the water flowing on the inside of the inner tube. R-114 is condensed on the annulus side of the condenser. The test section can be seen in Figure 2.4, and the system schematic is shown in Figure 2.5.

Two general notes should be made about the previous studies into particulate fouling in enhanced tubes. First, all of the studies referenced were performed at conditions more severe than would be expected in the field and, therefore, are not good indicators of how an enhanced tube might perform. Secondly, in most cases, despite the higher fouling rates compared to plain tubes, the enhanced tubes still had a much higher heat transfer rate then the plain tubes after fouling (Somerscales et al., 1991).

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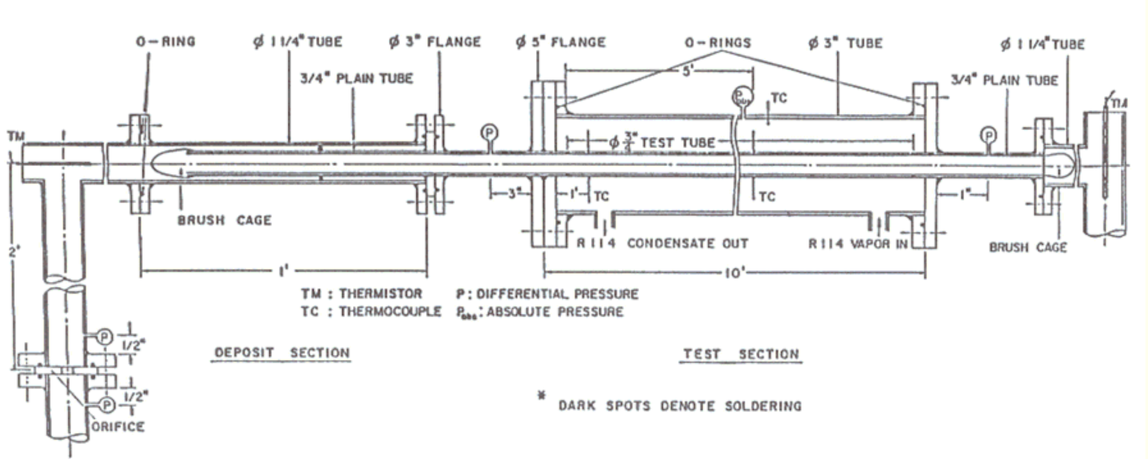

Figure 2.4: Test Section Used by Webb and His Colleagues

2.3 Precipitation Fouling

The other major form of fouling commonly found in cooling tower water is precipitation fouling, also known as scaling or crystallization. Precipitation fouling occurs when a dissolved material comes out of solution and deposits on the heat transfer surface. In cooling water, the precipitants are inverse soluble salts and, most commonly, calcium carbonate. Precipitation fouling usually follows a linear fouling curve. In general, for precipitation to occur, the solubility limit at given conditions, particularly the temperature must be exceeded, or in other words for the solution to be supersaturated. The temperature distribution, which is dependent on the flow conditions as well as the available overall temperature difference across the heat exchanger, affects the location of the precipitation. If the region of supersaturation is at the heat transfer surface, then precipitation is likely. If the supersaturation is away from the heat transfer surface,

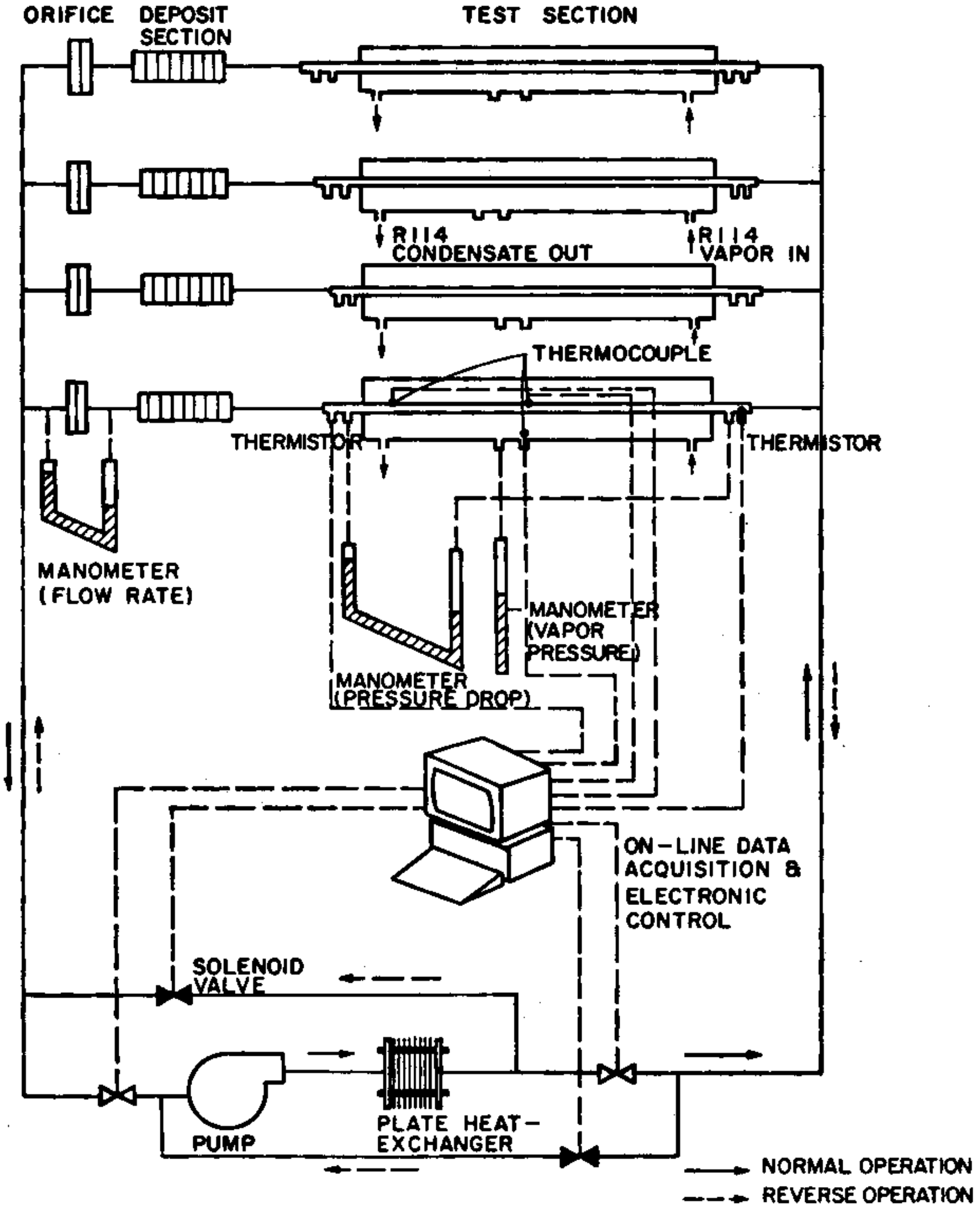

Figure 2.5: Schematic of the Apparatus Used by Webb and His Colleagues

crystals will form in the bulk fluid and deposit in the same manner as a particulate (Bott, 1997). The degree of supersaturation was found to affect what type of crystals form. Calcium carbonate will crystallize in two forms, calcite and aragonite. Aragonite forms at higher supersaturation ratios and has the greater effect on the fouling resistance, while calcite forms at lower supersaturation ratios and has less of an effect on the fouling resistance (Turner and Smith, 1998).

Ritter (1983) conducted scaling tests for two salts, lithium sulfate and calcium sulfate. He found that the scaling rates of the different salts could be correlated using the following six parameters:

- Supersaturation
- Mass transfer coefficient
- Surface temperature
- Sheer stress
- Heat flux
- Reynolds number

Ritter found that supersaturation was the most important parameter in determining the fouling rate. The other parameters varied in importance depending on which salt was tested. For example, the mass transfer coefficients was the second most important parameter in correlating the fouling in calcium sulfate and surface temperature in lithium sulfate. Hasson (1981) lists three process conditions which lead to supersaturation:

1. A solution is evaporated beyond the solubility limits of a dissolved salt.

2. A solution containing a dissolved salt of normal solubility is cooled below its solubility temperature or a solution containing a dissolved salt of inverse solubility is heated above its solubility temperature.
3. Mixing of different streams may also lead to the creation of supersaturated conditions, as is the case of $CaSO_4$ scale formation in phosphoric acid evaporators.

Hasson (1981) also lists the significant parameters which determine the superaturation potential that causes precipitation fouling:

1. The composition of the fresh water feed or of the process feed solution
2. The concentration effects occurring in the process through the separation of near pure water by evaporation or by a single-phase diffusion process
3. The temperature level of the process or operation which affects the solubility limits of the scaling salts, many of which have inverse solubility characteristics
4. The temperature gradient characterizing the heat-transfer operation to which the solution is exposed and the heat transfer mechanism

Precipitation Fouling Models

Somerscales (1990) reports that the first researcher to model fouling as a mass transfer process was Hasson in 1962 as he modeled calcium carbonate precipitation. Hasson assumed that the rate of growth of the deposit was given by

$$\phi_r = \frac{([Ca(HCO_3)_2] - K_s^{'})}{1/K_m + 1/k_r} \qquad (2.10)$$

where K_m is the mass transfer coefficient at the deposit-fluid interface and K_r is the reaction rate associated with the formation of the crystalline solid on the foulant surface. The solubility product, $K'_{s,}$ of the deposit at the deposit-fluid interface is available from the literature. Hasson et al. (1968) extended his calcium carbonate model and verified by more accurate data obtained with an improved experimental technique on the rate of scale growth. Hasson et al. used the following equation for the over-all rate of $CaCO_3$ deposition, in moles per unit area per unit time:

$$\frac{w}{k} = (C_f - 2\frac{w}{k_{BF}})^2 - (\frac{K_1^{'}}{K_2^{'}}) \cdot (C_E + \frac{w}{k_E}) \cdot [\frac{w}{k_R} + \frac{K_s^{'}}{C_B - w(1/k_{BF} + 1/k_R)}] \qquad (2.11)$$

For diffusion-controlled scale growth, the above equation simplifies to

$$(C_E + \frac{w}{k_E}) = (\frac{K_2^{'}}{K_3^{'}} \cdot K_s^{'}) \cdot (C_F - 2\frac{w}{k_{BF}})^2 \cdot (C_B - \frac{w}{k_{BF}}) \qquad (2.12)$$

The experimental portion of the study considered two factors that effect the growth rate of the scale. The first was the velocity of the fluid. Hasson et al. varied the velocity between 25 cm/s and 82 cm/s, while maintaining relatively constant water qualities, surface temperature, and bulk temperatures. Equation 2.10 was solved for the given flow conditions, so that the scale growth rate was expressed as a function of Reynolds number. The model results were in close agreement with the experimental results for differing velocities. The second factor that was experimentally investigated was the quality of the water. The pH was kept relatively constant, while the calcium concentration, total alkalinity, and total dissolved solids were varied. The flow velocity used was 25.5 cm/s. The experimental results were compared to the model results using the following equation:

$$\frac{w}{k_{BF}} = C_B - C_{Bi} \tag{2.13}$$

The experimental results were in good agreement with those predicted by the model. The experimental results were correlated by Equation 2.14, and model predictions can be found in Equation 2.15.

$$w = 0.054\,\mathrm{Re}_f^{0.65} \tag{2.14}$$

$$w = 0.03\,\mathrm{Re}_f^{0.716} \tag{2.15}$$

Hasson et al. propose that the discrepancies can be explained by two factors:

1) Bulk precipitation, which can contribute to increased scale growth on the wall
2) Escape of gaseous CO_2 on the reaction surface under high supersaturation conditions.

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Taborek et al. (1972, 1972) developed a model for precipitation fouling in the presence of small, non-crystallized sedimentation in cooling tower water. They used the Kern and Seaton model for general fouling as a starting point. For the deposit rate, Taborek et al. proposed the following:

$$\phi_d = C_1 P_d \Omega^n \exp(-\frac{E}{R_g T_s}) \tag{2.16}$$

where C_1 is a constant, E is the activation energy, R_g is the universal gas constant, and T_s is the temperature of fouling deposit surface. Ω is the water characterization factor, which is a function of the Langelier Index. The removal rate was proposed to be

$$\phi_r = C_2 \frac{\tau}{\psi} x_f^m \tag{2.17}$$

where C_2 is a constant, τ is the sheer stress, ψ is a function of the deposit structure, and x_f is the thickness of the fouling deposit. In the case of cooling water with low suspended solids content, the ψ factor can be assumed to be a function of velocity only and the ratio of τ and ψ may be approximated to be a unique function of velocity. In the case of m = 1, equations 2.16 and 2.17 can be solved to get:

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$$R_f^* = \frac{C_1 P_d \Omega^n \exp(-\frac{E}{R_g T_s})}{C_2 \frac{\tau}{\psi}} \tag{2.18}$$

and

$$B = C_2 k_f \frac{\tau}{\psi} \tag{2.19}$$

Taborek et al. determined the values for the constants, activation energy, sticking probability and the water characterization factor by applying the model to existing data.

Experimental Studies of Calcium Carbonate Scaling

Most of the research done in the field of precipitation fouling of cooling water is on calcium carbonate. Watkinson et al. (1974) investigated precipitation of calcium carbonate in internally-finned tubes and spirally-indented tubes. The experiments were conducted on a shell-and-tube heat exchanger apparatus, which had water flowing from a mixing tank through two tubes in parallel in the shell. One of the tubes was plain, and the other was enhanced. Steam was condensed on the shell side of the heat exchanger. The effects of salt concentration were briefly studied, and the fouling resistance was found to increase as the concentration increased. For the internally-finned tubes, the fouling resistance was found to be between 15 and 35 % greater then in plain tubes for the same velocity. On the other hand, the spirally-indented tubes showed a fouling resistance 25 to 50% smaller than that of the plain tubes at water velocities greater then 3 ft/s.

Watkinson and Martinez (1975) conducted tests on a competing brand of spirally indented tubes from the ones used by Watkinson et al. (1974). The same set up and

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experimental procedure were used. The water had 300 ppm suspended particles and 3000 ppm dissolved solids. The tests were run at velocities between 0.5 m/s and 3.0 m/s. Watkinson and Martinez (1975) found that the spirally-indented tubes had roughly the same asymptotic fouling resistances as the plain tubes under the same condition, whereas in the previous study the fouling resistances were found to be less than the plain tube. They also observed that there appeared to be no clear effect of the pitch of the spirals on the fouling resistance.

Knudsen and a colleagues conducted a series of experiments to determine the factors affecting the formation of scale in cooling tower water. The tests were run by flowing the cooling tower water through a tube in which a heated rod was inserted. A schematic of the test section can be seen in Figure 2.6. Knudsen and Story (1978) reports the first of these tests. The experiment was conducted and published in 1975, and was later republished in 1978. Knudsen and Story studied the effect of heat transfer surface temperature on the scaling behavior of simulated cooling tower water. The velocity was held constant at 3.3 ft/s, and an attempt was made to hold the water quality constant. The water quality was monitored by the Ryznor stability index, which is defined as

$$STI = 2 \cdot pH_s - pH \tag{2.20}$$

where

$$pH_s = 9.30 + A + B - C - D \tag{2.21}$$

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where A, B, C, and D are a functions of total solids, water temperature, calcium hardness, and alkalinity, respectively.

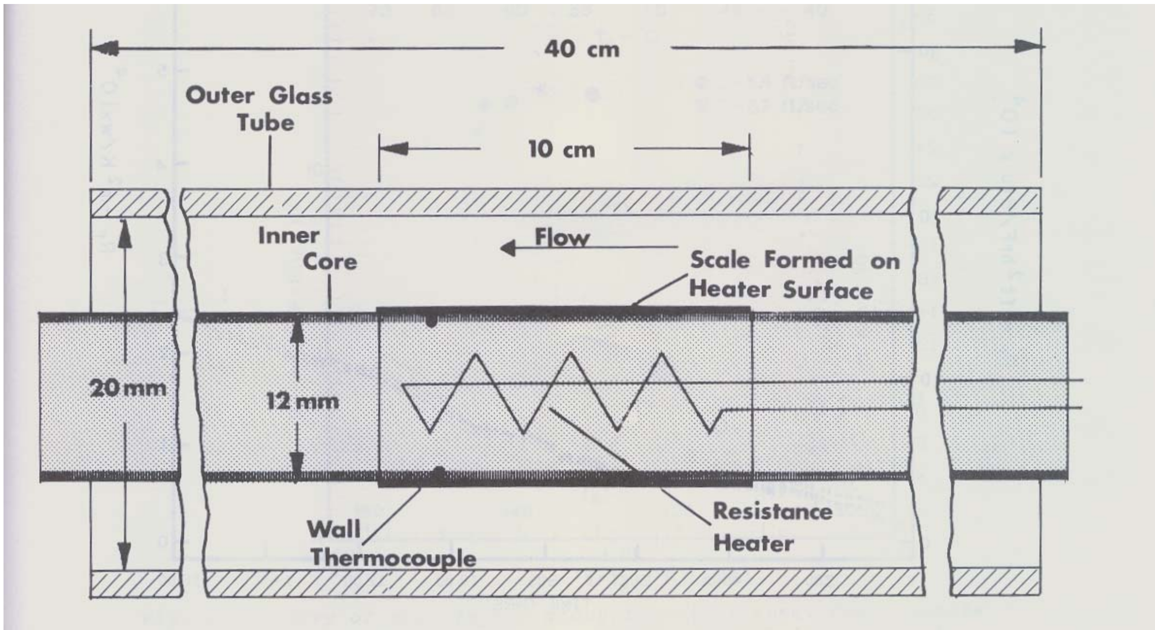

Figure 2.6: Test Section Used by Kunsden and His Colleagues

Tests were run until an asymptotic fouling resistance was reached and maintained for 50 to 100 hours. Knudsen and Story used the Taborek et al. model to analyze their results. They used a least squares fit of their data for Equation 2.18 and found

$$R_f^* = (3\times 10^{11})\exp(\frac{-11000}{R_g T_s}) \qquad (2.22)$$

These results are applicable only to the three test conditions. Kundsen and Story also observed that alkalinity seemed to effect the fouling resistance.

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Based on the observation of Knudsen and Story (1978), Morse and Knudsen (1977) studied the effects of alkalinity on scaling in simulated cooling tower waters. The alkalinity was varied from 115 to 180 ppm of calcium carbonate. Morse and Knudsen concluded that fouling resistance was affected by alkalinity through a complex relationship involving water quality factors and scale strength. From a minimum of 130 ppm, the asymptotic fouling resistance was found to increase with increasing alkalinity starting. Non-linear regression was used on the data. Morse and Knudsen found that this technique showed promise in following the progress of the tests and in determining when the asymptotic fouling resistance was reached. Of special note are two runs of the test that were conducted using actual cooling tower water. They found that the asymptotic fouling resistance in the actual cooling tower water was nearly twice that of the simulated water. This was possibly due to the presence of suspended particles in the cooling tower water that were not added to the simulated water. They also found that the scale strength was a function of the scale composition. Pure calcium carbonate was found to have a much stronger scale strength then scale having other crystalline structures.

Lee and Knudsen (1979) conducted a broader study then the previous two into the scaling characteristics of cooling tower water. The variety of water qualities was looked at as well as such factors of surface temperature, fluid velocity, and the presence of suspended particles. Twenty-four runs were made, of which three had suspended particles of Brazos River clay at 25 ppm. Most of the runs were at 5.4 ft/s where the shear stress on the heated surface is the same as that occurring in a 0.5-in. tube with a velocity of 6 ft/s. Three of the runs had velocities of 2.5 ft/s, 12.4 ft/s and 4.6 ft/s. The heat flux was varied from 15,000 to 113,000 Btu/hr-ft^2, resulting in a range of surface

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temperatures from 102°F to 165°F. Calcium hardness was maintained at 150 ± 2 ppm as $CaCO_3$. The total hardness was relatively constant at 225 ± 15 ppm as $CaCO_3$. Other water parameters varied over the duration of the experiment. The pH increased slightly from 8.8 to 9.2. The silica concentration increased from 80 to 120 ppm SiO_2. Total solids changed from an initial value of 420 to 750 ppm. Methyl orange alkalinity increased from an initial value of 150 to 270 ppm as $CaCO_3$.

Lee and Knudsen (1979) observed three different types of fouling deposits:

1) Magnesium silicate
2) Magnesium silicate and calcium carbonate mixture
3) Calcium carbonate

The reason for the different deposit compositions was not fully understood, but it seemed to very with methyl orange alkalinity. They also found that the asymptotic fouling resistance decreased with increasing velocity. The three runs made with the additional suspended particles indicated that the presence of suspended particles greatly affected the fouling resistances. The runs did not provide enough data to be conclusive, but Lee and Knudsen indicated that the fouling resistance increases greatly in the presence of suspended particles.

