Water and impurites

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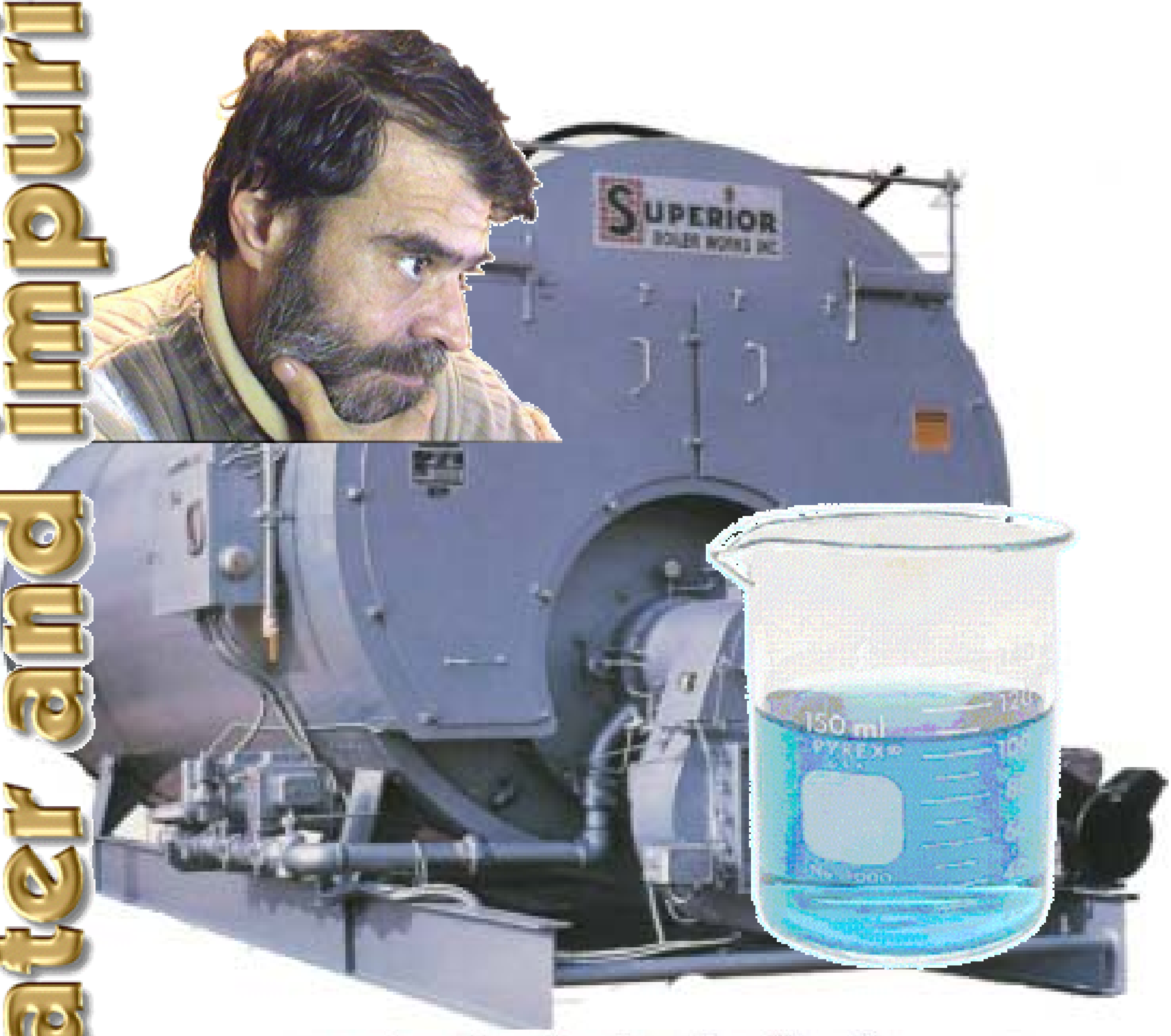

