

**STUDYING ELECTRIC FIELD EFFECT ON WATER BY ANALYSING THE  
INSTRUMENT “HYDRONIC”**

**By**

**Yasemin Catli**

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University tutor: Gian Domenico Sorarù

Corporate tutor: Gian Paolo Ghezzi



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## **ABSTRACT**

The study was conducted in order to understand how an electric field effects in an electronic water descaler and how does it change the formation of calcium carbonate crystals by applied electric field. The study was carried out in Artigiancavi Snc and Fondazione Bruno Kessler. The datas were gathered by using the precipitates after water heated and the scales from tubes, after examining under scanning electron microscope. The key to understanding this is to firstly consider how scale is formed. When hard water is heated the large amounts of dissolved chemicals present in the water react producing tiny crystals. Like snowflakes they can be large or small. In the case of limescale the small ones are known as calcite, the larger aragonite. Calcite crystals in addition to being small tend to stick both to each other and to the inside of pipes. On the other hand the aragonite crystals are less sticky and prefer to remain naturally in the water. The key to Hydronic approach is making aragonite dominant and controlling calcite. The reason for it may be, electric field forces the precipitation of calcium carbonate and similar crystals (nucleation), and redissolves the scale crystals which had deposited previously.

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## CHAPTER I. WATER BASICS

When we look at water, we might think that it's the most simple thing around. Water may be one of the most familiar substances on the planet, but it isn't absolutely ordinary. Pure water is colorless, odorless, and tasteless. Water is an incredibly important aspect of our daily lives. Every day we drink water, cook with water, bathe in water, and participate in many other activities involving water. If there is water, there is life. What is it about water that makes it so important to us? And what is it about water that makes it water? This part of the thesis will examine the chemical and physical properties of water and why water is so important for living things around.

### 1.1 Molecular Structure of Water

A molecule in chemistry is a combination of atomic nuclei and electrons that is sufficiently stable to have measurable properties. Water's composition was invented by the London scientist Henry Cavendish (1731-1810) in about 1781 [1]. Its chemical formula, "H<sub>2</sub>O", is probably the most well known of all chemical formulas. The molecules are tiny, V-shaped and have a molecular diameter about 2.75 Å. The molecular diameter is defined from interpolation of the effective ionic radii of the isoelectronic ions from crystal data of O<sup>2-</sup> (2.80 Å), OH<sup>-</sup> (2.74 Å) and H<sub>3</sub>O<sup>+</sup> (2.76 Å). And this diameter is similar to the length of the hydrogen bond. The water molecule (bond length 0.96 Å) is smaller than ammonia (NH<sub>3</sub>) (bond length 1.01 Å) or methane (CH<sub>4</sub>) (bond length 1.09 Å), with only H<sub>2</sub> (bond length 0.74 Å) and HF (bond length 0.92 Å) being smaller molecules.

The liquid form of water includes H<sub>2</sub>O, HDO, OH and H<sub>3</sub>O [3]. The pure liquid water including only H<sub>2</sub>O molecules, we can see in computer simulations. And this easy form even has two types like "para" and "ortho" forms [4]. So the scientists only use the form of H<sub>2</sub>O to avoid the confusion. The hydrogen atoms in water (H<sub>2</sub>) can state parallel (paramagnetic *ortho*-H<sub>2</sub>O, magnetic moment=1) or antiparallel (nonmagnetic *para*-H<sub>2</sub>O, magnetic moment=0) nuclear spin. The balance ratio of these nuclear spin states in H<sub>2</sub>O is Para at zero Kelvin, where the molecules have no rotational spin in their ground state, shifting to 3:1 *ortho:para* at less cold temperatures (>50 K). The equilibrium taking months to establish itself in ice (or gas) and nearly an hour in ambient water [5] *ortho*-H<sub>2</sub>O rotates in its ground state with energy 23.79 cm<sup>-1</sup>. Due to deuterium's nuclear spin of 1 (compare 1/2 for H's spin), the lowest energy form of D<sub>2</sub>O is *ortho*. D<sub>2</sub>O converts to a 2:1 *ortho:para* ratio at higher temperatures. HDO,



having non-equivalent hydrogen atoms, does not possess an *ortho/para* distinction. T<sub>2</sub>O behaves similarly to H<sub>2</sub>O as tritium also possesses a nuclear spin of ½ [6]. So by this way the water has a mixture of non-identical molecules and the properties of pure liquid *ortho*-H<sub>2</sub>O or *para*-H<sub>2</sub>O are unknown. The difference of these two forms are expected to be greater in an electric field which may be loaded externally, from surfaces or from water clustering itself [7]. Many materials adsorb *para*-H<sub>2</sub>O due to its non-rotation ground state. The apparent difference in energy between the two states is a significant 1-2 kJ mol<sup>-1</sup>, far greater than expected from spin-spin interactions (< μJ mol<sup>-1</sup>) [8]. Structural rearrangements may be induced by *ortho*-H<sub>2</sub>O : *para*-H<sub>2</sub>O conversion [9] as it is possible that Hydrogen bonds between *para*-H<sub>2</sub>O possessing no ground state spin, are stronger and last longer than Hydrogen bonds between *ortho*-H<sub>2</sub>O. It is possible that *ortho*-H<sub>2</sub>O and *para*-H<sub>2</sub>O form separate Hydrogen bond clusters.

In the liquid state, in spite of 80% of the electrons being concerned with bonding, the three atoms do not stay together as the hydrogen atoms are constantly exchanging between water molecules due to protonation/deprotonation process. Both acids and bases catalyze this exchange and even when at its slowest (at pH 7), the average time for the atoms in an H<sub>2</sub>O molecule to stay together is only about a millisecond. As this brief period is, however, much longer than the timescales met during investigations into water's Hydrogen bonding and Hydrogen properties, water is usually treated as a permanent structure. H<sub>2</sub>O molecules are symmetric with two mirror planes of symmetry and a two-fold rotation axis. The hydrogen atoms may possess parallel or antiparallel nuclear spin. The water molecule includes two light atoms (H) and an heavy atom (O). The roughly sixteen-fold difference in mass gives rise to its ease of rotation and the significant relative movements of the hydrogen nuclei, which are in constant and significant relative movement.

### 1.1.1 Lone Pairs of Water Molecule

As simply water described as; has four, tetrahedrally stated sp<sup>3</sup>- hybridized electron pairs, two of them are connected with Hydrogen atoms leaving the two remaining lone pairs. In a perfect tetrahedral arrangement the bond-bond, bond-lone pair and lone pair-lone pair angles would all be 109.47° and such tetrahedral bonding patterns are found in condensed phases such as hexagonal ice. From the beginning of the calculations, on molecules don't show the exist of significant directed electron density where lone pairs are expected. The negative charge is more concentrated on the line between where these lone pairs are expected, and lies closer to

the center of the Oxygen atom than the centers of positive charge on the Hydrogen atoms. The more exact calculated O-H length is 0.957854 Å and the H-O-H angle is 104.500°.



a schematic of an  $sp^3$  hybrid orbital

Figure 1  $sp^3$ - hybridization

The higher density of atoms are near Oxygen atom as shown in the image below. The polarizability of the molecule is centered around the Oxygen atom (1.4146 Å) with only small polarizabilities centered on the Hydrogen atoms (0.0836 Å). [10]

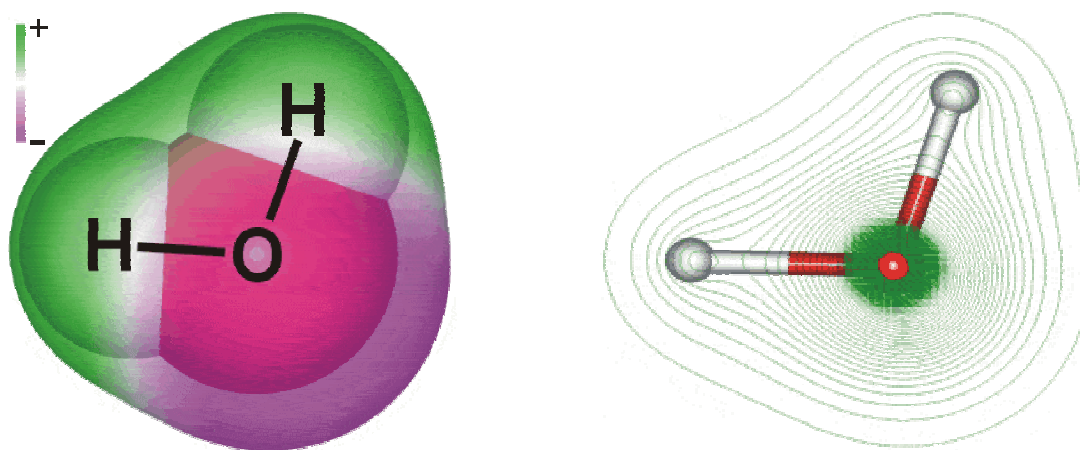


Figure 2 The charge distribution is lower near Hydrogen atoms.

Figure 3 The charge distribution is concentrated near Oxygen atom.

This charge distribution depends on atomic shape, approximately  $-0.7e$  on the Oxygen atom (with the equal but opposite positive charge equally divided between the Hydrogen atoms) for the isolated molecule [11]. The experimental values for gaseous water molecule are O-H length 0.95718 Å, H-O-H angle 104.474° [12].

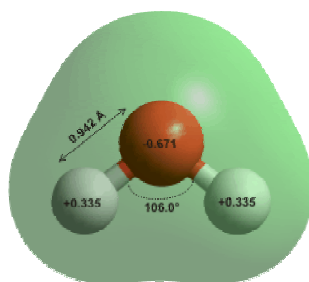


Figure 4 Water Molecule

But the values are changing for the liquid phase. Like O-H length 0.991 Å, H-O-H angle 105.5° [13]. And in the diffraction studies they become O-H length 1.01 Å, O-D length 0.98 Å; O-D length 0.970 Å, D-O-D angle 106°. They are high values because of the Hydrogen bonding makes weaker the covalent bonding and decreases the repulsion between the electron orbitals. But they can be changed in different polarization states, in different Hydrogen-bonded place and when the water molecules are attached to solutes and ions.

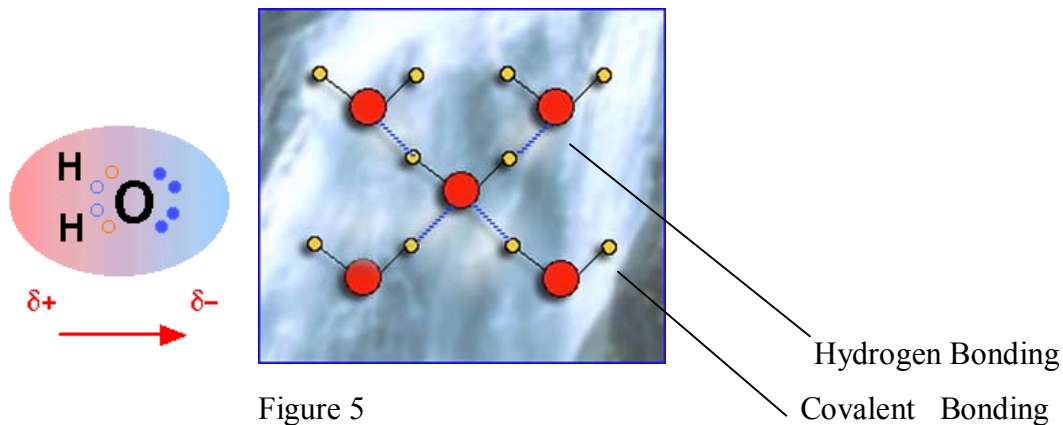
But mostly used numbers for O-H lengths of between 0.957 Å and 1.00 Å and H-O-H angles of 104.52° to 109.5°.

