Water Treatment Plant

Submitted By:

<table>
<thead>
<tr>
<th>Name</th>
<th>ID No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avik Roy</td>
<td>113-23-2664</td>
</tr>
<tr>
<td>Nabil Chowdhury</td>
<td>113-23-2674</td>
</tr>
<tr>
<td>Salikur Rahman</td>
<td>113-23-2796</td>
</tr>
</tbody>
</table>

Supervised by:
Tanvir Ahmed Chowdhury
Senior Lecturer
Department of Textile Engineering
Faculty of Engineering
Daffodil International University

Dissertation submitted to the Department of Textile Engineering of Daffodil International University in partial fulfillment of the requirement for the Degree of Bachelor of Science in Textile Engineering

Summer-2015
Letter of Approval

July 30, 2015

To
The Head
Department of Textile Engineering
Daffodil International University
102, Sukrabad, Mirpur Road, Dhaka 1207

Subject: Approval of final year project report.

Dear Sir,

I am writing to let you know that this project report titled as “Water Treatment Plant” has been completed for final evaluation. The whole report is prepared based on proper investigation and understanding though critical analysis of empirical data with required belongings. The students were directly involved in their project activities and the report becomes vital to spark off many valuable information for the readers.

Therefore, it will highly be appreciated if you kindly accept this project report and consider it for final evaluation.

Yours Sincerely,

Tanvir Ahmed Chowdhury
Senior Lecturer
Department of Textile Engineering
Faculty of Engineering
Daffodil International University
DECLARATION

We hereby declare that the work which is being presented in this thesis entitled, “Water Treatment Plant” is original work of our own, has not been presented for a degree of any other university and all the resource of materials uses for this project have been duly acknowledged.

_______________________       _________________
Avik Roy                        Date

_______________________       _________________
Nabil Chowdhury                 Date

_______________________       _________________
Salikur Rahman                  Date

This is to certify that the above declaration made by the candidate is correct to the best of my knowledge.

_______________________       _________________
Tanvir Ahmed Chowdhury          Date

                     Supervisor

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Acknowledgement

Above all, we praise the almighty Allah who gave us His enabling grace to successfully complete this research work.

With sincerity, we extend our warm and deep appreciation and gratitude to our supervisor, Tanvir Ahmed Chowdhury, Senior Lecturer for his unreserved guidance and support to come up with this research work. Being working with him, we have not only earned valuable knowledge but were also inspired by his innovativeness which helped to enrich our experience to a greater extent. His ideas and way of working was truly remarkable. We believe that this research could not be finished if he did not help us continuously.

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We are also grateful to Tanvir Ahmed Chowdhury, Senior Lecturer, Daffodil International University for his continuous support & Ideas during studies.

Finally, we express our sincere gratitude to our parents & friends for their encouragement in completing this project work.
Dedicated
To
“Our Parents & Teachers”
ABSTRACT

The study makes an assessment on water treatment plant that gives us knowledge about water treatment plant, temporary and permanent hardness of water, effect of hardness on fabric. To conduct this project work, we have examined two water treatment plants of three different industries. At first examine the total water treatment plant, then we examine initial hardness and after hardness of WTP. We examine that two industries use ion exchange process for removing their water hardness. Limit of soft water is 0 PPM to 50 PPM. Soft water increases the efficiency of easily exhaustion and fixation of dye.
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INTRODUCTION
1. Introduction:

Water is the most common liquid on Earth. It covers about 71.4% of the Earth. Pure water has no smell, taste, or color. Lakes, oceans, and rivers are made of water. Rain is water that falls from clouds in the sky. If water gets very cold (below 0 degrees Celsius), it freezes and becomes ice. Frozen rain is hail. Snow is formed from water vapour, not rain. If water gets very hot (above 100 degrees Celsius), it boils and becomes steam. Water is very important for life. However, some studies suggest that by 2025 more than half of the people around the world will not have enough water.

Water is a fluid. Water is the only substance on earth that exists naturally in three states. People know of over 40 anomalies about water. Unlike most other liquids such as alcohol or oil, when water freezes, it expands by about 9%. This expansion can cause pipes to break if the water inside them freezes.

Plants and animals (including people) are mostly water inside, and must drink water to live. It gives a medium for chemical reactions to take place, and is the main part of blood. It keeps the body temperature the same by sweating from the skin. Water helps blood carry nutrients from the stomach to all parts of the body to keep the body alive. Water also helps the blood carry oxygen from the lungs to the body. Saliva, which helps animals and people digest food, is mostly water. Water helps make urine. Urine helps remove bad chemicals from the body. The human body is between 60% and 70% water.

Water is a molecule made of 2 hydrogen atoms and 1 oxygen atom. Its chemical formula is $\text{H}_2\text{O}$. Water has a surface tension, so a little water can make drops on a surface, rather than always spreading out to wet the surface. Water can also be called 'aqua', which is the Roman word for water. Water is also used for recreational purposes. Though a human being can survive for up to a three weeks without food, they can only survive for a day or two without water.
1.1. Significance:

Since water treatment plant plays an important role in textile sectors specially in dyeing industries anyone studying in textile engineering must know the basic procedure and mechanism of a water treatment plant. For knowing best possible water quality it is essential to know the parameter used in water treatment plant and possible faults and remedies. As Bangladesh is a developing country and now we own a large share in world textile business it is high time we take some serious steps to develop our manufacturing system with highly efficient manufacturing plant to survive the increasing tough competition from other developing countries. As a part of highly efficient manufacturing system water treatment plant plays a vital role in determining product quality in textile wet processing. Therefore we had chosen —study on water treatment plant as our topic for thesis. To make this thesis report successful we have visited several industries and observed the techniques and procedure used to make water softening. We also sincerely observed the quality of water, parameter used and techniques used to ensure best possible quality. Thus we have gained a detailed knowledge about the water softening processes and their best possible implementation techniques in textile wet processing industries. This report covers the major water softening processes, hardness removal techniques, quality control, hardness measurement, survey result and comparison among different softening processes. We wish this report will help everyone to understand the basic information of water treatment plant of textile industries and make it possible to find out new techniques or at least further improve already existed ones.

We hope by the proper implementation of water treatment plant our country will be able to reach a benchmark in ensuring best product quality with a highly efficient modern manufacturing system and maintain its stronghold in worldwide textile business.
LITERATURE REVIEW
2. Literature Review

2.1. Water

Water is a substance that covers 70% of earth’s surface. Water is the only substance exist on earth in all three physical states of matter gas liquid and solid. Water is continuously moving through the cycle of evaporation, precipitation, and run off, back to the sea. chemically water is formed hydrogen and oxygen atom. Two hydrogen atoms is covalently bonded with one oxygen atom. The chemical formula of water is H₂O.pure water is colorless, tasteless and orderless. The necessisity of water is beyond imaginable….every day we drink water, bath in water, in our daily cleaning, our source of electric energy is water. In industry thousands of gallon of water is needed. In every sphere of life water is essential infect without water life is meaningless.

![Water Chemical Symbol: H₂O](image)

**Figure: chemical structure of water**

Properties of water:

<table>
<thead>
<tr>
<th>IUPAC ID:</th>
<th>Water, Oxidane</th>
</tr>
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<tbody>
<tr>
<td>Formula:</td>
<td>H₂O</td>
</tr>
<tr>
<td>Molar mass:</td>
<td>18.01528 g/mol</td>
</tr>
<tr>
<td>Density:</td>
<td>999.97 kg/m³</td>
</tr>
<tr>
<td>Melting point:</td>
<td>0 °C</td>
</tr>
<tr>
<td>Boiling point:</td>
<td>99.98 °C</td>
</tr>
<tr>
<td>Triple point temperature:</td>
<td>0.01 °C</td>
</tr>
<tr>
<td>Acidity(pKₐ):</td>
<td>15.74</td>
</tr>
<tr>
<td>Basicity(pKₐ):</td>
<td>15.74</td>
</tr>
</tbody>
</table>
2.2. Water Consumption in Textile Industry

Textile Industry is one of the top ten Industry which consume high amount of water. The raw material used greatly in textile wet processing is water. The quantity of water varies in different stages. Some textile mills have high water cost as they purchase water from municipal system. Therefore, quantity of water is a point to be observed in textile processing.

<table>
<thead>
<tr>
<th>Substrate Type</th>
<th>Quantity (gallon/pounds) [Approximately]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton</td>
<td>24.9-34.9</td>
</tr>
<tr>
<td>Wool</td>
<td>20-40</td>
</tr>
<tr>
<td>Nylon</td>
<td>12.5-15</td>
</tr>
<tr>
<td>Rayon</td>
<td>12.5-15</td>
</tr>
<tr>
<td>Polyester</td>
<td>10-20</td>
</tr>
<tr>
<td>Acrylic</td>
<td>10-20</td>
</tr>
<tr>
<td>Woven other</td>
<td>2-50</td>
</tr>
<tr>
<td>Knit other</td>
<td>3-40</td>
</tr>
<tr>
<td>Non woven</td>
<td>0.3-9</td>
</tr>
</tbody>
</table>

2.3. Source of Water

2.3.1. Main Source of Water

Main sources of water are:

1. **Rain water**: Rain water is the purest water of all natural sources. The water may contain traces of gases dissolved out small amount of finely divided solid matter derived from the air. It also contain dissolved impurities such as shoot traces of SO₂, NO₂, NH₃, H₂SO₄, CO₂ and other by products of industrialization. Suspended in it can be filtered by using sand bed. Rain water is suitable for boiling, washing and dyeing process.

2. **Subsoil water**: This type of water is collected from shallow springs and wells which are about 50ft (15cm) or so deep. It is usually free from suspended impurities because it has been filtered by its passage through the soil. It will, however, contain dissolve organic matter. Subsoil water is often rich in dissolved carbon dioxide, a gas abundantly present in the sin of the soil. Subsoil waters are
very variable with regard to the impurities which they contain. It is not suitable for dyeing and finishing.

3. **Surface water:** Surface water consist of rain water which is collected from streams, rivers or lakes. This type of water contains organic and inorganic matters which are dissolved in it and also contain suspended impurities. Then the Nutrifying bacteria will in time convert the organic substances into nitrates which are not objectionable in dyeing and finishing. Surface waters may receive considerable additions of dissolved mineral salts from shallow springs which feed the streams. It contains chloride, Sulphate, Carbonate, Bicarbonate of Sodium, Potassium, Calcium and Iron.

4. **Deep well water:** This type of water is obtained 500m below the surface. This is free from organic matters. The soluble impurities in water may be composed of a variety of substances, soluble organic compounds, ammonium salts, nitrites of animal or vegetable for quantities, the sewage contamination is undesirable for much textile purpose. The presence of salts of calcium or magnesium in solution can be most undesirable in many finishing process.

### 2.3.2. Other Source of Water

Other sources are:

1. **Municipal or public water system.**

2. **Reclaimed waste streams.**

The common compounds presents in almost all water supply in some extent are:

- Acidity, alkalinity.
- Aluminum.
- Chlorine.
- Heavy metal such as Iron, Copper, magnesium etc.
- Calcium and magnesium.
- Suspended matters.
- Dissolved solid.
- Oil, gases etc.
2.4. Impurities in Water

The brightness of color, performance of dye, whiteness etc. depends on water used in wet processing. So, it is essential to know what type of water is suitable for wet processing. To know this first we should understand about the impurities in water. There are mainly four types of impurities in water:

1. **Turbidity and color**: Turbidity is the presence of small and large particles in water which are soluble in water. These particles may be inorganic (silica, calcium carbonate) or organic (fats, vegetable matter, micro-organism) in nature. Large particles are removed by sedimentation. Filtration is used for small particles. Colors dissolve in water or colloidal organic matter disperse in water. These organic compounds are not visible normally. A Tintometer is used to measure the amount of color in water. Turbidity and water stain the fabric.

2. **Ions of Heavy metals**: Ions of heavy metals like iron, manganese, copper are harmful during wet processing. These causes following problems:
   - Act as catalyst in the decomposition of bleaching agents and cause activated attack with subsequent degradation of fiber.
   - Produce slight yellow color during scouring and bleaching and it is difficult to remove the color.
   - It may insolubilise the metal oxide during mercerization and reduce lusture, absorbency. In the dyeing stage, metal ions may combine with some dyes and cause dulling of shade.

3. **Alkalinity**: Generally when water contains carbonate and bicarbonate then water shows alkalinity. Amount of carbonate and bicarbonate is measured by Titration method.