Coates and Knusden (1980) continued the work of Lee and Knusden (1979). Coates and Knusden studied four different water qualities, which are delineated in Table 2.1. Water quality No. 1 produced magnesium silicate and showed a Arrhenius relationship with heater surface temperature. Water qualities Nos. 2 and 3 showed minimal deposition at surface temperatures less than 139°F. Water quality No. 4 showed minimal deposition over the whole range studied and gave asymptotic fouling resistances

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similar in magnitude to water quality No. 1. No quantitative effect of velocity was determined, but generally for the asymptotic mode of deposition, the higher the velocity the lower the asymptotic fouling resistance. Lahm and Knudsen (1986) present the combined results of Lee and Knudsen (1979) and Coates and Knudsen (1980).

Table 2.2: Water Qualities Studied by Lee and Knudsen, and Coates and Knudsen

	No. 1	No. 2	No. 3	No. 4	Make-up Water
Total Hardness (ppm CaCO3)	210	220	470	370*(800**)	40
Calcium Hardness (ppm CaCO3)	150	150	400	270(640)	30
m-Alkalinity (ppm CaCO3)	210	300	115	160(600)	42
Chloride (ppm)	300	400	600	500	40
Silica (ppm SiO2)	105	110	115	150	20
PH	9	9	9	9	7

Knudsen et al. (1987) performed experiments to determine the fouling characteristics of cooling tower water containing phosphate corrosions inhibitors. Tests were conducted using phosphate corrosions inhibitor (4-5 ppm polyphosphate and 5-6 ppm orthophosphate) at a variety of temperatures, flow velocities, and tube materials. The presence of the corrosion inhibitor caused calcium phosphate scale to form at rates higher then would be acceptable in industrial heat exchangers. To prevent the formation of calcium phosphate, copolymers are normally added, but the effects of these copolymers were not studied. They found that there was very little difference between the fouling behavior of the various metal surfaces.

Watkinson (1986) investigated the water quality effects on fouling from hard waters. He used artificial hard water and ran it through the annulus side of a double-pipe

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heat exchanger with steam condensing on the inside of the inner tube. The experiments were carried out in the constant heat flow mode using water of pH 6.9-8.1 and total alkalinity between 90 and 700 ppm as $CaCO_3$. The test section was 133-cm long and consisted of a 1.91cm OD copper tube inside a 3.72cm ID glass tube. The results were then compared against a ionic diffusion model proposed by Hasson, Sherman, and Biton for low pH. The fouling rate for the Hasson et al. model is given by

$$\frac{dR_f}{dt} = 0.5k_D[Ca^{++}][(1+4ac/b^2)^{1/2}-1]\frac{b}{a\rho_s k_s} \tag{2.23}$$

where

$$a = 1 - \frac{4K_2^{'}k_r[Ca^{++}]}{k_D K_1^{'}} \tag{2.24}$$

$$b = [CO_2]/[Ca^{++}] + 4K_2^{'}k_r[HCO_3^-]/K_1^{'}k_D + K_{sp}^{'}k_r[CO_2]/k_D[Ca^{++}] \tag{2.25}$$

$$c = K_2^{'}k_r[HCO_3^-]^2/K_1^{'}k_D[Ca^{++}] - K_{sp}^{'}k_r[CO_2]/k_D[Ca^{++}]^2 \tag{2.26}$$

Watkinson found that the ionic diffusion model results were in good agreement with the experimental results at scaling rates up to 4 x 10^{-6} m^2K/kJ, at which point major discrepancies occurred. Since these differences might have been caused by the effects of suspended particles, the tests were run again with filters to remove the suspended particles. This did not improve the results at the higher fouling rates. Although no reason was found for the discrepancy, the model was deemed valid for the conditions that would be typically found in industry. Particulate mass fluxes were calculated and found to be less than 10 % of the ionic fluxes, but which could account for 25 % of the thermal fouling.

Sheikholeslami and Watkinson (1986) performed scaling test on plain and externally-finned heat exchanger tubes. Sheikholeslami and Watkinson investigated the effect of tube material on scaling. Sheikholeslami and Watkinson also investigated if Hasson's ionic diffusion model was affected by tube material, and if predictions of scaling on externally-finned tubes from plain tube data could be made. A plain copper tube, a plain mild-steel tube, and a longitudinal-finned mild-steel tube were investigated. The tests were conducted at a fluid bulk temperature of 25°C and with water velocities of 0.3 to 0.8 m/s. The tubes used all had an OD of 19.1mm. The copper tube had an ID of 15.3 mm, while the mild steel tube had an ID of 13.3mm. The finned tube had 12 fins which were 6mm high by 0.5mm thick by 1.2m long. The finned tube showed a lower fouling resistance than the plain tube. The experimental results were compared to the model proposed by Hasson. The model predicted that the scaling rates should increase with increasing velocity as was the case in Watkinson (1986). However Sheikholeslami and Watkinson found that for the mild-steel tubes the opposite was true; the scaling rate decreased with increasing velocity. Sheikholeslami and Watkinson note that this would be the case if particulate fouling were dominant or if the deposits were fragile, but neither of these conditions were present.

Dreytser et al. (1984) performed precipitation tests on brass tubes with turbulence promoters. The enhancements tested are illustrated in Figure 2.7. One of the early concerns about enhanced tubes under fouling conditions was that the fouling deposits would “fill in” the enhancements and, thus, take away the added heat transfer surfaces. Drytser et al. found that this did not happen, but that the scale formed relatively uniformly along the test section and that the thickness of the scale on the enhanced tubes was half as thick as the plain tube.

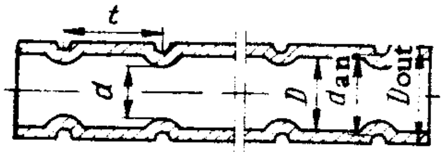

Figure 2.7: Ring-type Turbulence Promoters From Dreytser et al. (1984)

Zubair et al. (1997) attempted to model calcium carbonate scaling using a statistical model instead of the models describing the fouling processes. Zubair et al. argue that while there has been significant progress in understanding and modeling fouling, the previously published models had the following limitations:

1. There is a lack of information on many of the transport and chemical kinetic processes, particularly for the removal process. Specifically there is no precise information on rates of reaction, sticking probability, mass transfer rates, and the properties of foulant deposits such as density, thermal conductivity, and nutrient diffusivity.
2. The correlations proposed in these models are generally subject to simplifying assumptions. The errors so introduced could be substantial for practical applications in design, operation, and maintenance of heat exchangers.

To develop their model, Zubair et al. obtained experimental data on stainless steel tubes and used a filter to remove any suspended particles. The tests were repeated for each operating condition six times. They presented the random behavior of fouling growth laws in terms of the probability and reliability functions of the α-model. Although the model was developed for calcium carbonate fouling with a linear profile, the authors assert that the method of analysis could be used for any random fouling condition, even if the fouling resistance were not linear.

Khan et al. (2001) studied the effect of tube surface temperature, Reynolds number, tube diameter, and salt concentration on the growth of calcium carbonate scale in stainless steel tubes. The tube diameters tested were between .0053 and .02m. Khan et al. showed that fouling resistance increased as the concentration increased and that as the tube diameter decreased, the fouling resistance increased.

Experimental Studies of Coprecipitation of Salts

Another inversely soluble salt that is commonly found in the cooling tower water is calcium sulphate. Taborek et al. (1972, 1972) state that one-salt solutions form very strong scale deposits, which resist the removal process. However, in solutions containing large concentrations of multiple salts, such as cooling tower water, the crystalline structures form in irregular patterns. These irregularities lower the bond strength and result in cavities in the structure in which suspended particles can attach. This further lowers the strength of the crystalline structure. Sheikholeslami and Ng (2001) investigated the coprecipitation of calcium carbonate and calcium sulfate. Sheikholeslami and Ng found that the crystalline structures of calcium sulfate grew finer

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and more adherent as the concentration of calcium carbonate increased and that the rate of precipitation of calcium sulfate decreased as the concentration of calcium carbonate increased.

2.4. Combined Precipitation and Particulate Fouling

Fouling is normally studied as separate mechanisms, but in actual conditions, multiple fouling mechanisms occur at the same time. The interactions of these mechanisms can have a great effect on the fouling rates, but the interactions are little understood. In most cases where combined fouling was studied, the fouling curve was asymptotic.

Bansal et al. (1997) conducted experiments to determine the effects of suspended particles on crystallization fouling in plate heat exchangers. The study investigated calcium sulfate precipitation with two types of particulate particles, calcium sulfate and alumina. The calcium sulfate particles simulate when the solution precipitates in the bulk fluid or when shear stress breaks off particles into the fluid stream. Bansal et al. found that the presence of suspended calcium sulfate increased the growth rate of the scale. This may because the particles give the solution more nucleation sites. Conversely, when alumina particles settled, they reduced the deposit strength and, thus, increased the removal rate.

<u>Long-Term Fouling Tests</u>

There are very few references in the literature on long-term fouling tests. All of the previously-mentioned studies have been short-term or accelerated fouling studies.

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The first significant attempt to test fouling over a long period is found in Rabas et al. (1991). In Rabas et al. fouling data were taken in 12 TVA plant condensers over the period of a year. Nine of the condensers were fitted with enhanced, spirally-indented tubes. The cooling water used in the condensers was river water. During the tests, the fouling resistances for the plain or enhanced tubes never exceeded the recommended TEMA values. The fouling rates for the enhanced tubes were shown to be greater then for the plain tubes.

A second long-term fouling test of note was conducted by Haider et al. (1991, 1992) for flooded water chiller evaporators. They surveyed 61 actual plant sites about their setups and treatment practices. They also took samples from the evaporators to evaluate their potential for fouling. Haider et al. (1992) then conducted fouling tests by connecting a test evaporator in parallel with an existing evaporator at Penn State University. Three helically-ribbed tubes were tested along with a plain tube for two summer cooling seasons. The water sampling portion of the test showed that there was little potential for fouling in the evaporators, and this was confirmed by the experimental results.

Webb and Li (2000) and Li and Webb (2000) conducted long term fouling tests on condensers in a cooling tower loop. Web and Li attached test condenser in parallel with an actual condenser on the campus of Penn State University. The tests were conducted at a water velocity of 1.07 m/s. The water quality was approximately 800 ppm total calcium hardness, 1600-1800 μΩ electrical resistance, and a pH of 8.5. Eight helically-ribbed tubes of various helix angles, number of starts, and rib heights were tested along with plain tubes. The tests were run over two summer cooling seasons. The

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observed fouling mechanism was a combination of particulate and precipitation fouling. The three tubes with the largest number of starts and helix angles between 35 and 45° showed the greatest fouling resistance.

Table 2.3: Geometries of Tubes Studied By Webb and Li

Tube	e (mm)	n_s	$\alpha(°)$	p/e	A/A_p
1	n/a	0	n/a	n/a	1
2	0.33	45	45	2.81	1.59
3	0.4	30	45	3.5	1.48
4	0.43	10	45	9.88	1.17
5	0.47	40	35	3.31	1.65
6	0.49	25	35	5.02	1.43
7	0.53	25	25	7.05	1.42
8	0.53	18	25	9.77	1.31

Li and Webb examined the foulant deposits and found that the deposits had relatively loose structures. The loose structures show that both precipitation and particulate mechanisms occurred and suggests that particulate fouling is the dominant mechanism. The deposits were analyzed and found to have following composition:

1. 57% calcium carbonate
2. 2% calcium phosphate
3. 14% non-carbonate (either organic material or water)
4. 26% particulates

Li and Webb also compared previously-taken, accelerated particulate fouling data with the long-term data. They observed that the accelerated particulate fouling rates corresponded directly to the long-term combined fouling rates. A strong relationship was observed between the geometric parameters of the ribs and the asymptotic fouling rate. They proposed the following correlations for the asymptotic fouling resistance based on rib height, e, and pitch, p, for different numbers of starts:

$$R_f^* = 4.64 \times 10^{-3} (p/e)^{5.72} \quad n_s \leq 25 \tag{2.27}$$

$$R_f^* = 1.85 \times 10^{-} (p/e)^{0.92} \quad n_s \geq 25 \tag{2.28}$$

The fouling conditions used in Webb and Li and Li and Webb were more severe than would typically be found in the field.

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CHAPTER III

WATER ANALYSIS

3.1 Objective

The second phase of this research project was to establish a database of water quality data, collected from a sampling program for actual cooling towers. The reason for collecting this data is two-fold. First, the desire to look at what factors, such as geographic location and building type, affect the quality of water in cooling towers. Second, to establish an "average" fouling case for the experimental portion of the project to be completed in Phase III.

3.2 Questionnaire Development

To reach the first goal of the database, an understanding of what factors may contribute to the fouling potential of cooling tower water, a questionnaire of physical parameters for cooling tower setups was developed. The questionnaire covered geographical location, building use, maintenance practices, cooling tower setup, and water treatment. A copy of the questionnaire can be found in Table 3.1. Each site that was contacted was sent a copy of the questionnaire and asked to fill it out. They were also asked if they would be willing to send a water sample from their cooling towers.

Table 3.1: Site Questionnaire

COOLING TOWER INSTALLATION

Location:

Building Name: _________________ City: ________________ State: ___

Building Use (Please Check One):

___Hospital ___Hotel ___Office ___Convention Center ___Museum ___School ___Other (________________________)

Cooling Tower Manufacturer: ____

Cooling Tower Model: ____________________ Serial Number: _____________

What type of system is it (Please Check One)? ___Open ___Closed

Type of Service Piping (Please Check all That Apply):

___Iron ___Plastic ___Other (______________________)

CHILLER INSTALATION

Chiller Manufacturer: ____

Chiller Model: ____________________ Serial Number: __________________

Are there multiple chillers attached to a single cooling tower? ___Yes ___No

If yes, please give the model and serial numbers for the additional chillers:

____

____

____

OPERATING PROFILE

How often is the system running on average?

________Hours/Day ________Days/Week ________Weeks/Year

What is the operating velocity of the water? _________________

How many cycles of concentration does the cooling tower typically run? _______

MAINTENANCE PRACTICE

Are the condenser tubes cleaned? ___Yes ___No

How are they cleaned? ___Automatic Brushes ___Hand Brushes ___Acid

If cleaned, how frequently? ____

WATER IN CONDENSER TUBES

Source of Water (Please Check One):

___Municipal ___On-site Well ___On-site Surface Supply ___Other (________________)

Is the make up water softened? ___Yes ___No

Are corrosion/scale inhibitors used? ___Yes ___No

If yes, what kind (Check All That Apply):

___All-organic ___Organic ___ Molybdate ___Phosphate ___Other (_____________________)

Is acid used to control the pH of the condenser water? ___Yes ___No

If yes, what type of acid is used? _________________________________

Is the water treated for biological growth: ___Yes ___No

If yes, what type of biocide is used? ____________________________________

Potential sites were located based on search criteria such as building size and use. Each site was sent a letter explaining the project and a questionnaire to fill out. Over the course of six months, a total of two hundred and twenty sites in sixty-five cities were contacted in forty-two States and the District of Columbia. Of the sites contacted only nineteen sites in sixteen cities agreed to send water samples. Several other sites responded, but indicated that they did not have a cooling tower at their location. The geographic locations to which surveys were sent are indicated in Figure 3.1. The diamonds indicate those cities from which a water sample was collected. Circles indicate cites to which questionnaires were sent, but no samples were collected. The breakdown of where surveys were sent according to building use can be seen in Figure 3.2. As shown in Figure 3.2, most of the surveys were sent to hospitals and hotels because of the likelihood of these facilities having cooling towers and the ease of finding the contact information for these sites.

3.3 Water Sample Collection

Upon receiving agreement by a site to send a water sample, the site was provided with a sample collection kit. The kit included directions for collecting the sample, two water bottles, labels for the bottles, and an overnight prepaid mailing address label. At the request of the Mississippi State Chemical Laboratory two bottles were provided to the sites in order to have enough water to run all of the necessary tests. The Mississippi Chemical Laboratory also requested that the samples be refrigerated within 48 hours of being taken to preserve them. Unfortunately, almost half of the samples were not handled as instructed and were not refrigerated within 48 hours.

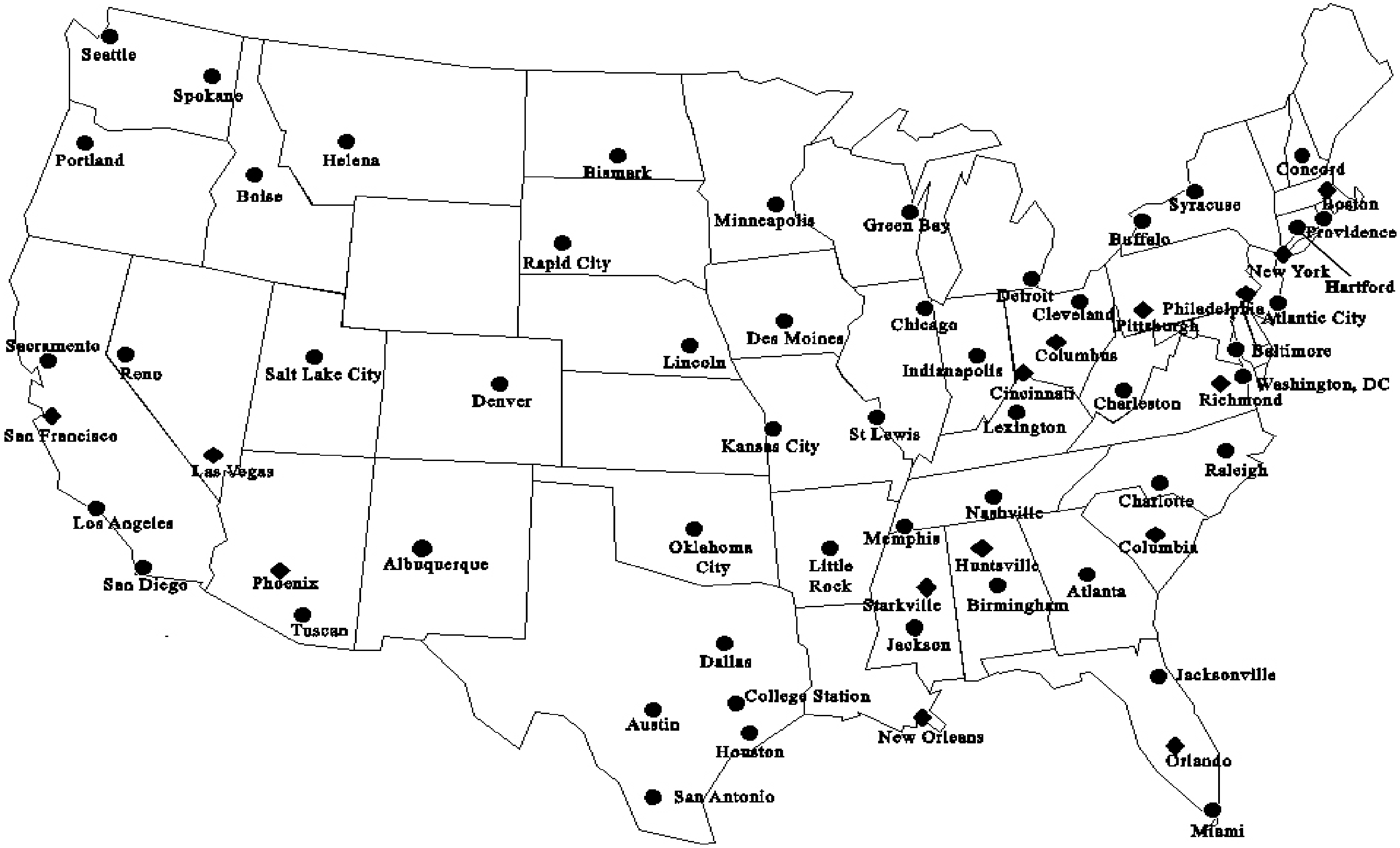

Figure 3.1: Geographical Locations of Potential Site

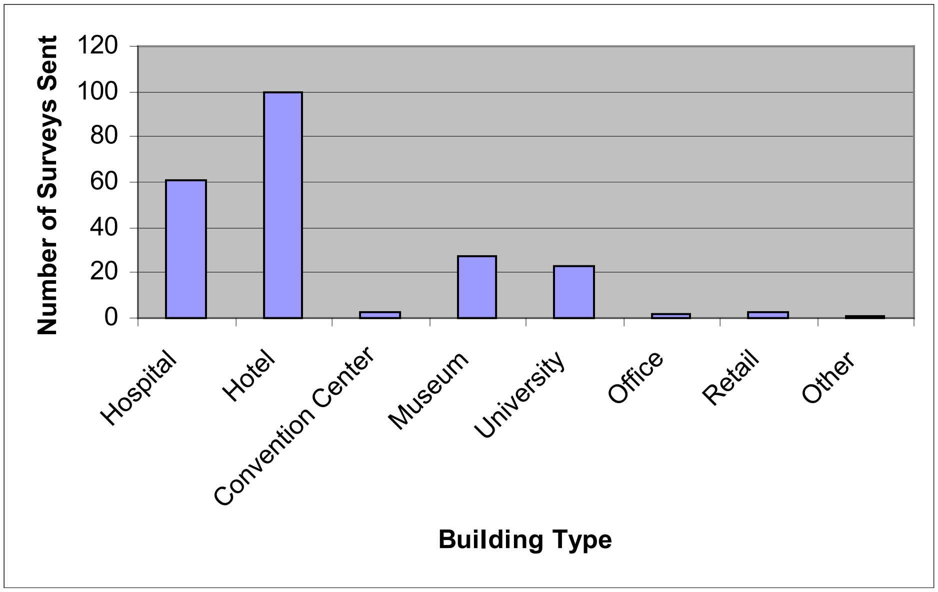

Figure 3.2: Surveys Sent by Building Use

From the nineteen sites that agreed to send samples, twenty-one samples were collected. One site put different samples from two cooling different cooling towers in each of the bottles. Another site provided two samples taken on two different dates.