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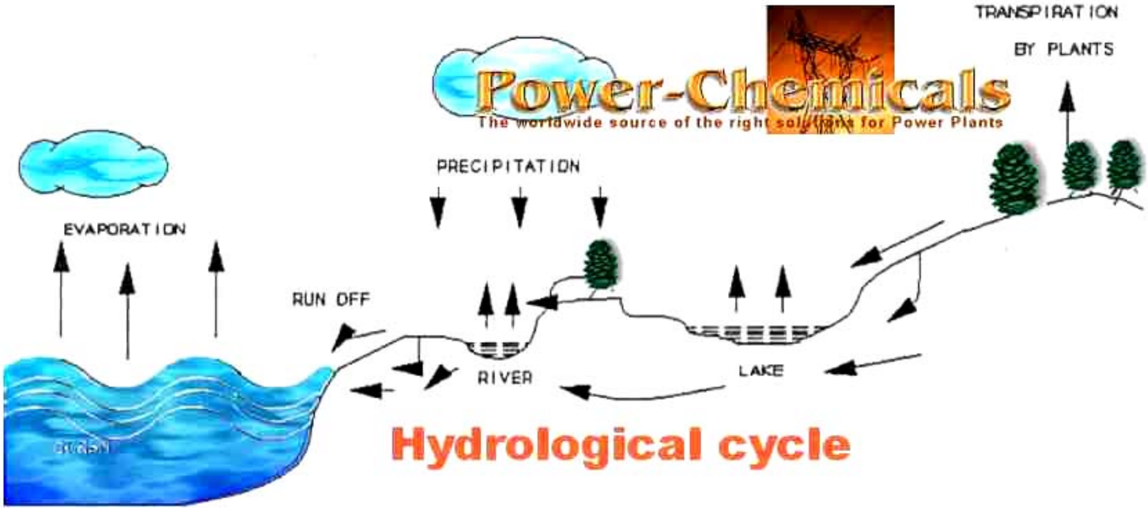
Water and impurites

Water has many features which make it the clear choice for industrial applications. It is capable of absorbing a great deal of heat, water is easy to handle, it is generally available and affordable. But the characteristics of water present problems to those of us responsible for operating and maintaining plant equipment.

In its pure form, water is odorless, colorless and tasteless, an ideal liquid for use in boilers and other plant equipment.



However, pure water simply does not exist in nature.

The earth's water follows an endless pattern of evaporation into the atmosphere, followed by precipitation back to earth. This is called the "hydrological cycle".

For a short interval, the evaporating water vapor is pure, leaving all the impurities behind in the water. After a short time, as the vapor condenses and forms water droplets, other gases and particles present in the atmosphere are absorbed, so that rain water may be saturated with oxygen, contain carbon dioxide and be contaminated with pollutants like sulphur and nitrogen oxide. The contaminated rain water then falls back to the earth where it picks up more impurities.

Water impurities fall into three categories:

- **Dissolved gases**

A first type of water impurity is dissolved gases such as oxygen and carbon dioxide. In the hydrologic cycle, various gases become dissolved in rainwater as it passes through the atmosphere. In addition, any equipment which is open to the atmosphere will permit gases to enter and be absorbed by the water.

- **Suspended solids**

These are impurities which do not dissolve in water. Suspended solids such as sand, mud, oil and decaying vegetation tend to separate from standing water. Suspended insoluble matter is also referred to as turbidity.

- **Dissolved solids**

Commonly encountered dissolved solids include calcium, magnesium, iron, chloride and silica.

The type and amount of impurities present in your plant's make-up water will depend largely on the water's source.

Well water picks up dissolved minerals as it percolates down through the earth's crust. This process also has a filtering effect, usually keeping the water free of suspended matter.

Surface waters from lakes, rivers and streams, on the other hand, may contain high levels of suspended matter such as sand, silt and leaf mold. Surface waters vary greatly in composition depending on factors such as the amount of rainfall, time of year, and the discharge of industrial pollution.

The amount of an impurity in a water sample is generally expressed in parts per million or ppm. One ppm is equal to one part of an impurity in one million parts of solution. For example, if certain water contains 1 ppm of silica, there is one kilogram of silica present in one million kilogram of that water. The amount of impurities that may be considered acceptable depends on the water's intended use.