4. **Hardness**: The presence of calcium, magnesium salt i.e. bi-carbonates, sulphates, chloride in water causes the hardness of water. The water which contains these salts is called hard water. Hard water does not easily form lather with soap as the salt of calcium and magnesium react with soap to form insoluble organic salts. There are two types of water hardness:
   - **Temporary hardness**: Temporary hardness is due to the presence of bicarbonates of calcium and magnesium. The types of hardness are called temporary hardness as it can be removed by boiling.
   - **Permanent hardness**: It is due to presence of chlorides or sulphates of calcium and magnesium. This type of hardness is called permanent hardness. These salts do not decompose on boiling. So permanent hardness cannot be removed easily.
2.5. Hardness

2.5.1. Hard Water

Hard water is water that has dissolved mineral (Bi-Carbonate, Sulphate, Chloride of Calcium and Magnesium). Hard water is not health risk. But it creates problem during wet processing. Hard water may be classified into two types:

1. Temporary hard water
2. Permanent hard water

Temporary hardness of water can be removed quite easily i.e. by boiling. But permanent hardness can be removed by applying some process. I will discuss these later.

Removing hardness from water is called softening and hardness is mainly caused by calcium and magnesium salts. These salts are dissolved from geologic deposits through which water travels. The length of time water is in contact with hardness producing material helps determine how much hardness there is in raw water.

The two basic methods of softening public water supplies are chemical precipitation and ion exchange. Other methods can also be used to soften water, such as electrodialysis, distillation, freezing, and reverse osmosis. These processes are complex and expensive and usually used only in unusual circumstances.

Water becomes hard by being in contact with soluble, divalent, metallic cations. The two main cations that cause water hardness are calcium (Ca^{2+}) and magnesium (Mg^{2+}). Calcium is dissolved in water as it passes over and through limestone deposits. Magnesium is dissolved as water passes over and through dolomite and other magnesium bearing formations. Because groundwater is in contact with these geologic formations for a longer period of time than surface water, groundwater is usually harder than surface water.

Although strontium, aluminum, barium, iron, manganese, and zinc also cause hardness in water, they are not usually present in large enough concentrations to contribute significantly to total hardness.

2.5.2. Hardness Expression Method

The hardness of water is expressed by the amount of Calcium present in water. In this method, chloride, sulphates and bi-carbonates of calcium and magnesium are not taken into consideration. Because, it is difficult to measure the components. Hardness is expressed:

PPM (parts per million): PPM is the way to express the dilute concentration of substance. In case of hard water, PPM is the number of grains of calcium carbonate which is present in one million grains of water. It is usually defined as 1mg CaCO_3 per liter and used in America.
In Degree (grains per gallon): The number of grains of Calcium carbonates which are present in 1 gallon (70,000 grains) of water.

Parts per 10^5: This is the weight of calcium carbonate present in 100000 unit water. It is used in England, France.

So, we find a relationship between PPM and Degree. That is

1000000 grains hard water contains X grain CaCO₃

\[ 1 \rightarrow \frac{X}{1000000} \rightarrow 70000 \times \frac{X}{1000000} \text{ grains} \]

Hence, Degree of hardness = 0.7 * PPM

PPM = Degree /0.07

2.5.3. Scales of Hardness

Now, let’s take a look about the scale used in different methods to measure the hardness of water.

1⁰dH hardness (German) --> 10mg of CaO per 1L water.

1⁰fH hardness (French) --> 10mg of CaCO₃ per 1L water.

1⁰eH hardness (English) --> 1 grain or 68.4mg of CaCO₃ per 4.455L water.

1⁰aH hardness (American) --> 1mg of CaCO₃ per 1L water.

gpg hardness --> 1 grain or 68.4mg of CaCO₃ per gallon (US) water.

2.5.4. Measurement of Hardness of Water

Water hardness is unfortunately, expressed in several different units and it is often necessary to convert from one unit to another when making calculations. Most commonly used units include grains per gallon (gpg), parts per million (ppm), and milligrams per liter (mg/L).

Grains per gallon are based on the old English system of weights and measures, and are based on the average weight of a dry kernel of grain (or wheat). Parts per million is a weight to weight ratio, where one ppm of calcium means 1 pound of calcium in 1 million pounds of water (or 1 gram of calcium in 1 million grams of water). Milligrams per liter (mg/L) are the same as ppm in the dilute solutions present in most raw and treated water (since pure water weights 1000 grams per liter).
Since calcium carbonate is one of the more common causes of hardness, total hardness is usually reported in terms of calcium carbonate concentration (mg/L as CaCO₃), using either of two methods:

➢ Calcium and Magnesium Hardness

Hardness caused by calcium is called calcium hardness, regardless of the salts associated with it. Likewise, hardness caused by magnesium is called magnesium hardness. Since calcium and magnesium are normally the only significant minerals that cause hardness, it is generally assumed that:

\[
\text{Total Hardness} = \text{Calcium Hardness} + \text{Magnesium Hardness}
\]

\[
= 2.50 \times \text{Calcium conc. (mg/L as Ca}^{2+}\text{)} + 4.12 \times \text{Magnesium conc. (mg/L as Mg}^{2+}\text{)}
\]

➢ Carbonate and Non-carbonate Hardness

Carbonate hardness is primarily caused by the carbonate and bicarbonate salts of calcium and magnesium. Non-carbonate hardness is a measure of calcium and magnesium salts other than carbonate and bicarbonate salts (such as calcium sulfate, CaSO₄, or magnesium chloride, MgCl₂). Total hardness (which varies based on alkalinity) is expressed as the sum of carbonate hardness and non-carbonate hardness:

\[
\text{Total hardness} = \text{Carbonate hardness} + \text{Non-carbonate hardness}
\]

色々 Measurement of Hardness of water:

<table>
<thead>
<tr>
<th>Classification</th>
<th>mg/l or ppm</th>
<th>grains/gal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soft</td>
<td>0 – 17.1</td>
<td>0 – 1</td>
</tr>
<tr>
<td>Slightly hard</td>
<td>17.1 – 60</td>
<td>1 – 3.5</td>
</tr>
<tr>
<td>Moderately hard</td>
<td>60 – 120</td>
<td>3.5 – 7.0</td>
</tr>
<tr>
<td>Hard</td>
<td>120 – 180</td>
<td>7.0 – 10.5</td>
</tr>
<tr>
<td>Very Hard</td>
<td>180 &amp; over</td>
<td>10.5 &amp; over</td>
</tr>
</tbody>
</table>
2.5.5. Hardness Unit Conversion

If we convert the different system, then we get a table like this:

<table>
<thead>
<tr>
<th></th>
<th>Ppm</th>
<th>Gpg</th>
<th>°dH</th>
<th>°eH</th>
<th>°fH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parts per million (ppm)</td>
<td>1</td>
<td>0.058</td>
<td>0.056</td>
<td>0.07</td>
<td>0.1</td>
</tr>
<tr>
<td>Grains per gallon (gpg)</td>
<td>17.118</td>
<td>1</td>
<td>0.96</td>
<td>1.2</td>
<td>1.7</td>
</tr>
<tr>
<td>German degree (°dH)</td>
<td>17.80</td>
<td>1.04</td>
<td>1</td>
<td>1.25</td>
<td>1.78</td>
</tr>
<tr>
<td>English degree (°eH)</td>
<td>14.30</td>
<td>0.83</td>
<td>0.798</td>
<td>1</td>
<td>1.43</td>
</tr>
<tr>
<td>French degree (°fH)</td>
<td>10</td>
<td>0.584</td>
<td>0.56</td>
<td>0.702</td>
<td>1</td>
</tr>
</tbody>
</table>

2.6. Soft Water

The water which does not contain \( \text{HCO}_3^- \), \( \text{Cl}^- \), \( \text{SO}_4^{2-} \) salt of \( \text{Ca}^{2+} \), \( \text{Mg}^{2+} \), \( \text{Fe}^{2+} \), \( \text{Al}^{3+} \) & form foam easily by reacting with soap is called soft water e.g. Rain water.

2.7. Difference Between Hard Water and Soft Water

<table>
<thead>
<tr>
<th></th>
<th>Hard water</th>
<th>Soft water</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contains</td>
<td>Hard water contains high amount of calcium and magnesium.</td>
<td>Soft water contains high amount of sodium.</td>
</tr>
<tr>
<td>Benefits</td>
<td>Hard water is a good source of calcium and magnesium in the body. Hard water also reduces the solubility of toxic metal ions.</td>
<td>Soft water is not harsh on the skin, clothes, dishes, etc.</td>
</tr>
<tr>
<td>Problems</td>
<td>Hard water can leave the clothes rough and worn out during washing; hard water also makes it difficult to take off dirt from the skin and leaves a film on skin and dishes when washing them. Build up of limescale and galvanic erosion are also problems caused by hard water.</td>
<td>Soft water does not give off any problems, though it is less beneficial than hard water in consumption. Softened water is also known to emit lead from old pipes in the supply system.</td>
</tr>
</tbody>
</table>
2.8. Water Softening methods

Water softening process is done in order to remove Ca$^{2+}$ and Mg$^{2+}$ ions from water. Since, Na and Mg are nonvolatile salt, it is needed to separate them from water by precipitation or any other way.

There is a simple process of softening temporary hardness of water and it is boiling. When water is boiled the dissolved Calcium & Magnesium salt converted to Calcium Carbonate and Magnesium Carbonate & precipitated. That way they can be separated from water. The reaction is here:

\[
\begin{align*}
\text{Ca(HCO}_3\text{)} & \rightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \\
\text{Mg(HCO}_3\text{)} & \rightarrow \text{MgCO}_3 + \text{CO}_2 + \text{H}_2\text{O}
\end{align*}
\]

ppm.

For both temporary and permanent hard water there are three industrial softening methods. These are:

1. Soda lime method
2. Base exchange method (permuit)
3. Demineralisation method.

➢ Lime Soda Process:

Hydrated lime Ca(OH)$_2$ and sodium Carbonate are used in this method to precipitate Calcium and Magnesium ions. Particularly, Ca(OH)$_2$ is used for Carbonate ions and NaCO$_3$ is used for non Carbonate ions.

For temporary hardness,

\[
\begin{align*}
\text{Ca(HCO}_3\text{)} + \text{Ca(OH}_2\text{)} & \rightarrow 2\text{CaCO}_3\downarrow + 2\text{H}_2\text{O} \\
\text{Mg(HCO}_3\text{)} + \text{Ca(OH}_2\text{)} & \rightarrow 2\text{MgCO}_3\downarrow + 2\text{H}_2\text{O}
\end{align*}
\]

Here, the solubility of Ca(HCO$_3$) is lower than that of Mg(HCO$_3$). CaCO$_3$ precipitate first while water is treated with Ca(OH)$_2$ and at $100^0$C temperature the solubility of CO$_3$ is 12-75 ppm.

For permanent hardness.

\[
\begin{align*}
\text{CaSO}_4 + \text{NaCO}_3 & \rightarrow \text{CaCO}_3 + \text{Na}_2\text{SO}_4 \\
\text{MgCl}_2 + \text{Ca(OH}_2\text{)} & \rightarrow \text{CaCl}_2 + \text{Mg(OH}_2\text{)}
\end{align*}
\]

In 2$^{nd}$ reaction from above CaCl$_2$ is produced which is replaced by CaCO$_3$ by using Na$_2$CO$_3$. 
\[ \text{CaCl}_2 + \text{Na}_2\text{CO}_3 = \text{CaCO}_3 + \text{NaCl} \]

The main parts of the process are:

1. Reagent tanks (Soda lime + Coagulants)
2. Reaction tank
3. Filter
4. Soft water storage tank.

**Process:**
The lime and soda are entered into the reagent tank. At the same time, predetermined amount of raw hard water is pumped into the Reaction tank. A large propeller acts as an agitator into the Reaction tank. The agitation is increased to get more amount of ppm, steam is passed through the sideway pipe to increase the temperature of the mixer. The water is filtered to remove CaCO\(_3\) after precipitation is completed and finally passed to the soft water storage tank.

Precipitation rate can be increased by:

1. By increasing Temperature.
2. By using excess reagent and stirring.
3. By using sand grain.

The residual hardness that presents in water as CaCO\(_3\) can be decreased by either hot or cold method. For cold method it can be reduced to 5-20 ppm and for hot process it is 5-15 ppm.