Briefly without numbers and angles the structure of water molecule;

Each Hydrogen nucleus attaches to the central Oxygen atom by a pair of electrons that are shared between them; this shared electron pair is called covalent bonding. In H<sub>2</sub>O, only two of the six outer-shell electrons of Oxygen are used for this cause, leaving four electrons which are organized into two non-bonding pairs. The four electron pairs surrounding the Oxygen tend to arrange themselves as far from each other as possible in order to minimize repulsions between these clouds of negative charge. This can result in a tetrahedral geometry in which the angle between electron pairs (and therefore the H-O-H bond angle) is 109.5°. However, because of the two non-bonding pairs remain closer to the Oxygen atom, these consume a stronger repulsion against the two covalent bonding pairs, effectively pushing the two Hydrogen atoms closer together. The result is a damaged tetrahedral arrangement, and makes the H-O-H angle is 104.5°.

### **1.1.2 Hydrogen Bonding**

The water molecule is electrically neutral but as I wrote before the negative and positive charges are not distributed equally. The negative electronic charge is concentrated in the end of the Oxygen atom, has partly nonbonding pairs (solid blues), and Oxygen's high nuclear charge consumes strong attractions on electrons. This event produces an electric dipole, showing in the image for the red arrow.



Hydrogen bonds (blue dotted lines) are noncovalent bonds that form between neighboring molecules of water and give liquid water its unusual properties.

The partially-positive Hydrogen atom on one water molecule is electrostatically attracted to the partially-negative Oxygen. This process is called Hydrogen Bonding. These Hydrogen Bonds' length is longer than the O-H Covalent Bonding length. So this makes it weaker.

### 1.1.3 The Polarity of Water

Molecular polarity exists because of the electronegativity difference between molecules. Also the diameter of the radio af an atom can role a part. If in a molcul there is no electronegativity difference, it means these atoms are the same atoms. So by this way they can not be polar. We call them as apolar molecules. The electrons that they share between them will spend the same time near both the same atoms. For example like (monoatomic)  $O_2$ ,  $N_2$ ,  $H_2$ ,  $C_{12}$ ,  $F_2$ ,  $I_2$ ,  $Br_2$ .

Sometimes the molecules including different types of atoms can also behave like a polar molecule. In example for  $CO_2$  molecule, the electrons between Carbon atom and Oxygen atoms, are balanced and equally distributed.

If the electronegativity difference between two atoms are high (higher than 2) we can say that; there is a situation like using the electrons in common (one electron is leaving its atom to another atom) (Ionic Bonding), if the difference is low (lower than 2) there is a case like sharing the electrons, this makes the Covalent Bonding. And it's called Polar Covalent Bond. Water molecule is the most well-known polar molecule. The electronegativity difference (3.5 for Oxygen atom, 2.1 for Hydrogen atoms) is  $1.4 < 2$ . Electrons are exerting much time near Oxygen atom compare to Hydrogen atoms. The molecule is totally neutral but it's a polar

molecule. Why CO<sub>2</sub> apolar, why H<sub>2</sub>O polar? The reason is the geometries of the molecules. CO<sub>2</sub> molecule is linear (bond angle 180°), H<sub>2</sub>O is nonlinear. For this reason the partial charges are zero, but H<sub>2</sub>O is partially charged.

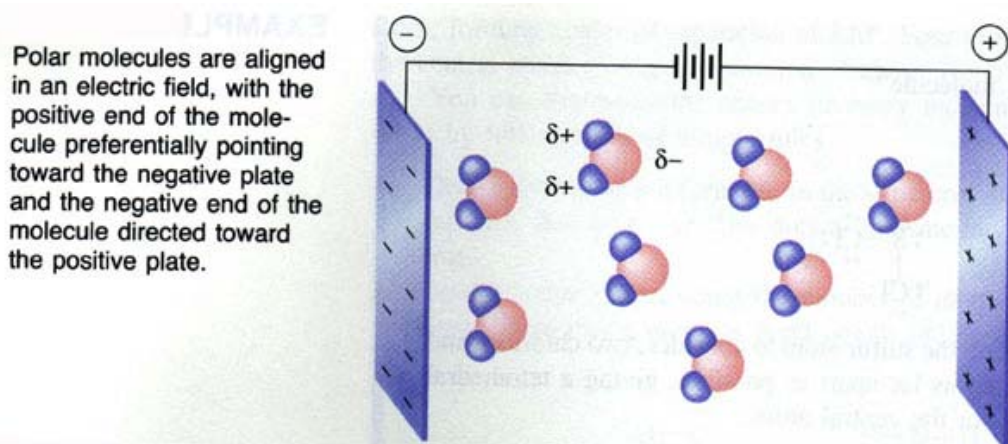


Figure 6 Electric Field On Water

*Prof. Jill Granger (The Chemistry of Water)*

## 1.2 Why is Water Liquid?

It has been studying for many years about the nature of liquid water and how H<sub>2</sub>O molecules arranged and interact. There has been always an intensive study about it and we can find huge literature about this. These phenomenons are well-verified; -H<sub>2</sub>O molecules attract each other within a special type of dipole-dipole interactions is so-called hydrogen bonding.

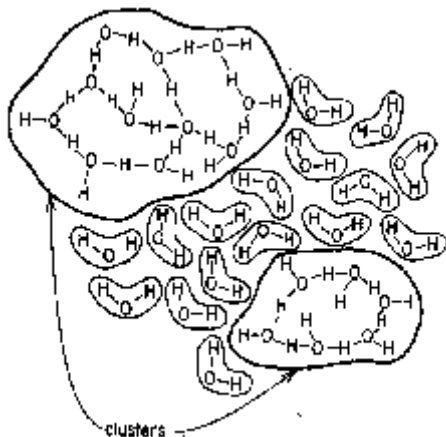


Figure 7 The first view in 1950s. The clusters with different sizes.

-A hydrogen bonded cluster that has four H<sub>2</sub>O's settled at the corners of an imaginary tetrahedron has an definite. One of the reasons for it is; the structure and the water clusters depend on the time frame and the volume.

Recent studies beginning from the 1980s after the molecular modeling simulations is; in a very short time scale (less than a picosecond) water behaves like gel, having a huge, single cluster. On a 10<sup>-12</sup>-10<sup>-9</sup> second time scale, geometry and the thermal motions cause breaking

the Hydrogen Bonds and re-build in new configurations. An it causes ever-changing place discontinuities whose influence and lenght depends on the two parameters; temperature and pressure.

Every individual water molecule can form Hydrogen Bonds by pointing its two Hydrogen atoms towards the Oxygen atom of one of its adjacent neighbors. When water exists as ice, the hydrogen bonds form a complete network, with each molecule donating two bonds and accepting two bonds from its neighbors. When the same amount of water is melted and becomes liquid, it loses about ten percent of those hydrogen bonds. The controversy has revolved around the nature of the missing Hydrogen Bonds. The water molecules toggle between ice-like and broken Hydrogen Bond structures. The scientists explained how changes in temperature affect measurements made through Raman Spectroscopy, a technique widely used in physical and chemical research to characterize substances. The two-state model of liquid water have based their arguments on the temperature dependence of liquid water's Raman Spectra. These features include the asymmetric band profile, the isosbestic point indicating temperature invariance. At any given moment, some of the Hydrogen Bonds in a quantity of liquid water must be greatly distorted; otherwise the water would be in a solid rather than a liquid state. However, their new and more detailed Raman Spectroscopy measurements show that any broken Hydrogen Bonds in a sample of water reform so quickly, nearly in 200 femtoseconds.

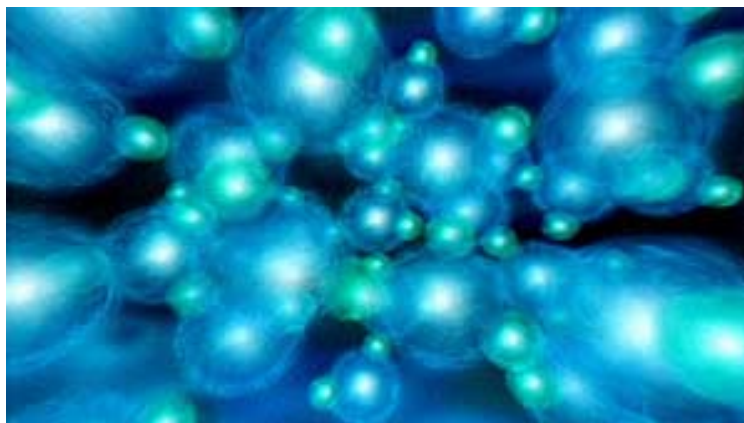


Figure 8 New Raman spectroscopy data points to the continuum model of liquid water, on which many of the biological simulations used today are based. *The Sacred Balance*

The widely held idea that there exists a stable population of water molecules with broken Hydrogen Bonds in the liquid appears to be incorrect. Hydrogen Bonds in liquid water are

continually breaking and reforming and moving around. Given that 90% of our blood consists of water and that the human body is 60% of water, it is important that scientists are trying to understand water's microscopic structure. Among other applications, the biological simulations used in various research efforts, including medical studies, are based on models that mimic the continuum model of liquid water [14].

### 1.2.1 Liquid and Solid Water

Solid ice has a well defined structure and each water molecule has four neighbor H<sub>2</sub>Os. Two of these are Hydrogen-bonded to the Oxygen atom on the central H<sub>2</sub>O molecule, and each of the two Hydrogen atoms are similarly bonded to another neighboring H<sub>2</sub>O. The hydrogen bonds are represented by the blue lines in the figure below. In reality, the four bonds from each Oxygen atom point toward the four corners of a tetrahedron centered on the Oxygen atom. This basic assembly repeats itself in three dimensions to build the ice crystal.

When ice melts to form liquid water, the uniform three-dimensional tetrahedral organization of the solid breaks down as thermal motions distort, and break hydrogen bonds. The methods used to determine the positions of molecules in a solid do not work with liquids, so there is no exact way of determining the detailed structure of water. The illustration here is probably typical of the arrangement of neighbors around any particular H<sub>2</sub>O molecule, but very little is known about the extent to which an arrangement like this gets generated to more distant molecules.

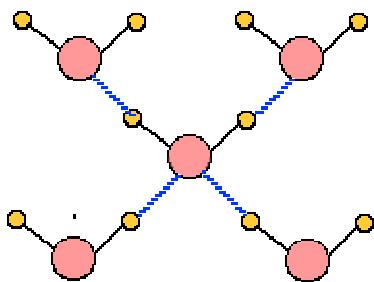


Figure 9 Solid ice structure

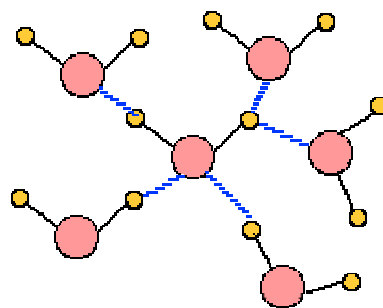


Figure 10 Liquid water structure

The stable arrangement of Hydrogen-bonded water molecules in ice gives rise to the beautiful hexagonal symmetry that shows itself in every snowflake.



Figure 11 A Snowflake

## CHAPTER II. HARDNESS OF WATER

We need to determine the water before using it in living places, industrial areas, domestic usage and agricultural production. The main factors that are taken into consideration when determining water quality are; acidity & alkalinity, microorganisms, turbidity, trace elements and nutrients such as Nitrogen, Phosphorus, Halogens (Chloride and Fluoride ions), alkali metals (Sodium and Potassium ions), Calcium and Magnesium ions, dissolved oxygen content (DO).