3.4 Water Sample Testing

With the help of Amanda Meitz, a microbiologist at Biosolutions, Inc., a number of parameters that effect water quality were identified. Each of these parameters is an indicator of the potential for fouling. The types of fouling that the parameters are indicators for and the degree of that relationship (Haider et. al, 1991) are shown in Table 3.2. A single asterisk (*) indicates a minor indicator, while two asterisks (**) indicate a major indicator.

Table 3.2: Test Results as Indicators of Fouling

	Precipitation	Particulate	Corrosion
Calcium Hardness as CaCO3	**		*
Magnesium Hardness of CaCO3	*		*
Phenolphthalein Alkalinity as CaCO3	*		
Total Alkalinity as CaCO3	**		
Sulfate as SO4	*		
Chloride as Cl			*
Silica as SiO	**		*
PH	**		**
Specific Conductance			*
Total Phosphate	*		*
Orthophosphate	*		*
Total Dissolved Solids	**		*
Total Suspended Solids		**	

The results of the water analysis performed by the Mississippi State Chemical Laboratory are shown in Table 3.3. The table reports the average value, standard deviation, maximum and minimum values obtained for each of the parameters.

Table 3.3: Water Analysis Results

Water Quality Variable	Average	Standard Deviation	Max	Min
pH	8.58	0.41	9.2	7.8
Calcium Hardness as CaCO3	314.76	190.83	700	10
Magnesium Hardness of CaCO3	142.67	150.99	690	14
Total Alkalintiy as CaCO3	323.81	233.67	970	62
Phenolphthalein Alkalinity as CaCO3	36.29	37.86	970	0
Sulfate as SO4	274.51	259.91	844	6.7
Chloride as Cl	254.81	297.40	1200	28
Silica as SiO2	35.57	21.67	96	10
Specific Conductance	2080.19	2110.56	8560	380
Total Dissolved Solids	1079.90	1071.79	4650	200
Iron	0.60	1.38	6.6	0.016
Copper	0.23	0.22	1	0.041
Total Suspended Particles	20.11	28.92	128	4.2

-

Phosphate and orthophosphate appear in Table 3.2, but not in Table 3.3 because the results obtained by the Mississippi State Chemical Laboratory were not considered to be valid. Three factors account for the invalid results. First, due to a miscommunication with the Mississippi State Chemical Laboratory, the samples were not preserved in such a way as to obtain valid results. Second, as stated before, the samples did not always arrive within the 48 hours that were requested. Third, the uncertainties for the procedure used are quite large and some of the results were physically impossible, but may have been within the uncertainty of the experiment. Phosphate and orthophosphate are used in some corrosion inhibitors. Their presence in the water is simply an indication that a corrosion inhibitor was present. In all of the returned questionnaires, the use of corrosion inhibitors was indicated. Therefore, the phosphate and orthophosphate results are not presented here.

3.5 Questionnaire Results

The goal of the questionnaires that were sent to the sites was to try and identify field practices which might contribute to the fouling potential of the water. Nine parameters in the operational and maintenance data were identified as independent variables which could have an impact on the water quality:

1) Geographic location
2) Building use, i.e., university, hotel, hospital
3) Whether the make-up water was softened
4) Whether a corrosion inhibitor was used
5) Whether acid was used to control the pH
6) Whether biocide was added to the water

7) Whether more then one chiller unit was attached to the cooling tower loop
8) If the tubes were cleaned, and how often
9) How many hours per year was the cooling tower used

The geographic locations from which samples were received can be seen in Figure 3.1. The types of buildings that provided water samples are shown in Figure 3.3. Despite sending nearly half of the questionnaires (see Figure 3.2) to hotels, only two sent water samples. Five universities and five hospitals responded, as did four museums.

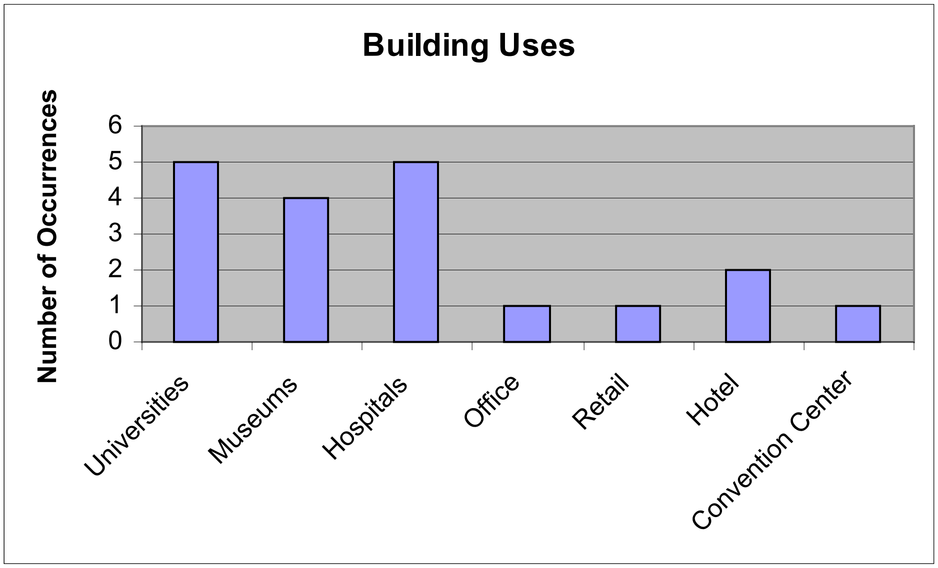

Figure 3.3: Building Uses of Responding Sites

The third through sixth variables are related to the water treatment program employed by the sites. Figure 3.4 presents the responses to these questions on the questionnaire. In cases where the make-up water is particularly hard, chemicals are sometimes added to the water to soften it. Water hardness, especially calcium hardness, is the primary indicator that scaling will occur. Biocides are added to kill microbiological growth in the water. Corrosion inhibitors are added to the water to

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prevent corrosion. Corrosion inhibitors are normally basic in composition. Therefore, acid is sometimes added to the water to lower the pH.

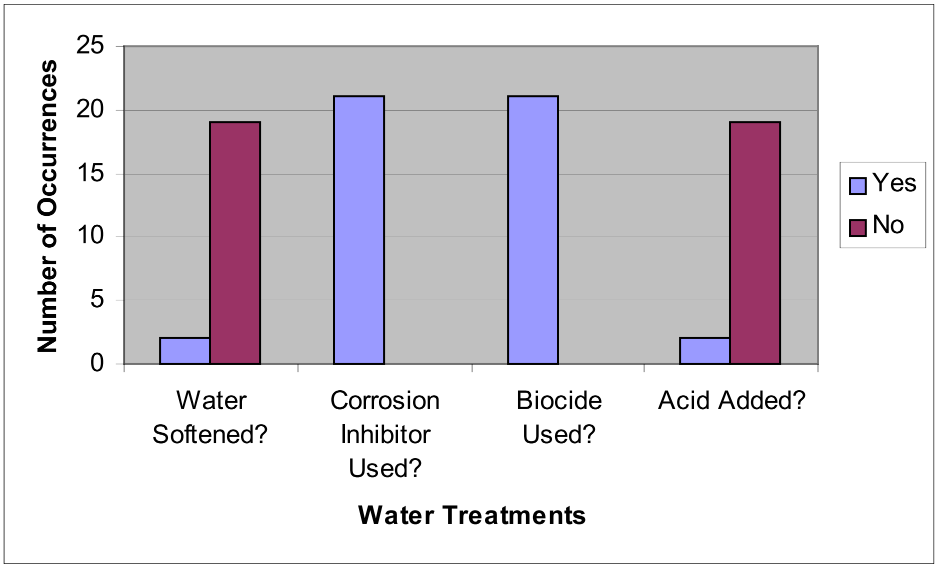

Figure 3.4: Water Treatments Used

The seventh variable, which was identified as an independent variable, was the use of multiple chillers with a single cooling tower. Figure 3.5 shows the breakdown of this variable. Two of the sites left this question blank when they returned their questionnaires.

The eighth variable that was examined was whether the condenser tubes of the chillers were cleaned and, if so, how often. Except for one site, all of the sites responded that the condenser tubes were cleaned. Sixteen of those sites said that the condenser tubes were cleaned annually. Two sites said that the condenser tubes were cleaned but not annually. One site said the condenser tubes were cleaned every three years, and the other site, which had an on-line cleaning system, said the tubes were cleaned three times a day. The ninth variable was the hours per year that the cooling towers operated. The

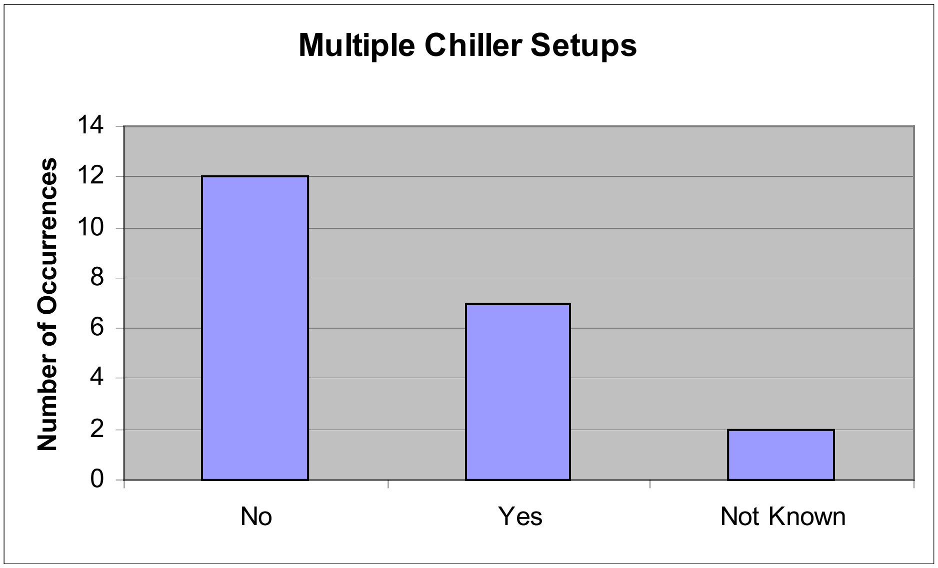

Figure 3.5: Use of Multiple Chillers

average was 8082 hours/year. Thirteen of the sites reported that their cooling towers ran 24 hours a day, 365 days a year.

Most of the variables that were identified as independent variables were the same for all or most of the sites that responded. Therefore, the variables effect on the fouling potential cannot be examined. For example, all of the cooling towers used corrosion inhibitors; therefore, the effect of not using a corrosion inhibitor on the potential for corrosion fouling cannot be examined.

3.6 Fouling Potentials

Statistical Analysis

A statistical approach will be followed to interpret the data and assess the probability of fouling. The statistical approach will define the probability that a specific

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fouling indicator is below or above a given threshold value, x_c. The threshold values indicate the potentials for fouling and are defined for specific fouling mechanisms. The derivations of the equations to determine the probability of a value falling below or above the threshold value are taken from Haider et al. (1991). A normal probability distribution is assumed for the systems.

$$Y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}(\frac{x-\mu}{\sigma})^2} \tag{3.1}$$

Where Y is the probability distribution of the fouling indicator value x, μ is the mean, and σ is the standard deviation. Let

$$z = \frac{x-\mu}{\sigma} \tag{3.2}$$

and Equation 3.1 becomes

$$Y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}z^2} \tag{3.3}$$

If z_c correspond to the threshold value of the fouling indicator, then Equation 3.2 can be expressed as

$$z_c = \frac{x_c-\mu}{\sigma} \tag{3.4}$$

The cumulative probability of occurrence below z_c is given by

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$$P_b = \int_{-\infty}^{x_c} Y dx = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^{z_c} e^{-\frac{1}{2}z^2} \sigma dz \qquad (3.5)$$

$$P_b = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{z_c} e^{-\frac{1}{2}z^2} dz \qquad (3.6)$$

Let

$$b^2 = \frac{1}{2} z^2$$

Substitute into Equation 3.6 to obtain

$$P_b = \frac{1}{\sqrt{\pi}} \left(\int_0^{\infty} e^{-b^2} db + \int_0^{\frac{z_c}{2}} e^{-b^2} db \right) \qquad (3.6)$$

Recalling the definition of error function

$$erf(b) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-b^2} db \qquad (3.7)$$

$$\int_0^{\infty} e^{-b^2} dt = \frac{\sqrt{\pi}}{2} erf\left(\frac{z_c}{\sqrt{2}} \right) \qquad (3.8)$$

$$\int_0^{\frac{z_c}{2}} e^{-b^2} dt = \frac{\sqrt{\pi}}{2} erf\left(\frac{z_c}{\sqrt{2}} \right) \qquad (3.9)$$

Equation 3.6 implies that

-

$$P_b = \tfrac{1}{2} + \tfrac{1}{2} erf\left(\frac{z_c}{\sqrt{2}}\right) \tag{3.10}$$

Using the identity

$$erf\left(\frac{z_c}{\sqrt{2}}\right) = 1 - erfc\left(\frac{z_c}{\sqrt{2}}\right)$$

the probability of occurrence of x below x_c is

$$P_b = 1 - \frac{1}{2} erfc(\frac{z_c}{\sqrt{2}}) \tag{3.11}$$

Where erfc is the complementary error function. Similarly the probability of occurrence of x above x_c is

$$P_a = 1 - P_b \tag{3.12}$$

Therefore

$$P_a = \frac{1}{2} erfc(\frac{z_c}{\sqrt{2}}) \tag{3.13}$$

Equations 3.11 and 3.13 are valid for positive values of z_c. For negative values of z_c, equations 3.11 and 3.13 can be transformed using the identity

$$erfc\left(\frac{z_c}{\sqrt{2}}\right) = 2 - erfc\left(\frac{-z_c}{\sqrt{2}}\right) \tag{3.14}$$

Equation 3.11 can now be written as

$$P_b = \tfrac{1}{2} erfc\left(\frac{-z_c}{\sqrt{2}}\right) \tag{3.15}$$

Similarly, Equation 3.13 can now be written as

$$P_a = 1 - \tfrac{1}{2} erfc\left(\frac{-z_c}{\sqrt{2}}\right) \tag{3.16}$$

Langelier Saturation Index

The fouling indicator that will be used for the analysis of the corrosion and precipitation fouling potential will be the Langelier Saturation Index. The Langelier Saturation Index is used to predict whether water will tend to precipitate or dissolve calcium carbonate. If calcium carbonate precipitates, scale will form on the tube wall. If the water dissolves calcium carbonate, it has a corrosive tendency. The Langelier Index is defined as the difference between the actual pH of the water and the calculated pH of water saturated with calcium carbonate. The Langelier Index is

$$\mathrm{LSI} = \mathrm{pH_a} - \mathrm{pH_s} \tag{3.17}$$

-

where

pH_a = pH of water sample, measured:

pH_s = pH of water saturated with calcium carbonate.

The pH of water saturated with calcium carbonate is

$$pH_s = 11.017 + 0.197\log(TDS) - 0.995\log(Ca) - 0.016\log(Mg) - 1.041\log(Alk) + 0.021\log(SO_4) \quad (3.18)$$

where

TDS = total dissolved solids, ppm

Ca = calcium, ppm

Mg = magnesium, ppm

Alk = alkalinity, ppm

SO_4 = sulfur as sulphate, ppm.

A suggested guide for how to interpret the Langelier Saturation Index, taken from Haider et al. (1991), is

If LSI = -2.0 the water is corrosive but not scale forming;

If LSI = -0.5 the water is slightly corrosive but not scale forming;

If LSI = 0 the water is slightly corrosive only;

If LSI = +0.5 the water is slightly corrosive and slightly scale forming;

If LSI = +2.0 the water is non-corrosive and definitely scale forming.

Corrosion Potential

The Langelier Saturation Index was used to analyze the potential of the water to corrode the condenser tubes. The analysis showed a no chance for significant corrosion to occur. The lack of potential for corrosion fouling was expected since all of the sites employed some form of corrosion inhibitor. Also, the water was tested for the presence of iron and copper. A high concentration of these metals indicates that the tubes or service piping were eroding, a type of corrosion fouling. However, the average concentration of both metals was extremely low, with the average concentration of copper being 0.232 ppm and the average concentration of iron being 0.600 ppm. The complete potentials for corrosion fouling can be found in Table 3.4.

Table 3.4: Corrosion Fouling Potential

Definitely Corrosive (LSI < -2)	0%
Mildly Corrosive (-2 < LSI <-0.5)	0%
Slightly Corrosive (-.05 < LSI < 2)	57%
Non-Corrosive (LSI > 2)	22%

Particulate Fouling Potential

The potential for particulate fouling was determined using the total suspended particles concentration of a water sample. Webb and Kim (1989) observed that particulate fouling did not occur at concentrations of less than 1000 ppm. Haider et al. (1991) used a threshold value of 300 ppm in evaluating the fouling potential of water in flooded water chiller evaporators. For this analysis, the 300 ppm threshold was used. The average value for total suspended solids was 232.5 ppm, but this includes a single value of 4480 ppm, which is significantly higher than the suspended solids of the rest of the samples. The average drops to 20.11 ppm, when this sample is removed from the group. This sample will be rejected for the calculation of the fouling potential. Without the sample with a suspended solids concentration of 4480 ppm, the analysis shows that there is no chance that there will be particulate fouling.

The numbers returned by the Mississippi State Chemical Laboratory may not be truly reflective of the amount of suspended particles in the samples. The Mississippi State Chemical Laboratory originally used a 45μm filter to obtain the total suspended solids concentration. Almost none of the samples registered any suspended solids. After discovering the filter size used, the Mississippi State Chemical Laboratory was asked to rerun the tests with the smallest filter they had available. The tests were then rerun with a 10μm filter to obtain the results presented in Table 3.3. However, Chamra (1992) reports that for Ohio River and Mississippi River water, 90 % of the suspended particles found in the water were between 1 and 16μm in diameter. Therefore much higher concentrations of suspended particles then those found by the analysis run of these samples could be possible.

The literature shows that cooling tower water has primarily been modeled as precipitation fouling with little or no particulate fouling. However, several researchers have shown that the presence of suspended particles affects the formation of scale and allows the fouling resistance to reach an asymptotic value. Pure precipitation fouling is linear in nature. The conclusion that can be drawn from the literature and the total suspended particle concentrations in this study is that there is very little potential for pure particulate fouling, but that the suspended solids are expected to effect the formation of scale.

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Precipitation or Scaling Fouling Potential

The Langelier Saturation Index was used to evaluate the potential for scale formation. The results show that 96 % of the cooling tower systems show at least some potential for scale formation, and 41 % have definite potential to scale. The effect of having multiple chillers attached to a single cooling tower was also investigated. The presence of multiple chillers increased the potential for scaling. The percentage of systems with definite scaling potential was 71 % for systems with multiple chillers, and only 39 % for those without multiple chillers. Unfortunately, there are too few samples to draw definite conclusions, but the result does warrant further investigation. The complete results of the scaling potential analysis are presented in Table 3.5.

Table 3.5: Scaling Fouling Potentials

	Overall	With Multiple Chillers	Without Multiple Chillers
No Scaling (LSI < 0)	1%	0%	2%
No Scaling to Mild Scaling (0 < LSI < 0.5)	3%	0%	5%
Mildly to Definitely Scaling (0.5 < LSI < 2)	55%	29%	53%
Definitely Scaling (LSI > 2)	41%	71%	39%

Effect of Building Type on LSI

The second independent variable to be examined was the building use. Since only one retail center, one office building and two hotels responded, they will not be used in the comparison. The average LSI was calculated for each of the remaining building types. The building type with the highest average LSI was universities followed by hospitals and museums. The results are shown in Figure 3.6.