After processing with lime soda method if the water contains some hardness, then it can be removed by adding phosphate. In this process, some NaOH are also used.

\[ 10\text{CaCO}_3 + 6\text{Na}_3(\text{PO}_4) + 2\text{NaOH} \rightarrow \{\text{Ca}(\text{PO}_4)_2\}_3\text{Ca(OH)}_2 + \text{NaCO}_3 \]
**Base Exchange Process:**

It is the most simple and used process. Water obtained by using this process has a hardness of 0-2°. Water is softened by exchanging Ca\(^{2+}\) and Mg\(^{2+}\) ion with the help of zeolite. That’s why it is also called Zeolite or permuit process. While water is passed into Zeolite the ions are exchanged. Zeolite is the Hydrated silicate of sodium and aluminium. The general formula is:

\[(\text{Na}_2\text{O})_x(\text{Al}_2\text{O}_3)_y(\text{SiO}_2)_z(\text{H}_2\text{O})_n\]

Let, Zeolite \(= Z = (\text{Al}_2\text{O}_3)_y(\text{SiO}_2)_z(\text{H}_2\text{O})_n\)

For temporary hardness:

\[\text{Ca}(\text{HCO}_3) + \text{Na}_2\text{O}.Z \rightarrow \text{CaO}.Z + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}\]

\[\text{Mg}(\text{HCO}_3) + \text{Na}_2\text{O}.Z \rightarrow \text{MgO}.Z + \text{Na}_2\text{CO}_3 + 2\text{H}_2\text{O}\]

For permanent hardness:

\[\text{CaSO}_4 + \text{Na}_2\text{O}.Z \rightarrow \text{CaO}.Z + \text{Na}_2\text{SO}_4\]

\[\text{MgSO}_4 + \text{Na}_2\text{O}.Z \rightarrow \text{MgO}.Z + \text{Na}_2\text{SO}_4\]

\[\text{MgCl}_2 + \text{Na}_2\text{O}.Z \rightarrow \text{MgO}.Z + \text{NaCl}\]

**Process:**
Zeolite are taken into the tank. Then hard raw water is entered into the inlet pipe. While water comes to the contact of Zeolite in Zeolite bed, the water softened. Then soft water is collected from downward outlet.
Regeneration:
When water is softened by this process for many times Zeolite is exhausted. For this reason, Zeolite is not used for every time while softening water. 10% NaCl is used through the Zeolites and the Zeolites are regenerated again.

\[ \text{CaO}_2 \text{Z} + 2\text{NaCl} \rightarrow \text{Na}_2\text{O}_2 \text{Z} + \text{CaCl}_2 \]

➢ **Demineralization Method:**

Demineralization process is the modern water softening process. By applying this process the water obtained may be as pure as distilled water. Because not only the ions are removed those are responsible for water hardness but also some dissolved salt i.e. FeCO₃, CaCl₂ etc. can be removed. In this process strong acid cation resin and strong base anion resin are used. Cation in water like Sodium, Calcium, Magnesium removed by cation resin. And for anion like Chloride, Sulphate anion resins are used.

**Process:** The demineralization plant consist of both cation and anion unit. Control over cation and anion unit is essential. Predetermined amount of resin bed are taken according to the composition of hard water. Then, the process is done by two steps:

1. **Hydrogen Cation exchanger:** Cation resin can be in Hydrogen (R-SO₃H) or Sodium form (R-SO₃Na). Sulphonated resin (Cation acid resin) in Hydrogen form is used as cation exchanger for water softening.

   \[ \text{CaCl}_2 + \text{H}_2\text{R} \rightarrow \text{CaR} \downarrow + 2\text{HCl} \]
   \[ \text{Ca(HCO}_3\text{)} + \text{H}_2\text{R} \rightarrow \text{CaR} \downarrow + 2\text{H}_2\text{O} + 2\text{CO}_2 \]

2. **Anion exchanger:** Amino resin (anion base resin) is used and produced HCl is removed.

   \[ \text{HCl} + \text{HOR}_1 \rightarrow \text{ClR}_1 \downarrow + \text{H}_2\text{O} \text{ (soft water)} \]
**Regeneration:** We know, regeneration is done to get back the resins which are used to softening water are exhausted and we have to apply some acid & alkali to regenerate them again.

For step 1, regeneration is performed by using acid. Less than 2% H₂SO₄ is used.

\[
\text{CaR} + \text{H}_2\text{SO}_4 \rightarrow \text{CaSO}_4 + \text{H}_2\text{R} \text{ (regenerated resin)}
\]

For step 2, regeneration is done by using 1% solution of NaOH.

\[
\text{ClR}_1 + \text{NaOH} \rightarrow \text{NaCl} + \text{HOR}_1 \text{ (regenerated resin)}
\]

**2.9. Advantages and Disadvantages**

**Advantages of water softening are:**
- Water Softening will deal with the problems caused by hard water such as excessive soap use and scaling.
- Depending on the type of water softening process used, softening may also aid in other water treatment processes.
- Water Softening often removes iron and manganese, reduces tastes and odors, reduces total solids content, and removes radioactivity.
- The high pH associated with lime softening can aid in disinfection.
- When water is stabilized using recarbonation at the end of the lime water softening process, corrosion in the distribution system is avoided.

**Disadvantages of Softening are:**
- Water softening processes are expensive.
- The high pH associated with lime softening tends to form hypo chlorate as the dominant free chlorine residual, which is less powerful disinfectant than other free chlorine residuals.
- The high pH may also increase tri halomethane levels in the water.
- If the water is not properly stabilized after treatment, then corrosive water may be produced which will corrode the distribution system.
- Ion exchange water softening can also cause problems due to the high levels of sodium in the treated water.
- Both lime softening and ion exchange softening create waste disposal problems.

**2.10. Ion Exchange**

**2.10.1. Classification of Ion Exchange resins**

Ionizable groups attached to the resin bead determine the functional capability of the resin. Industrial water treatment resins are classified into four basic categories:

- Strong Acid Cation (SAC)
- Weak Acid Cation (WAC)
- Strong Base Anion (SBA)
Weak Base Anion (WBA)

SAC resins can neutralize strong bases and convert neutral salts into their corresponding acids. SBA resins can neutralize strong acids and convert neutral salts into their corresponding bases. These resins are utilized in most softening and full demineralization applications. WAC and WBA resins are able to neutralize strong bases and acids, respectively. These resins are used for dealkalization, partial demineralization, or (in combination with strong resins) full demineralization.

SAC resins derive their functionality from sulfonic acid groups ($\text{HSO}_3^-$). When used in demineralization, SAC resins remove nearly all raw water cations, replacing them with hydrogen ions, as shown below:

$$\begin{align*}
\left[ \begin{array}{c}
\text{Ca} \\
\text{Mg} \\
\text{2Na}
\end{array} \right] & \cdot \left[ \begin{array}{c}
\text{2HCO}_3^- \\
\text{SO}_4^- \\
\text{2Cl}^{-}
\end{array} \right] + 2\text{ZSO}_3^- \cdot \text{H} & \iff & 2\text{ZSO}_3^- + \left[ \begin{array}{c}
\text{Ca} \\
\text{Mg} \\
\text{2Na}
\end{array} \right]
\end{align*}$$

The exchange reaction is reversible. When its capacity is exhausted, the resin can be regenerated with an excess of mineral acid.

Strong acid cation exchangers function well at all pH ranges. These resins have found a wide range of applications. For example, they are used in the sodium cycle (sodium as the mobile ion) for softening and in the hydrogen cycle for decationization.

Weak acid cation exchange resins derive their exchange activity from a carboxylic group (-COOH). When operated in the hydrogen form, WAC resins remove cations that are associated with alkalinity, producing carbonic acid as shown:

$$\begin{align*}
\left[ \begin{array}{c}
\text{Ca} \\
\text{Mg} \\
\text{2Na}
\end{array} \right] & \cdot \left( \text{HCO}_3^- \right)_2 + 2\text{ZCOO}^- \cdot \text{H} & \iff & 2\text{ZCOO}^- + \left[ \begin{array}{c}
\text{Ca} \\
\text{Mg} \\
\text{2Na}
\end{array} \right] + 2\text{H}_2\text{CO}_3
\end{align*}$$

These reactions are also reversible and permit the return of the exhausted WAC resin to the regenerated form. WAC resins are not able to remove all of the cations in most water supplies. Their primary asset is their high regeneration efficiency in comparison with SAC resins. This high efficiency reduces the amount of acid required to regenerate the resin, thereby reducing the waste acid and minimizing disposal problems.

Weak acid cation resins are used primarily for softening and dealkalization of high-hardness, high-alkalinity waters, frequently in conjunction with SAC sodium cycle polishing systems. In full demineralization systems, the use of WAC and SAC resins in combination provides the economy of the more efficient WAC resin along with the full exchange capabilities of the SAC resin.
SBA resins derive their functionality from quaternary ammonium functional groups. Two types of quaternary ammonium groups, referred to as Type I and Type II, are used. Type I sites have three methyl groups:

\[
(R \begin{array}c \quad \text{N} \quad \text{CH}_3 \\ \text{CH}_3 \end{array})^+
\]

In a Type II resin one of the methyl groups is replaced with an ethanol group. The Type I resin has a greater stability than the Type II resin and is able to remove more of the weakly ionized acids. Type II resins provide a greater regeneration efficiency and a greater capacity for the same amount of regenerant chemical used.

When in the hydroxide form, SBA resins remove all commonly encountered anions as shown below:

\[
\begin{align*}
\text{H}_2\text{SO}_4 & + 2Z \cdot \text{OH} \implies 2Z \cdot \frac{\text{SO}_4^{2-}}{2\text{Cl}^{-}} + 2\text{H}_2\text{O} \\
\text{2HCl} & \quad \text{2H}_2\text{SiO}_3 \\
\text{2H}_2\text{CO}_3 & \quad 2\text{H}_2\text{CO}_3
\end{align*}
\]

As with the cation resins, these reactions are reversible, allowing for the regeneration of the resin with a strong alkali, such as caustic soda, to return the resin to the hydroxide form.

Weak base resin functionality originates in primary (R-NH₂), secondary (R-NHR'), or tertiary (R-NR''₂) amine groups. WBA resins readily remove sulfuric, nitric, and hydrochloric acids, as represented by the following reaction:

\[
\begin{align*}
\text{H}_2\text{SO}_4 & + 2Z \cdot \text{OH} \implies 2Z \cdot \frac{\text{SO}_4^{2-}}{2\text{Cl}^{-}} + 2\text{H}_2\text{O} \\
\text{2HCl} & \quad \text{2H}_2\text{SiO}_3 \\
\text{2HNO}_3 & \quad 2\text{HNO}_3
\end{align*}
\]

2.10.2. Sodium Zeolite Softening

Sodium zeolite softening is the most widely applied use of ion exchange. In zeolite softening, water containing scale-forming ions, such as calcium and magnesium, passes through a resin bed containing SAC resin in the sodium form. In the resin, the hardness ions are exchanged with the sodium, and the sodium diffuses into the bulk water solution. The hardness-free water, termed soft water, can then be used for low to medium pressure boiler feedwater, reverse osmosis system makeup, some chemical processes, and commercial applications, such as laundries.
Principles of Zeolite Softening

The removal of hardness from water by a zeolite softening process is described by the following reaction:

\[
\begin{align*}
\text{Ca} & \quad \text{Mg} \\
\text{SO}_4 & \quad \text{2Cl} \\
\text{2HCO}_3 & \quad \text{Na}_2 \quad \text{Z} \quad \rightarrow \quad \text{Z} \quad \text{Ca} \\
& \quad \text{Mg} \\
& \quad \text{2Na}_2\text{SO}_4 \\
& \quad \text{2NaCl} \\
& \quad \text{2NaHCO}_3
\end{align*}
\]

Water from a properly operated zeolite softener is nearly free from detectable hardness. However, some small amounts of hardness, known as leakage, are present in the treated water. The level of hardness leakage is dependent on the hardness and sodium level in the influent water and the amount of salt used for regeneration.

Figure is a typical profile of effluent hardness from a zeolite softener during a service cycle.