Table 1 This is an example of water quality in a typical aquatic system

The Quality	Sea Water	River Water
pH	8	6.8
Dissolved Oxygen	6-8 ppm	6-8 ppm
Na <sup>+</sup>	1.1 x 10 <sup>4</sup> ppm	6.7 ppm
K <sup>+</sup>	380 ppm	1.5 ppm
Ca <sup>2+</sup>	400 ppm	17.5 ppm
Mg <sup>2+</sup>	1.3 x 10 <sup>3</sup> ppm	4.8 ppm
Cl <sup>-</sup>	1.9 x 10 <sup>4</sup> ppm	4.2 ppm
SO <sub>4</sub> <sup>2-</sup> /HSO <sub>4</sub> <sup>-</sup>	2.6 x 10 <sup>3</sup> ppm	17.5 ppm
CO <sub>3</sub> <sup>2-</sup> /HCO <sub>3</sub> <sup>-</sup>	142 ppm	33 ppm
Hg <sup>2+</sup>	0.03 ppb	< 1 ppb
Cd <sup>2+</sup>	0.1 ppb	< 1 ppb
Pb <sup>2+</sup>	4-5 ppb	< 1 ppb



## **2.1 Main Tests for Water Analysis**

### **2.1.1 The Temperature**

Using a simple thermometer in a hard plastic cover is enough. Temperature influences the amount of dissolved oxygen in water which in turn influences the survival of aquatic organisms. Increasing the temperature of a freshwater stream from 20 to 30°C will decrease the dissolved oxygen saturation level from about 9.2 ppm to 7.6 ppm. Increasing temperature also increases the rates of chemical reactions taking place in the water. Increases in temperature are often associated with hot water discharge from power stations and industries that use water as a coolant.

### **2.1.2 pH**

It is a measure of the Hydrogen ion concentration. There are digital pH meters, pH papers and special solutions. We can learn the acidity and alkalinity of water. pH of rain water is about 5.5-6.0. Typically, natural water has pH 6.5-8.5. A pH<5 (acidic water) is most damaging to eggs and larvae of aquatic organisms. Most aquatic life (except for some bacteria and algae) cannot survive pH<4. Natural alkalinity is due to CO<sub>2</sub>(g), HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and OH<sup>-</sup>, carbonate rocks such as limestone and dolomite increase alkalinity. Alkalinity is increased by caustic substances from industry (KOH, NaOH), soil additives in agriculture such as lime Ca(OH)<sub>2</sub>, superphosphate which is mixture of Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> and CaSO<sub>4</sub>, and soaps and detergents. Natural acidity is due to CO<sub>2</sub>(g), HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, H<sub>2</sub>S, Fe<sup>3+</sup>, other acidic metal ions, proteins & organic acids. Increases in acidity can be due to acids used in industry, acid mine drainage, acid rain.

### **2.1.3 Turbidity**

A Secchi disc or 500 ml of water in a measuring cylinder standing on paper marked with a black cross can help us to test it. Turbidity is a measure of water clarity. Suspended solids in water can stop light reaching submerged plants and can raise water temperature. Suspended solids often present in water are mud, clay, bacteria and minerals such as silica, calcium carbonate and ochre (iron oxide). Suspended solids can be increased by the discharge of

wastes (domestic sewage, industrial and agricultural effluents), leaching of wastes (from mines), and agitation (dredging or shipping).

#### **2.1.4 Total Dissolved Solids (TDS)**

There are TDS meters. Freshwater meters: 0-1990 ppm (parts per million). Dual range brackish water meters: 0-19,900 ppm. Salt-water meters: to above 35,000 ppm. This is a conductivity test of available ions in the water, including  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{HCO}_3^-$  and ions containing P, S & N. High levels of  $\text{Na}^+$  is associated with excessive salinity and is found in many minerals. Potassium is incorporated into plant material and is released into water systems when plant matter is decayed or burnt.

#### **2.1.5 Dissolved Oxygen (DO)**

The Dissolved Oxygen test measures the Oxygen level in the water. The DO level varies with temperature. DO levels are highest in the afternoon due to photosynthesis and lowest just before dawn. DO is lowered by an increase in temperature (as from a discharge of hot water from a power station), increases in aerobic oxidation (due to increases in organic matter from sewage or due to inorganic fertilisers such as phosphates and nitrate which overstimulate algal growth). Water with  $\text{DO} < 1\text{ppm}$  is dead. There are methods like Winkler Titration Method and Colorimetric Method.

#### **2.1.6 Biochemical Oxygen Demand (BOD)**

BOD measures the rate of consumption of oxygen by organisms in the water over five days period. Increases in BOD can be due to animal and crop wastes and domestic sewage. The first water sample from above is kept in the dark for five days at the temperature at which the sample was collected. Then the dissolved oxygen is determined using the Winkler Titration Method.

#### **2.1.7 Salinity**

Many water organisms can only survive in a narrow range of salt concentrations since salt controls their osmotic pressure. Titrate a known volume of the water sample with silver nitrate

solution (2.73g AgNO<sub>3</sub> per 100 ml distilled water) using K<sub>2</sub>CrO<sub>4</sub> as indicator. The end-point of the titration is given by the reddening of the silver chloride precipitate (AgCl<sub>(s)</sub>). Volume of AgNO<sub>3</sub> used = chloride content in g/L.

### **2.1.7 Hardness**

Calcium ions are a major contributor to water hardness and are due to water running through rocks containing minerals such as gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), calcite (CaCO<sub>3</sub>), dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>). Hard water has a noticeable taste, produces precipitates with soaps which inhibits lathering and forms precipitates (scale) in boilers, hot water systems and kettles. Temporary hardness (or 'bicarbonate hardness') is due to Ca(HCO<sub>3</sub>)<sub>2</sub> which deposits CaCO<sub>3</sub>(s) as scale on boiling the water. Magnesium ion levels are often high in irrigation water and can cause scouring in stock. Ca<sup>2+</sup> and Mg<sup>2+</sup> can combine with Cl<sup>-</sup> and/or SO<sub>4</sub><sup>2-</sup> causing permanent hardness which can't be removed by boiling. Water can be softened by an ion exchange process using a solid material such as a resin or clay that is capable of exchanging Na<sup>+</sup> or H<sup>+</sup> for Ca<sup>2+</sup> and Mg<sup>2+</sup>. For testing; it can be used complexometric titration using EDTA , Atomic Absorption Spectroscopy, or Flame Test.

### **2.1.8 Total Phosphate Test**

Total Phosphate is used as an indicator of pollution from run-off in agricultural areas or domestic sewage. Concentrations of 0.2mg/l are common. Coloremometrically it can be measured.

### **2.1.9 Total Nitrogen Test**

Total Nitrogen is an important indicator of eutrophic waters, especially for those contaminated by animal wastes, fertiliser run-off and domestic sewage. Coloremometrically it can be measured.

### **2.1.10 Microorganisms**

Microorganisms in a water sample are counted under a microscope. Many protozoa, bacteria, viruses, algae and fungi are found in natural water systems.

### **2.1.11 Heavy Metals**

Heavy metals in concentrations above trace amounts are generally toxic to living things.  $\text{Ni}^{2+}$   $\text{Fe}^{3+}$   $\text{Cu}^{2+}$   $\text{Cd}^{2+}$   $\text{Pb}^{2+}$   $\text{Zn}^{2+}$ . And other ions like  $\text{Al}^{3+}$   $\text{Mg}^{2+}$   $\text{Na}^+$   $\text{K}^+$ .

## **2.2 How Minerals Affect Water Supplies**

Groundwater with high amounts of minerals is common in both municipal and private water supplies. Dissolved minerals can affect the usefulness of groundwater and surface water. If the problem is bad enough, chemical treatment may help. Sometimes another source of water is needed. Some common minerals affect water supplies like [15];

### **2.2.1 Total Dissolved Solids**

High concentrations of total dissolved solids can cause water to taste bad, forcing consumers to use other water sources. Highly mineralized water also deteriorates plumbing and appliances. Waters containing more than 500 milligrams per liter (mg/l) of dissolved solids should not be used if other less mineralized supplies are available. This does not mean that any water in excess of 500 mg/l is unusable. People may eventually adjust to drinking water containing high total dissolved solids.

### **2.2.2 Hardness**

Hardness is the amount of calcium and magnesium dissolved in the water. Hard water has no adverse health effects and may even taste better than soft waters. But hard water is less desirable because it requires more soap for effective cleansing, forms scum and curd, causes yellowing of fabrics, toughens vegetables during cooking, and forms scales in boilers, hot water heaters, pipes, and on cooking utensils. The hardness of good quality water should not exceed 270 mg/l measured as calcium carbonate ( $\text{CaCO}_3$ ). Water softer than 30-50 mg/l may be corrosive to piping, depending on pH, alkalinity and dissolved oxygen. Whether or not to soften hard water is a matter of personal preference and depends on the natural sodium level. The most common types of commercial water softeners replace the calcium and magnesium ions with sodium. Water softened in this way may affect individuals on sodium-restricted

diets. The treated water should be tested for sodium. A personal physician should be consulted about the results.

### **2.2.3 Nitrate**

High nitrate concentrations can occur in wells located near feedlots, barnyards, sewage disposal systems or areas of high fertilizer application, and often indicate the presence of other forms of groundwater contamination. High nitrate water should never be used in infant feeding. In infants, nitrate can destroy the oxygen-carrying capacity of the blood, causing a condition known as methemoglobinemia. This results in an oxygen starvation condition and the infant appears blue. Serious poisonings, sometimes fatal, have occurred in infants less than six months old after drinking water containing nitrate as nitrogen at concentrations greater than 10 mg/l.

### **2.2.4 Iron and Manganese**

The primary source of iron is the water bearing strata. Iron is typically dissolved in water and when brought to the surface, can form “rust” which may settle out. Another source of iron is iron-reducing bacteria, which depend upon iron to live. These bacteria add iron to the water by attacking the piping of the system. Removing naturally-occurring iron in the water may require special water treatment equipment. Iron-reducing bacteria may be controlled or eliminated by adequate chlorination. The most common water complaints are those of red water, laundry spotting, metallic tastes, and staining of plumbing fixtures. These are usually due to the presence of iron above 0.3 mg/l. Iron and manganese have similar adverse effects and frequently occur together in natural waters. Concentrations of manganese greater than 0.05 mg/l may cause brown/black stains and deposits.

### **2.2.5 Sodium**

A person's intake of sodium is mostly influenced by the use of salt, where its role in the body is to help maintain water balance. The contribution of sodium from drinking water is small in comparison to other sources. Commercial water softeners may significantly increase the amount of sodium in drinking water. A diet for someone who must restrict sodium intake can be designed to allow for sodium from the water supply. The person can also use another source of drinking water. High concentrations of sodium can make water less suitable for irrigation purposes by altering soil chemistry and absorption properties. With continued use,

the soil will eventually be unable to absorb moisture. Although no evidence has shown that high sodium levels affect healthy individuals, recommended levels have been set at 100-200 mg/l.

### **2.2.6 Sulfate**

Three reasons for limiting the concentration of sulfates in drinking water are:

- a) sulfates can cause laxative effects with high intake, especially in combination with magnesium or sodium,
  - b) water containing large amounts of sulfate tends to form hard scales in boilers and heat exchangers,
  - c) sulfates can impact taste. The laxative effect is commonly noted by people not used to water high in sulfates. These effects vary from one person to another and appear to fade with time.
- For these reasons, the recommended limit is 250-500 mg/l.