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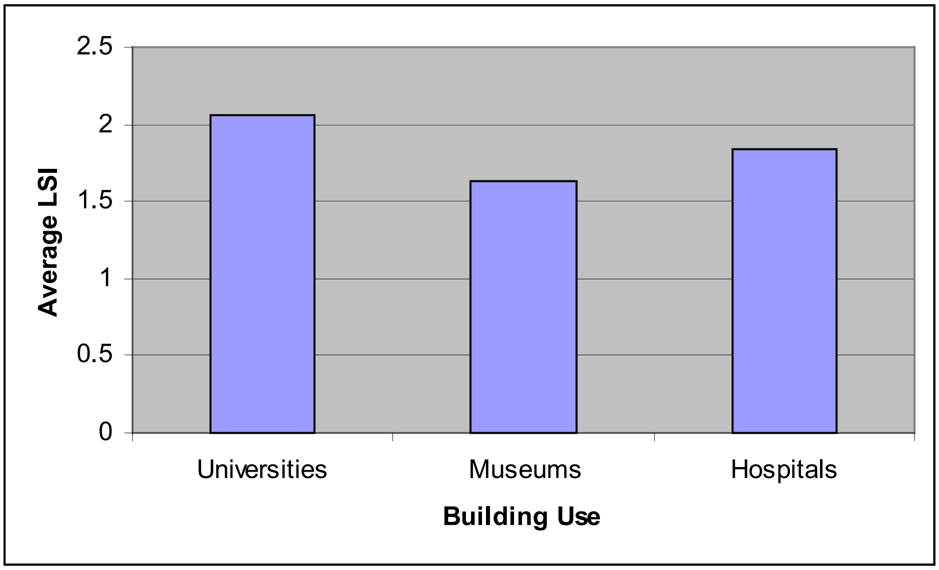

Figure 3.6: Average LSI by Building Use

3.7 Recommendations for Water Quality of Phase III

Phase III of the project calls for the experimental determination of fouling in enhanced tubes using simulated cooling tower water. It is planned to run three different water qualities with an average fouling potential, a severe fouling potential, and a light fouling potential are planned for different runs. It is recommended that only the water quality factors that contribute to the scaling be varied, while the total suspended solids remain constant. There are two reasons for this recommendation. First, the suspended solids did not vary very much between the samples and had very low concentrations. Second, the interaction between the precipitation and particulate fouling modes is not fully understood. For example, increasing both the potentials for particulate and precipitation fouling may lower the overall fouling potential by making the scaling deposits easier to break free of the wall. Recommendations for water qualities are in Table 3.6.

Table 3.6: Recommended Water Qualities for Phase III

	ppm				
	Calcium Hardness	Magnesium Hardness	Sulfate	Total Suspended Solids	Silica
Low Fouling Potential	115	15	25	150	35
Average Fouling Potential	315	145	275	150	35
High Fouling Potential	515	300	525	150	35

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CHAPTER IV

EXPERIMENTAL SET-UP

4.1 Introduction

Phase III of this project will be the construction of a laboratory facility to test fouling behavior in helically-finned copper tubes. The apparatus will be constructed in Patterson Engineering Laboratories on the campus of Mississippi State University. This chapter will describe the proposed experimental apparatus to be constructed, the data reduction equations that will be used to evaluate the data, and the test parameters to be run.

4.2 Experimental Apparatus

The apparatus will have nine parallel test sections. Eight of the test sections will have helically finned tubes, and the ninth test section will have a plain tube. A schematic of the instrumentation for the apparatus is shown in Figure 4.1. This figure is not to scale and the wiring for only one test section is illustrated.

Each test section is nine feet in length and consists of a counterflow double-tube heat exchanger. The simulated cooling tower water runs through the inner tube, while

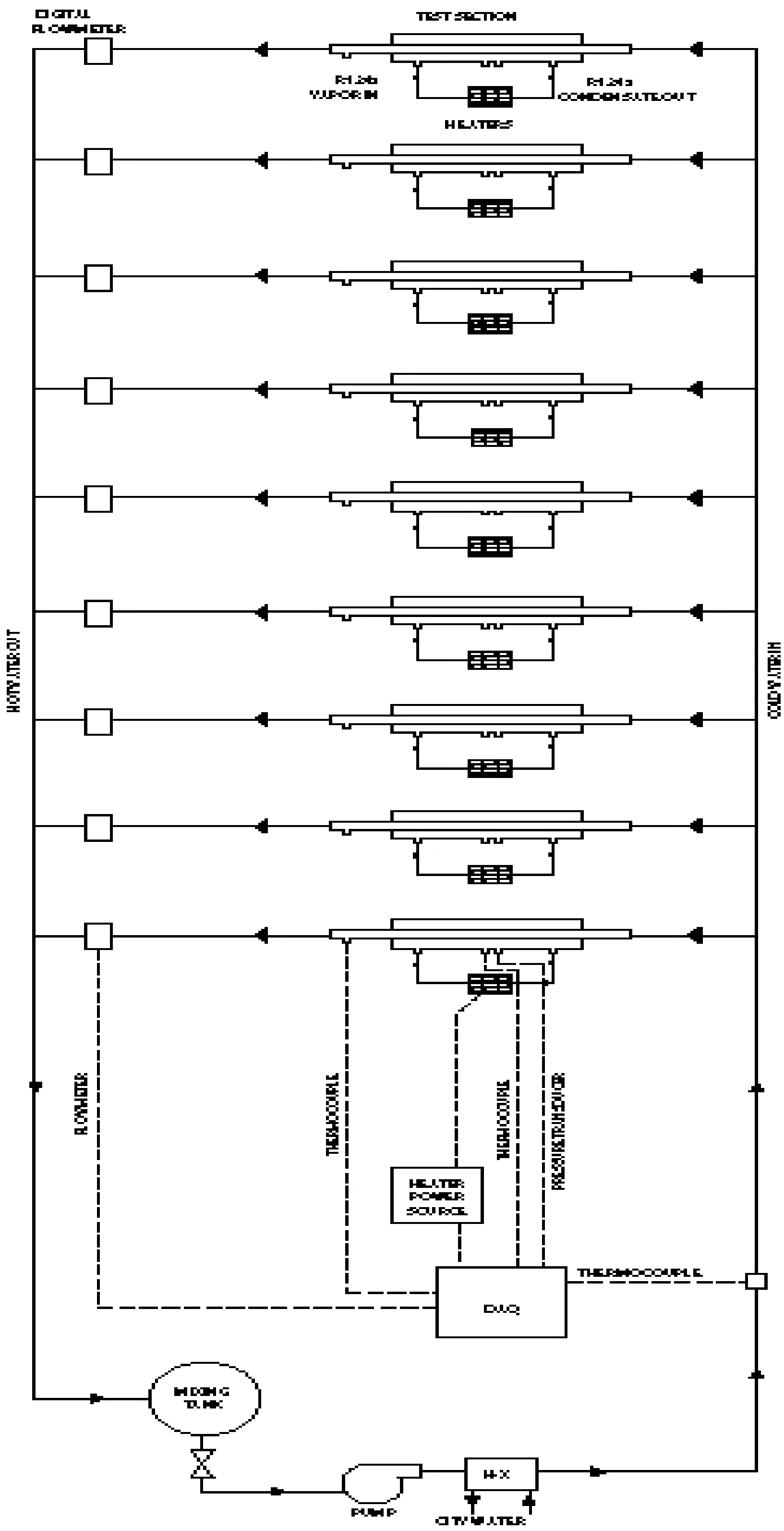

Figure 4.1: Test Apparatus Schematic

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refrigerant condenses on the outside of the tube. The eight tubes will have inside geometries with varying numbers of starts, helix angles, and fin heights. The outside of the inner tube will also be finned. The external fins will be the same for all tubes, including the plain tube.

R134a has been selected as the refrigerant because its condensing pressure is higher than atmospheric, making leaks easier to detect. The refrigerant will be evaporated using electric heater around a tank below the test section. The refrigerant vapor will then flow into the annulus of the test section where vapor will be condensed. Gravity will be used to drain the refrigerant back into the tank. A thermocouple and a pressure transducer will be mounted in the annulus of each test section to monitor the saturation temperature and pressure of the refrigerant. An emergency shut-off program will be used to turn off the heaters if the temperature or pressure gets too high in the annulus of the test section while the apparatus is running unattended.

On the waterside, there will be one thermocouple, which will measure the inlet temperature for all of the test sections, mounted on the main feed line. There will also be a thermocouple on the end of each test section to measure the outlet temperature. A flow meter will be mounted on the outlet of each test section to measure the flow rate of the water in the test section. A detailed drawing of the test section can be found in the Figure 4.2. The possibility of cleaning the tubes between experimental reuns was discussed, but then rejected. Webb and Kim (1989) showed for particulate fouling that brushing was adequate to clean the tubes. However, a study by Cho et al. (2000) determined that brushing does not remove scale deposits unless the test section was allowed to dry for a

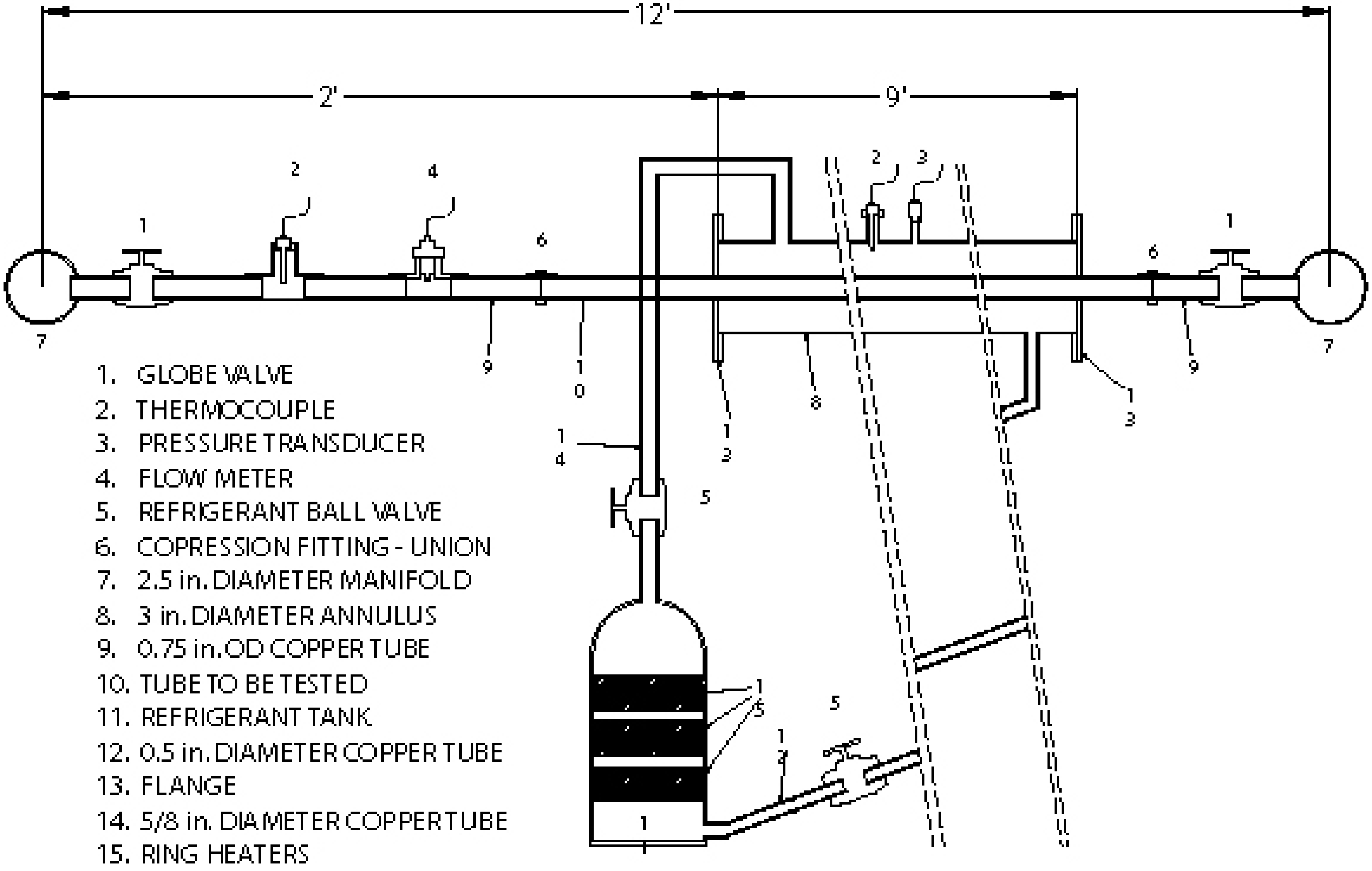

Figure 4.2: Apparatus Test Section

month. For this reason and to ensure that no damage is done to the tubes by the brushes, the tubes will be replaced after each test set.

A mixing tank is connected to the common water loop. The tank will be used to mix foulants into the water in order to maintain the desired water quality. Foulants may be added to the mixing tank during the test in order to keep water quality constant throughout the duration of the test. In addition to the mixing tank two counterflow heat exchangers in parallel with each other will be used to reject heat from the water. Regular tap water will be used as the coolant in these heat exchangers. The setup of the apparatus in the laboratory is illustrated in Figure 4.3.

4.3 Data Reduction

The fouling resistance is calculated by

$$R_f = \frac{1}{U_f} - \frac{1}{U_c} \tag{4.1}$$

where U_f is the over-all heat transfer coefficient when fouling is present, and U_c is the over-all heat transfer coefficient when the tubes are clean. The energy balance equation along with the log mean temperature difference (LMTD) method will be used to determine the overall heat transfer coefficients, U_c and U_f. The heat transfer rate from the water to the test section is given by the energy balance

$$\dot{Q} = \dot{m}_w c_{p,w} (T_{w,out} - T_{w,in}) , \tag{4.2}$$

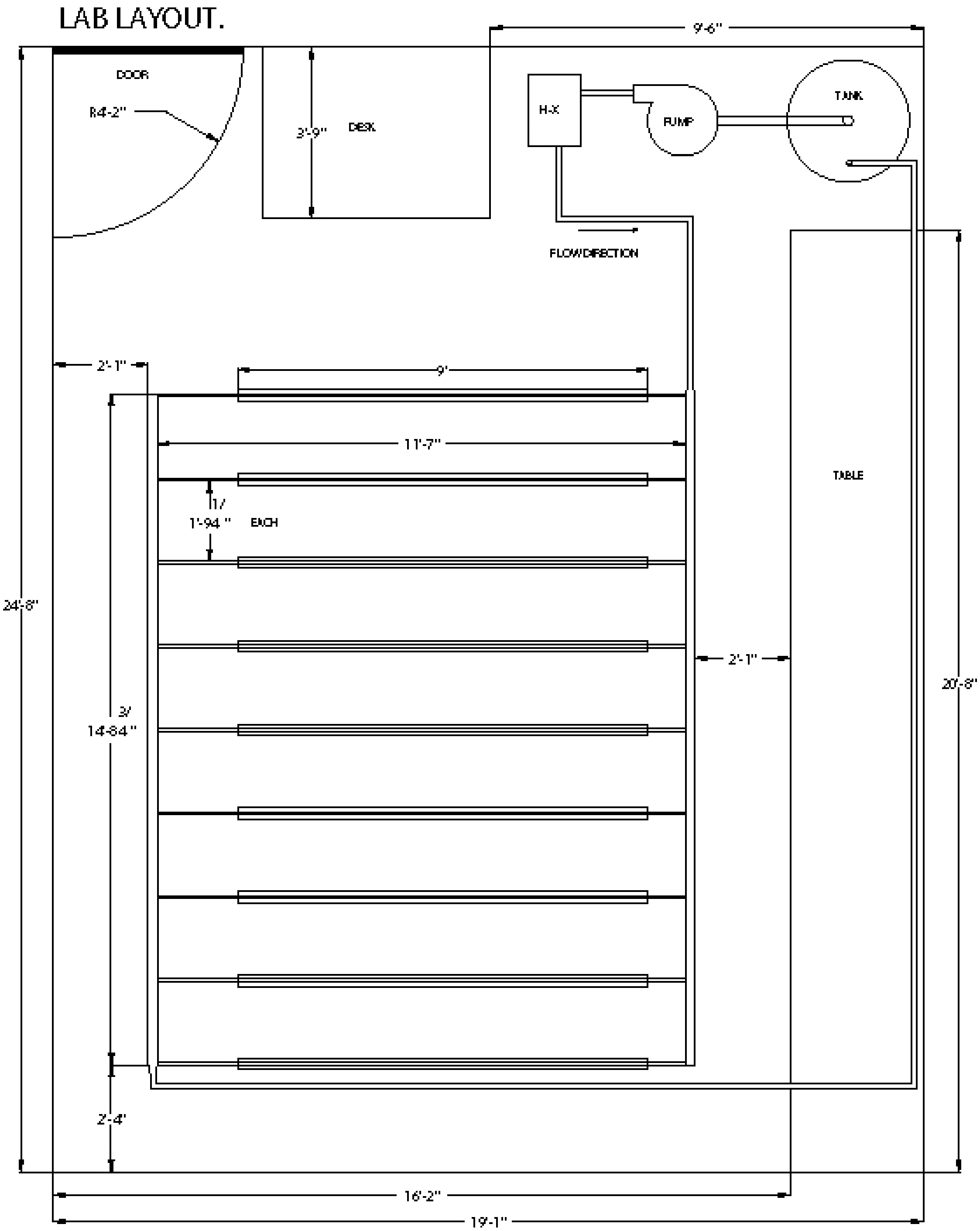

Figure 4.3: Laboratory Layout with Apparatus

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and $$\dot{Q} = U \cdot A \times LMTD\,. \tag{4.3}$$

where A is the inside surface area, which is defined as $\pi D_i L$

Therefore: $$U = \frac{\dot{Q}}{A * LMTD} \tag{4.4}$$

During the test, the water velocity may vary some. To account for this variation, the overall heat transfer coefficient needs to have a correction factor. The correction will be found by plotting U_c as a function of water velocity and performing a regression analysis of the plot. The resulting regression equation will be used to determine the overall heat transfer coefficient at the actual velocity in the fouled tube.

The asymptotic fouling resistance (R_f^*) and the initial fouling rate (dR_f/dt_o) will be calculated by curve-fitting the reduced fouling data into the following form:

$$R_f = R_f^*(1 - e^{-Bt}) \tag{4.5}$$

$$\frac{dR}{dt_o} = BR_f^* \tag{4.6}$$

4.4 Experimental Procedure

The experiment will consist of nine runs. Three water velocities will be run, each at a three water qualities. The three velocities to be tested are 4, 6 and 8 ft/s. The water qualities to be tested are presented in Table 3.6.

Table 4.1 shows the internal fin geometries to be tested. Li and Webb (2000) proposed relationships between fouling resistance and helix angle, fin height and number of starts. For this study, these parameters will be further investigated and compared with the results of Webb and Li (2000), and Li and Webb (2000). Tubes 1, 2, and 4 investigate the effect of number of starts on fouling. Tubes 5,6, and 7 investigate the effect of ridge height on fouling. Tubes 4, 6, 8 investigate the effect of the helix angle on fouling.

Table 4.1: Geometries to be Tested

Tube	d_o (Inch)	d_i (Inch)	e (Inch)	α	n_s
1	0.75	0.612	0.015	25	10
2	0.75	0.612	0.015	25	30
3	0.75	0.612	0.015	45	30
4	0.75	0.612	0.015	25	45
5	0.75	0.612	0.012	35	45
6	0.75	0.612	0.015	35	45
7	0.75	0.612	0.020	35	45
8	0.75	0.612	0.015	45	45
9	0.75	0.612	-	-	-

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CHAPTER V

CONCLUSIONS

Twenty-one water samples were collected from nineteen sites for this project. Each of these water samples was analyzed for several parameters that effect water quality. These parameters were then compared with several variables in the maintenance and operational information obtained on the sites through the questionnaire. Several conclusions were drawn about the fouling potential of the water sampled. The conclusions are

1. The condenser tubes in the cooling towers sampled had very little chance for corrosion fouling. This result was expected because all of the sites sampled employed some form of corrosion inhibitor.
2. The potential to have particulate fouling was inconclusive, since the Mississippi State Chemical Laboratory was able to filter out only particles with a diameter greater than 10 μm. The results showed that there was no chance of particulate fouling. This result is in line with previous attempts in the literature to model cooling tower water.
3. The condensers sampled showed a significant potential for precipitation fouling; 96 % have at least some potential and 41 % have the potential to definitely form scale

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4. The samples that were taken from systems with multiple chillers attached to a single cooling tower showed significantly more potential to form scale then those with only a single chiller attached to the cooling tower. This result warrants further investigation.

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CHAPTER VI

FUTURE WORK

Phase III of this project needs to be completed. The apparatus for Phase III, which is described in Chapter 4 of this thesis, needs to be built. The water qualities to be used in Phase III of this study are shown in Figure 3.6. The fouling tests need to be run, and data examined using the data reduction equations described in Chapter 4. Further investigating the effect of multiple chiller configurations on fouling potential would be useful, but such an investigation is outside of the scope of Phase III of this project.