After final rinse, the softener produces a low, nearly constant level of hardness until the ion exchange resin nears exhaustion. At exhaustion, the effluent hardness increases sharply, and regeneration is required. As illustrated by the softening reactions, SAC resin readily accepts calcium and magnesium ions in exchange for sodium ions. When exhausted resin is regenerated, a high concentration of sodium ions is applied to the resin to replace calcium and magnesium. The resin is treated with a 10% sodium chloride solution, and regeneration proceeds according to the following equation:

\[
\text{Z} \quad \text{Ca} \\
\text{Mg} \quad \text{(concentrated)} \quad + \quad 2\text{NaCl} \quad \rightarrow \quad \text{Na}_2 \quad \text{Z} \quad + \quad \text{Ca} \\
\text{Mg} \quad \text{Cl}_2
\]

During regeneration, a large excess of regenerant (approximately 3 times the amount of calcium and magnesium in the resin) is used. The eluted hardness is removed from the softening unit in the waste brine and by rinsing. After regeneration, small residual amounts of hardness remain in the resin. If resin is allowed to sit in a stagnant vessel of water, some hardness will diffuse into the bulk water. Therefore, at the initiation of flow, the water effluent from a zeolite softener can contain hardness even if it has been regenerated recently. After a few minutes of flow, the hardness is rinsed from the softener, and the treated water is soft. The duration of a service cycle depends on the rate of softener flow, the hardness level in the water, and the amount of salt used for regeneration. Table 8-1 shows the effect of regenerant level on the softening capacity of a gelular strong cation resin. Note that the capacity of the resin increases as the regenerant dosage increases, but the increase is not proportional. The regeneration is less efficient at the higher regenerant levels. Therefore, softener operating costs increase as the regenerant level increases. As shown by the data...
in Table 8-1, a 150% increase in regenerant salt provides only a 67% increase in operating capacity.

**Table.** Effect of regenerate salt level on strong acid cation resin softening capacity.

<table>
<thead>
<tr>
<th>Salt (lb/ft³)</th>
<th>Capacity (gr/ft³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>18,000</td>
</tr>
<tr>
<td>8</td>
<td>20,000</td>
</tr>
<tr>
<td>10</td>
<td>24,000</td>
</tr>
<tr>
<td>15</td>
<td>30,000</td>
</tr>
</tbody>
</table>

**Equipment**
The equipment used for sodium zeolite softening consists of a softener exchange vessel, control valves and piping, and a system for brining, or regenerating, the resin.

![Diagram of softener exchange vessel](image)

Usually, the softener tank is a vertical steel pressure vessel with dished heads as shown in Figure.

Major features of the softening vessel include an inlet distribution system, free-board space, a regenerant distribution system, ion exchange resin, and a resin-retaining underdrain collection system.

The inlet distribution system is usually located at the top of the tank. The inlet system provides even distribution of influent water. This prevents the water from hollowing out flow channels in the resin bed, which would reduce system capacity and effluent quality. The inlet system also acts as a collector for backwash water.

The inlet distributor consists of a central header/hub with distributing laterals/radials or simple baffle plates, which direct the flow of water evenly over the resin bed. If water is not prevented from flowing directly onto the bed or tank walls, channeling will result. The volume between the inlet distributor and the top of the resin bed is called the free-board space. The free-board allows for the expansion of the resin during the backwash portion of the regeneration without loss of resin. It should be a minimum of 50% of the resin volume (80% preferred).
The regenerant distributor is usually a header-lateral system that evenly distributes the regenerant brine during regeneration. The location of the distributor, 6 in. above the top of the resin bed, prevents the dilution of regenerant by water in the free-board space. It also reduces water and time requirements for displacement and fast rinse. The regenerant distributor should be secured to the tank structure to prevent breakage and subsequent channeling of the regenerant.

Water is softened by the bed of strong acid cation exchange resin in the sodium form. The quantity of resin required depends on the water flow, total hardness, and time desired between regeneration cycles. A minimum bed depth of 24 in. is recommended for all systems.

The underdrain system, located at the bottom of the vessel, retains ion exchange resin in the tank, evenly collects the service flow, and evenly distributes the backwash flow. Uneven collection of water in service or uneven distribution of the backwash water can result in channeling, resin fouling, or resin loss.

Although several underdrain designs are used, there are two primary types—subfill and resin-retaining. A subfill system consists of multiple layers of support media (such as graded gravel or anthracite) which support the resin, and a collection system incorporating drilled pipes or subfill strainers. As long as the support layers remain intact, the resin will remain in place. If the supporting media becomes disturbed, usually due to improper backwash, the resin can move through the disrupted layers and exit the vessel. A resin-retaining collector, such as a screened lateral or profile wire strainer, is more expensive than a subfill system but protects against resin loss.

The main valve and piping system directs the flow of water and regenerant to the proper locations. The valve system consists of a valve nest or a single multiport valve. A valve nest includes six main valves: service inlet and outlet, backwash inlet and outlet, regenerant inlet, and regenerant/rinse drain. The valves may be operated manually, or automatically controlled by air, electrical impulse, or water pressure. In some systems, a single multiport valve is used in place of the valve nest. As the valve rotates through a series of fixed positions, ports in the valve direct flow in the same manner as a valve nest. Multiport valves can eliminate operational errors caused by opening of the incorrect valve but must be properly maintained to avoid leaks through the port seals.

The brining system consists of salt dissolving/brine measuring equipment, and dilution control equipment to provide the desired regenerant strength. The dissolving/measuring equipment is designed to provide the correct amount of concentrated brine (approximately 26% NaCl) for each regeneration, without allowing any undissolved salt into the resin. Most systems use a float-operated valve to control the fill and draw-down of the supply tank, thereby controlling the amount of salt used in the regeneration. Usually, the concentrated brine is removed from the tank by means of an eductor system, which also dilutes the brine to the optimum regenerant strength (8-10% NaCl). The brine can also be pumped from the concentrated salt tank and mixed with dilution water to provide the desired regenerant strength.

- **Softener Operation**

A sodium zeolite softener operates through two basic cycles: the service cycle, which produces soft water for use, and the regeneration cycle, which restores resin capacity at exhaustion.
In the service cycle, water enters the softener through the inlet distribution system and flows through the bed. The hardness ions diffuse into the resin and exchange with sodium ions, which return to the bulk water. Soft water is collected in the underdrain system and discharged. Service water flow to the softener should be as constant as possible to prevent sudden surges and frequent on-off operation.

Due to resin requirements and vessel designs, the softening operation is most efficient when a service flow rate between 6 and 12 gpm per square foot of resin surface area is maintained. Most equipment is designed to operate in this range, but some special designs utilize a deep resin bed to permit operation at 15-20 gpm/ft². Continuous operation above the manufacturer's suggested limits can lead to bed compaction, channeling, premature hardness breakthrough, and hardness leakage. Operating well below the manufacturer's recommended flow rates can also negatively affect softener performance. At low flow rates, the water is not sufficiently distributed, and the optimum resin-water contact cannot take place.

When a softener is exhausted, the resin must be regenerated. Monitoring of the effluent hardness reveals resin exhaustion. When hardness increases, the unit is exhausted. Automatic monitors provide a more constant indication of the condition of the softener than periodic operator sampling and testing, but require frequent maintenance to ensure accuracy. Many facilities regenerate softeners before exhaustion, based on a predetermined time period or number of gallons processed.

Most softening systems consist of more than one softener. They are often operated so that one softener is in regeneration or standby while the other units are in service. This ensures an uninterrupted flow of soft water. Prior to placing a standby softener into service, the unit should be rinsed to remove any hardness that has entered the water during the standing time.

**Softener Regeneration**

The regeneration cycle of a sodium zeolite softener consists of four steps: backwash, regeneration (brining), displacement (slow rinse), and fast rinse.

Backwash: During the service cycle, the downward flow of water causes suspended material to accumulate on the resin bed. Resin is an excellent filter and can trap particulate matter that has passed through upstream filtration equipment. The backwash step removes accumulated material and reclassifies the resin bed. In the backwash step, water flows from the under drain distributor up through the resin bed and out the service distributor to waste. The upward flow lifts and expands the resin, allowing for removal of particulate material and resin fines and the classification of the resin. Resin classification brings the smaller beads to the top of the unit while the larger beads settle to the bottom. This enhances the distribution of the regenerant chemical and service water.

Backwashing should continue for a minimum of 10 min or until effluent from the backwash outlet is clear. The backwash flow should be sufficient to expand the resin bed volume by 50% or more, depending on the available free-board. Insufficient backwash can lead to bed fouling and channeling. Excessive backwash flow rates result in the loss of resin. Backwash flow rates usually vary between 4-8 (ambient temperature) and 12-15 (hot service) gpm per square foot of bed area, but each manufacturer's recommendation should be followed. The ability of water to expand the resin is greatly affected by
temperature. Less flow is required to expand the bed with cold water than with warm water. Resin bed expansion should be checked regularly and the flow rate adjusted as needed to maintain proper bed expansion.

Usually, the backwash water is filtered raw water. Water leaving the backwash outlet is unchanged in chemistry but can contain suspended solids. In order to conserve water, the backwash effluent can be returned to the clarifier or filter influent for treatment.

Regeneration (Brining): After backwash, regenerant brine is applied. The brine stream enters the unit through the regenerant distributor and flows down through the resin bed at a slow rate (usually between 0.5 and 1 gpm per square foot of resin). Brine flow is collected through the underdrain and sent to waste. The slow flow rate increases contact between the brine and resin. To achieve optimum efficiency from the brine, the solution strength should be 10% during brine introduction.

Displacement (Slow Rinse): Following the introduction of regenerant brine, a slow flow of water continues through the regenerant distribution system. This water flow displaces the regenerant through the bed at the desired flow rate. The displacement step completes the regeneration of the resin by ensuring proper contact of the regenerant with the bottom of the resin bed. The flow rate for the displacement water is usually the same rate used for the dilution of the concentrated brine. The duration of the displacement step should be sufficient to allow for approximately one resin bed volume of water to pass through the unit. This provides a "plug" of displacement water which gradually moves the brine completely through the bed.

Fast Rinse: After completion of the displacement rinse, water is introduced through the inlet distributor at a high flow rate. This rinse water removes the remaining brine as well as any residual hardness from the resin bed. The fast rinse flow rate is normally between 1.5 and 2 gpm per square foot of resin. Sometimes it is determined by the service rate for the softener.

Initially, the rinse effluent contains large amounts of hardness and sodium chloride. Usually, hardness is rinsed from the softener before excess sodium chloride. In many operations, the softener can be returned to service as soon as the hardness reaches a predetermined level, but some uses require rinsing until the effluent chlorides or conductivity are near influent levels. An effective fast rinse is important to ensure high effluent quality during the service run. If the softener has been in standby following regeneration, a second fast rinse, known as a service rinse, can be used to remove any hardness that has entered the water during standby.

2.10.3. **Hot Zeolite Softening**

Zeolite softeners can be used to remove residual hardness in the effluent from a hot process lime or lime-soda softener. The hot process effluent flows through filters and then through a bed of strong acid cation resin in the sodium form (Figure).
Figure: Hot Zeolite Softening

The equipment and operation of a hot zeolite softener is identical to that of an ambient temperature softener, except that the valves, piping, controllers, and instrumentation must be suitable for the high temperature (220-250°F). Standard strong cation resin can be used at temperatures of up to 270°F, but for a longer service life a premium gel or macrolenticular resin is recommended. When operating a zeolite system following a hot process softener, it is important to design the system to eliminate flow surges in the hot lime unit. Common designs include the use of backwash water storage tanks in the hot lime unit and extended slow rinses for the zeolite in lieu of a standard fast rinse.

Applications and Advantages

Scale and deposit buildup in boilers and the formation of insoluble soap curds in washing operations have created a large demand for softened water. Because sodium zeolite softeners are able to satisfy this demand economically, they are widely used in the preparation of water for low and medium pressure boilers, laundries, and chemical processes. Sodium zeolite softening also offers the following advantages over other softening methods:

- treated water has a very low scaling tendency because zeolite softening reduces the hardness level of most water supplies to less than 2 ppm
- operation is simple and reliable; automatic and semiautomatic regeneration controls are available at a reasonable cost
- salt is inexpensive and easy to handle
- no waste sludge is produced; usually, waste disposal is not a problem
- within certain limits, variations in water flow rate have little effect on treated water quality
- because efficient operation can be obtained in units of almost any size, sodium zeolite softeners are suitable for both large and small installations

Limitations
Although sodium zeolite softeners efficiently reduce the amount of dissolved hardness in a water supply, the total solids content, alkalinity, and silica in the water remain unaffected. A sodium zeolite softener is not a direct replacement for a hot lime-soda softener. Plants that have replaced their hot process softeners with only zeolite softeners have experienced problems with silica and alkalinity levels in their boilers.

Because the resin is such an efficient filter, sodium zeolite softeners do not function efficiently on turbid waters. Continued operation with an influent turbidity in excess of 1.0 JTU causes bed fouling, short service runs, and poor effluent quality. Most city and well waters are suitable, but many surface supplies must be clarified and filtered before use.

The resin can be fouled by heavy metal contaminants, such as iron and aluminum, which are not removed during the course of a normal regeneration. If excess iron or manganese is present in the water supply, the resin must be cleaned periodically. Whenever aluminum coagulants are used ahead of zeolite softeners, proper equipment operation and close control of clarifier pH are essential to good softener performance.