### **2.2.7 Alkalinity**

Alkalinity is a measure of the water's ability to neutralize acids. Natural waters usually contain carbonates, bicarbonates, and hydroxides. The bicarbonate ion is usually the most common. The ratio of these ions is a function of pH, mineral composition, temperature, and ionic strength. Water may have low alkalinity but a relatively high pH value, so alkalinity alone is not of major importance as a measure of water quality. Alkalinity is not considered harmful to humans but may cause a distinct unpleasant taste.

### **2.2.8 Chloride**

Chloride in drinking water can have two effects. First, it can affect the taste. Second, the water may corrode hot water pipes. Consumers can decrease chloride levels by treating the water or by finding another water supply. A recommended limit of 250 mg/l has been set for chloride. For many years, chloride has been used as an indicator of pollution of the water source. Any sudden increase in the chloride content of a water supply should be investigated as a possible indication of pollution.

### **2.2.9 Fluoride**

Fluoride can affect teeth during the period when permanent teeth are being formed. When the concentration is best, 1.2 mg/l, no ill effects will result. High fluoride (more than 4.0 mg/l) in water can cause a brown color on teeth.

## **CHAPTER III. LIMESCALING**

Water is classified as hard or soft depending on the type and amount of naturally occurring minerals and salts dissolved in it. The mineral content usually consists the metal ions of calcium and magnesium in the form of their carbonates, calcium carbonate and magnesium carbonate but may include several other metals as well as sulphates and bicarbonates. When water has a high content of dissolved minerals (solids) it is described as hard, whereas soft water has a low dissolved content. Two common types of hardness in water are temporary hardness and permanent hardness:

### **3.1 Temporary Hardness**

Temporary hardness of water can be removed by boiling or by the addition of lime (calcium hydroxide). It is caused by dissolved calcium bicarbonate in the water. Calcium carbonate is less soluble in hot water than in cold water; therefore, boiling (which promotes the formation of carbonate) precipitates calcium carbonate out of solution, leaving water that is less hard on cooling. And this is what causes the kettle to become coated with limescale.

### **3.2 Permanent Hardness**

Permanent hardness of water can not be removed by boiling. It is usually caused by the concentration of calcium and magnesium sulphates and chlorides in the water, which are more soluble as the temperature rises.

### **3.3 What Makes Water Hard?**

Acid in rain. Most people have heard of acid rain produced by absorption of sulphur and nitrogen oxides by rainfall; however, the presence of pollutants like these gases is not the only

source of acidity. Carbon dioxide constitutes 0.3% of the Earth's atmosphere, and is easily absorbed by water to form carbonic acid-the acid found in carbonated drinks. For this reason, all rain is acidic to some extent, and has a strong bent to dissolve minerals and rocks with which it comes into contact.

Water is a good solvent and collects impurities easily. Pure water, which is tasteless, colorless, and odorless, is often called the universal solvent. As rain falls, it becomes slowly acidic as described above. As the water travels through soil and rock, it dissolves small amounts of minerals and holds them in solution. Calcium and magnesium dissolved in water are the two most common minerals that make water 'hard.' The degree of hardness becomes greater as the magnesium and calcium content increases, and is related to the concentration of multivalent cations dissolved in the water.

### **3.3.1 Degree of Measure**

The hardness of water is measured as milligrams per litre of calcium carbonate, e.g. 200 mg/litre  $\text{CaCO}_3$ . Milligrams per litre is the same as parts per million (ppm). It can be also seen like mg/litre of calcium. These can be changed into mg/litre of  $\text{CaCO}_3$  by multiplying the reading by 2.5.

### **3.3.2 Is Hard Water Bad For Us?**

It is not generally dangerous to safety or health, hard water causes potentially costly problems in the home and in industry. The mineral build-up on plumbing, and heating elements of household products affects their performance and service life. However, the calcium and magnesium in drinking water is actually beneficial to us. Many people and other countries need to soften their water. Standard salt fed "ionic exchange" or "reverse osmosis" water softener systems remove these beneficial minerals and add potentially unhealthy sodium to the water from salt. The electronic water treatment device does not remove the healthy calcium from drinking water, nor does it add any chemicals to the water.

Researchers are continually studying the relationship between water hardness and cardiovascular disease mortality. Such studies have been 'epidemiological studies,' which are statistical relationship studies. Some studies suggest a relation between hard water and lower cardiovascular disease mortality, other studies do not suggest an association.



### **3.3.3 How can we know the hardness of water?**

The simplest way to understand if water is hard or soft is the lather/froth test. Soft water lathers easily with soap, but hard water does not. Toothpaste also does not froth well in hard water. More definite methods of hardness detection using a wet titration method to determine hardness.

Any of the marks below can also determine the presence of hard water; Furred up kettle, soap scum in sinks and bathtubs, bathtub rings, clogged showerheads, spots on dishes, shower doors, and foundation of taps, reduced foaming and cleaning abilities of soaps and detergents, dingy and yellowed clothes with soapy residues that require extra rinsing to remove, clogged pipes from buildup of minerals, increased water heating costs from buildup of minerals, reducing efficiency of water heaters, possible skin infections from bacteria trapped in pores underneath soap scum. To find out the state of the water in an area it can be can find out how hard or soft the water is by contacting the water company in that particular area. These companies are usually very co-operative, and most of them even send a free water hardness testing pack to test area own water supply.

### **3.4 Limescale**

Scale, or limescale is a hard, whitish coating that builds up on surfaces that come into contact with hard water. Hard water causes limescale because it contains calcium carbonate (lime) and other minerals that stick to pipes and water heaters as water is heated. The collected limescale inside water heaters reduces their life and energy efficiency. Water from a groundwater source is harder because minerals comes into it from the soil. Water from river sources is generally softer.

When water is heated, it causes the dissolved salts to attach themselves to any metal they come into contact with, forming a hard crust called limescale or scale. It's a familiar sight on the heating elements in electric kettles and other boilers. In areas of the country where the water is naturally soft, the build-up takes a longer time to be noticed. In hard water areas, the limescale build-up can be relatively quicker.

Most substances, most calcium salts become less soluble as the temperature rises. These salts are naturally present to some degree in all mains water supplies. So, any system where mains water is heated is liable to suffer from limescale formation. Considering a water containing

300 milligrams per litre (mg/l) of calcium carbonate hardness. The potential weight of limescale produced in a 100 litre central heating system is 30 grams, and this is from only the initial fill of water. After formed, calcium scale doesn't dissolve and water lost from the system for whatever reason will leave it behind. The fresh make-up water will then bring more calcium salts into the system to begin the process again producing an ever-increasing thickness of scale. Being a direct result of increased temperature, limescale will form in the hottest part of the system, usually the heat transfer surface in the boiler. In contrast, iron oxide first forms as sludge at the point of corrosion, and only turns into limescale if it is carried by the water to the heat exchanger where it can become hardened by baking.

### 3.4.1 Effects of Limescale

Limescale can be a big problem when it occurs in the pipe work or water heating elements of kitchen equipment which uses running mains water and heating elements, such as dishwashers, combi-ovens, coffee machines and vending machines. It can even be a potentially dangerous cause of overheating in these appliances. Where scale build-up occurs inside pipes, it restricts the flow of water causing serious and expensive damage to equipment. Where scale build-up occurs on heating elements, it insulates the elements and forces them to use far more energy than needed to heat the water, leading to early burn-out.



Figure 12 The Limescaling

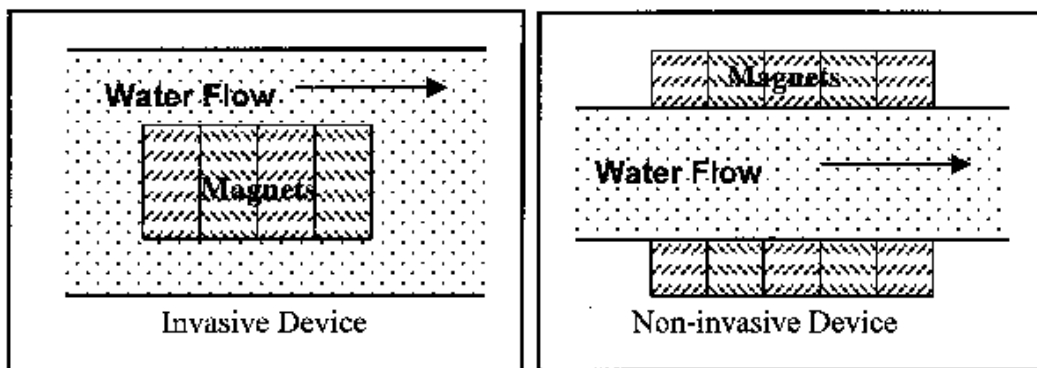
There are dissolved salts in all types of water and scale build-up will occur eventually. Even when the normal water supply is considered to have soft water, should the water be drawn from deep boreholes in times of drought, its hardness level will change. Water companies move water around from region to region through underground pipe work, which also changes the hardness level.

Limescale in hard water areas cause high running costs of heating and hot water systems used in both building services and industrial applications. The cost of limescale formation to industry environment through wasting energy is equally significant.

### 3.5 Water Softening and Limescale Treatments

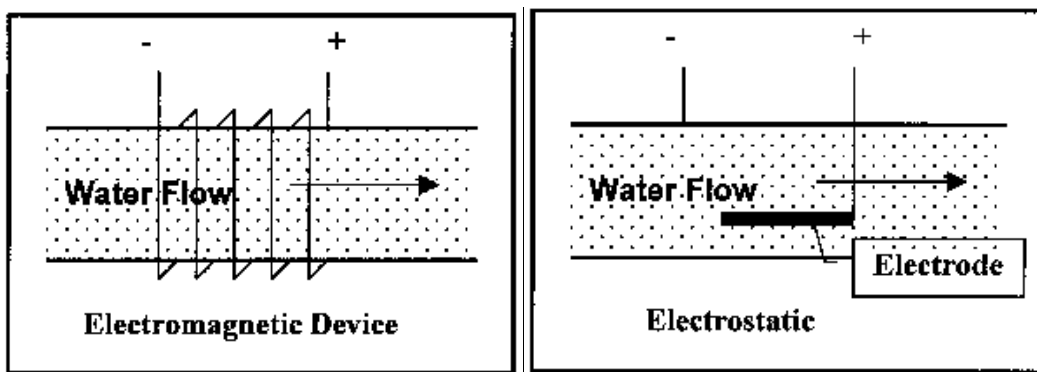
#### 3.5.1 Electronic or Magnetic Water Descalers

These devices operate by wrapping coils of wire or fixed magnets around the incoming water main to pass a magnetic field through the water. This causes the calcium in the water to stay in solution, thereby inhibiting it from adhering to taps, baths and kettles. Electronic descalers typically operate with one coil, but a few use two. This feature increases the time for which the water is exposed to the magnetic waveform.



*Nielsen Technical Trading*

Figure 13 Magnetic Devices



*Nielsen Technical Trading*

Figure 14 Non-Permanent Magnet Devices

So in the first magnetic devices there is always a permanent magnet. For Electromagnetic devices magnetic field is generated by electromagnets. In electrostatic like the working way of Hydronic; an electric field is distributed in the water flow which attracts and repels the ions, in the result generates a magnetic field.

### 3.5.2 Water Softeners

A water softener works on the principle of cation (ion exchange) in which ions of the hardness minerals (such as calcium and magnesium) are exchanged for sodium or potassium ions, effectively reducing the concentration of hardness minerals to tolerable levels. Water softeners add a slight amount of salt to the water, which has the effect of greatly reducing the amount of dissolved limescale. They are suitable for dishwashing or laundry, or other purposes where the water is not directly used for consumption. The least expensive form of water treatment, it can lead to streaking of glasses in glass washers and over time, the salt can corrode welds on internal pipe-work.