While relatively high concentrations of impurities can be tolerated in water used for open recirculating cooling systems, ultra high purity water is required for high pressure steam generating systems. The problem with even relatively small amounts of impurities in boiler feedwater is the fact that these impurities concentrate in the boiler.

Just as river water leaves impurities behind as it evaporates, boiler water leaves impurities behind in the boiler as it turns to steam. This is explained as follows, starting from a beaker of tap water containing 2 ppm of calcium, the amount of calcium left behind becomes twice as concentrated to 4 ppm. If half the water again evaporates, the calcium concentration again doubles to 8 ppm. Adding more tap water to make-up for the water lost by evaporation adds even more calcium.

The same thing happens in your boiler: As water turns to steam and escapes in the steam drum, the water left behind in the boiler becomes more concentrated with impurities.

Cycles of concentration

Cycles of concentration is a term used to indicate the number of times the solids in a particular volume of water are concentrated.

In the following section we'll go into more detail about monitoring boiler water and steps you can take to keep impurities in your boiler at an acceptable level.

Cycles of concentration in a boiler may be determined by dividing the amount of chloride in the boiler water by the amount of chloride in the feedwater. Cycles are regulated by adjusting the blowdown rate. To reduce cycles of concentration, the blowdown rate is increased. Your Drew representative will determine the optimum number of cycles for your boiler.

Our understanding of chemistry and chemical reactions helps us to monitor and control substances which dissolve in water. Over one hundred elements are known to man. Of them only eight make up over 98% of the earth's crust.

The elements are arranged on a periodic table which provides information on their properties. Each element can be divided into individual atoms. Atoms of various elements combine to form an infinite number of compounds that are soluble in water to some degree.

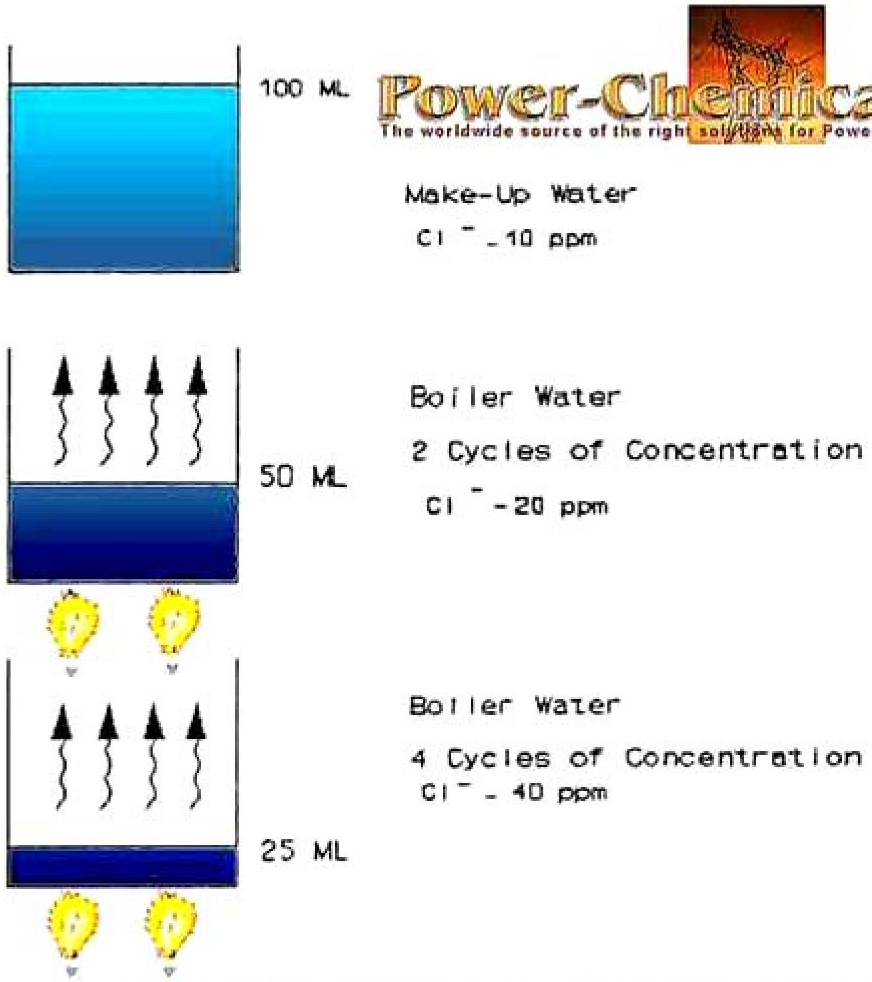
An example of a compound is water itself which is a combination of two atoms of hydrogen with one atom of oxygen. Another example is common table salt which is composed of one atom of sodium and one atom of chloride.