Strong oxidizing agents in the raw water attack and degrade the resin. Chlorine, present in most municipal supplies, is a strong oxidant and should be removed prior to zeolite softening by activated carbon filtration or reaction with sodium sulfite.

### 2.10.4 Demineralization

Softening alone is insufficient for most high-pressure boiler feedwaters and for many process streams, especially those used in the manufacture of electronics equipment. In addition to the removal of hardness, these processes require removal of all dissolved solids, such as sodium, silica, alkalinity, and the mineral anions (Cl\(^{-}\), SO\(_4^{2-}\), NO\(_3^{-}\)).

Demineralization of water is the removal of essentially all inorganic salts by ion exchange. In this process, strong acid cation resin in the hydrogen form converts dissolved salts into their corresponding acids, and strong base anion resin in the hydroxide form removes these acids. Demineralization produces water similar in quality to distillation at a lower cost for most fresh waters.

#### Principles of Demineralization

A demineralizer system consists of one or more ion exchange resin columns, which include a strong acid cation unit and a strong base anion unit. The cation resin exchanges hydrogen for the raw water cations as shown by the following reactions:

\[
\begin{align*}
\left[ \begin{array}{c} \text{Ca} \\ \text{Mg} \\ \text{2Na}
\end{array} \right] 
& \cdot \left[ \begin{array}{c} 2\text{HCO}_3^- \\ \text{SO}_4^{2-} \\ 2\text{Cl}^- \\ 2\text{NO}_3^-
\end{array} \right] 
+ 2\text{Z} \cdot \text{H} 
\rightarrow 
2\text{Z} \cdot \left[ \begin{array}{c} \text{Ca} \\ \text{Mg} \\ \text{2Na}
\end{array} \right] 
+ \left[ \begin{array}{c} 2\text{H}_2\text{CO}_3^- \\ \text{H}_2\text{SO}_4 \\ 2\text{HCl} \\ 2\text{HNO}_3
\end{array} \right]
\end{align*}
\]
A measure of the total concentration of the strong acids in the cation effluent is the free mineral acidity (FMA).

In a typical service run, the FMA content is stable most of the time, as shown in Figure.

If cation exchange were 100% efficient, the FMA from the exchanger would be equal to the theoretical mineral acidity (TMA) of the water. The FMA is usually slightly lower than the TMA because a small amount of sodium leaks through the cation exchanger. The amount of sodium leakage depends on the regenerant level, the flow rate, and the proportion of sodium to the other cations in the raw water. In general, sodium leakage increases as the ratio of sodium to total cations increases.

As a cation exchange unit nears exhaustion, FMA in the effluent drops sharply, indicating that the exchanger should be removed from service. At this time the resin should be regenerated with an acid solution, which returns the exchange sites to the hydrogen form. Sulfuric acid is normally used due to its affordable cost and its availability. However, improper use of sulfuric acid can cause irreversible fouling of the resin with calcium sulfate.

To prevent this occurrence, the sulfuric acid is usually applied at a high flow rate (1 gpm per square foot of resin) and an initial concentration of 2% or less. The acid concentration is gradually increased to 6-8% to complete regeneration.

Some installations use hydrochloric acid for regeneration. This necessitates the use of special materials of construction in the regenerant system. As with a sodium zeolite unit, an excess of regenerant (sulfuric or hydrochloric acid) is required up to three times the theoretical dose.

To complete the demineralization process, water from the cation unit is passed through a strong base anion exchange resin in the hydroxide form. The resin exchanges hydrogen ions for both highly ionized mineral ions and the more weakly ionized carbonic and silicic acids, as shown below:

\[
\begin{align*}
\left[ \text{H}_2\text{SO}_4 \right] + 2\text{Z} \cdot \text{OH} & \rightleftharpoons 2\text{Z} \cdot \left[ \text{SO}_4^{2-} \right] + 2\text{H}_2\text{O} \\
2\text{HCl} & \\
2\text{H}_2\text{SiO}_3 & \\
2\text{H}_2\text{CO}_3 & \\
2\text{HNO}_3 &
\end{align*}
\]
The above reactions indicate that demineralization completely removes the cations and anions from the water. In reality, because ion exchange reactions are equilibrium reactions, some leakage occurs. Most leakage from cation units is sodium. This sodium leakage is converted to sodium hydroxide in the anion units. Therefore, the effluent pH of a two bed cation-anion demineralizer system is slightly alkaline. The caustic produced in the anions causes a small amount of silica leakage. The extent of leakage from the anions depends on the chemistry of the water being processed and the regenerant dosage being used.

Demineralization using strong anion resins removes silica as well as other dissolved solids. Effluent silica and conductivity are important parameters to monitor during a demineralizer service run.

Both silica and conductivity are low at the end of the fast rinse, as shown in Figure.

When silica breakthrough occurs at the end of a service run, the treated water silica level increases sharply. Often, the conductivity of the water decreases momentarily, then rises rapidly. This temporary drop in conductivity is easily explained. During the normal service run, most of the effluent conductivity is attributed to the small level of sodium hydroxide produced in the anion exchanger. When silica breakthrough occurs, the hydroxide is no longer available, and the sodium from the cation exchanger is converted to sodium silicate, which is much less conductive than sodium hydroxide. As anion resin exhaustion progresses, the more conductive mineral ions break through, causing a subsequent increase in conductivity.

When the end of a demineralizer run is detected, the unit must be removed from service immediately. If the demineralizer is allowed to remain in service past the breakpoint, the level of silica in the treated water can rise above that of the influent water, due to the concentrating of silica that takes place in the anion resin during the service run.

Strong base anion exchangers are regenerated with a 4% sodium hydroxide solution. As with cation regeneration, the relatively high concentration of hydroxide drives the regeneration reaction. To improve the removal of silica from the resin bed, the regenerant caustic is usually heated to 120°F or to the temperature specified by the resin manufacturer. Silica removal is also enhanced by a resin bed preheat step before the introduction of warm caustic.
Equipment and Operation

The equipment used for cation-anion demineralization is similar to that used in zeolite softening. The primary difference is that the vessels, valves, and piping must be made of (or lined with) corrosion-resistant materials. Rubber and polyvinyl chloride (PVC) are commonly used for ion exchange vessel linings. The controls and regenerant systems for demineralizers are more complex, to allow for such enhancements as stepwise acid and warm caustic regenerations.

Demineralizers are similar in operation to zeolite softeners. The service flow rate guidelines for a demineralizer range from 6 to 10 gpm per square foot of resin. Flow rates of over 10 gpm per square foot of resin cause increased sodium and silica leakage with certain waters. Anion resin is much lighter than cation resin. Therefore, the backwash flow rates for anion exchange resins are much lower than those for cation resins, and anion resin expansion is affected by the temperature of the water more than cation resin expansion. The water used for each step of anion resin regeneration should be free from hardness, to prevent precipitation of hardness salts in the alkaline anion resin bed.

Continuous conductivity instruments and silica analyzers are commonly used to monitor anion effluent water quality and detect the need for regeneration. In some instances, conductivity probes are placed in the resin bed above the underdrain collectors to detect resin exhaustion before silica breakthrough into the treated water occurs.

Advantages and Limitations

Demineralizers can produce high-purity water for nearly every use. Demineralized water is widely used for high pressure boiler feedwater and for many process waters. The quality of water produced is comparable to distilled water, usually at a fraction of the cost. Demineralizers come in a wide variety of sizes. Systems range from laboratory columns that produce only a few gallons per hour to systems that produce thousands of gallons per minute.

Like other ion exchange systems, demineralizers require filtered water in order to function efficiently. Resin foulants and degrading agents, such as iron and chlorine, should be avoided or removed prior to demineralization. Anion resins are very susceptible to fouling and attack from the organic materials present in many surface water supplies. Some forms of silica, known as colloidal, or non-reactive, are not removed by a demineralizer. Hot, alkaline boiler water dissolves the colloidal material, forming simple silicates that are similar to those that enter the boiler in a soluble form. As such, they can form deposits on tube surfaces and volatilize into the steam.

2.10.5. Dealkalization

Often, boiler or process operating conditions require the removal of hardness and the reduction of alkalinity but not the removal of the other solids. Zeolite softening does not reduce alkalinity, and demineralization is too costly. For these situations, a dealkalization
process is used. Sodium zeolite/hydrogen zeolite (split stream) dealkalization, chloride-anion dealkalization, and weak acid cation dealkalization are the most frequently used processes.

**Sodium Zeolite/Hydrogen Zeolite (Split Stream) Dealkalization**

In a split stream dealkalizer, a portion of the raw water flows through a sodium zeolite softener. The remainder flows through a hydrogen-form strong acid cation unit (hydrogen zeolite). The effluent from the sodium zeolite is combined with the hydrogen zeolite effluent. The effluent from the hydrogen zeolite unit contains carbonic acid, produced from the raw water alkalinity, and free mineral acids. When the two streams are combined, free mineral acidity in the hydrogen zeolite effluent converts sodium carbonate and bicarbonate alkalinity in the sodium zeolite effluent to carbonic acid as shown below:

\[
2\text{NaHCO}_3 + \begin{cases} 2\text{HCl} \\ \text{H}_2\text{SO}_4 \\ 2\text{HNO}_3 \end{cases} \rightarrow \begin{cases} 2\text{NaCl} \\ \text{Na}_2\text{SO}_4 \\ 2\text{NaNO}_3 \end{cases} + 2\text{H}_2\text{CO}_3
\]

Carbonic acid is unstable in water. It forms carbon dioxide gas and water. The blended effluents are sent to a decarbonator or degasser, where the carbon dioxide is stripped from the water by a countercurrent stream of air.

**Figure shows a typical split stream dealkalization system.**

The desired level of blended water alkalinity can be maintained through control of the percentage of sodium zeolite and hydrogen zeolite water in the mixture. A higher percentage of sodium zeolite water results in higher alkalinity, and an increased percentage of hydrogen zeolite water reduces alkalinity.

In addition to reducing alkalinity, a split stream dealkalizer reduces the total dissolved solids of the water. This is important in high alkalinity waters, because the conductivity of these waters affects the process and can limit boiler cycles of concentration.
Strong base anion resin in the chloride form can be used to reduce the alkalinity of a water. Water flows through a zeolite softener and then an anion unit, which replaces the carbonate, bicarbonate, sulfate, and nitrate ions with chloride ions as shown in these reactions:

\[
\begin{align*}
&\text{Na}_2\text{SO}_4 \\
&2\text{NaHCO}_3 \\
&2\text{NaCO}_3 \\
&2\text{NaNO}_3
\end{align*}
\]

\[
\rightarrow 2\text{Z} \cdot \text{Cl} \rightarrow 2\text{NaCl} + 2\text{Z} \cdot \begin{align*}
&\text{SO}_4 \\
&2\text{HCO}_3 \\
&2\text{NO}_3
\end{align*}
\]

The chloride anion dealkalizer reduces alkalinity by approximately 90% but does not reduce total solids. When the resin nears exhaustion, treated water alkalinity increases rapidly, signaling the need for regeneration.

The zeolite softener is regenerated as previously described. In addition, the anion resin is also regenerated with sodium chloride brine that returns the resin to the chloride form. Frequently, a small amount of caustic soda is added to the regenerate brine to enhance alkalinity removal.

Weak Acid Cation Dealkalization

Another method of dealkalization uses weak acid cation resins. Weak acid resins are similar in operation to strong acid cation resins, but only exchange for cations that are associated with alkalinity, as shown by these reactions:

\[
\begin{align*}
&\text{Ca} \\
&\text{Mg} \\
&2\text{Na}
\end{align*}
\] \cdot 2\text{HCO}_3 + 2\text{Z} \cdot \text{H} \rightarrow 2\text{Z} \cdot \begin{align*}
&\text{Ca} \\
&\text{Mg} \\
&2\text{Na}
\end{align*} + 2\text{H}_2\text{CO}_3
\]

where Z represents the resin. The carbonic acid (H$_2$CO$_3$) formed is removed by a decarbonator or degasser as in a split stream system.