## CHAPTER IV. METHODOLOGY

Before beginning the experiments parts, I would like to give some informations about the partner company Artigiancavi Snc and FBK-Irst that I carried out my Project and my internship.

### Artigiancavi Snc



The company has 30 years experience, professionalism and advanced technology for the people needs; the highest reliability of steel cables, the solution for thanks to machining, the safety of water and pure sound thanks to Hydronic and reliability of Skim to ensure maximum performance of the skis. From thirty years Artigiancavi is a craft, private mechanic. Born in 1975 for the production of flexible brake (which at present has a marginal role in the supply business), over the years has expanded its branches diversifying its production coming to understand the majority of working Mechanical and production safety cables for market. Since 1983 the company has seen an evolution that has taken her to become a company specialized in the executions of machining personalized (functional needs of customers and small to medium quantities) and to access and enter the European market (in the case the production of cables).

Currently producing Cables ; cutting and assembly of wire ropes of various kinds from  $\varnothing 0.7$  to  $\varnothing 8.5$  carbon steel or stainless steel. Funi brake clutch of vehicles: cars, machinery, muletti, trailers, agricultural, garage doors, etc..They design stainless steel cables for repair or decoration of swimming pools, parapets, guards, etc..

The mechanical part; Precision Machining with CNC machines. Turning centers with up to 7 axes. Turning from bar  $\varnothing 5$  to  $\varnothing 80$  mm. Turning maximum  $\varnothing 650$  mm. Milling machining centers with up to 6 axes. Milling maximum  $900 \times 900 \times 3000$  mm.

The Hydronic part; Hydronic srl is a company that deals with studies, research, production and assistance in the field of water treatment and protection from fouling limestone. Associated with the District Technology Trentino and the Canada Green Building Council, is connected with major research institutes in the sector in Italy and Europe. Hydronic's commitment is to produce devices that, in total respect for the environment and health, achieve maximum effectiveness of treatment.

In the absence of any treatment limestone deposits in the structure aragonitica: crystals aghiiformi is firmly interwoven with each other and form deposits fouling compact, causing damage to equipment.

### **The System Hydronic**



Hydronic device works with the same principle is on equipment for private homes and for the application greater scope for the industry. Treatment of Hydronic system solves the problem; electrical impulses generated by the power of the system and carefully graduated compared to the scope and degree of hardness of water, changing the nature of crystalline calcium carbonate in water to form crystals coming aghiiform, the which are unable to adhere to the walls. Microcrystals do not deposit anymore, the water runs away and the equipment does not suffer any damage.

The advantages;

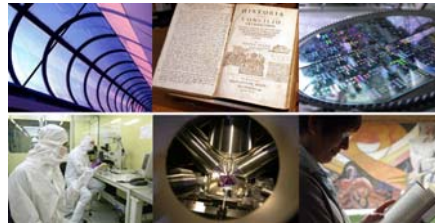
The system is guaranteed Hydronic two years, but it can maintain its power and strength for a longer period of time. The cleaning of the product is very simple that can be executed directly without the need for contact or technical personnel. The device requires no salt or other

chemicals; There are no operating costs or supply problems later. Hygiene is absolute; the components of which are in contact with water are only in stainless steel, the materials are suitable for food. In addition, the design does not allow any stagnant water and the absence of resins together avoids any risk of chemical or bacteriological. The composition of water remains unchanged. It is not necessary to add salt or chlorine then the composition of the water is not changed.

#### Long Term Effects

- Extended life of water appliances and lower maintenance costs
- Removes existing scale
- Kinder to skin and hair - ideal for babies
- Saves energy - lower water heating costs

#### **FBK- Fondazione Bruno Kessler**



The Foundation was created on 1 March 2007. FBK inherits the activities of the Istituto Trentino di Cultura, which was based on the ideas of Bruno Kessler, a long-time member of the local government and founder of the University of Trento. Established by a law of the Autonomous Province of Trento, FBK operates as private entity. Fondazione Bruno Kessler is situated in Trentino, a province in northern Italy governed under a special autonomy statute. The foundation, with more than 350 researchers, conducts studies in the areas of Information Technology, Materials and Microsystems.

## 4.1 The Technical Datas for Hydronic



Figure 15 The installation for trials in the company

Hydronic<sup>1</sup> is a compact, computerised electronic water conditioner which descale existing system, prevent new scale forming. The electronic unit works by sending out a signal which changes the electrical and physical properties of scale forming calcium molecules. This action stops any further build-up of scale by preventing molecules from adhering to themselves or any other surface. The solubility of the water is also increased, therefore existing scale is dissolved back into the water and gradually reduced. The most important difference when we compare Hydronic to other devices; it has no wrapping coils of wire for the tubes, inside the cylindrical there are small sticks (electrodes) attached to electrical unit. And the other difference is changing the calcium carbonate calcite form to aragonite form. And this was the main aim of this project; to control the crystal forms and to find out the reason as well. First I want to give some informations about the Calcium Carbonates polymorphs.

### 4.1.1 Calcite

The most common carbonate mineral is Calcite ( $\text{CaCO}_3$ ). It is the main constituent of limestone and its metamorphic equivalent-marble. Deposits of fine grained calcite in powder form are referred to as chalk. It forms the cementing agent in many sandstones, and is one of the more common minerals precipitated by living organisms to form their skeletal structures. Calcite is also precipitated from groundwater where it form veins, or in open cavities like caves and caverns can form the cave decorations-like stalactites and stalagmites, and encrustations. It is also precipitated from hot springs where it is called travertine. Calcite occurs in rare igneous rocks called carbonatites. These form from carbonate magmas. Calcite

is also precipitated from hydrothermal fluids to form veins associated with sulfide bearing ores.

#### *Properties*

In hand specimen, calcite is distinguished by its rhombohedral cleavage, its hardness of 3, and by its foaming in dilute HCl. It can range in color from white, to slightly pink, to clear, but dark colored crystals can also occur. In thin section it is most readily distinguished by its high birefringence, showing high order white interference colors, by its rhombohedral cleavage and its uniaxial negative character. Because of its high birefringence, it shows a large change in relief on rotation of the stage. Furthermore, its  $n_e$  refractive index direction (low RI direction) when parallel to the polarizer shows a negative relief when compared to the mounting medium of the thin section. Calcite can be distinguished from Aragonite by the lack of rhombohedral cleavage and biaxial nature of Aragonite [16].

#### **4.1.2 Aragonite**

The Aragonite group of minerals are all orthorhombic, can be distinguished from minerals of the calcite group by their lack of rhombohedral cleavage. Aragonite ( $\text{CaCO}_3$ ) is the most common mineral in this group. Aragonite is the higher pressure form of  $\text{CaCO}_3$  but, nevertheless occurs and forms at surface temperatures and pressures. When found in metamorphic rocks it is a good indicator of the low temperature, high pressure conditions of metamorphism. Water containing high concentrations of Ca and Carbonate can precipitate Aragonite. Warm water favors Aragonite, while cold water favors calcite, thus Aragonite is commonly found as a deposit of hot springs. Aragonite can also form by biological precipitation, and the pearly shells of many organisms are composed of Aragonite. Fine needle-like crystals of Aragonite are produced by carbonate secreting algae.

#### *Properties*

In hand specimen, Aragonite, like calcite, foams in cold HCl. But, unlike Calcite, Aragonite does not show a rhombohedral cleavage. Instead it has single good {010} cleavage. It is usually transparent to white in color and forms in long bladed crystals. Twinning is common on {110}, and this can produce both cyclical twins, which when present, make it look pseudo-hexagonal, and single twins. In thin section Aragonite is distinguished by its high birefringence, showing high order white interference colors, its biaxial character with a  $2V$  of about  $18^\circ$ , and extinction parallel to the {010} cleavage [17].



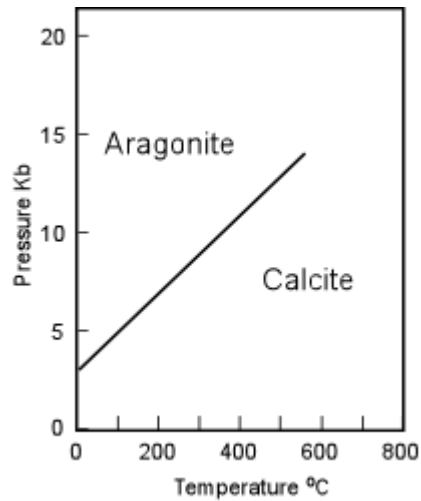


Figure 16 P-T Relation of Calcite and Aragonite

#### 4.2 The Methods of Research and Analysis

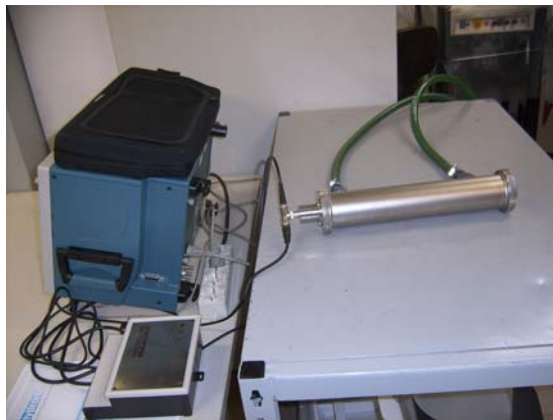


Figure 17 The installation in FBK

The general datas from oscilloscope that readable are; it gives a wave form of square , 2/3 place for positive and 1/3 place for negative, the frequency is 260mSec for both at 3850 Hz. In the laboratory of FBK-Irst we made an experimental set up to control the electrical datas. And the data from the oscilloscope shows the characteristic of the electrical unit.