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-

APPENDIX A

RESPONSE DATA TO QUESTIONNAIRES

-

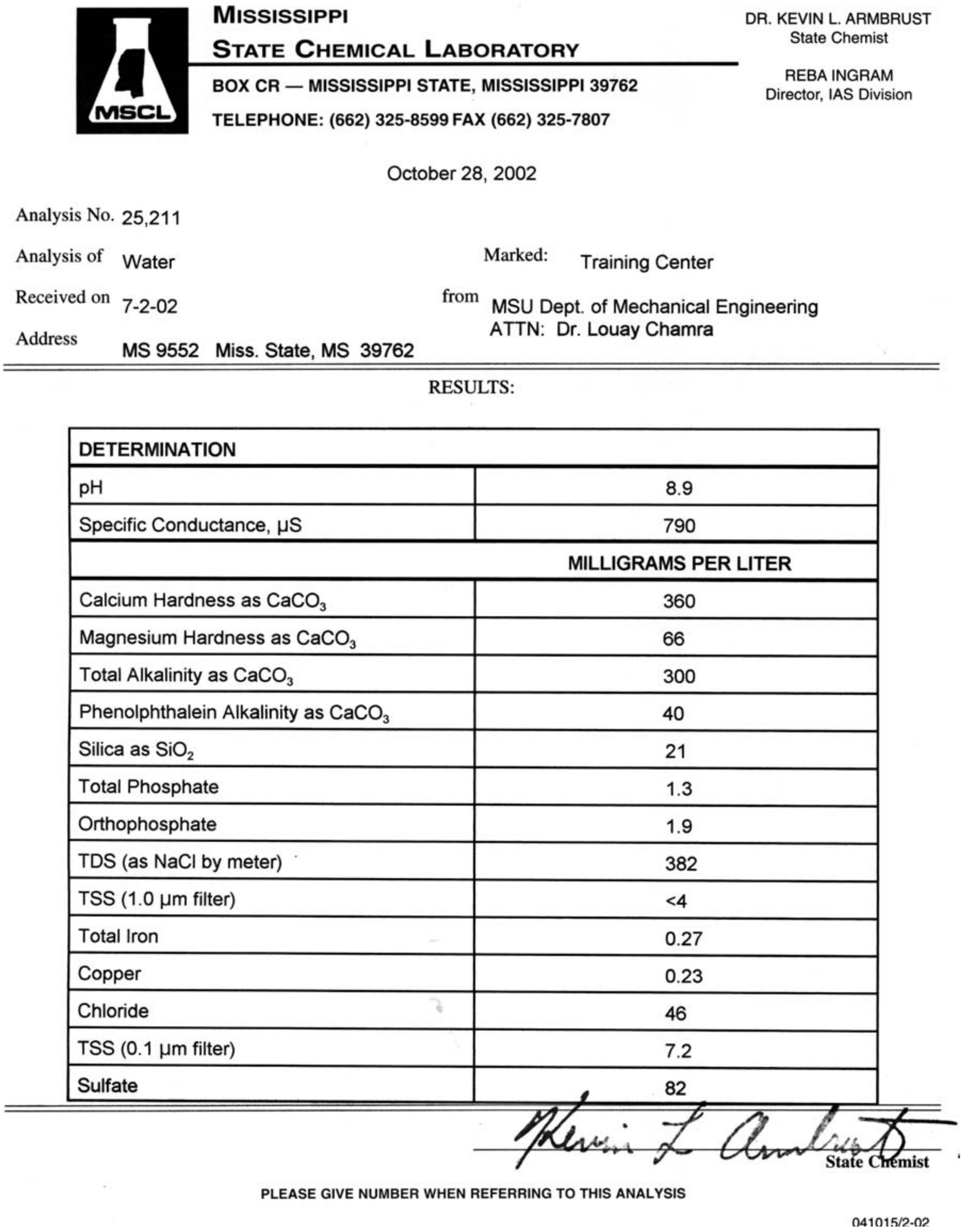
Table A.1: Questionnaire Response Data

Sample #	Location	City	State	Building Use	Corrosion Inhibitor	Type of Corrosion Inhibitor	Water Softened	Acid Used	Biocide Used	Multiple Chillers	hours/ year	Cleaned ?	Cleaning Type	Frequency of Cleaning	Water Source	Number of Cycles
1a	Space and Rocket Center	Huntsville	AL	Museum	Yes	Organic, Molybdate	No	No	Yes	No	8030	Yes	Automatic brushes	Annually	Municipal	3
1b	Space and Rocket Center	Huntsville	AL	Museum	Yes	Organic, Molybdate	No	No	Yes	No	8030	Yes	Automatic brushes	Annually	Municipal	3
2	University of Alabama	Huntsville	AL	University												
4	California Academy of Science	San Francisco	CA	Museum	Yes		No	No	Yes	No	8760	No			Municipal	
5	Valley Hospital	Las Vegas	NV	Hospital	Yes	Phosphate	Yes	No	Yes	No	8760	Yes	Automatic brushes	Annually	Municipal	
6	Palmento Richland Hospital	Columbia	SC	Hospital	Yes	Molybdate	No	No	Yes	No	8760	Yes	Automatic brushes	3 Times Daily	Municipal	7
7	Hyatt Regency	Las Vegas	NV	Hotel	Yes		No	No	Yes	Yes	8760	Yes	Hand Brushes	Annually	Municipal	3
8	Museum of Fine Arts	Boston	MA	Museum	Yes	Phosphate	No	No	Yes	Yes	4704	Yes	Automatic brushes	Annually	Municipal	8
10	Embassy Suites Hotel	Richmond	VA	Hotel	Yes		No	No	Yes	No	8760	Yes	Hand Brushes	Annually	Municipal	
11	Florida Hospital	Orlando	FL	Hospital	es	All-Organic, Phosphonate, Azole	No	No	Yes	No	8760	Yes	Hand Brushes	Annually	Municipal	3
12	University of Pittsburgh	Pittsburgh	PA	University	Yes		No	No	Yes	Yes	8760	Yes	Automatic Brushes	Annually	Municipal	7
13	Museum of Science	Boston	MA	Museum	Yes		No	No	Yes	No	8760	Yes	Automatic brushes	Annually	Municipal	4
14	Pennsylvania Convention Center	Philadelphia	PA	Convention Center	Yes	Organic, Molybdate, Phosphate	No	No	Yes	Yes	8760	Yes	Hand Brushes	Annually	Municipal	
15	Maryville Hospital	Phoenix	AZ	Hospital	Yes	Molybdate, Phosphate	No	Yes	Yes	No	8760	Yes	Automatic Brushes	Annually	Municipal	4
16	Riverwalk	New Orleans	LA	Retail	Yes	Molybdate, Phosphate	No	No	Yes	Yes	5840	Yes	Automatic Brushes	Every 3 Years	Municipal	
17	Indianapolis University	Indianapolis	IN	University	Yes	Molybdate	No	No	Yes		8760	Yes	Hand Brushes	Annually	Municipal	3
18	University of Cincinnati	Cincinnati	OH	University	Yes	Molybdate, Phosphate	No	No	Yes	No	5000	Yes	Hand Brushes	Annually	Municipal	5
19	James Cancer Center	Columbus	OH	Hospital	Yes	Organic, Molybdate, Phosphate	Yes	No	Yes	No		Yes	Hand Brushes	Annually	Municipal	5
20	Fedex	Memphis	TN	Office	Yes		No	Yes	Yes	Yes	8760	Yes	Hand Brushes	Annually	On-site Well	6
21	California Academy of Science	San Francisco	CA	Museum	Yes		No	No	Yes	No	8760	No			Municipal	
22	Mississippi State Steam Plant	Starkville	MS	University			??	??	Yes	Yes						

-

APPENDIX B

RESULTS OF WATER ANALYSIS BY MISSISSIPPI STATE CHEMICAL LABORATORY



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STATE CHEMICAL LABORATORY
BOX CR — MISSISSIPPI STATE, MISSISSIPPI 39762
TELEPHONE: (662) 325-8599 FAX (662) 325-7807

DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,211

Analysis of Water

Marked: Training Center

Received on 7-2-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.9
Specific Conductance, µS	790
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	360
Magnesium Hardness as $CaCO_3$	66
Total Alkalinity as $CaCO_3$	300
Phenolphthalein Alkalinity as $CaCO_3$	40
Silica as SiO_2	21
Total Phosphate	1.3
Orthophosphate	1.9
TDS (as NaCl by meter)	382
TSS (1.0 µm filter)	<4
Total Iron	0.27
Copper	0.23
Chloride	46
TSS (0.1 µm filter)	7.2
Sulfate	82

Kevin L. Armbrust
State Chemist

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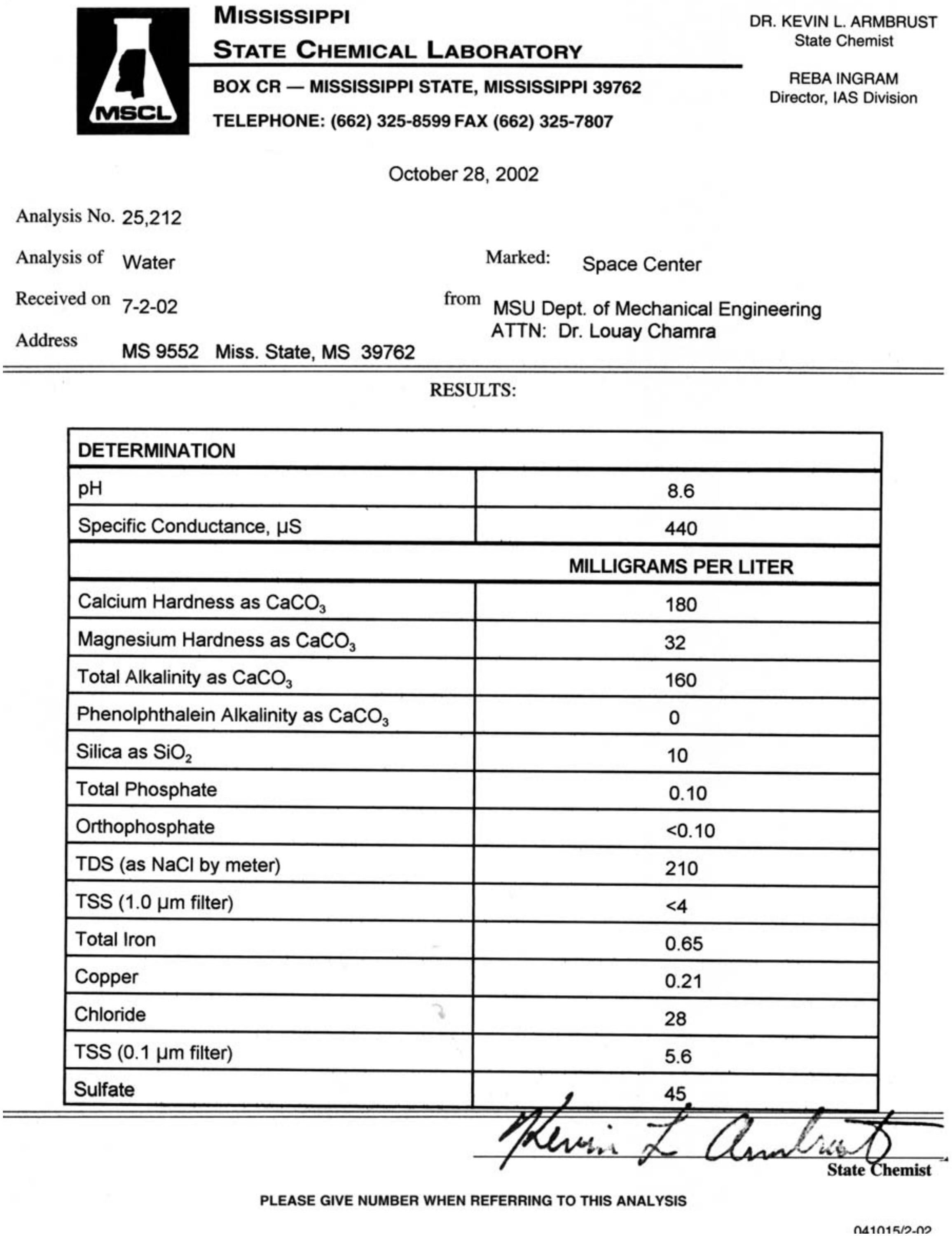

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MSCL

DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,212

Analysis of Water

Marked: Space Center

Received on 7-2-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.6
Specific Conductance, μS	440
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	180
Magnesium Hardness as $CaCO_3$	32
Total Alkalinity as $CaCO_3$	160
Phenolphthalein Alkalinity as $CaCO_3$	0
Silica as SiO_2	10
Total Phosphate	0.10
Orthophosphate	<0.10
TDS (as NaCl by meter)	210
TSS (1.0 μm filter)	<4
Total Iron	0.65
Copper	0.21
Chloride	28
TSS (0.1 μm filter)	5.6
Sulfate	45

Kevin L. Armbrust
State Chemist

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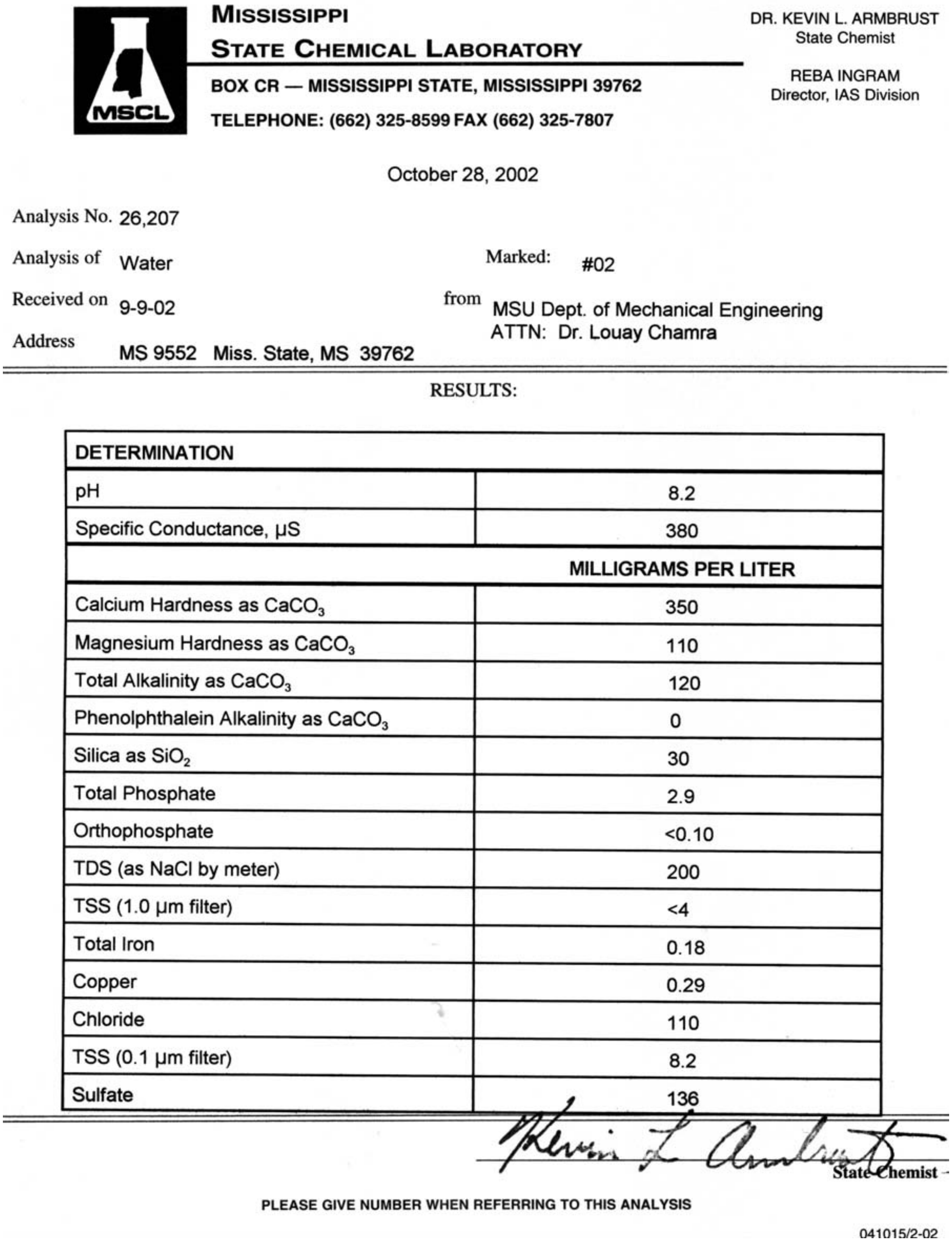

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 26,207

Analysis of Water

Marked: #02

Received on 9-9-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.2
Specific Conductance, µS	380
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	350
Magnesium Hardness as $CaCO_3$	110
Total Alkalinity as $CaCO_3$	120
Phenolphthalein Alkalinity as $CaCO_3$	0
Silica as SiO_2	30
Total Phosphate	2.9
Orthophosphate	<0.10
TDS (as NaCl by meter)	200
TSS (1.0 µm filter)	<4
Total Iron	0.18
Copper	0.29
Chloride	110
TSS (0.1 µm filter)	8.2
Sulfate	136

Kevin L. Armbrust
State Chemist

PLEASE GIVE NUMBER WHEN REFERRING TO THIS ANALYSIS

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TELEPHONE: (662) 325-8599 FAX (662) 325-7807

DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 26,237

Analysis of Water

Marked: #04

Received on 9-10-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.9
Specific Conductance, µS	5,400
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	230
Magnesium Hardness as $CaCO_3$	690
Total Alkalinity as $CaCO_3$	970
Phenolphthalein Alkalinity as $CaCO_3$	96
Silica as SiO_2	96
Total Phosphate	20.0
Orthophosphate	<0.10
TDS (as NaCl by meter)	3,020
TSS (1.0 µm filter)	550
Total Iron	0.71
Copper	0.30
Chloride	1,000
TSS (0.1 µm filter)	4,480
Sulfate	685

Kevin L. Armbrust
State Chemist

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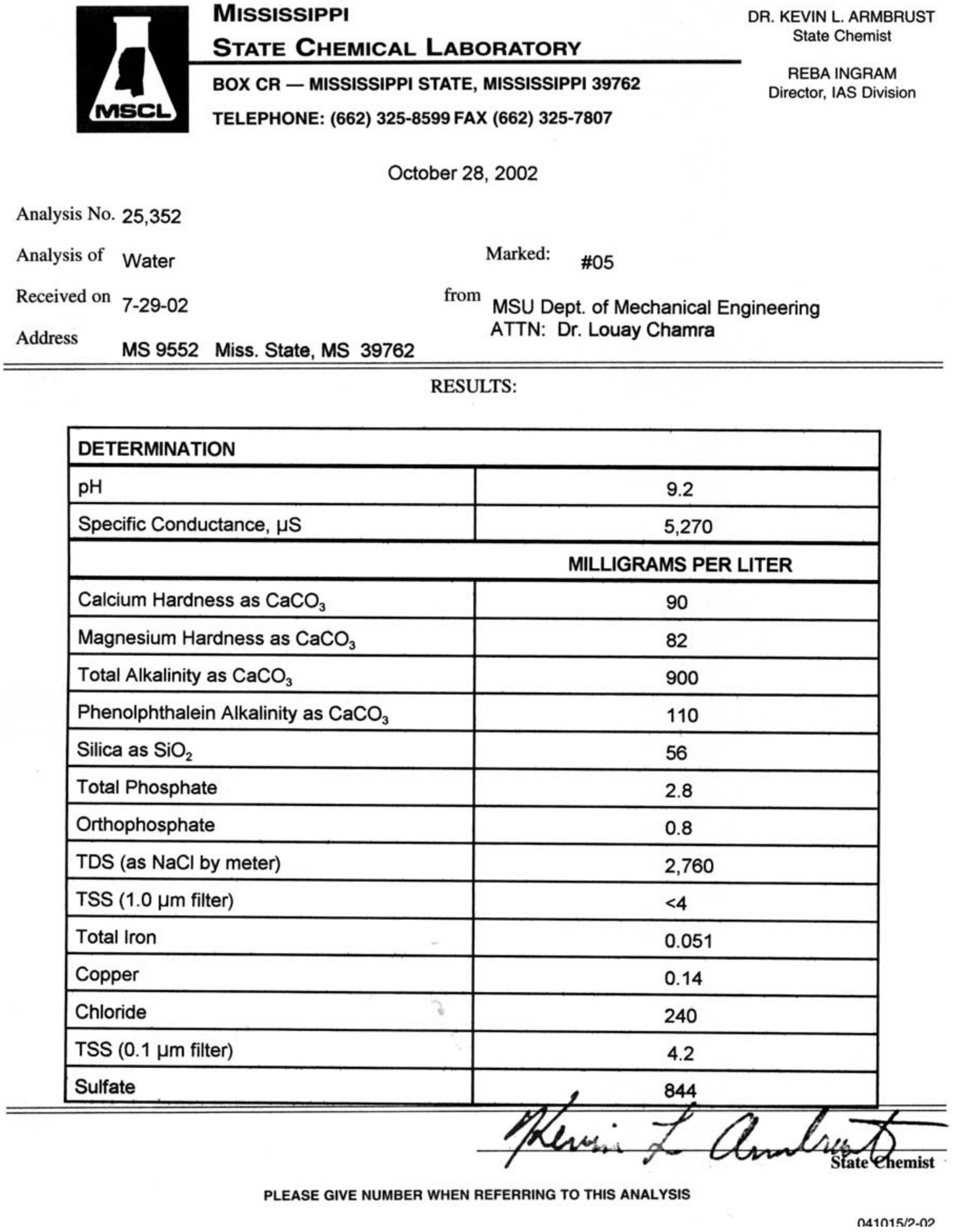

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,352

Analysis of Water

Marked: #05

Received on 7-29-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	9.2
Specific Conductance, µS	5,270
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	90
Magnesium Hardness as $CaCO_3$	82
Total Alkalinity as $CaCO_3$	900
Phenolphthalein Alkalinity as $CaCO_3$	110
Silica as SiO_2	56
Total Phosphate	2.8
Orthophosphate	0.8
TDS (as NaCl by meter)	2,760
TSS (1.0 µm filter)	<4
Total Iron	0.051
Copper	0.14
Chloride	240
TSS (0.1 µm filter)	4.2
Sulfate	844