The ideal influent for a weak acid cation system has a hardness level equal to the alkalinity (both expressed in ppm as CaCO$_3$). In waters that are higher in alkalinity than hardness, the alkalinity is not removed to its lowest level. In waters containing more hardness than alkalinity, some hardness remains after treatment. Usually, these waters must be polished by a sodium zeolite softener to remove hardness. During the initial portion of a weak acid cation service run (the first 40-60%) some cations associated with mineral anions exchange, producing small amounts of mineral acids in the effluent. As the service cycle progresses, alkalinity appears in the effluent. When the alkalinity in the effluent exceeds 10% of the influent alkalinity, the unit is removed from service and regenerated with a 0.5% sulfuric acid solution. The concentration of regenerant acid should be kept below 0.5-0.7%, to prevent calcium sulfate precipitation in the resin. Weak acid cation resin exchange is very efficient. Therefore, the amount of acid required is virtually equal (chemically) to the amount of cations removed during the service cycle.
If the materials of construction for the down-stream equipment or overall process cannot tolerate the mineral acidity present during the initial portions of the service cycle, a brine solution is passed through the regenerated weak acid resin prior to the final rinse. This solution removes the mineral acidity without a significant impact on the quality or length of the subsequent run.

Equipment used for a weak acid cation dealkalizer is similar to that used for a strong acid cation exchanger, with the exception of the resin. One variation of the standard design uses a layer of weak acid resin on top of strong acid cation resin. Because it is lighter, the weak acid resin remains on top. The layered resin system is regenerated with sulfuric acid and then with sodium chloride brine. The brine solution converts the strong acid resin to the sodium form. This resin then acts as a polishing softener.

- **Direct Acid Injection**

In the process of direct acid injection and decarbonation, acid is used to convert alkalinity to carbonic acid. The carbonic acid dissociates to form carbon dioxide and water and the carbon dioxide is removed in a decarbonator. The use of an acid injection system should be approached with caution, because an acid overfeed or a breakdown in the pH control system can produce acidic feedwater, which corrodes the iron surfaces of feedwater systems and boilers. Proper pH monitoring and controlled caustic feed after decarbonation are required.

- **Advantages and Limitations of Dealkalization Systems**

Ion exchange dealkalization systems produce hardness-free, low-alkalinity water at a reasonable cost, and with a high degree of reliability. They are well suited for processing feedwater for medium-pressure boilers, and for process water for the beverage industry. Split stream and weak acid cation systems also reduce the total dissolved solids. In addition to these advantages, the following disadvantages must be considered:

  - dealkalizers do not remove all of the alkalinity and do not affect the silica content of a water
  - dealkalizers require the same influent purity as other ion exchange processes; filtered water that is low in potential foulants must be used
  - the water produced by a dealkalization system using a forced draft decarbonator becomes saturated with oxygen, so it is potentially corrosive
2.10.6. Other Demineralization Processes

The standard cation-anion process has been modified in many systems to reduce the use of costly regenerants and the production of waste. Modifications include the use of decarbonators and degassers, weak acid and weak base resins, strong base anion caustic waste (to regenerate weak base anion exchangers), and reclamation of a portion of spent caustic for subsequent regeneration cycles.

Several different approaches to demineralization using these processes are shown in Figure.

- **Decarbonators and Degassers**
  Decarbonators and degassers are economically beneficial to many demineralization systems, because they reduce the amount of caustic required for regeneration. Water from a cation exchanger is broken into small droplets by sprays and trays or packing in a decarbonator. The water then flows through a stream of air flowing in the opposite direction. Carbonic acid present in the cation effluent dissociates into carbon dioxide and water. The carbon dioxide is stripped from the water by the air, reducing the load to the anion exchangers. Typical forced draft decarbonators are capable of removing carbon dioxide down to 10-15 ppm. However, water effluent from a decarbonator is saturated with oxygen.

  In a vacuum degasser, water droplets are introduced into a packed column that is operated under a vacuum. Carbon dioxide is removed from the water due to its decreased partial pressure in a vacuum. A vacuum degasser usually reduces carbon dioxide to less...
than 2 ppm and also removes most of the oxygen from the water. However, vacuum degassers are more expensive to purchase and operate than forced draft decarbonators.

- **Weak Acid and Weak Base Resins**
  Weak functionality resins have a much higher regeneration efficiency than their strong functionality counterparts. Weak acid cation resins, as described in the dealkalization section, exchange with cations associated with alkalinity. Weak base resins exchange with the mineral acid anions (SO₄²⁻, Cl⁻, NO₃⁻) in a strong acid solution. The regeneration efficiency of weak resins is virtually stoichiometric, the removal of 1 kg of ions (as CaCO₃) requires only slightly more than 1 kg of the regenerant ion (as CaCO₃). Strong resins require three to four times the regenerant for the same contaminant removal.
  Weak base resins are so efficient that it is common practice to regenerate a weak base exchanger with a portion of the "spent" caustic from regeneration of the strong base anion resin. The first fraction of the caustic from the strong base unit is sent to waste to prevent silica fouling of the weak base resin. The remaining caustic is used to regenerate the weak base resin. An additional feature of weak base resins is their ability to hold natural organic materials that foul strong base resins and release them during the regeneration cycle. Due to this ability, weak base resins are commonly used to protect strong base resins from harmful organic fouling.

- **Regenerant Reuse**
  Due to the high cost of caustic soda and the increasing problems of waste disposal, many demineralization systems are now equipped with a caustic reclaim feature. The reclaim system uses a portion of the spent caustic from the previous regeneration at the beginning of the next regeneration cycle. The reused caustic is followed by fresh caustic to complete the regeneration. The new caustic is then reclaimed for use in the next regeneration. Typically, sulfuric acid is not reclaimed, because it is lower in cost and calcium sulfate precipitation is a potential problem.

### 2.10.7. Common Ion Exchange System Problems

As in any dynamic operating system incorporating electrical and mechanical equipment and chemical operations, problems do occur in ion exchange systems. The problems usually result in poor effluent quality, decreased service run lengths, or increased consumption of regenerant. To keep the ion exchange system operating efficiently and reliably, changes in water quality, run lengths, or regenerant consumption should be considered whenever problems are detected.
Show that there are many possible causes for reduced performance of a demineralization system. Some of the more common problems are discussed below.

**Operational Problems**
Changes in raw water quality have a significant impact on both the run length and the effluent quality produced by an ion exchange unit. Although most well waters have a consistent quality, most surface water compositions vary widely over time. A 10% increase in the hardness of the water to a sodium zeolite softener causes a 10% decrease in the service run length. An increase in the ratio of sodium to total cations causes increased sodium leakage from a demineralizer system. Regular chemical analysis of the influent water to ion exchangers should be performed to reveal such variations.

Other causes of ion exchange operational problems include:

- Improper regenerations, caused by incorrect regenerant flows, times, or concentrations. Manufacturer’s recommendations should be followed when regenerating ion exchange resins.
• Channeling, resulting from either high or low flow rates, increased suspended solids loading or poor backwashing. This causes premature exhaustion even when much of the bed is in a regenerated state.
• Resin fouling or degradation, caused by poor-quality regenerant.
• Failure to remove silica from the resin, which can result from low regenerant caustic temperature. This can lead to increased silica leakage and short service runs.
• Excess contaminants in the resin, due to previous operation past exhaustion loads. Because the resin becomes loaded with more contaminants than a normal regeneration is designed to remove, a double regeneration is required following an extended service run.

➢ Mechanical Problems

Typical mechanical problems associated with ion exchange systems include:

• Leaking valves, which cause poor quality effluent and prolonged rinses.
• Broken or clogged distributor, which leads to channeling.
• Resin loss, due to excessive backwashing or failure in the under drain screening or support media.
• Cation resin in the anion unit, causing extended rinse times and sodium leakage into the demineralized water.
• Instrumentation problems, such as faulty tantalizers or conductivity meters, which may indicate a problem when none exists, or may introduce poor quality water to service. Instrumentation in the demineralizer area should be checked regularly.

2.11. Resin Fouling and Degradation

Resin can become fouled with contaminants that hinder the exchange process.

![Figure: Shows a resin fouled with iron.](image)
The resin can also be attacked by chemicals that cause irreversible destruction.

![Figure: Natural Organics of resin foul](image)

Some materials, such as natural organics (Figure), foul resins at first and then degrade the resin as time passes.

This is the most common cause of fouling and degradation in ion exchange systems, and is discussed under "Organic Fouling," later in this chapter.

### Causes of Resin Fouling

**Iron and Manganese.** Iron may exist in water as a ferrous or ferric inorganic salt or as a sequestered organic complex. Ferrous iron exchanges in resin, but ferric iron is insoluble and does not. Ferric iron coats cation resin, preventing exchange. An acid or a strong reducing agent must be used to remove this iron. Organically bound iron passes through a cation unit and fouls the anion resin. It must be removed along with the organic material. Manganese, present in some well waters, fouls a resin in the same manner as iron.

**Aluminum.** Aluminum is usually present as aluminum hydroxide, resulting from alum or sodium aluminate use in clarification or precipitation softening. Aluminum floc, if carried through filters, coats the resin in a sodium zeolite softener. It is removed by cleaning with either acid or caustic. Usually, aluminum is not a foulant in a demineralizer system, because it is removed from the resin during a normal regeneration.

**Hardness Precipitates.** Hardness precipitates carry through a filter from a precipitation softener or form after filtration by post-precipitation. These precipitates foul resins used for sodium zeolite softening. They are removed with acid.

Sulfate Precipitation. Calcium sulfate precipitation can occur in a strong acid cation unit operated in the hydrogen cycle. At the end of a service cycle, the top of the resin bed is rich in calcium. If sulfuric acid is used as the regenerant, and it is introduced at too high a concentration or too low a flow rate, precipitation of calcium sulfate occurs, fouling the resin. After calcium sulfate has formed, it is very difficult to redissolve; therefore, resin fouled by calcium sulfate is usually discarded. Mild cases of calcium sulfate fouling may be reversed with a prolonged soak in hydrochloric acid.

Barium sulfate is even less soluble than calcium sulfate. If a water source contains measurable amounts of barium, hydrochloric acid regeneration should be considered.
**Oil Fouling.** Oil coats resin, blocking the passage of ions to and from exchange sites. A surfactant can be used to remove oil. Care must be exercised to select a surfactant that does not foul resin. Oil-fouled anion resins should be cleaned with nonionic surfactants only.

Microbiological Fouling. Microbiological fouling can occur in resin beds, especially beds that are allowed to sit without service flow. Microbiological fouling can lead to severe plugging of the resin bed, and even mechanical damage due to an excessive pressure drop across the fouled resin. If microbiological fouling in standby units is a problem, a constant flow of recirculating water should be used to minimize the problem. Severe conditions may require the application of suitable sterilization agents and surfactants.

**Silica Fouling.** Silica fouling can occur in strong base anion resins if the regenerant temperature is too low, or in weak base resins if the effluent caustic from the SBA unit used to regenerate the weak base unit contains too much silica. At low pH levels, polymerization of the silica can occur in a weak base resin. It can also be a problem in an exhausted strong base anion resin. Silica fouling is removed by a prolonged soak in warm (120°F) caustic soda.

- **Causes of Irreversible Resin Degradation**

**Oxidation.** Oxidizing agents, such as chlorine, degrade both cation and anion resins. Oxidants attack the divinylbenzene cross-links in a cation resin, reducing the overall strength of the resin bead. As the attack continues, the cation resin begins to lose its spherical shape and rigidity, causing it to compact during service. This compaction increases the pressure drop across the resin bed and leads to channeling, which reduces the effective capacity of the unit.

In the case of raw water chlorine, the anion resin is not directly affected, because the chlorine is consumed by the cation resin. However, downstream strong base anion resins are fouled by certain degradation products from oxidized cation resin.

If chlorine is present in raw water, it should be removed prior to ion exchange with activated carbon filtration or sodium sulfite. Approximately 1.8 ppm of sodium sulfite is required to consume 1 ppm of chlorine.

Oxygen-saturated water, such as that found following forced draft decarbonation, accelerates the destruction of strong base exchange sites that occurs naturally over time. It also accelerates degradation due to organic fouling.

**Thermal Degradation.** Thermal degradation occurs if the anion resin becomes overheated during the service or regeneration cycle. This is especially true for acrylic resins, which have temperature limitations as low as 100°F, and Type II strong base anion resins, which have a temperature limit of 105°F when in the hydroxide form.
Organic Fouling

Organic fouling is the most common and expensive form of resin fouling and degradation. Usually, only low levels of organic materials are found in well waters. However, surface waters can contain hundreds of parts per million of natural and man-made organic matter. Natural organics are derived from decaying vegetation. They are aromatic and acidic in nature, and can complex heavy metals, such as iron. These contaminants include tannins, tannic acid, humic acid, and folic acid.