Natural water generally contains a variety of dissolved compounds.

As a compound dissolves, it separates into atoms having either a positive or negative charge. These charged atoms are called ions. Ions with a positive charge are called cations and ions with a negative charge are called anions.

When a water sample is analyzed, usually no attempt is made to determine the original compounds which introduced the various ions.

For example, calcium bicarbonate is a compound frequently present in ground water. In a chemical analysis, calcium cations and bicarbonate anions are determined and reported simply as calcium ions and bicarbonate ions. This provides sufficient information to determine the amount and type of impurities present in the water.



Cycles of concentration

Conductivity

You have the ability to determine the total amount of dissolved solids in your plant's boiler water by measuring conductivity.

Conductivity is the measure of a solution's ability to conduct electricity. Electrical current is carried by dissolved solids present in the water.

Therefore, current is negligible in pure water. But current is measurable in water which contains dissolved solids.

Measuring conductivity gives no indication of what is in the water, but it will give you a good indication of the total amount of dissolved solids present.

Total dissolved solids may be controlled by the continuous blowdown, which typically is removed from the steam drum, or by manual blowdown. Guidelines for maximum TDS levels in boilers operating at various steam pressures are shown in tables.

It is advisable to keep the TDS in the boiler water just below the maximum allowed in order to save fuel, water and treatment chemicals.

Because of the time it takes to determine the TDS by evaporation, the TDS is calculated from the water's conductivity.

The relationship between TDS and conductivity varies depending on the water quality.

For boilers that use synthetic polymers as a sludge dispersant, a factor of 0.7 times the neutralized conductivity (in µmhos) may be used.

For boilers that use Quebracho tannin, the factor will vary from 0.7 to 1.0 depending on the amount of tannin in the water.

pH

pH is another term you'll hear often in regard to water testing.

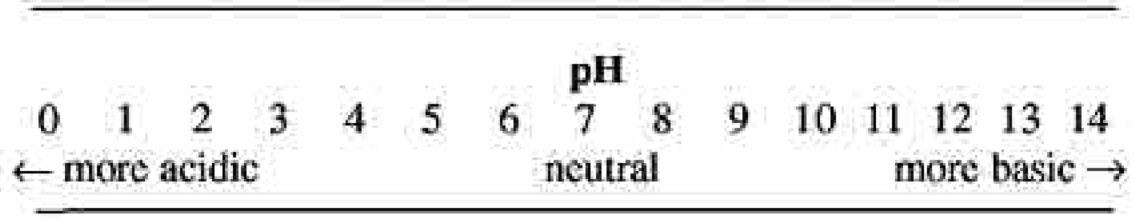
Compounds dissolve in water, separating into positively charged ions called cations and negatively charged ions called anions.

Cations and anions combine in a number of ways forming molecules of various salts, acids and bases.

Water high in acid is termed "acidic" while water high in bases is termed "alkaline".

pH is a measurement of the acidity-alkalinity balance of water, with a pH of 7 considered neutral. We find that in boilers, the ideal pH is around 10. Water with a pH above or below 10 becomes aggressive to metal surfaces and causes damage to plant equipment.

It is critical to monitor pH frequently.



Alkalinity.

a. Sources of alkalinity.