Kevin L. Armbrust
State Chemist

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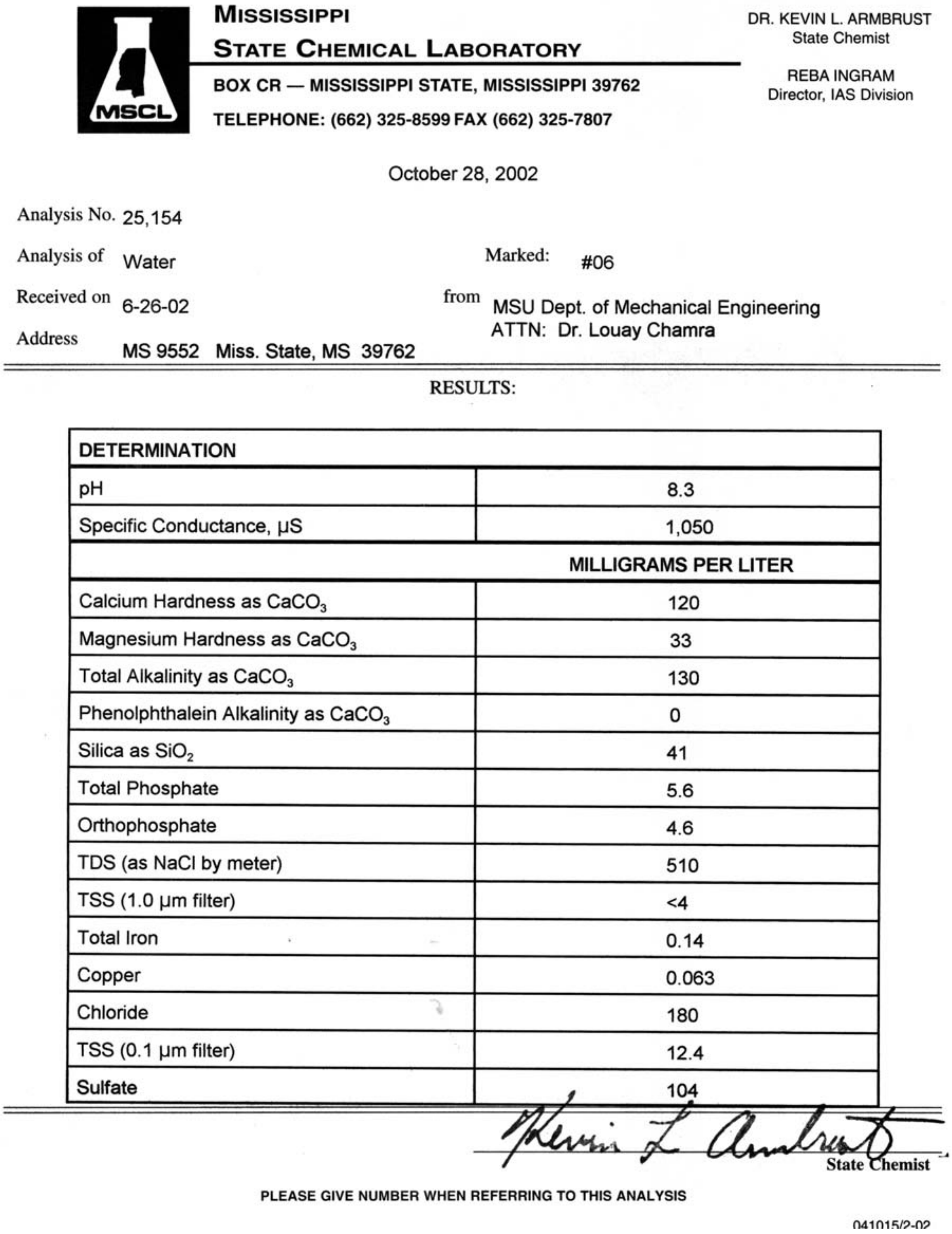

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,154

Analysis of Water

Marked: #06

Received on 6-26-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.3
Specific Conductance, µS	1,050
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	120
Magnesium Hardness as $CaCO_3$	33
Total Alkalinity as $CaCO_3$	130
Phenolphthalein Alkalinity as $CaCO_3$	0
Silica as SiO_2	41
Total Phosphate	5.6
Orthophosphate	4.6
TDS (as NaCl by meter)	510
TSS (1.0 µm filter)	<4
Total Iron	0.14
Copper	0.063
Chloride	180
TSS (0.1 µm filter)	12.4
Sulfate	104

Kevin L. Armbrust
State Chemist

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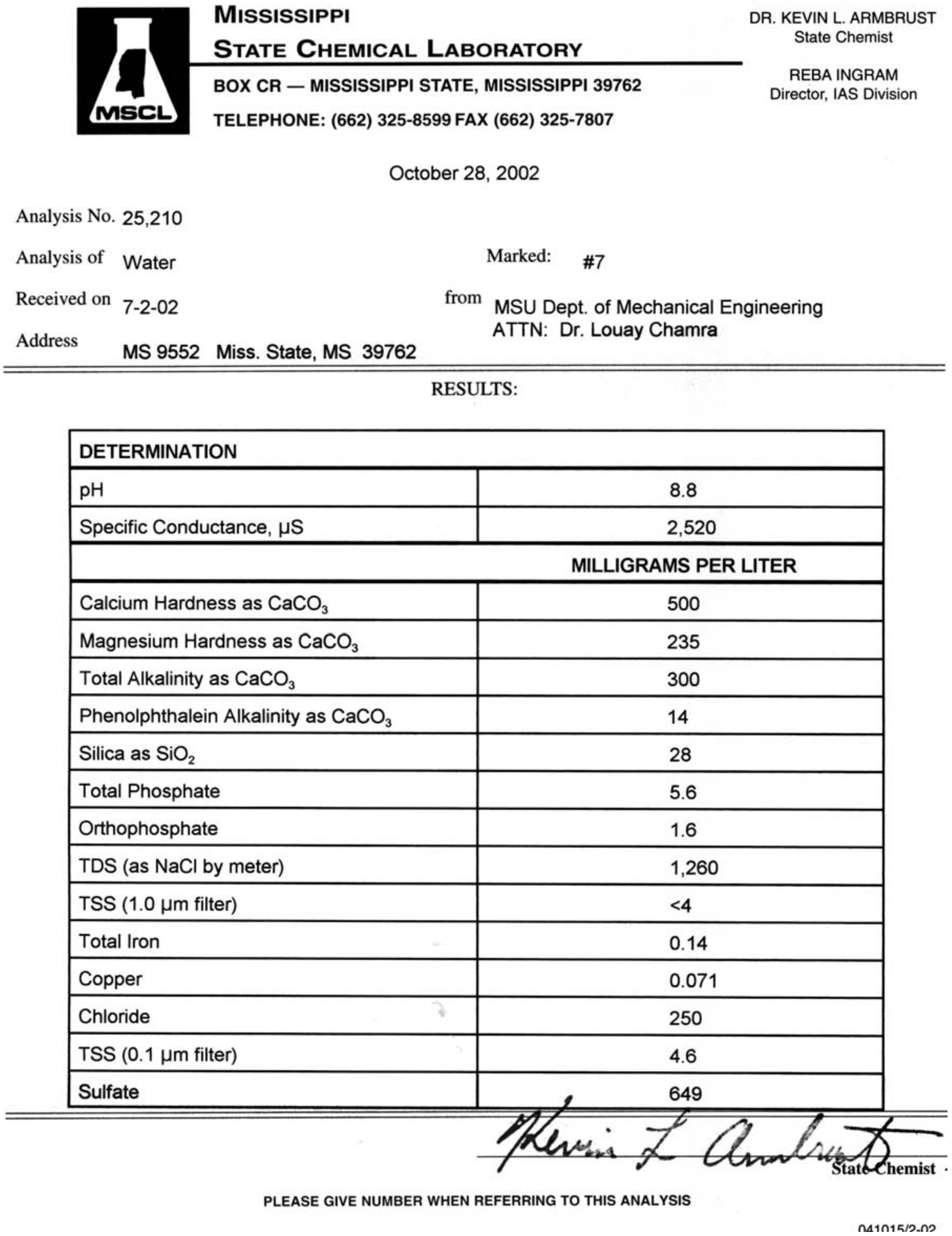

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State Chemist

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October 28, 2002

Analysis No. 25,210

Analysis of Water

Marked: #7

Received on 7-2-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.8
Specific Conductance, µS	2,520
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	500
Magnesium Hardness as $CaCO_3$	235
Total Alkalinity as $CaCO_3$	300
Phenolphthalein Alkalinity as $CaCO_3$	14
Silica as SiO_2	28
Total Phosphate	5.6
Orthophosphate	1.6
TDS (as NaCl by meter)	1,260
TSS (1.0 µm filter)	<4
Total Iron	0.14
Copper	0.071
Chloride	250
TSS (0.1 µm filter)	4.6
Sulfate	649

Kevin L. Armbrust
State Chemist

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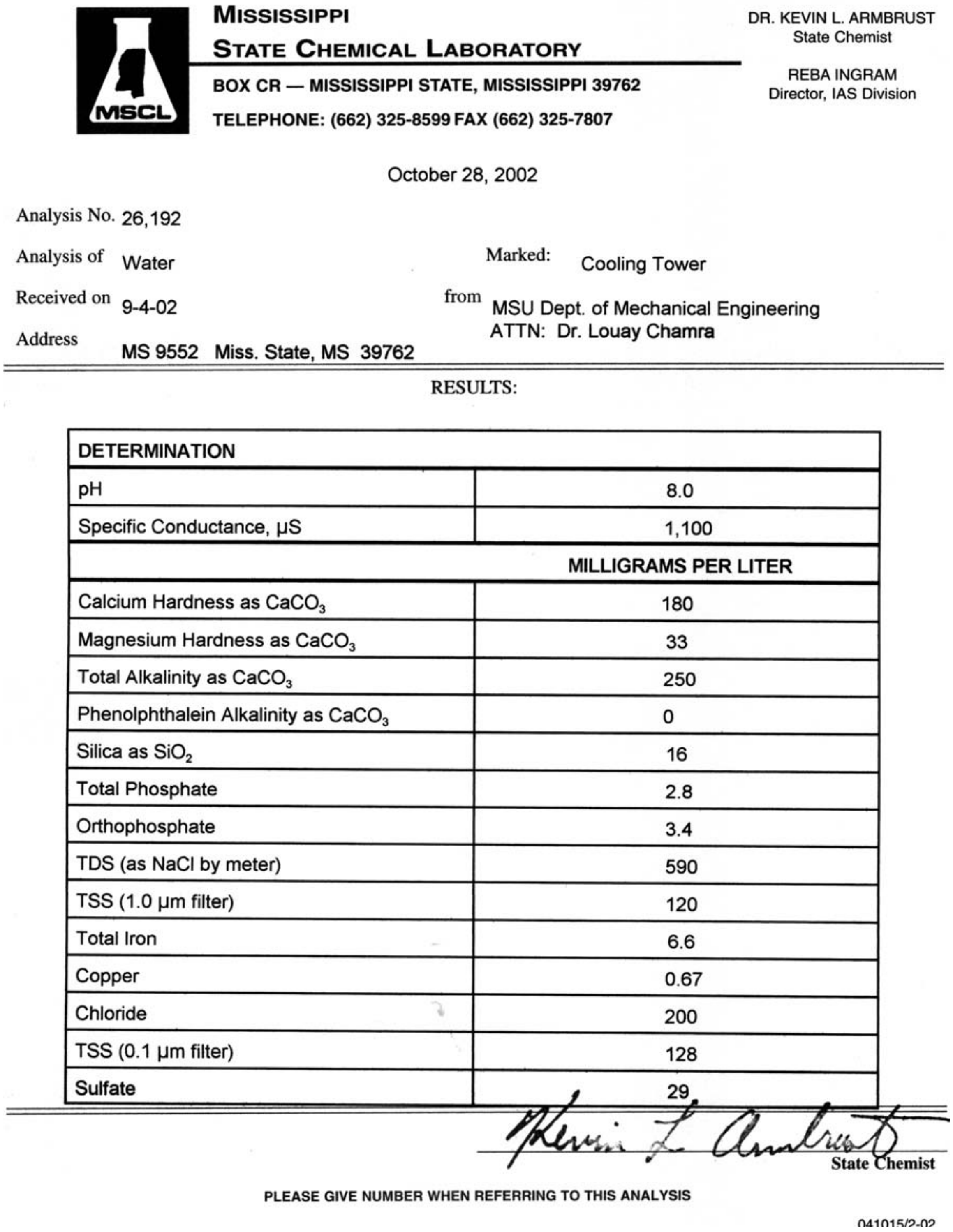

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 26,192

Analysis of Water

Marked: Cooling Tower

Received on 9-4-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.0
Specific Conductance, µS	1,100
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	180
Magnesium Hardness as $CaCO_3$	33
Total Alkalinity as $CaCO_3$	250
Phenolphthalein Alkalinity as $CaCO_3$	0
Silica as SiO_2	16
Total Phosphate	2.8
Orthophosphate	3.4
TDS (as NaCl by meter)	590
TSS (1.0 µm filter)	120
Total Iron	6.6
Copper	0.67
Chloride	200
TSS (0.1 µm filter)	128
Sulfate	29

Kevin L. Armbrust
State Chemist

PLEASE GIVE NUMBER WHEN REFERRING TO THIS ANALYSIS

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 26,255

Analysis of Water

Marked: No Identification Number

Received on 9-13-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	7.8
Specific Conductance, µS	1,100
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	270
Magnesium Hardness as $CaCO_3$	60
Total Alkalinity as $CaCO_3$	62
Phenolphthalein Alkalinity as $CaCO_3$	0
Silica as SiO_2	24
Total Phosphate	4.4
Orthophosphate	<0.10
TDS (as NaCl by meter)	560
TSS (1.0 µm filter)	<4
Total Iron	0.039
Copper	0.15
Chloride	100
TSS (0.1 µm filter)	11
Sulfate	362

Kevin L. Armbrust
State Chemist

PLEASE GIVE NUMBER WHEN REFERRING TO THIS ANALYSIS

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 26,318

Analysis of Water

Marked: #11

Received on 9-25-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

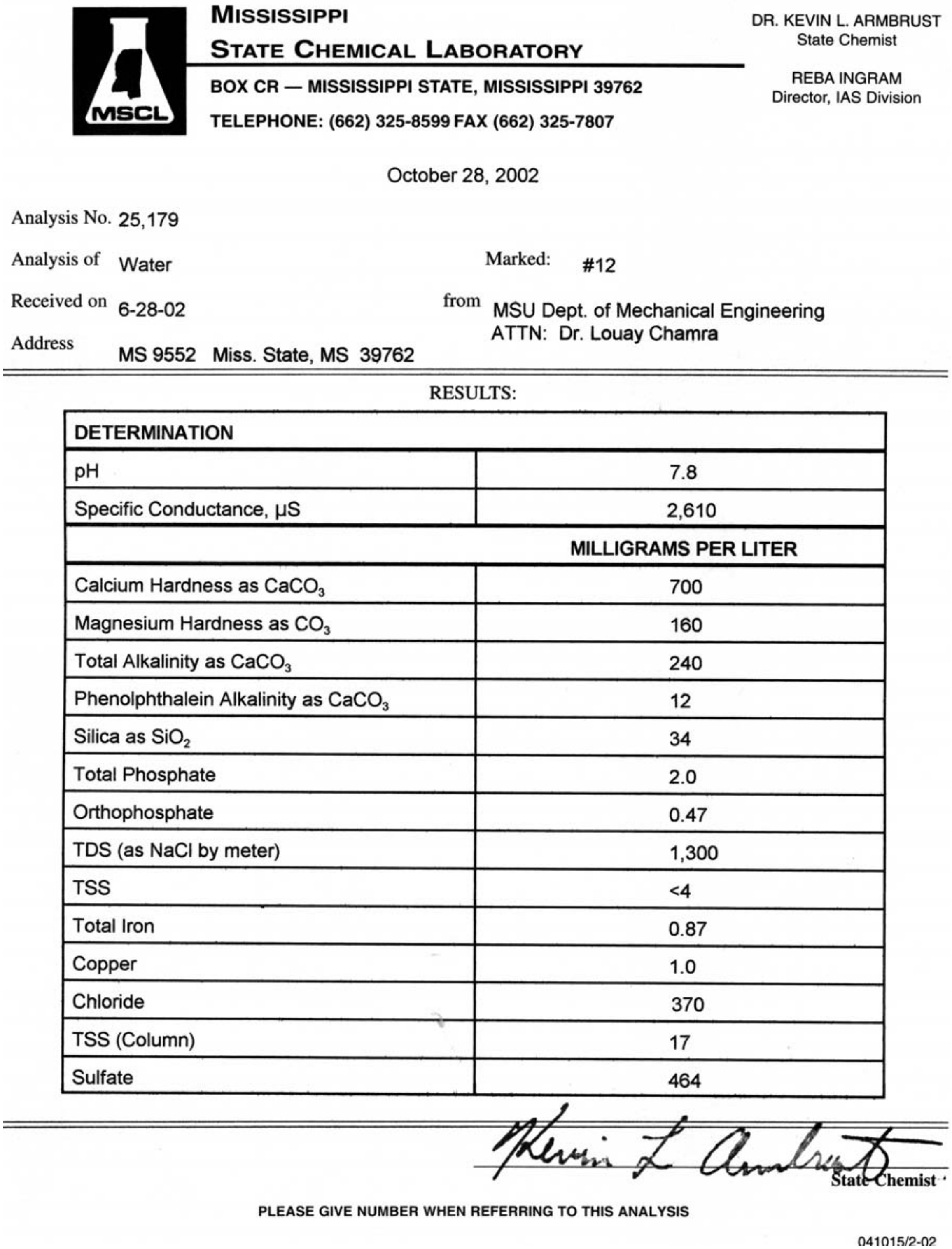
Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	9.0
Specific Conductance, µS	820
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	310
Magnesium Hardness as $CaCO_3$	130
Total Alkalinity as $CaCO_3$	450
Phenolphthalein Alkalinity as $CaCO_3$	110
Silica as SiO_2	39
Total Phosphate	0.70
Orthophosphate	0.81
TDS (as NaCl by meter)	450
TSS (1.0 µm filter)	<4
Total Iron	0.054
Copper	0.096
Chloride	54
TSS (0.1 µm filter)	4.2
Sulfate	24

Kevin L. Armbrust
State Chemist

PLEASE GIVE NUMBER WHEN REFERRING TO THIS ANALYSIS



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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,179

Analysis of Water

Marked: #12

Received on 6-28-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	7.8
Specific Conductance, µS	2,610
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	700
Magnesium Hardness as CO_3	160
Total Alkalinity as $CaCO_3$	240
Phenolphthalein Alkalinity as $CaCO_3$	12
Silica as SiO_2	34
Total Phosphate	2.0
Orthophosphate	0.47
TDS (as NaCl by meter)	1,300
TSS	<4
Total Iron	0.87
Copper	1.0
Chloride	370
TSS (Column)	17
Sulfate	464

Kevin L. Armbrust
State Chemist

PLEASE GIVE NUMBER WHEN REFERRING TO THIS ANALYSIS

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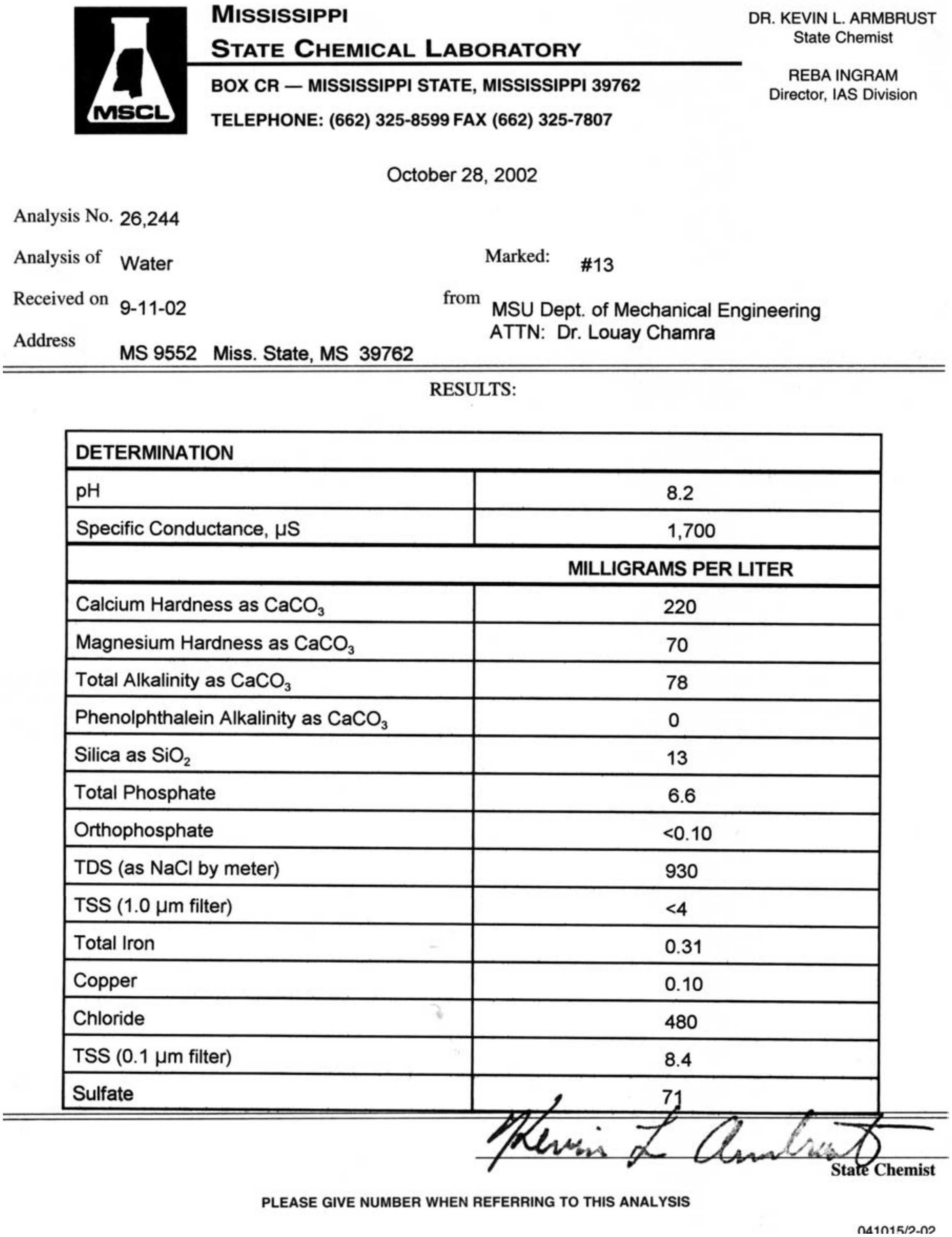