Initially, organics block the strong base sites on a resin. This blockage causes long final rinses and reduces salt splitting capacity. As the foulant continues to remain on the resin, it begins to degrade the strong base sites, reducing the salt splitting capacity of the resin. The functionality of the site changes from strong base to weak base, and finally to a nonactive site. Thus, a resin in the early stages of degradation exhibits high total capacity, but reduced salt splitting capacity. At this stage, cleaning of the resin can still return some, but not all, of the lost operating capacity. A loss in salt splitting capacity reduces the ability of the resin to remove silica and carbonic acid.

Organic fouling of anion resin is evidenced by the color of the effluent from the anion unit during regeneration, which ranges from tea-colored to dark brown. During operation, the treated water has higher conductivity and a lower pH.

Prevention: The following methods are used, either alone or in combination, to reduce organic fouling:

- Prechlorination and clarification. Water is prechlorinated at the source, and then clarified with an organic removal aid.
- Filtration through activated carbon. It should be noted that a carbon filter has a finite capacity for removal of organic material and that the removal performance of the carbon should be monitored frequently.
- Macroporous and weak base resin ahead of strong base resin. The weak base or macroporous resin absorbs the organic material and is eluted during regeneration.
- Specialty resins. Acrylic and other specialty resins that are less susceptible to organic fouling have been developed.

Inspection and Cleaning. In addition to these preventive procedures, a program of regular inspection and cleaning of the ion exchange system helps to preserve the life of anion resin. Most cleaning procedures use one of the following:

- Warm (120°F) brine and caustic. Mild oxidants or solubilizing agents can be added to improve the cleaning.
- Hydrochloric acid. When resins are also fouled with significant amounts of iron, hydrochloric acids are used.
- Solutions of 0.25-0.5% sodium hypochlorite. This procedure destroys the organic material but also significantly degrades the resin. Hypochlorite cleaning is considered a last resort.
It is important to clean an organically fouled resin before excessive permanent degradation of the strong base sites occurs. Cleaning after permanent degradation has occurred removes significant amounts of organic material but does not improve unit performance. The condition of the resin should be closely monitored to identify the optimum schedule for cleaning.

2.12. Resin Testing and Analysis
To track the condition of ion exchange resin and determine the best time for cleaning it, the resin should be periodically sampled and analyzed for physical stability, foulant levels, and the ability to perform the required ion exchange. Samples should be representative of the entire resin bed. Therefore, samples should be collected at different levels within the bed, or a grain thief or hollow pipe should be used to obtain a "core" sample. During sampling, the inlet and regenerant distributor should be examined, and the condition of the top of the resin bed should be noted. Excessive hills or valleys in the resin bed are an indication of flow distribution problems. The resin sample should be examined microscopically for signs of fouling and cracked or broken beads. The level of organic and inorganic foulants in the resin should be determined and compared to known standards and the previous condition of the resin. Finally, the salt splitting and total capacity should be measured on anion resin samples to evaluate the rate of degradation or organic fouling.

Expression of Analytic Results:

- **Parts per million**

  Water analysis involves the detection of minute amounts of a variety of substances. The expression of results in percentage would require the use of cumbersome figures. For this reason, the results of a water analysis are usually expressed in parts per million (ppm) instead of percentage. One part per million equals one ten-thousandth of one percent (0.0001%), or one part (by weight) in a million parts—for example, 1 oz in 1,000,000 oz of water, or 1 lb in 1,000,000 lb of water. It makes no difference what units are used as long as both weights are expressed in the same units.

  When elements are present in minute or trace quantities, the use of parts per million results in small decimal values. Therefore, it is more convenient to use parts per billion (ppb) in these cases. One part per billion is equal to one-thousandth of one part per million (0.001 ppm). For example, in studies of steam purity using a specific ion electrode to measure sodium content, values as low as 0.001 ppm are not uncommon. This is more conveniently reported as 1.0 ppb.

  In recent times, the convention for reporting analytical results has been shifting toward the use of milligrams per liter (mg/L) as a replacement for parts per million and micrograms per liter (µg/L) as a replacement for parts per billion.
Test procedures and calculations of results are based on the milliliter (mL) rather than the more common cubic centimeter (cc or cm³). The distinction between the two terms is very slight. By definition, a milliliter is the volume occupied by 1 g of water at 4°C, whereas a cubic centimeter is the volume enclosed within a cube 1 cm on each edge (1 mL = 1.000028 cm³).

- **Milligrams per litre**

  The milligrams per liter (mg/L) convention is closely related to parts per million (ppm). This relationship is given by:

  \[
  \text{ppm} \times \text{solution density} = \text{mg/L}
  \]

  Thus, if the solution density is close or equal to 1, then ppm = mg/L. This is normally the case in dilute, aqueous solutions of the type typically found in industrial water systems. Control testing is usually conducted without measurement of a solution's density. For common water samples, this poses no great inaccuracy, because the density of the sample is approximately 1. Milligrams per liter (mg/L) and parts per million (ppm) begin to diverge as the solution density varies from 1. Examples of this are a dense sludge from a clarifier underflow (density greater than 1) or closed cooling system water with high concentrations of organic compounds (density less than 1). All of the analytical methods discussed in this text contain calculations required to obtain the results in milligrams or micrograms per liter.

- **Equivalents per million**

  In reporting water analyses on an ion basis, results are also expressed in equivalents per million (epm). Closely allied to the use of parts per million, this approach reduces all constituents to a common denominator—the chemical equivalent weight.

  The use of equivalents per million is not recommended for normal plant control. Parts per million is a simpler form of expressing results and is accepted as the common standard basis of reporting a water analysis. However, whenever extensive calculations must be performed, the use of equivalents per million greatly simplifies the mathematics, because all constituents are on a chemical equivalent weight basis. The remainder of this section provides a discussion of parts per million and equivalents per million for those who desire a working knowledge of these methods of expression for purposes of calculations.

  The units of ppm and epm are commonly combined in normal reporting of water analyses, and many different constituents are frequently reported on a common unit weight basis. For example, calcium (equivalent weight 20.0) is reported in terms of "calcium as CaCO₃" (equivalent weight 50.0). The test for calcium is calibrated in terms of CaCO₃, so the conversion factor 2.5 (50/20) is not needed. Hardness,
magnesium, alkalinity, and free mineral acid are often reported in terms of CaCO3; the value reported is the weight of CaCO3 that is chemically equivalent to the amount of material present. Among these substances, ionic balances may be calculated. When constituents are of the same unit weight basis, they can be added or subtracted directly. For example, ppm total hardness as CaCO3 minus ppm calcium as CaCO3 equals ppm magnesium as CaCO3. However, ppm magnesium as Mg$^{2+}$ equals 12.2 (magnesium equivalent weight) divided by 50.0 (CaCO3 equivalent weight) times the ppm magnesium as CaCO3.

In every case, it is necessary to define the unit weight basis of the results—"ppm alkalinity as CaCO3" or "ppm sulfate as SO$_4^{2-}$" or "ppm silica as SiO$_2$". Where the unit weight basis is different, calculations must be based on the use of chemical equations.

The following rules outline where ppm can be used and where epm must be used. In general, either may be used where an exact chemical formula is known. When such knowledge is lacking, ppm must be used.

- The concentration of all dissolved salts of the individually determined ions must be in ppm.
- Two or more ions of similar properties whose joint effect is measured by a single determination (e.g., total hardness, acidity, or alkalinity) may be reported in either ppm or epm.
- The concentration of undissolved or suspended solids should be reported in ppm only.
- The concentration of organic matter should be reported in ppm only.
- The concentration of dissolved solids (by evaporation) should be expressed as ppm only.
- Total dissolved solids by calculation may be expressed in either ppm or epm.
- Concentration of individual gases dissolved in water should be reported in ppm. The total concentration of each gas when combined in water may be calculated to its respective ionic concentration in either ppm or epm.

### 2.13. Problems caused by Hard Water in Textile Industry

Hard water can create so many problems during wet processing from desizing to finishing in textile mills. Since every process is related to the next process, so all processes should be done precisely to get best result. To do it first we have to know what problems hard water can create in different stage of wet processing.

**In Boiler:** If hard water is used in boiler, then a layer is formed on the inner surface of the vessel or in the inner side of tube. This layer is very hard just like as stone which is not removed without hammer or chaser or tassel. This is called scale. In boiler, temporary hard water produce CaCO$_3$ & Mg(OH)$_2$, the combination of CaCO$_3$ & Mg(OH)$_2$ is called scale.
Ca (HCO3)2 --> CaCO3 + CO2 + H2O  
Mg (HCO3)2 --> Mg CO3 + CO2 + H2O  
MgCO3 + H2O --> Mg (OH)2 + CO2  
[CaCO3 + Mg (OH)2 ] --> Scale.

As a result, in boiler more heat will be needed & for that, more fuel will be required. For scale formation, equally heat transformation in boiler tube is not possible very often. As a result, for excess heat of a particular part of the tube, the tube may burst.

Heat loss of tube up to 40% according to the diameter of the tube. Heat loss by pipe scaling up to 40% for 20 mm scale.

<table>
<thead>
<tr>
<th>SCALE THICKNESS</th>
<th>HEAT LOSS</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 mm</td>
<td>approximately 10%</td>
</tr>
<tr>
<td>3 mm</td>
<td>17%</td>
</tr>
<tr>
<td>5 mm</td>
<td>22%</td>
</tr>
<tr>
<td>10 mm</td>
<td>30%</td>
</tr>
<tr>
<td>20 mm</td>
<td>43%</td>
</tr>
</tbody>
</table>

Corrosion can be a serious problem in boiler, if hard water is used in it. Dissolved O2 in the presence of CO2 is the common cause of corrosion. Fe present in hard water reacts with CO2 to form Fe CO3, which is the main process of corrosion. This Fe CO3 is hydrolyzed & produce Fe(OH)2, this agent / component damage the boiler.

Fe + H2O + CO2 --> Fe CO3 + H2O  
Fe CO3 + H2O     --> Fe(OH)2 + CO2

Desizing: Hard water de-active enzymes & insolubilize size materials such as starch, PVA etc.

Scouring: Hard react with soap during scouring. Soap is the Na & K salt of higher fatty acid (C17H35COONa). The Hard water does not easily form lather by reacting with soap. The Ca & Mg salt of hard water react with soap and produce insoluble organic salts which becomes the wastage of soap.

CaSO4 + 2 C17H35COONa --> (C17H35COO)2Ca + Na2SO4  
Insoluble organic salt

If we use hard water in wet processing, then they produce insoluble salt which is deposited with the fabric. As a result, the surface of scoured fabric become harsh, hard & non-flexible which creates problem in the next process like produced uneven dyeing.

Bleaching: Hard water decompose bleach bath.  
H2O2 --> H2O + [O]

Mercerizing: It forms insoluble metal acid, reduce absorbency and luster.

Dyeing: Ca2+ and Mg2+ ions of hard water react with dye molecules and precipitated the dye. As a result dyestuff is spoilt. Hence, uneven shade (depth of dyeing) of color is produced.
**Printing:** It break the emulsion, change it’s thickness and efficiency and it is also harmful for thickener. Hard water cause problems in printing process like dyeing.

**Finishing:** Hard water interferes with catalysts, because resins and other additives to become non reactive, break emulsion and deactives soap.

From above, we saw that hard water causes problems in every process of wet processing. So, we have to use such water that is suitable for wet processing and don’t create any problem. Ideal quality of feed water for textile industry is:

- pH should be in the range of 7 – 8.
- Water should be odorless & colorless.
- Water hardness: maximum 5° dH.
- Solid content: < 50 mg/L.
- Dissolved solids: < 1 mg/L.
- Inorganic salts: < 500 mg/L.
- Organic salts: < 20 mg/L.
- Iron (Fe): < 0.1 mg/L.
- Mn : < 0.02 mg/L.
- Cu: < 0.005 mg/L.
- Nitrate: < 50 mg/L.
- Nitrite: < 5 mg/L.
STUDY & SURVEY
3. STUDY AND SURVEY

3.1. Zaber & Zubair Fabrics Limited

3.1.1. Water Treatment Flow Chart:

```
   Deep Water
      |                |
      | Raw water      |
      | reservoir      |
      |                |
      | Stone Tank     |
      |                |
      | Resin Tank     |
      |                |
      | Salt Mixing    |
      |                |
      | Delivery       |
      | Pump           |
      |                |
      | Soft Water     |
      | Reservoir      |
      |                |
      | Dyeing / Boiler|
```
3.1.2 Diagram:

STONE TANK

Softening / RESIN TANK
Capacity - 80,000 Ltr
Resin - 3,600 Ltr

Dosing Tank
[Mixing Salt]

MOTOR
Dosing Tank

WASH BACK
WASH

Motor 01
Motor 02
Motor 03
Motor 04

Water Reservoir / Water House

Deep Water

Feling Material

Drain

WATER

MOTOR

Mixing Salt

Motor 01
Motor 02
Motor 03
Motor 04

PUMP

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3.1.3 Function of different parts:

**Mass water storage:**
- It is a house where total water is stored primarily.
- It is also a reservoir for continuous flow.
- From here water goes through tank 1 (Stone Tank).