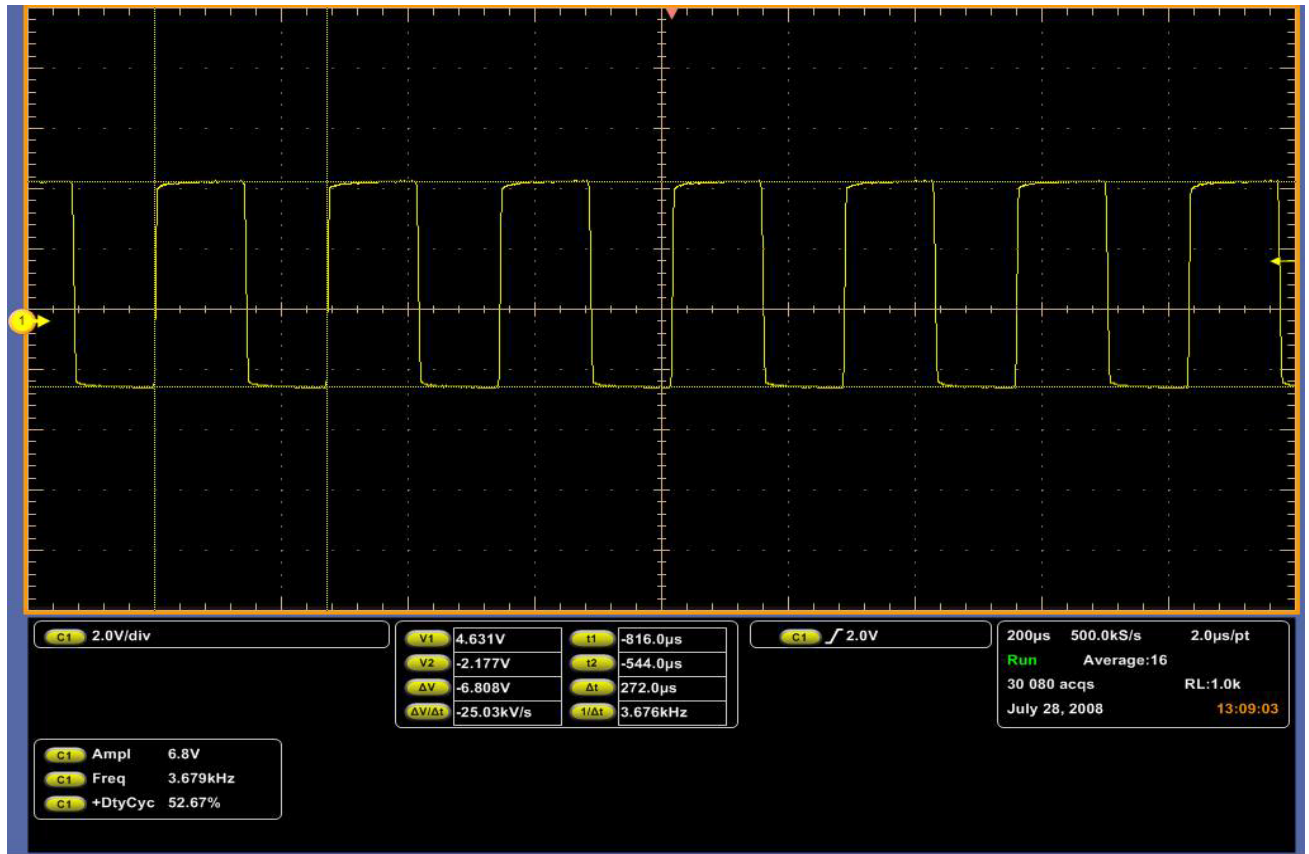


Figure 18 Data From Oscilloscope

Methods of preparing the samples of an aqua is not a simple way. Because water is not a solid material and is hard to prepare it for the experiments. I have consulted many people who are studying chemistry and are good at with preparing samples for microscope and the best method I found is;

First, I took water samples from the company's water trial system. Two types of water are taken; water treated with Hydronic and water not treated with Hydronic. In the laboratory of Fbk, I used an electronic heater to boil the water and to create precipitates of Calcium Carbonate on the glass. At  $80^{\circ}\text{C}$ , 3 hours, in two types of glass, one is filled with water type 1, one is filled with water type 2 and inside there were two thin glasses to make the residues stucked on. After three hours, it was easy to see the residuals on the glass. By these samples it's more easy to maket hem ready for the SEM .

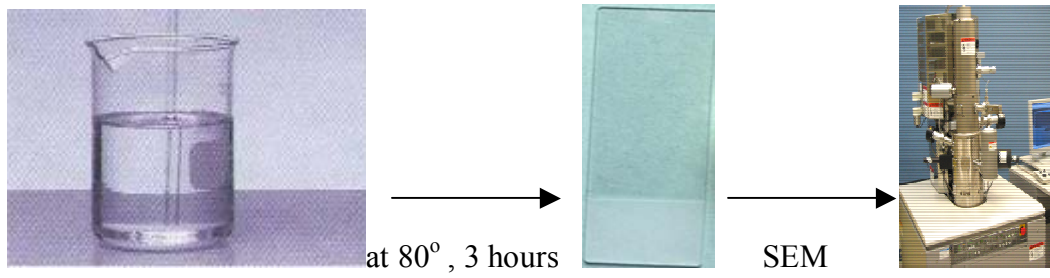


Figure 19 Preparation of Samples

Some images from these trials;

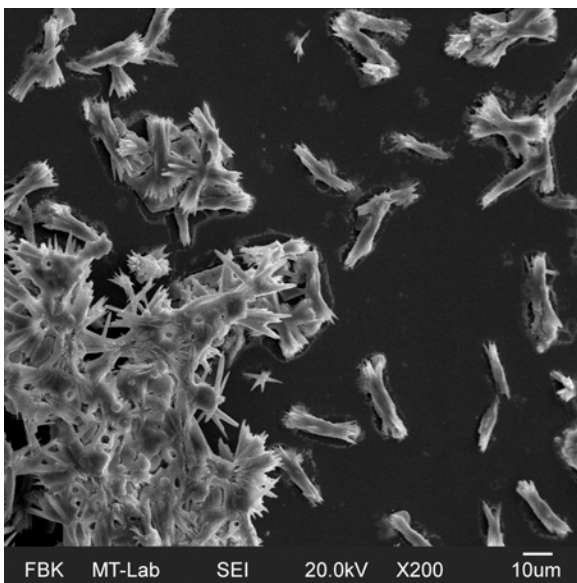


Figure 20 Nontreated water

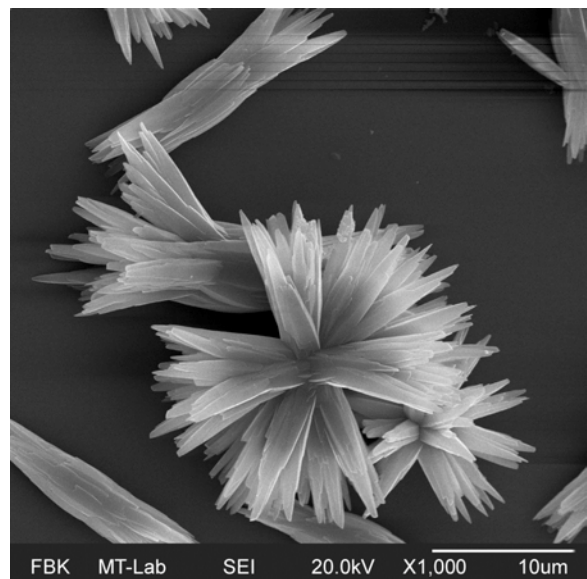


Figure 21 Treated water with Hydronic

The other way to see the calcium carbonate crystals; was to examine the residues (yellow scales) from the tubes. For this, some residues were taken from the company's Hydronic installation.



Figure 22 Scales from tubes

Like I did before, we collected two types of residues from the tubes, like treated with Hydronic, non-treated water passing tube.

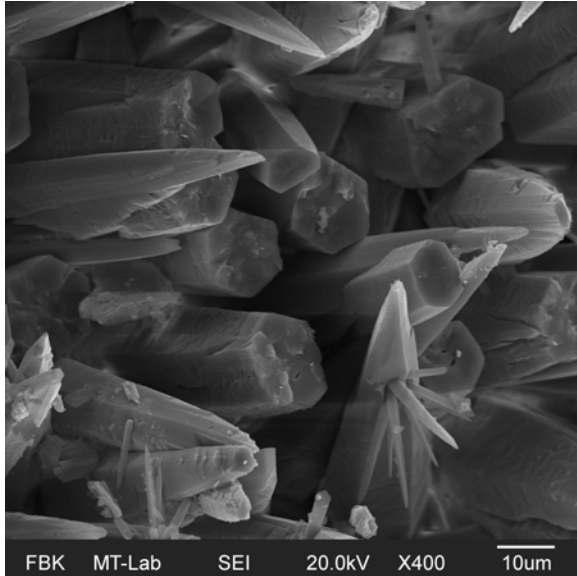


Figure 23 From non-treated water's sacale

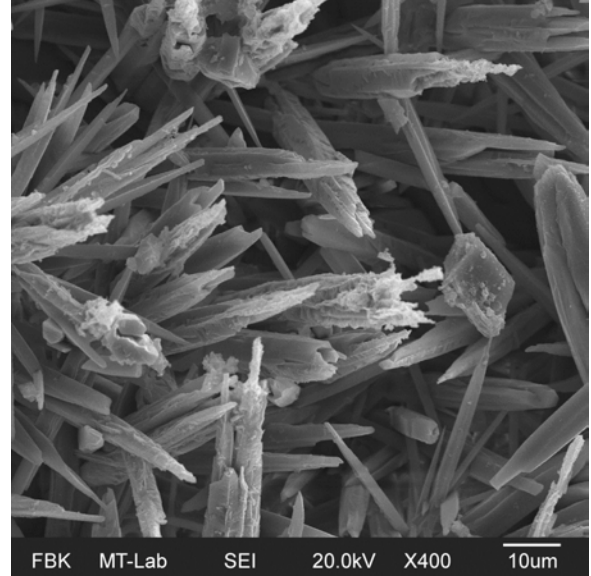


Figure 24 From treated water's scale

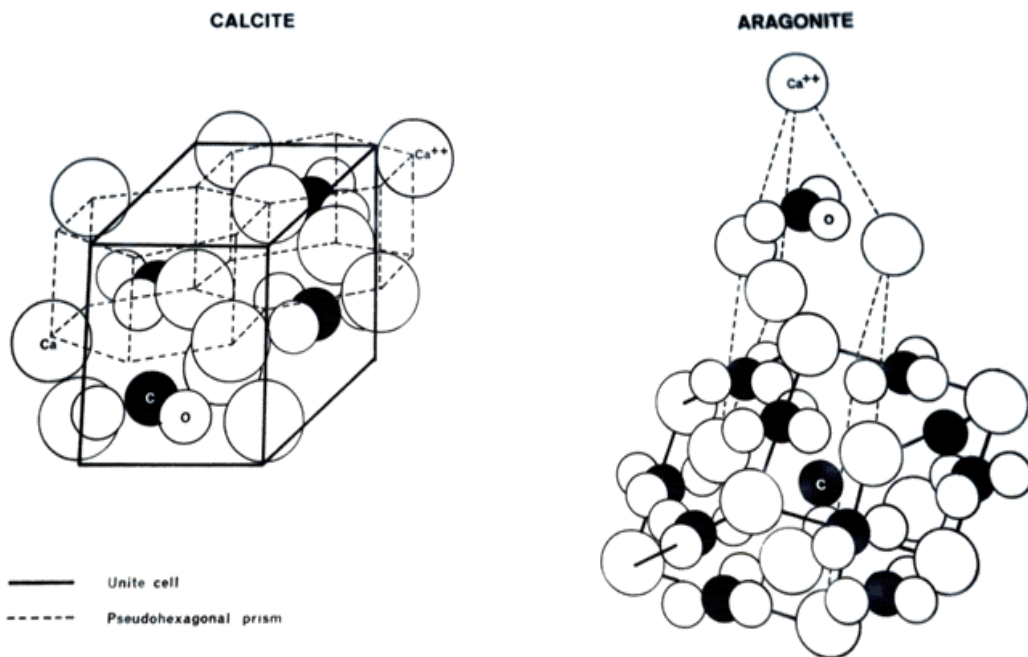


Figure 25 *William Pengelly Cave Studies Trust*

Here in this comparison the shape of calcium carbonate crystals have two different morphologies.

One experiment by changing the frequency of the electric circuit with the waveform generator (Agilent 33250A Function / Arbitrary Waveform Generator, 80 MHz) was also carried out.