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 26,244

Analysis of Water

Marked: #13

Received on 9-11-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.2
Specific Conductance, µS	1,700
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	220
Magnesium Hardness as $CaCO_3$	70
Total Alkalinity as $CaCO_3$	78
Phenolphthalein Alkalinity as $CaCO_3$	0
Silica as SiO_2	13
Total Phosphate	6.6
Orthophosphate	<0.10
TDS (as NaCl by meter)	930
TSS (1.0 µm filter)	<4
Total Iron	0.31
Copper	0.10
Chloride	480
TSS (0.1 µm filter)	8.4
Sulfate	71

Kevin L. Armbrust
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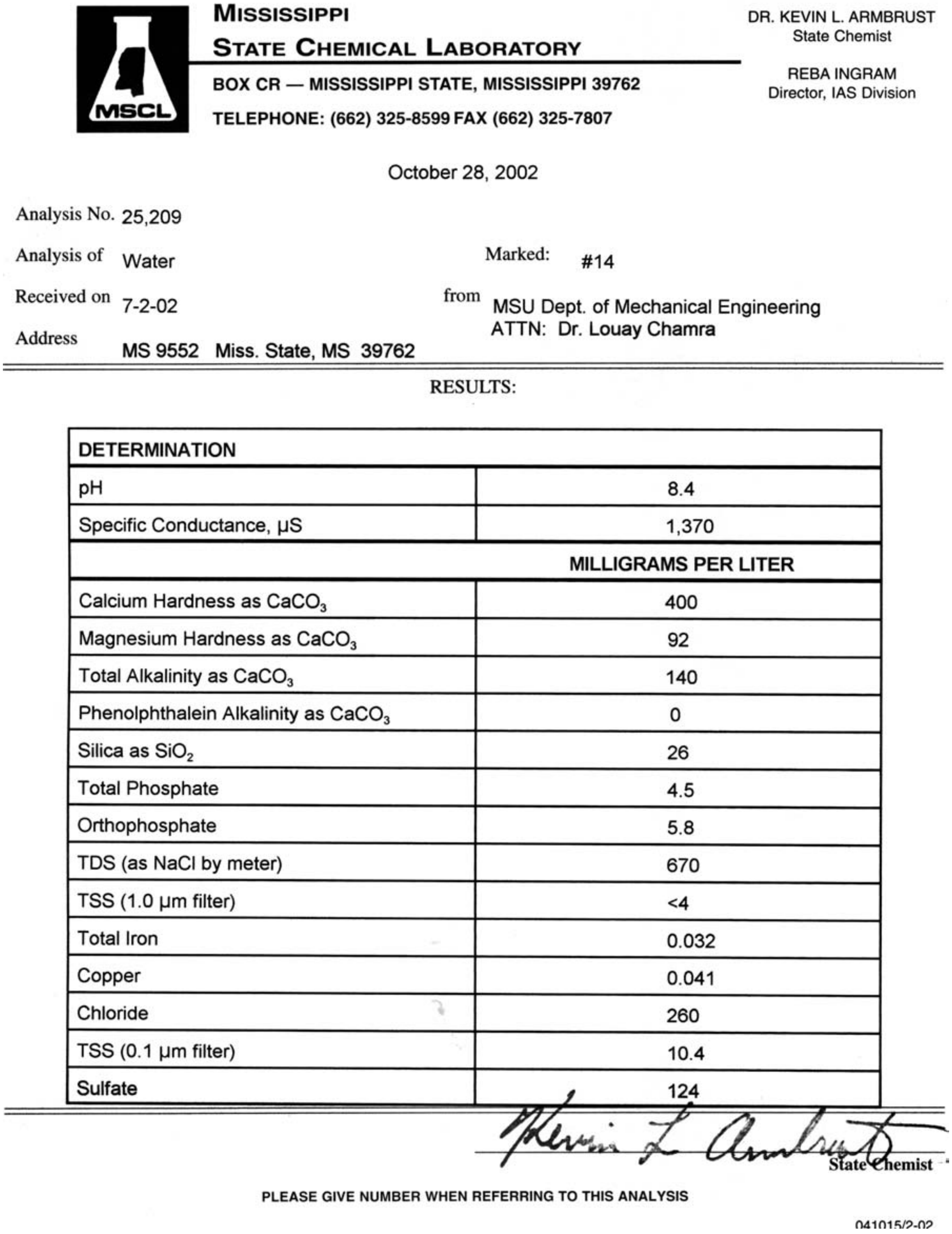

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,209
Analysis of Water
Marked: #14
Received on 7-2-02
from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra
Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.4
Specific Conductance, µS	1,370
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	400
Magnesium Hardness as $CaCO_3$	92
Total Alkalinity as $CaCO_3$	140
Phenolphthalein Alkalinity as $CaCO_3$	0
Silica as SiO_2	26
Total Phosphate	4.5
Orthophosphate	5.8
TDS (as NaCl by meter)	670
TSS (1.0 µm filter)	<4
Total Iron	0.032
Copper	0.041
Chloride	260
TSS (0.1 µm filter)	10.4
Sulfate	124

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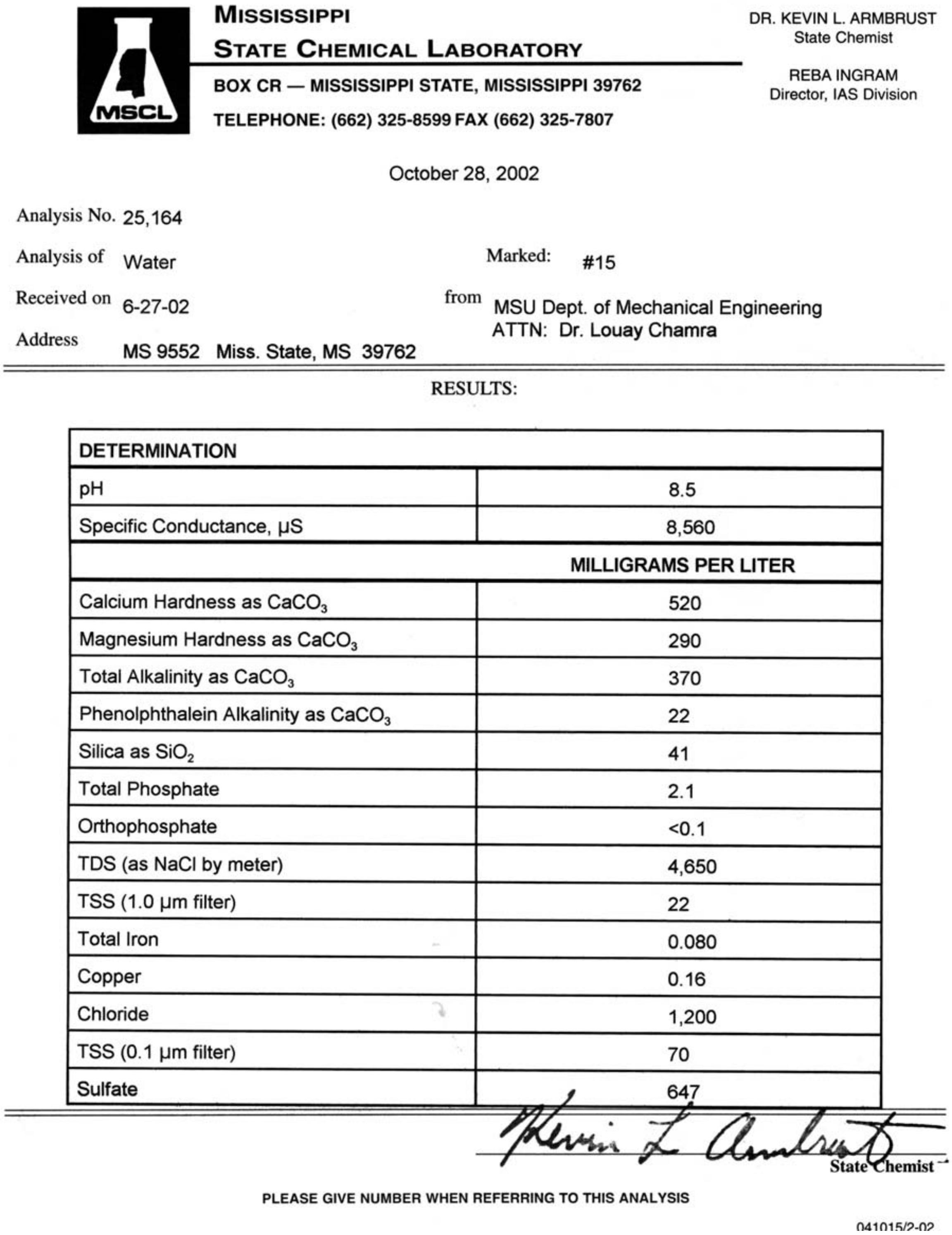

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October 28, 2002

Analysis No. 25,164
Analysis of Water
Marked: #15
Received on 6-27-02
from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra
Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.5
Specific Conductance, µS	8,560
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	520
Magnesium Hardness as $CaCO_3$	290
Total Alkalinity as $CaCO_3$	370
Phenolphthalein Alkalinity as $CaCO_3$	22
Silica as SiO_2	41
Total Phosphate	2.1
Orthophosphate	<0.1
TDS (as NaCl by meter)	4,650
TSS (1.0 µm filter)	22
Total Iron	0.080
Copper	0.16
Chloride	1,200
TSS (0.1 µm filter)	70
Sulfate	647

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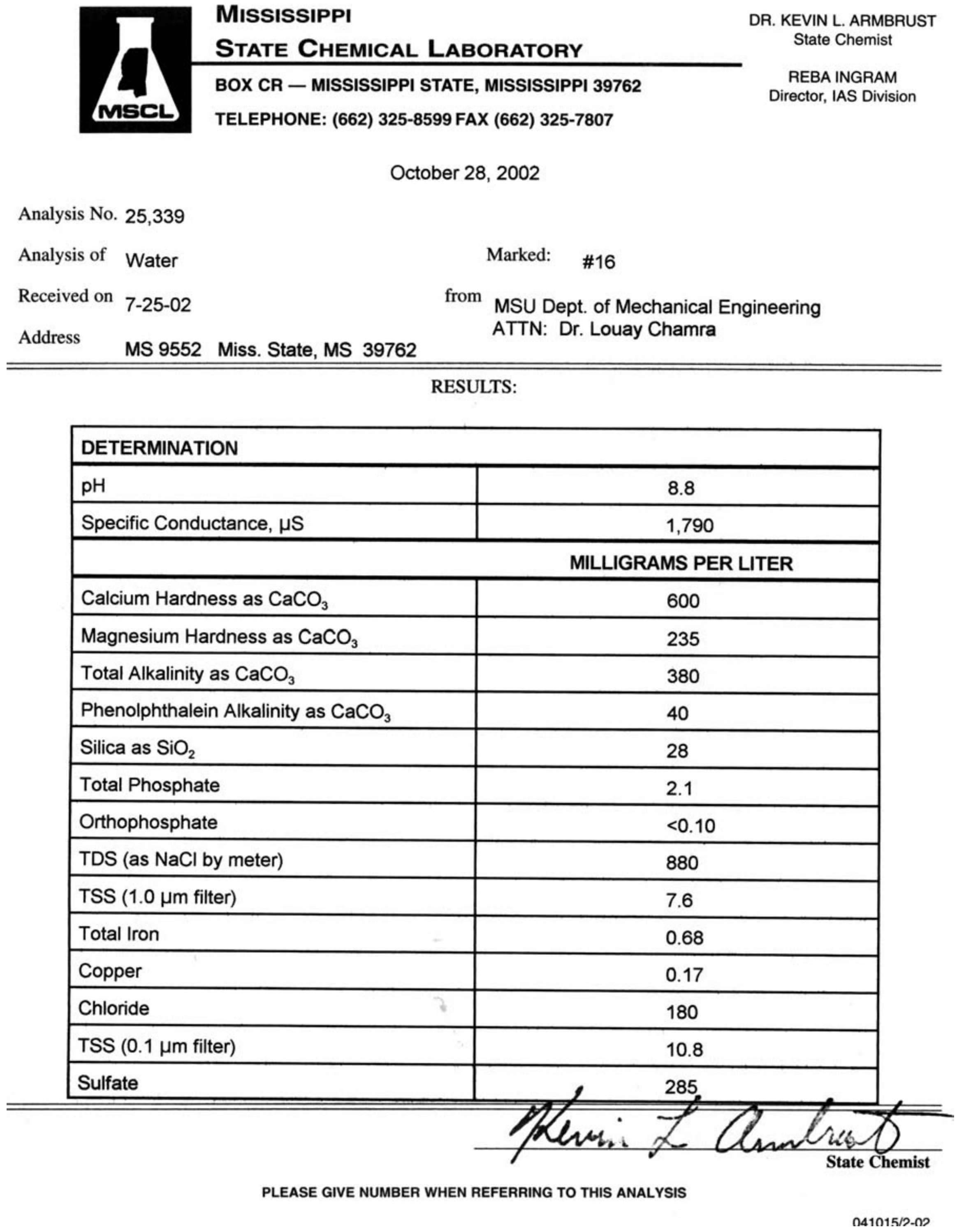

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DR. KEVIN L. ARMBRUST
State Chemist

REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,339

Analysis of Water

Marked: #16

Received on 7-25-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.8
Specific Conductance, µS	1,790
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	600
Magnesium Hardness as $CaCO_3$	235
Total Alkalinity as $CaCO_3$	380
Phenolphthalein Alkalinity as $CaCO_3$	40
Silica as SiO_2	28
Total Phosphate	2.1
Orthophosphate	<0.10
TDS (as NaCl by meter)	880
TSS (1.0 µm filter)	7.6
Total Iron	0.68
Copper	0.17
Chloride	180
TSS (0.1 µm filter)	10.8
Sulfate	285

Kevin L. Armbrust
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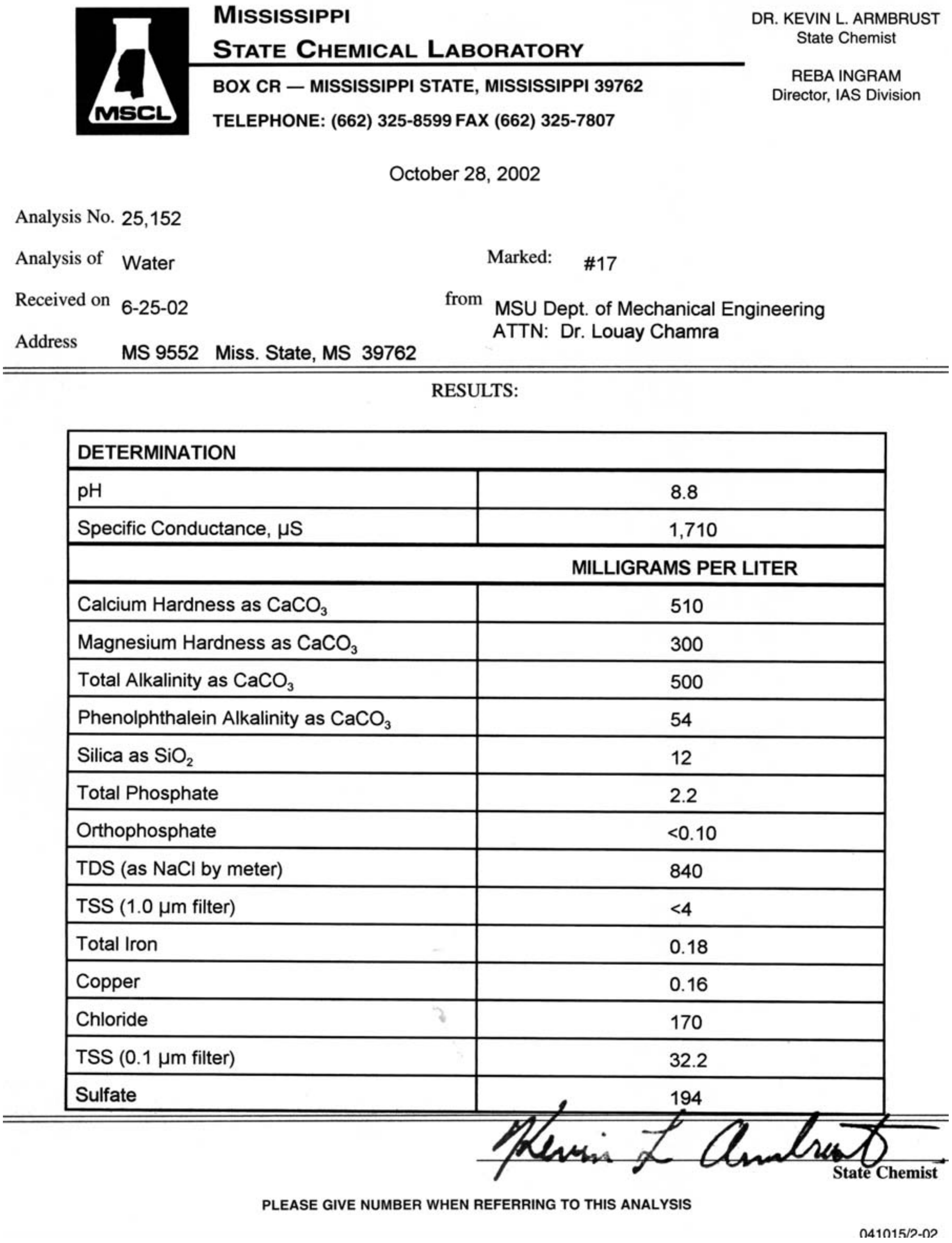

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REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 25,152

Analysis of Water

Marked: #17

Received on 6-25-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.8
Specific Conductance, µS	1,710
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	510
Magnesium Hardness as $CaCO_3$	300
Total Alkalinity as $CaCO_3$	500
Phenolphthalein Alkalinity as $CaCO_3$	54
Silica as SiO_2	12
Total Phosphate	2.2
Orthophosphate	<0.10
TDS (as NaCl by meter)	840
TSS (1.0 µm filter)	<4
Total Iron	0.18
Copper	0.16
Chloride	170
TSS (0.1 µm filter)	32.2
Sulfate	194