The three basic sources of alkalinity in water are: alkalinity resulting from the bicarbonate ion (HCO_3^-), the carbonate ion ($CO_3^=$), and the hydroxyl ion (OH^-). The amount of each of these in water can be determined by titrating with an acid to certain pH levels (end points) using phenolphthalein (P alkalinity) and a methyl orange (M alkalinity) end points. The relationship between pH and these alkalinities is shown in figure.

b. Relationship of P, M and OH alkalinities.

Test procedures for determining the P and M alkalinities are included in commercially available test kits. The OH alkalinity can be determined by a specific test or it can be calculated from the P and M alkalinities.

The OH alkalinity is the result of the hydroxyl ion (OH^-) in the water, and is also known as "caustic alkalinity" or "causticity".

The relationship between the measured P and M alkalinities and level of hydroxyl, carbonate, and bicarbonate forms of the alkalinity is shown in table 6-4 and is discussed below.

Alkalinity in boiler water essentially results from the presence of hydroxyl and carbonate ions.

(1) Hydroxyl alkalinity (causticity) in boiler water is necessary to protect the boiler against corrosion. Proper dosage of sodium hydroxide is covered in paragraph 3-19. Too high a causticity causes other operating problems, such as foaming. Excessively high causticity levels can

result in a type of caustic attack of the boiler called "embrittlement".

(2) With the phosphate control program phosphate in the boiler water combines with calcium to precipitate calcium phosphate, removing calcium from the boiler water.

Calcium phosphate, under proper conditions, forms a finely divided, fluid sludge, which can be carried by the boiler circulation and can, in general, be readily removed by blowdown.

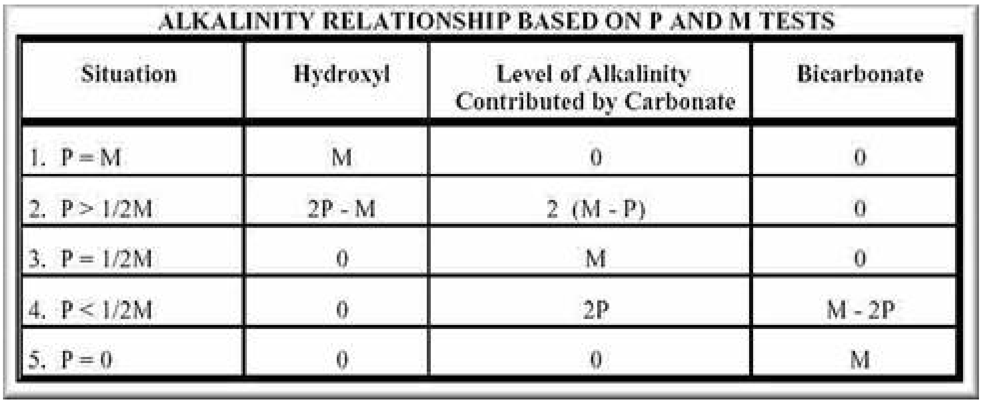
Because calcium phosphate is the least soluble of the calcium salts in boiler water, phosphate control prevents formation of other calcium scales, such as calcium carbonate, calcium sulfate, or calcium silicate.

The pH in the boiler must be kept above 11.0 to prevent possible formation of a sticky sludge that adheres to the boiler surfaces.

(3) Causticity in boiler water is the result of the addition of sodium hydroxide (NaOH) or the breakdown of bicarbonate alkalinity in the feedwater under the influence of heat to produce sodium carbonate, carbon dioxide and water:

$$2NaHCO_3 \rightarrow NaCO_3 + CO_2 + H_2O$$

Sodium   Sodium Carbon Water
Bicarbonate   Carbonate Dioxide



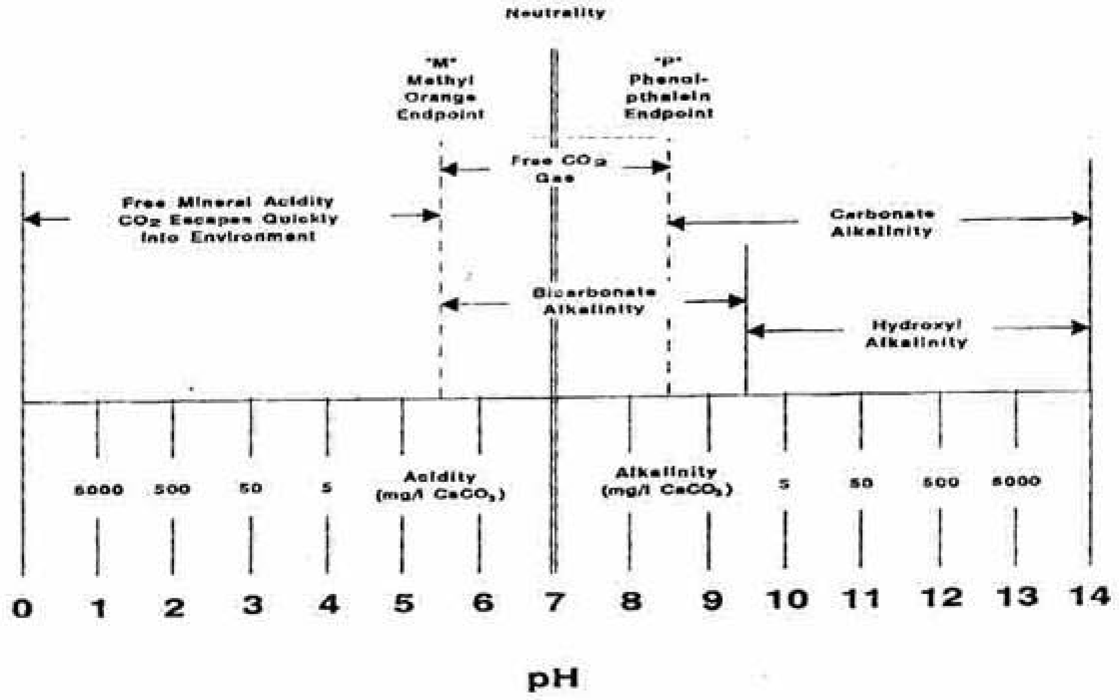
ALKALINITY RELATIONSHIP BASED ON P AND M TESTS

Situation	Hydroxyl	Level of Alkalinity Contributed by Carbonate	Bicarbonate
1. P = M	M	0	0
2. P > 1/2M	2P - M	2 (M - P)	0
3. P = 1/2M	0	M	0
4. P < 1/2M	0	2P	M - 2P
5. P = 0	0	0	M

Carbonates react with the hot boiler water, although not as fast or as complete as the bicarbonate reaction, to form carbon dioxide and sodium hydroxide which increases the causticity in the boiler and the acidity of the steam.

$$Na_2CO_3 + H_2O \longrightarrow 2NaOH + CO_2$$

ACIDITY & VARIOUS TYPES OF ALKALINITY & THEIR pH RANGES



source US Army TECHNICAL BULLETIN 420-49-05

Water Hardness

The presence of calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions in a water supply is commonly known as **"hardness."** It is usually expressed as **parts per million** (ppm). Hardness minerals exist to some degree in virtually every water supply. The following table classifies the degree of hardness:

Hardness mg/L	Classification
0-17	soft water
17-60	slightly hard water
60-120	moderately hard water
120-180	hard water
>180	very hard water

Iron

Iron, which makes up 5% of the earth's crust, is a common water contaminant. It can be difficult to remove because it may change valence states - that is, change from the water-soluble ferrous state (Fe2+) to the insoluble ferric state (Fe3+). When oxygen or an oxidizing agent is introduced, ferrous iron becomes ferric which is insoluble and so precipitates, leading to a rusty (red-brown) appearance in water.

This change can occur when deep well water is pumped into a distribution system where it adsorbs oxygen. Ferric iron can create havoc with valves, piping, water treatment equipment, and water-using devices.