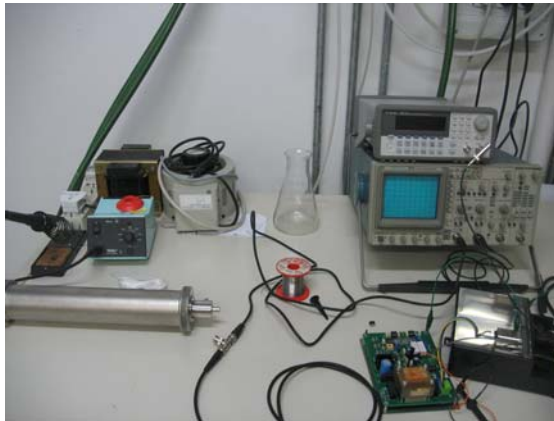


Figure 26 Installation with Waveform Generator

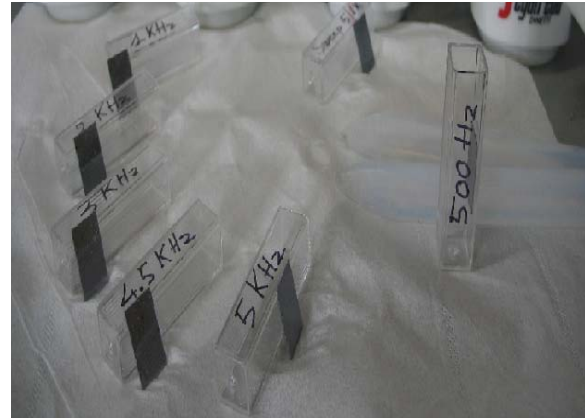
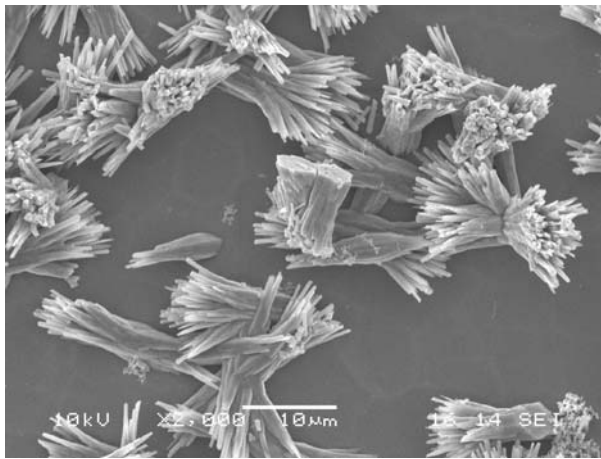
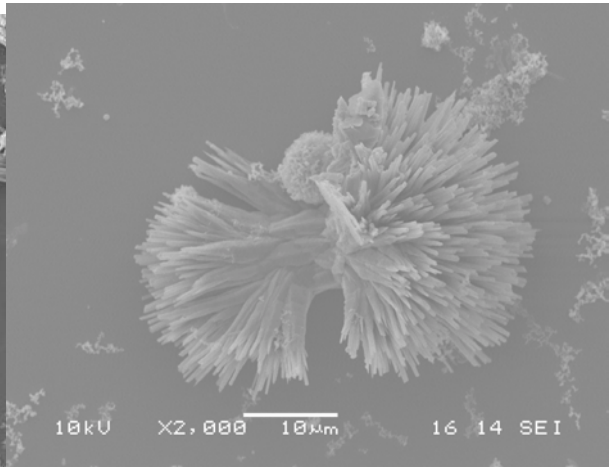


Figure 27 Small silicon wafers

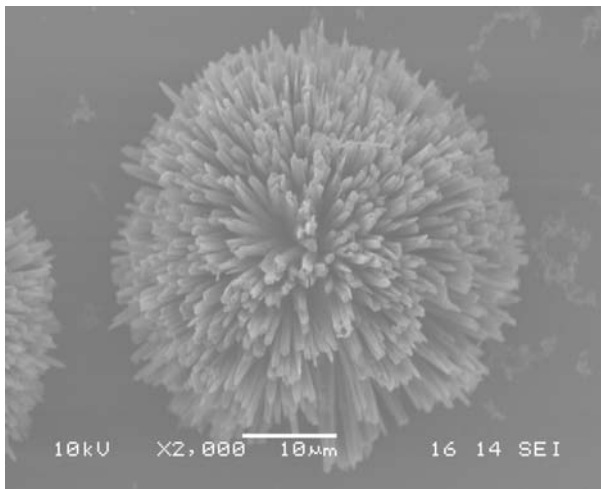
The water that we have taken from the company (hard water) has been tried for all different seven frequencies. Like 500 Hz, 1KHz, 2KHz, 3KHz, 4.5KHz, 5KHz and sweep in frequency between 0.5 -6 KHz. In seven different small containers after adding water we have put small silicon wafers for the residues. After treating them with various frequencies, we left them in electric furnace with 50°C degrees for one day. The day before the silicons were ready for the electron microscope.



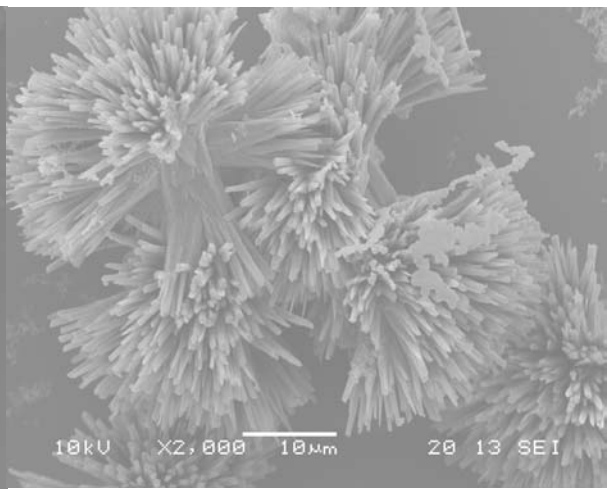
500 Hz



2KHz

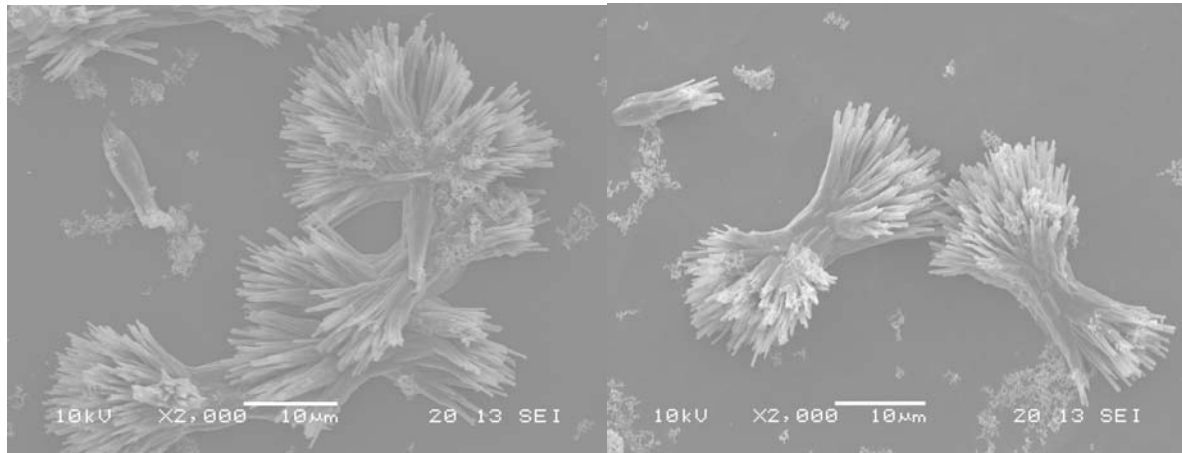


1KHz



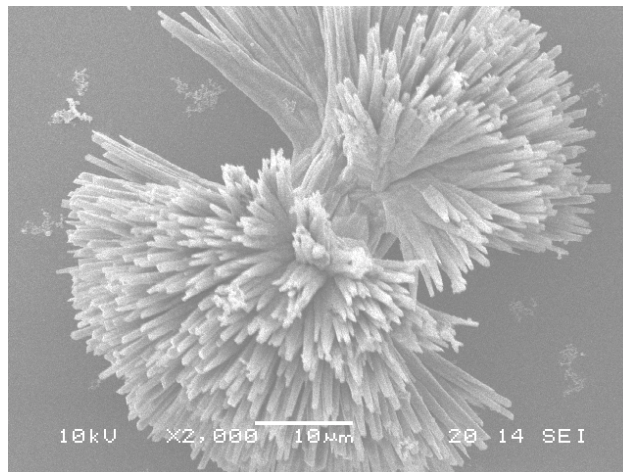
3KHz

Figure 28 The images from SEM of the samples treated with various frequencies



4.5 KHz

5KHz



Sweep in Frequency between 0.5 -6 KHz

Figure 29 The images from SEM of the samples treated with various frequencies

The pictures show us an aragonite form of the calcium carbonate crystals. Without changing the form due to various frequencies.

#### *Determination of Chemical Composition*

With the scanning electron microscope, by EDS we have also tried to see if the particles after heating are calcium carbonate or not. The residues on the small silicon wafer were searched.

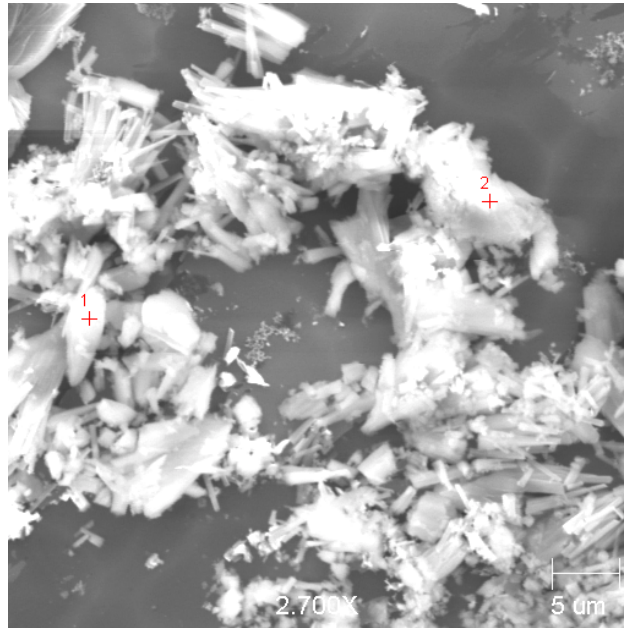


Figure 30 Determining the places we want to know the chemical composition

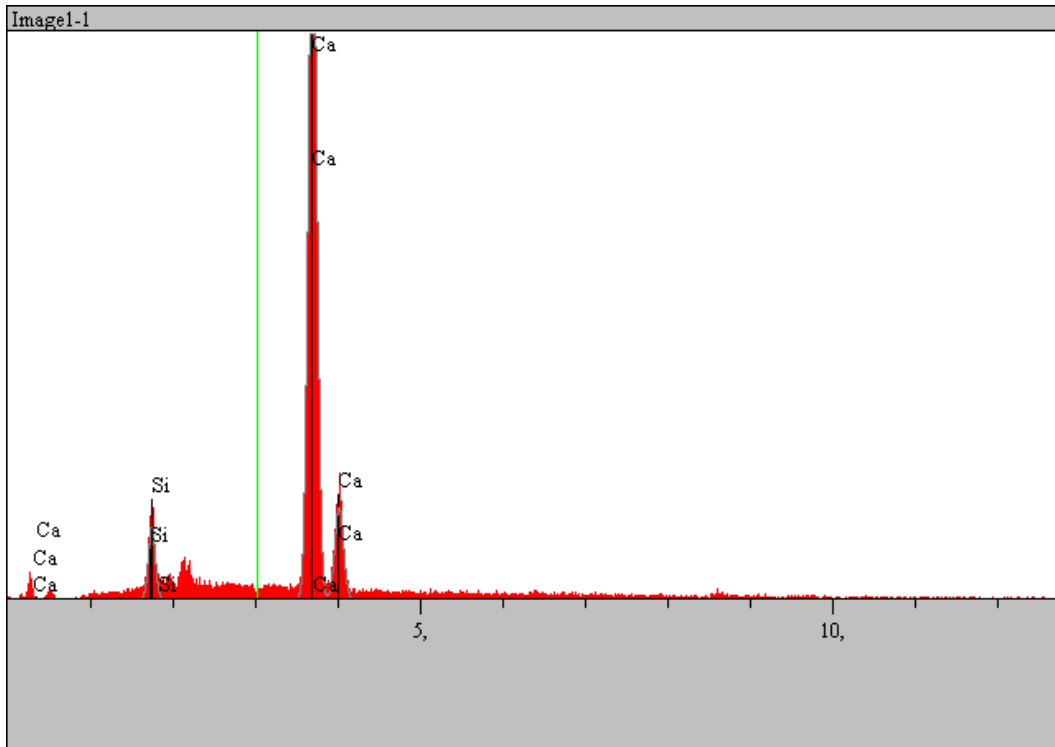


Figure 31 Ca and Si compositions

Elt.	Line	Intensity (c/s)	Error 2-sig	Atomic Wt %	Conc	Units	
Si	Ka	44,51	2,436	8,941	6,438	wt.%	
Ca	Ka	560,69	8,646	91,059	93,562	wt.%	
				100,000	100,000	wt.%	Total

Table 2 Concentrations



We can see that the residues are calcium carbonates. But to get more information about crystals if they precipitate like calcite or aragonite we need to use X-Ray Diffractometer.