Kevin L. Armbrust
State Chemist

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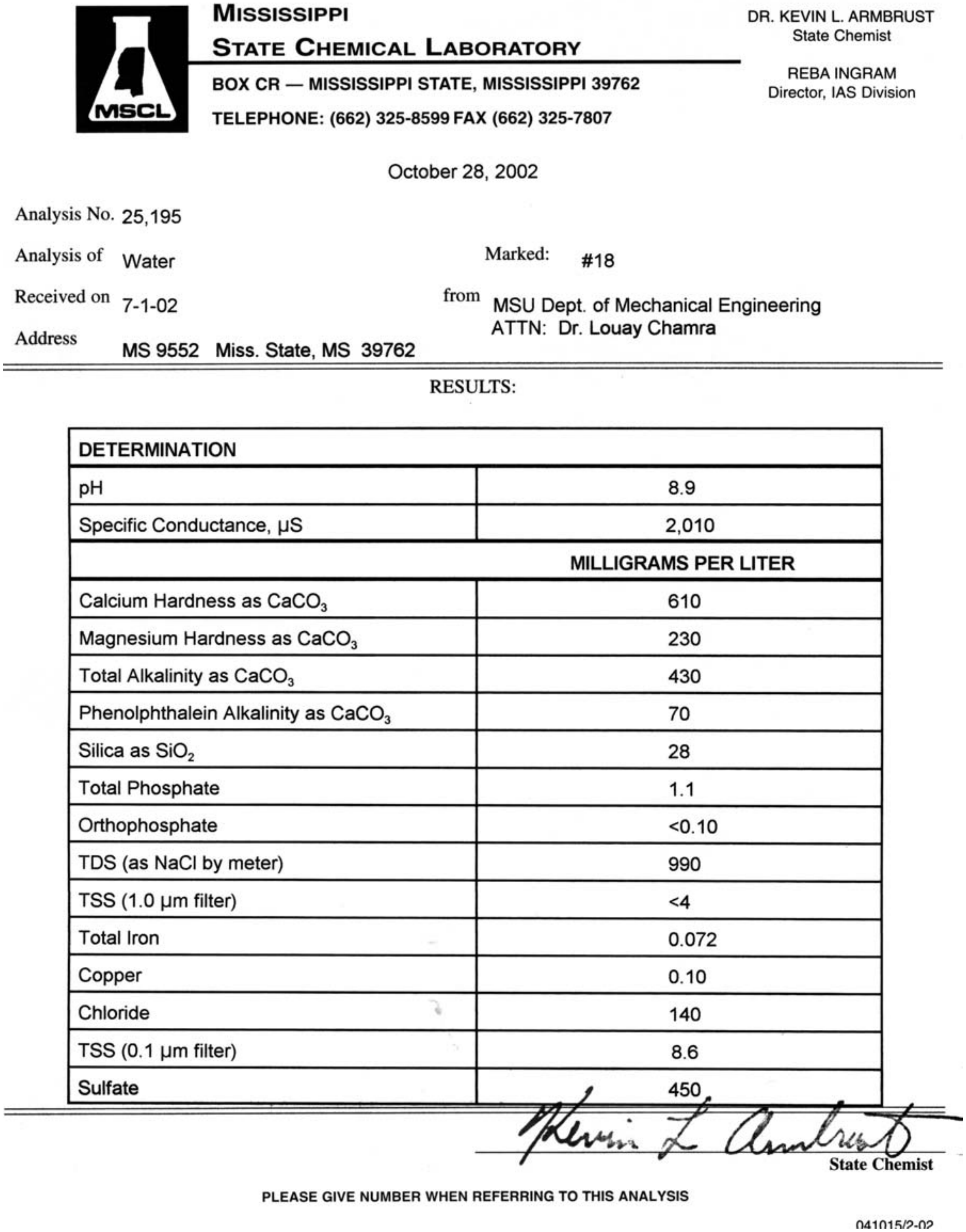

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October 28, 2002

Analysis No.	25,195		
Analysis of	Water	Marked:	#18
Received on	7-1-02	from	MSU Dept. of Mechanical Engineering ATTN: Dr. Louay Chamra
Address	MS 9552 Miss. State, MS 39762		

RESULTS:

DETERMINATION	
pH	8.9
Specific Conductance, µS	2,010
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	610
Magnesium Hardness as $CaCO_3$	230
Total Alkalinity as $CaCO_3$	430
Phenolphthalein Alkalinity as $CaCO_3$	70
Silica as SiO_2	28
Total Phosphate	1.1
Orthophosphate	<0.10
TDS (as NaCl by meter)	990
TSS (1.0 µm filter)	<4
Total Iron	0.072
Copper	0.10
Chloride	140
TSS (0.1 µm filter)	8.6
Sulfate	450

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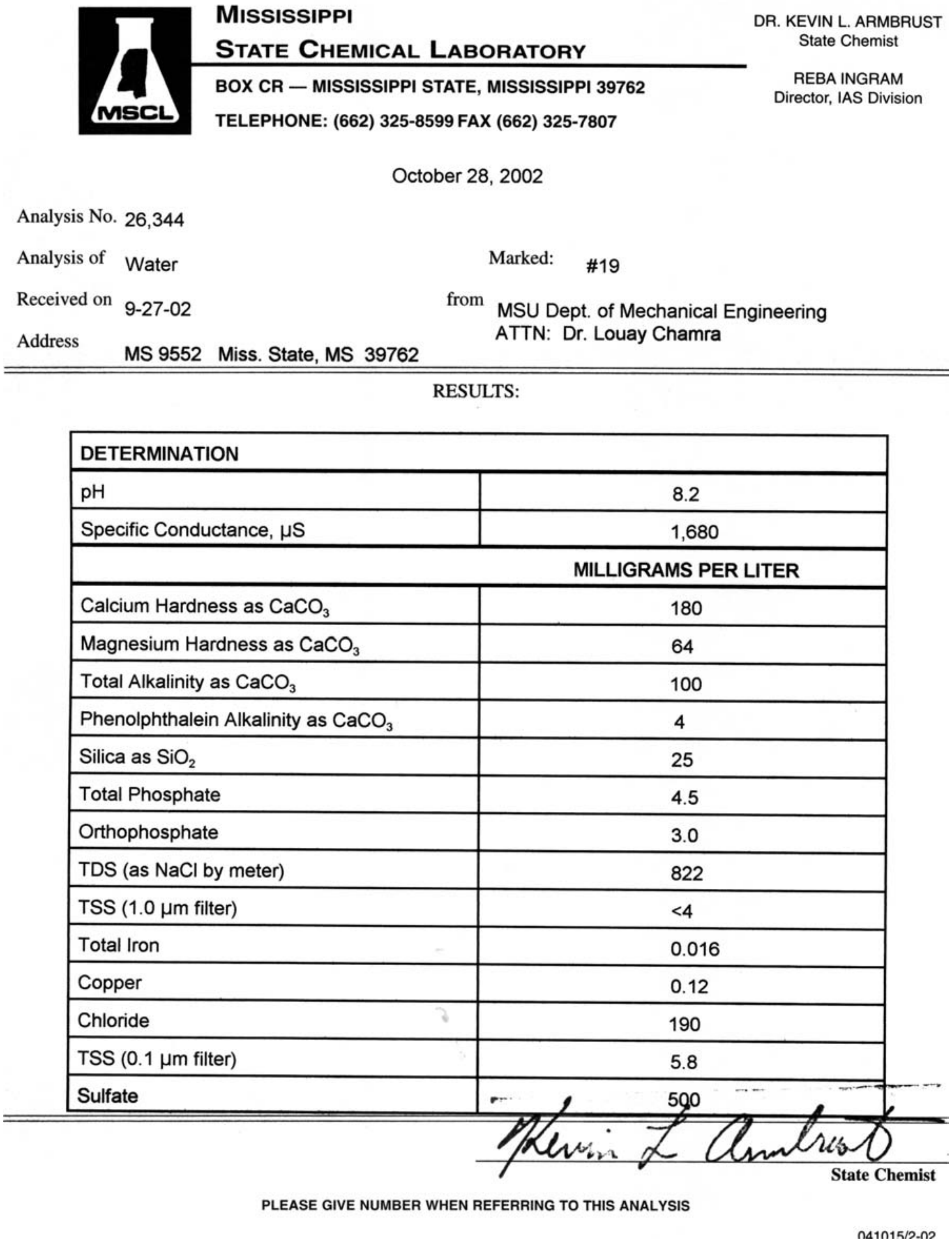

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Director, IAS Division

October 28, 2002

Analysis No. 26,344
Analysis of Water
Marked: #19
Received on 9-27-02
from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra
Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.2
Specific Conductance, µS	1,680
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	180
Magnesium Hardness as $CaCO_3$	64
Total Alkalinity as $CaCO_3$	100
Phenolphthalein Alkalinity as $CaCO_3$	4
Silica as SiO_2	25
Total Phosphate	4.5
Orthophosphate	3.0
TDS (as NaCl by meter)	822
TSS (1.0 µm filter)	<4
Total Iron	0.016
Copper	0.12
Chloride	190
TSS (0.1 µm filter)	5.8
Sulfate	500

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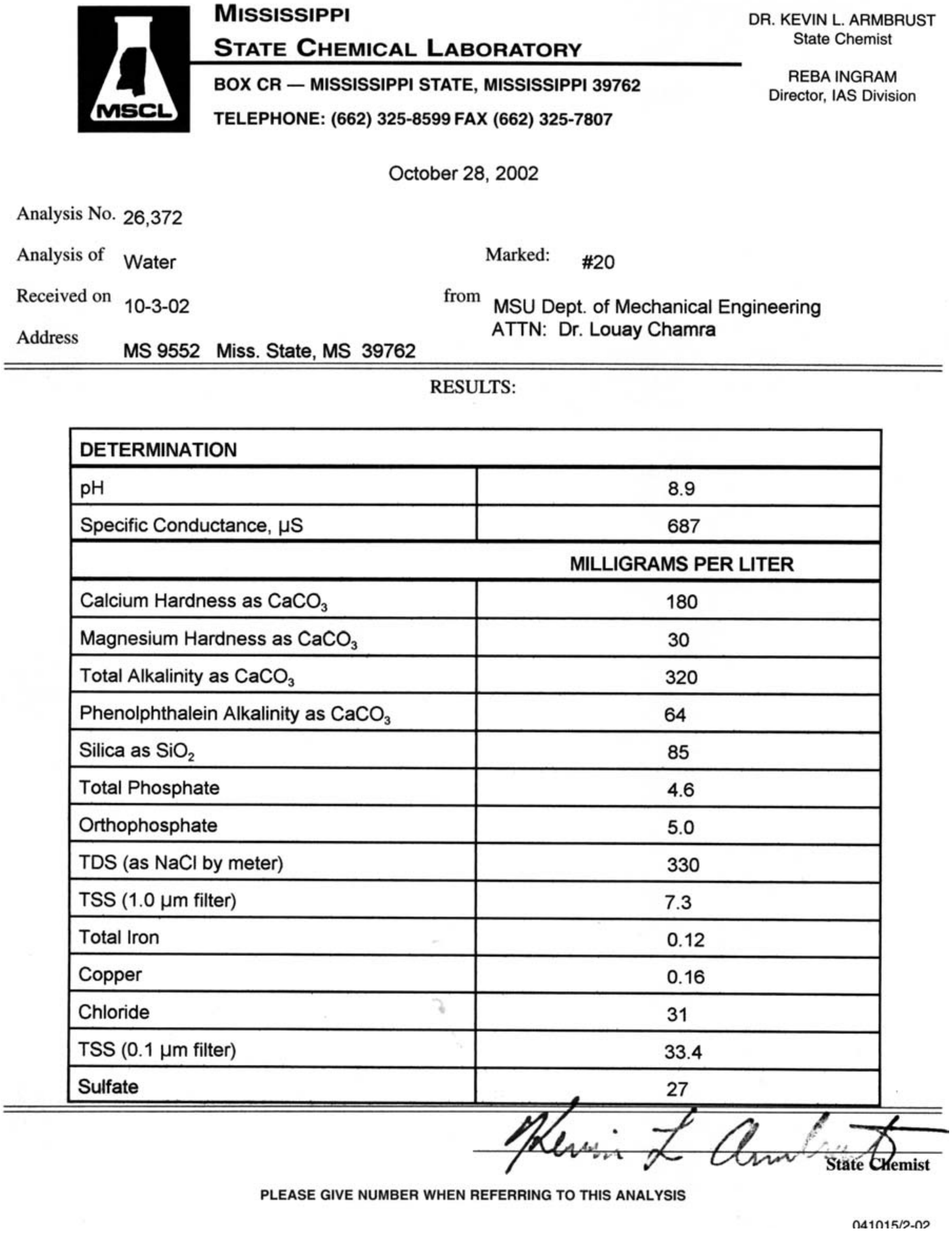

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REBA INGRAM
Director, IAS Division

October 28, 2002

Analysis No. 26,372

Analysis of Water

Marked: #20

Received on 10-3-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.9
Specific Conductance, µS	687
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	180
Magnesium Hardness as $CaCO_3$	30
Total Alkalinity as $CaCO_3$	320
Phenolphthalein Alkalinity as $CaCO_3$	64
Silica as SiO_2	85
Total Phosphate	4.6
Orthophosphate	5.0
TDS (as NaCl by meter)	330
TSS (1.0 µm filter)	7.3
Total Iron	0.12
Copper	0.16
Chloride	31
TSS (0.1 µm filter)	33.4
Sulfate	27

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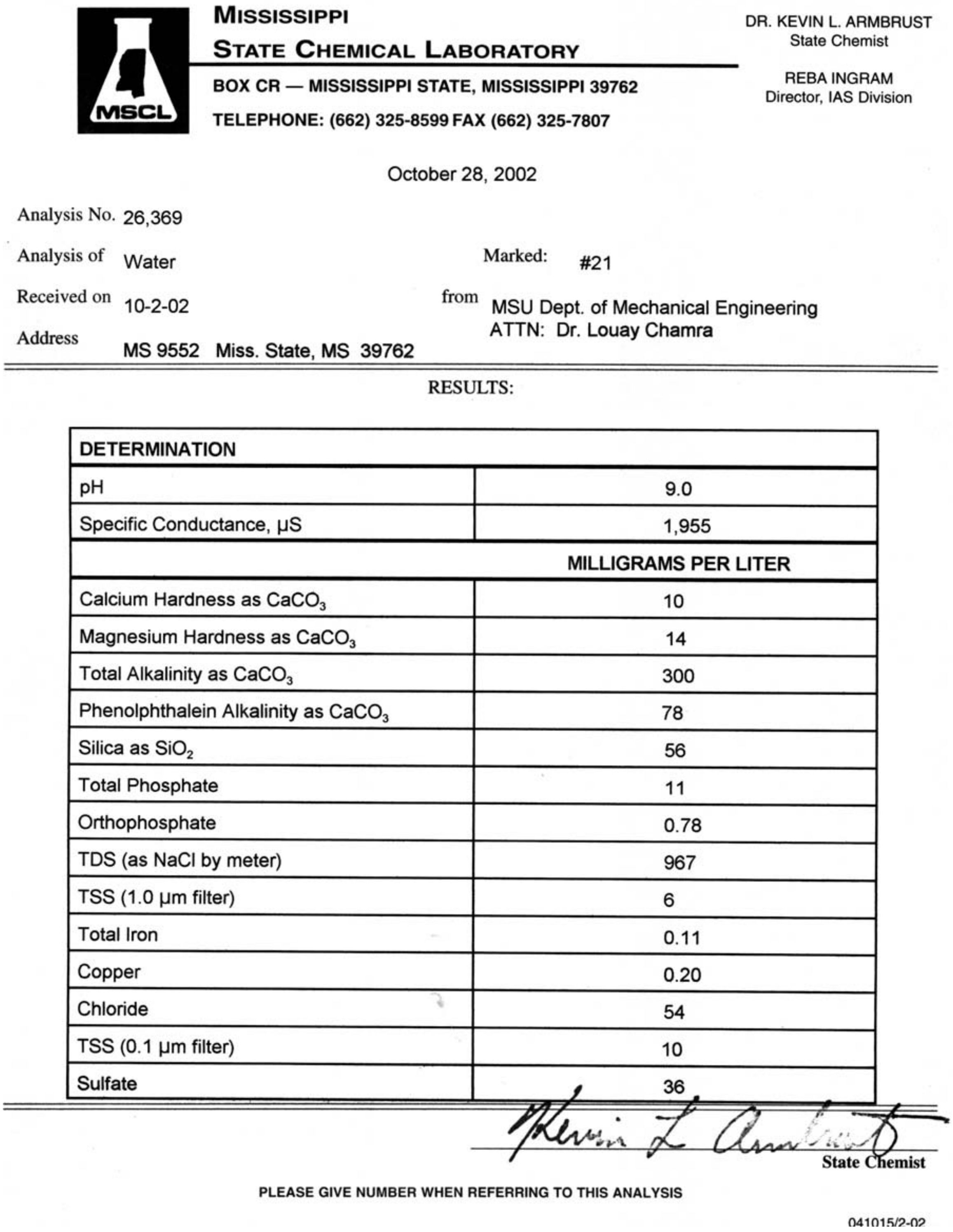

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October 28, 2002

Analysis No. 26,369
Analysis of Water
Marked: #21
Received on 10-2-02
from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra
Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	9.0
Specific Conductance, µS	1,955
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	10
Magnesium Hardness as $CaCO_3$	14
Total Alkalinity as $CaCO_3$	300
Phenolphthalein Alkalinity as $CaCO_3$	78
Silica as SiO_2	56
Total Phosphate	11
Orthophosphate	0.78
TDS (as NaCl by meter)	967
TSS (1.0 µm filter)	6
Total Iron	0.11
Copper	0.20
Chloride	54
TSS (0.1 µm filter)	10
Sulfate	36

Kevin L. Armbrust
State Chemist

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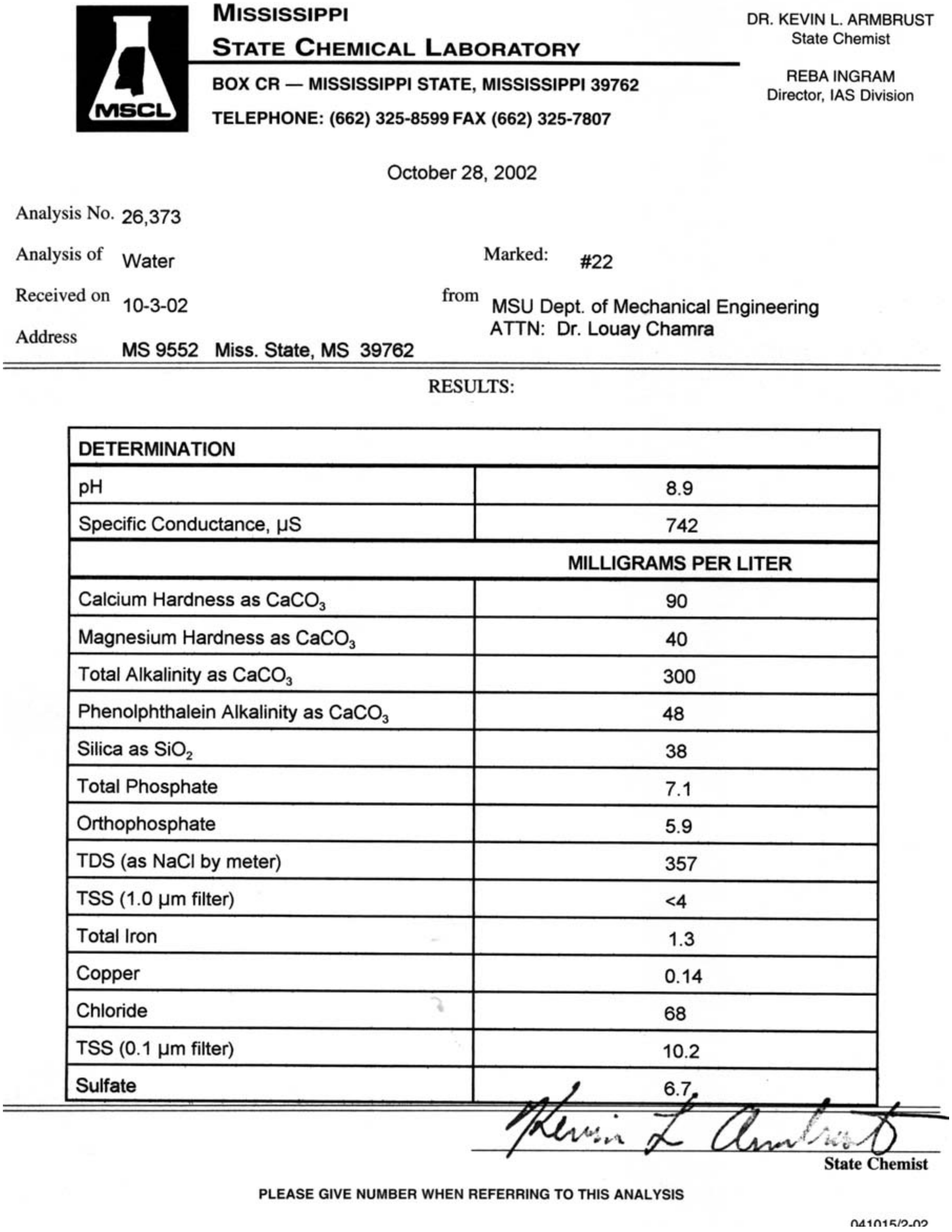

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October 28, 2002

Analysis No. 26,373

Analysis of Water

Marked: #22

Received on 10-3-02

from MSU Dept. of Mechanical Engineering
ATTN: Dr. Louay Chamra

Address MS 9552 Miss. State, MS 39762

RESULTS:

DETERMINATION	
pH	8.9
Specific Conductance, µS	742
	MILLIGRAMS PER LITER
Calcium Hardness as $CaCO_3$	90
Magnesium Hardness as $CaCO_3$	40
Total Alkalinity as $CaCO_3$	300
Phenolphthalein Alkalinity as $CaCO_3$	48
Silica as SiO_2	38
Total Phosphate	7.1
Orthophosphate	5.9
TDS (as NaCl by meter)	357
TSS (1.0 µm filter)	<4
Total Iron	1.3
Copper	0.14
Chloride	68
TSS (0.1 µm filter)	10.2
Sulfate	6.7

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