Certain bacteria can further complicate iron problems. Organisms such as Crenothrix, Sphaerotilus and Gallionella use iron as an energy source. These iron-reducing bacteria eventually form a rusty, gelatinous sludge that can plug a water pipe. When diagnosing an *iron problem, it is very important to determine whether or not such bacteria are present.*

Manganese

Although manganese behaves like iron, much lower concentrations can cause water system problems. However, manganese does not occur as frequently as iron. Manganese forms a dark, almost black, precipitate.

Sulfate

Sulfate (S042~) is very common. When present at lower levels, sulfate salts create problems only for critical manufacturing processes. At higher levels, they are associated with a bitter taste and laxative effect. Many divalent metal-sulfate salts are virtually insoluble and precipitate at low concentrations.

Chloride

Chloride (Cl~) salts are common water contaminants. The critical level of chloride depends on the intended use of the water. At high levels, chloride causes a salty or brackish taste and can interfere with certain water treatment methods. Chlorides also corrode the metals of water supply systems, including some stainless steels.

Total Organic Carbon (TOC)

TOC is a direct measure of the organic, oxidizable, carbon-based material in water. TOC is a vital measurement used in sophisticated water treatment systems - such as electronics grade - where any amount of contamination can adversely affect product quality and yield.

Biochemical Oxygen Demand (BOD)

BOD is a measure of organic material contamination in water, specified in mg/L. BOD is the amount of dissolved oxygen required for the biochemical decomposition of organic compounds and the oxidation of certain inorganic materials (e.g., iron, sulfites). Typically the test for BOD is conducted over a five-day period.

Chemical Oxygen Demand (COD)

COD is another measure of organic material contamination in water specified in mg/L. COD is the amount of dissolved oxygen required to cause chemical oxidation of the organic material in water.

Both BOD and COD are key indicators of the environmental health of a surface water supply. They are commonly used in waste water treatment but rarely in general water treatment.

Dissolved Gases

- ### Carbon Dioxide

Dissolved carbon dioxide (C02) associates with water molecules to form carbonic acid (H2C03), reducing the pH and contributing to corrosion in water lines, especially steam and condensate lines.

Carbonic acid, in turn, dissociates to bicarbonate (HC03~) or carbonate (C032~), depending on pH. Most of the C02 found in water comes not from the atmosphere but from carbonate that the water has dissolved from rock formations.

- ### Oxygen

Dissolved oxygen (02) can corrode water lines, boilers and heat exchangers, but is only soluble to about 14 ppm at atmospheric pressure

Control Tests

In order to minimise scaling and/or corrosion of these systems, the following control tests must be performed, and all water test results must be documented on a dedicated record sheet (see typical record sheet overleaf):

(a) Log the quantity of water softened/dealkalised between regenerations;

(b) Log the make-up water meter reading at least once per month;

(c) At least once per day on large systems and 3 times per week on small systems, perform the following tests on boiler water samples and log these test results:

(i) neutralised total dissolved solids.... must be 1500-3000 ppm (2000-4000 micromhos/cm);

(ii) phosphate ……………………must be 40-80 ppm PO4;

(iii) hydroxide alkalinity………must be 150-300 ppm CaCO3;

(iv) total alkalinity ………………must be less than 700 ppm CaCO3;

(v) sulphite…………………………must be 30-60 ppm SO3; (50 ppm Na2 SO3)

(vi) pH ……………………………must be 10.5-11.5.

(d) At least once per day on large systems and 3 times per week on small systems, determine and log the pH level of the condensate return—it must be 8.5-9.5 pH for systems that are not used for humidity control and 8.0-8.5 pH for systems that are used for humidity control;

(e) At least once per day on large systems and 3 times per week on small systems, determine and log the TDS concentration of the condensate return—it must be less than 40 ppm (50 micromhos/cm);

(f) At least once per day on large systems and 3 times per week on small systems, determine and log the total hardness concentration of the condensate return & softener effluent—they both must be less than 2 ppm CaCO3;

(g) While performing the above tests, note the general appearance of the water samples—the boiler water samples may be colourless or amber & contain either no sediment or a small amount of sediment, whereas the condensate & softener samples must be clear & colourless with no sediment.