## **CHAPTER V. RESULTS and DISCUSSIONS**

To probe the scale inhibition mechanisms, calcium carbonate scale occurring before and after the addition of Hydronic was collected. The results from scale SEM may show that, without Hydronic, calcium carbonate scale shows rhombohedron and hexagon, which are the characteristics of calcite. After addition of Hydronic, morphology of scale is changed. It can be concluded that the alteration of morphology is ascribed to the change of crystal form. There are three stages in the crystallizing process including occurrence and disappearing of unstable phase, occurrence and disappearing of metastable phase, development of stable phase. Without scale inhibitors, metastable phases usually transform into stable phase, thus the main constitute of formed scale is calcite [18]. When scale inhibitors are added, both formation and transformation of metastable phases are inhibited, which results in the occurrence of aragonite and vaterite. From the fact that more aragonite presents in scale with Hydronic, we can see that the function of scale inhibitor is realized mainly by controlling the crystallizing process at the second stage.

And another information about the effect of an electric field on water; water is very sensitive to an electric field. The field strongly "polarizes" water, lining up the charges in the molecules [19]. Applying an electric field to water, we expect the molecules to align their dipoles along the field lines, on average, like so many compass needles aligning in Earth's magnetic field. The degree to which they align with and augment the electric field is called polarizability. But in the Hydrogen-bonded network of water, the dipoles are already partially aligned with each other, even before applying the field. Clusters of nearby molecules act as a single, larger dipole, enhancing the field more than they would on their own. This so-called collective effect is one reason for water's large polarizability. But researchers have wondered how this effect compares with a second one; Each oxygen pulls the hydrogens further from the oxygen in neighboring molecules, which increases the charge separation within each molecule and therefore the strength of each molecule's individual dipole.

Hydronic unit effects the formation of the limescale. Forces the precipitation of calcium carbonate and similar crystals, and redissolves the scale crystals which had deposited previously. For explaining these effects, crystals forming process is important.

### *Crystal Formation*

The crystallization of dissolved solids follows three very different phases. The Hydronic unit works by changing the nucleation phase.

Solution phase → nucleation → crystal growth

### *Nucleation*

Nucleation is the beginning of crystal formation. During the nucleation process, the dissolved ions are constantly colliding with each other. Only a small portion of the collisions will result in nuclei, since the molecules must have a certain amount of energy and must be oriented properly to begin forming the proper crystal structure. The rate that nuclei are formed is given by the following equation.

Rate of Nucleation = [collision factor] x exp [Energy of activation/kT]

The collision factor means the fraction of collisions which results in a nucleus formation. The factor generally depends on the total number of collisions and on how the ions are oriented when they collide. The energy of activation signifies how much energy is needed to get the nucleus started. Once this energy is put in, the nucleus will then continue to grow into a crystal. If this amount of energy is not available, the nucleus will re-dissolve back into a solution. The energy is the result of the kinetic energy from the moving ions, the energy released when the ions bond together, and the energy required to form the outer surface of the nucleus. Affecting the rate of nucleus formation is by increasing the number of collisions and the energy of the collisions of the ions in the water.

The scale causing minerals in water are present as dissolved ions. As charged ions, they will move in an electric field and magnetic field. Using *Ampere's Law*, the electric unit sends a current inside the fluid and generates an electric field. Because an alternating signal is used, the electromagnetic field alternates from one direction to the opposite direction. It is, this change in magnetic field which induces an alternating electric field. This is known as *Faraday's Law*. All particles having an electrical charge are affected by these fields. Number of collisions and their energy will increase. There are two important results of this increased nucleation rate;

The result is that the cations will move in one direction, and anions will move to the opposite direction. These ions are now moving in line, be it opposite be it in the same direction, instead at random directions, the number of collisions increase. In addition, since they are accelerated by the electric field, they have more energy when they collide. Hardness causing ions (such as  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{HCO}_3$ ) will form crystals faster in the presence of the electric field.

Without this treatment, the nucleation will typically occur at breaks, points or other sites on the pipe wall. The scale will form layer by layer, eventually closing off the pipe. With treatment, the crystals nucleate and grow in the solution phase in the liquid.

### *Nucleation Rate*

The nucleation rate,  $I$ , depends on the average number of critical clusters,  $n^*$  and the diffusion of molecules to the cluster,  $\beta$ .

$$I = n^* \beta$$

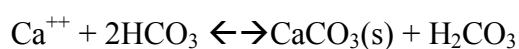
Where the average population of critical nuclei is

$$n^* = N \exp\left(\frac{-\Delta G^*}{k_B T}\right)$$

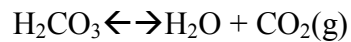
Where:

- $\Delta G^*$  is critical free energy needed.
- $N$  is the number of potential nucleation sites per unit volume
- $k_B$  is the Boltzmann Constant

These crystals will be carried along with the flowing water, setting as loose sediment in tanks or boilers. It will not be hard, adherent scale as compared to untreated water. The second result of electronic water treatment is the shift in the other components of the chemical equilibrium of the water. As calcium carbonate is forced to precipitate, this drives the following reaction to form carbonic acid ( $\text{H}_2\text{CO}_3$ ).



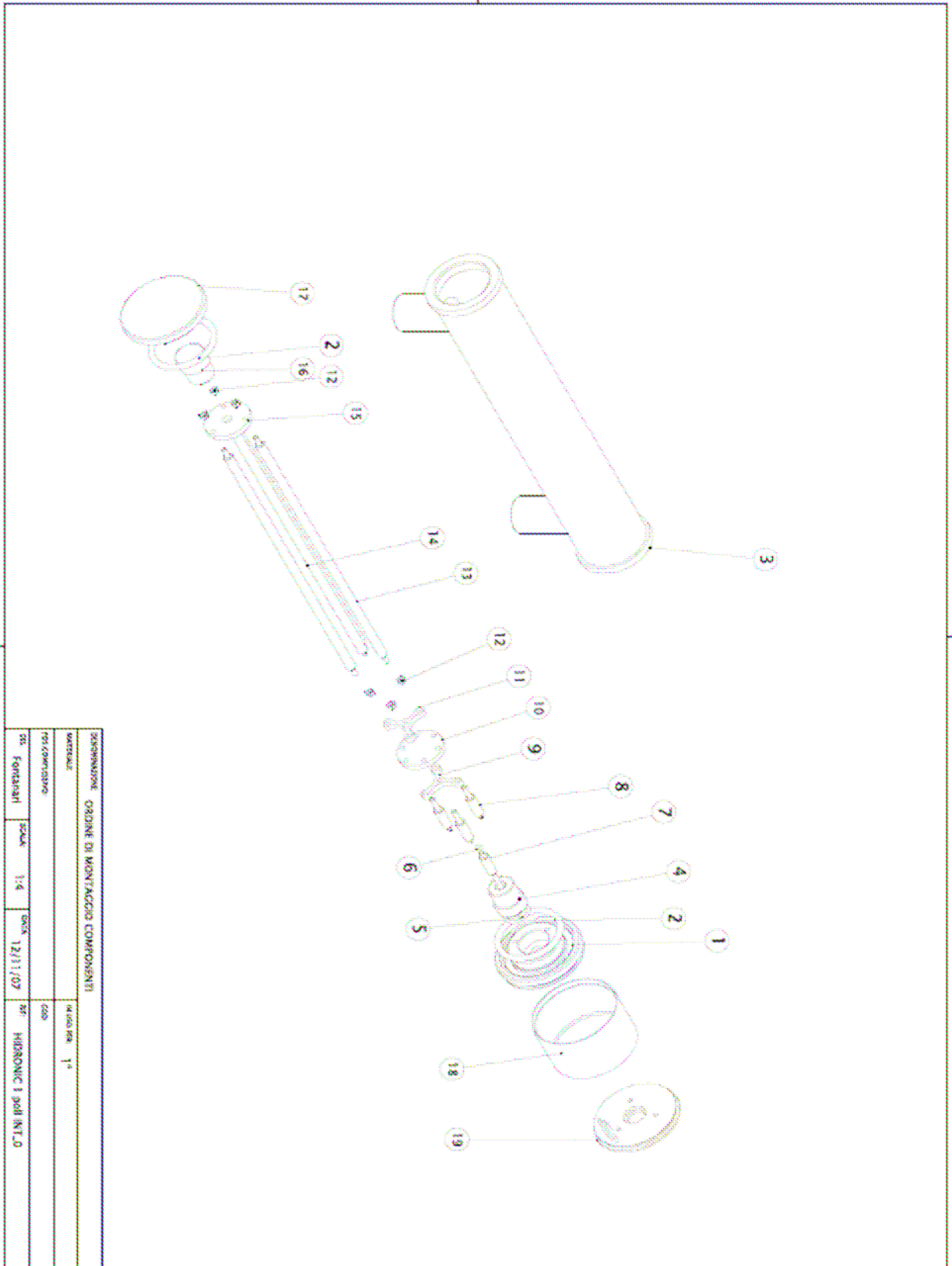
However, the carbonic acid which is formed will further dissociate. This is because the carbonic acid is in balance with its own equilibrium equation.



Most of the carbonic acid that is formed will break down further and form water and carbon dioxide. The final result therefore, of forced precipitation of calcium carbonate is the reaction of carbon dioxide gas. The carbon dioxide gas bubbles being formed are the key to the removal of old scale deposits. The thin layer of water immediately surrounding the gas bubbles will have a low pH due to the fact that the liquid wants to dissolve the carbon dioxide gas. As the gas bubbles flow downstream, they come in contact with old scale deposits. Since calcium carbonate is more soluble in acidic solutions, the scale will be dissolved by the acidic boundary layer surrounding the gas bubbles [20].

### **5.1 Future works**

In this stage and project period, we have consulted to many professors in Faculty of Engineering in Mesiano (Prof. Giuliano Ziglio) and in University of Padova (Prof. Gilberto Artioli), who are familiar with the water sample preparation. I may be also useful to take the precipitates from water, without boiling it. And an easy microfiltrator for water may be used for it. And after the precipitates inside microfilter can be examined by X-ray Diffractometer. To learn more about the calcium carbonate crystals, either they are formed like Calcites or Aragonites. And we may also learn the percentages of the crystals.



1 The three dimensional figure of Hydronic

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