**Tank 1 (Stone Tank):**
- This tank contains three layers of stone.
- In first layer or in upper layer contain small size of stones.
- In second layer medium size of stones are stored.
- In third layer or lower layer large size of stones are stored.
- Water passes from the upper layer to lower layer.
- Those three layers primarily remove water impurities.
- Then by using valve water go to resin tank

![Stone Tank Diagram](image)

Figure: Stone Tank
Tank 2 (Resin Tank):
- Tank 2 contains resin.
- The water from tank 1 passes through tank 2.
- At first water passed through resin.
- Cat-ion resin remove hardness of water
- Resin is regenerated in every 24 hours
- Common salt is used for regeneration
- pH should controlled here
- At least 300kg salt use daily.
- Mixing Tank capacity 1000litre

Alternative tank (3, 4):
- Alternative tank 3 does as same as tank 1.
- Alternative tank 4 does as same as tank 2.
- Both tank 3, 4 maintains continuous supply of water.

Soft water storage tank:
- Soft water comes from tank 2, tank 4.
- This water storage tank reserves the total soft water.
- Soft water storage tank supply water to dyeing machine and boiler.

Dyeing machine:
- Soft water used for desizing, scouring, bleaching, dyeing and washing process.

Soft water storage tank for boiler:
- This tank stores water for boiler use.
- Soft water supplied by two automatic pumps to boiler.

Boiler:
- Boiler use water for steam generation.
- Soft water is used for low corrosion formation in boiler.

3.1.4 Working Procedure:

1. At first water is sucked from underground by suction pump
2. Then water is stored in a water tank
3. Then water enters in a sand and stone filter and purified from dirt dust and sediments and un dissolved solid
4. Then water enters in a set of ion exchange resins where hard water is purified by exchanging its metal ions like calcium ions and magnesium ions with sodium ions of ion exchange resin where following reaction occurs
Temporary hardness

\[
\text{Ca(HO}_3\text{)}_2 + \text{Na2OZ} = \text{CaO.Z + 2NaHCO}_3
\]

\[
\text{Mg(HO}_3\text{)}_2 + \text{Na2OZ} = \text{MgO.Z + 2NaHCO}_3
\]

Permanent hardness

\[
\text{CaSO}_4 + \text{Na2OZ} = \text{CaO.Z + Na2SO}_4
\]

\[
\text{MgSO}_4 + \text{Na2OZ} = \text{MgO.Z + Na2SO}_4
\]


In this tank after every 15 minutes around 300kgs of salt is added to regenerate the resin by following reaction

\[
\text{CaO.Z + 2NaCl} = \text{Na2O.Z + CaCl}_2
\]

5. Then water is kept on a soft water tank for 30 to 40 minute
6. From this soft water tank water is pumped to supply the water to boiler and dye house

3.1.5 Chemistry Involved in WTP :

- NaCl used for control hardness.
- Acetic acid used for pH control.
- Clamagite for pH test etc.

3.1.6 Water Quality :

<table>
<thead>
<tr>
<th>Parameter</th>
<th>before softening</th>
<th>after softening</th>
</tr>
</thead>
<tbody>
<tr>
<td>PH</td>
<td>7.5-8</td>
<td>6.9-7.2</td>
</tr>
<tr>
<td>Hardness</td>
<td>45-55 PPM</td>
<td>3-5 PPM</td>
</tr>
</tbody>
</table>
3.2. Dulal Brothers Limited [DBL]

3.2.1. Water Treatment Flow Chart:

- Ground Water
- Submersible Pump
- Raw Water Reserve Tank
- Centrifugal Pump
- Multi-grade Filter
- Activate Carbon Filter
- Softener Filter
- Soft Water Reserve Tank
- Delivery Pump
- Boiler / Dyeing
3.2.2 Diagram:

3.2.3 Main Functional Part:

1. Submersible Pump:
   This Pump pulls water from underground.

2. Raw water reserve Tank:
   This tank reserves the raw water which was pulled out by Submersible Pump.

3. Centrifugal Pump:
   This Pump supplies the raw water from raw water reserve Tank to Multi-grade filter.
4. Multi-grade filter:

This filter vessel consists:

- Sand: 4600kg
- Gables: 800kg
- Pebbles-II: 750kg
- Pebbles-I: 850kg

Fig: Multi-grade filter
5. **Active Carbon Filter:**

This filter vessel consists:

- Carbon : 1200kg
- Sand    : 4600kg
- Gables  : 800kg
- Pebbles-II: 750kg
- Pebbles-I: 850kg
6. **Softener Filter:**

This filter vessel consist sand and 7000kg cat-ion resin.

![Softener Filter Diagram](image)

Fig: Softener Filter

7. **Soft water reserve tank:** This tank stores the soft water.

8. **Booster pressure Pump:** This Pump supplies the soft water from Soft water reserve tank to where needed with pressure.
3.2.4 Working Procedure:

1. At first water is sucked from underground by suction pump
2. Then water is stored in a water tank
3. Then water enters in a sand and stone filter and purified from dirt dust and sediments and un dissolved solid
4. Then water enters activated carbon resin where water is further purified
5. Then water enters in a set of ion exchange resins where hard water is purified by exchanging its metal ions like calcium ions and magnesium ions with sodium ions of ion exchange resin where following reaction occurs

Temporary hardness

\[
\begin{align*}
\text{Ca}(\text{HO}_3)_2 + \text{Na}_2\text{OZ} &= \text{CaO}.\text{Z} + 2\text{NaHCO}_3 \\
\text{Mg}(\text{HO}_3)_2 + \text{Na}_2\text{OZ} &= \text{MgO}.\text{Z} + 2\text{NaHCO}_3
\end{align*}
\]

Permanent hardness

\[
\begin{align*}
\text{CaSO}_4 + \text{Na}_2\text{OZ} &= \text{CaO}.\text{Z} + \text{Na}_2\text{SO}_4 \\
\text{MgSO}_4 + \text{Na}_2\text{OZ} &= \text{MgO}.\text{Z} + \text{Na}_2\text{SO}_4
\end{align*}
\]

Where \( Z = \text{Al}_2\text{O}_3.\text{SiO}_2.\text{H}_2\text{O} \)

In this tank after every 15 minutes around 3002kgs of salt is added to regenerate the resin by following reaction

\[
\text{CaO}.\text{Z} + 2\text{NaCl} = \text{Na}_2\text{O}.\text{Z} + \text{CaCl}_2
\]

5. Then water is kept on a soft water tank
6. From this soft water tank water is pumped to supply the water to boiler and dye house

3.2.5 Water Quality:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before softening</th>
<th>After softening</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>30-40ppm</td>
<td>2-4 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>8-9</td>
<td>6-7</td>
</tr>
</tbody>
</table>
3.3 Determination of Hardness of Water / Water Hardness :

Name of the Hardness tester: Hardness test kit

Hardness of Water:
The presence of Calcium, Magnesium salt i.e. bi-carbonates, sulphates, Chloride in water is called causes of hardness of water. The water which contains these salts is called hard water. Water's hardness is determined by the concentration of multivalent cations in the water.

Reagent:
1. Hardness buffer
2. Calmagite Indicator
3. HI 3812-0 EDTA Solution

Procedure:

For High Range – 0 to 300 mg/L CaCO3

1. Remove the cap from the small plastic beaker. Rinse the plastic beaker with the water sample, fill to the 5 ml mark and replace the cap.

2. Add 5 drops of Hardness Buffer through the cap port and mix carefully swirling the beaker in tight circles.

3. Add 1 drop of Calmagite Indicator through the cap port and mix as described above. The solution becomes a red violet color.

4. Take the titration syringe and push the plunger completely into the syringe. Insert tip into HI 3812-0 EDTA Solution and pull the plunger out until the lower edge of the seal is on the 0 ML mark of the syringe.

5. Place the syringe tip into the cap port of the plastic beaker and slowly add the titration solution drop wise, swirling to mix after each drop.
6. Continue adding the titration solution until the solution becomes purple, then mix for 15 seconds after each additional drop until the solution turns blue.

7. Read off the milliliters of titration solution from the syringe scale and multiply by 300 to obtain mg/L (ppm) CaCO₃.

**For Low Range – 0.0 to 30.0 mg/L CaCO₃**

If result is lower than 30 mg/L, the precision of the test can be improved by following the procedure below.

1. Remove the cap from the large plastic beaker. Rinse it with the water sample, fill to the 50 ml mark and replace the cap.
2. Proceed with the titration as for the high range test.
3. Read off the milliliters of titration solution from the syringe scale and
4. Multiply by 30 to obtain mg/L (ppm) CaCO₃
DISCUSSION OF RESULTS
4.1 **Input & Output Quality of water:**

1. Zaber & Zubair Fabrics Ltd.

<table>
<thead>
<tr>
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</table>

2. Dulal Brothers Ltd.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Before softening</th>
<th>After softening</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>30-40ppm</td>
<td>2-4 ppm</td>
</tr>
<tr>
<td>pH</td>
<td>8-9</td>
<td>6-7</td>
</tr>
</tbody>
</table>
4.2. Difference:

<table>
<thead>
<tr>
<th>Serial No.</th>
<th>Parameter</th>
<th>Zaber &amp; Zubair Fabrics Ltd.</th>
<th>Dulal Brothers Ltd.</th>
</tr>
</thead>
</table>
| 01         | 1<sup>st</sup> vessel consist | Sand and stone Filter  
This filter contains 3 types of stone i.e.  
Small stone  
Medium stone  
Large stone | Multi-grade Filter  
This filter contains  
Sand : 4600 kg  
Gables : 800 kg  
Pebbles-II : 750 kg  
Pebbles-I : 850 kg |
| 02         | 2<sup>nd</sup> vessel consist | This type of filter does not use  
Active Carbon Filter  
This filter contains  
Carbon : 1200 kg  
Sand : 4600 kg  
Gables : 800 kg  
Pebbles-II : 750 kg  
Pebbles-I : 850 kg | |
| 03         | 3<sup>rd</sup> vessel consist | This filter contains 3600 liter of resin  
Softener Filter  
This filter vessel consist sand and  
7000kg cat-ion resin. | |
| 04         | Raw water reserve tank | Yes | Yes |
| 05         | Soft water reserve tank | Yes | Yes |
| 06         | Input hardness       | 45-55 ppm | 30-40 ppm |
| 07         | Output hardness      | 3-5 ppm | 2-4 ppm |
| 08         | Run time             | 6 hrs | 5-6 hrs |
| 09         | Soften water amount  | 0.32 million liter | 0.25 million liter |
CONCLUSION
In textile wet processing all the process requires water. Without it no process can be carried out. It’s estimated that for processing 1kg of textile at least 80-100 litter of water is required. But water cannot use directly from underground. It contains many impurities. Among all the impurities hardness is most dangerous for textile production. It remains caused effect in Textile processing. A water treatment is a process that makes the water more suitable to use for the end users, as it can be in use by industries, individuals or others. Therefore Water treatment plant is one of the most important unit in textile wet processing technology that determines the result next processes. Water quality is a determining factor in textile finishing section. Water treatment plant ensures best water quality and perfect finishing for textile material. As fibres are highly sensitive to the quality of water used during processing it is highly recommended to avoid the use of hard water at any cost. Without treatment is should damage uniform dyeing, accurate color etc. It will hamper economically. In textile dyeing section it is highly recommended to use water of a predefined quality which is free from hardness, odor and other impurities. There is a standard for the quality of dye house water that every industry must maintain if it wants to get desired quality. Boiler is the one of the most valuable section in textile. Hardness cause damage in boiler. So that Boiler water treatment is a popular treatment process in industrial plants because of the problem caused by scale formation and corrosion within the system which comes with stream. Water treatment plant has to be environmental friendly therefore waste from water treatment plant requires further processing in ETP. Water treatment plant is the first in a series of modern textile finishing system. Without it no process will get desired end result. Hard water must be softened before application in any process. Otherwise it creates a lot of problems that hampers production badly. So if we want to survive the challenge to produce quality textile product without hampering environment we must use an efficient water treatment plant that will generate best quality soft water for all the coloration and finishing processes.