SPIROCARE® WATER CHEMISTRY

In both open and closed cooling and heating systems, water is one of the most important components of the installation. Often, the interchange between the water chemistry (such as the pH value, oxygen and calcium quantities), the mechanical components (pipes, radiators and heat exchangers) and the physical characteristics (such as pressure and temperature) of the installation is often insufficiently known or is underestimated. However, this can lead to problems with potentially poor heat transfer, mechanical failures, a high degree of maintenance or a shorter service life, which ultimately has a negative impact on the energy and operating costs. The water chemistry is an important component and requires knowledge of the principal properties of water and the potential effects, such as the formation of scale and corrosion.

GUIDELINES

As soon as the quality of the heating or cooling water is no longer adequate, major failures, serious damage and efficiency losses can occur. This is not only relevant in legal terms, in view of guarantee claims, but also in business economic terms, because the business, repair and maintenance costs do not make a positive contribution to the operating result. For the monitoring of the correct water quality in heating and cooling installations, reference is made to various guidelines, including the VDI 2035. Many suppliers originate from Germany or have their main markets there. This is one of the reasons why the guarantee provisions of suppliers of appendages are often related to the VDI 2035. Nevertheless, some system installation or parts manufacturers refer to other guidelines.

The various system water parameters must be measured 8-12 weeks after the first filling and then once a year. If additives are added to the system, the concentration of these must also be measured annually.

BASIC PARAMETERS OF SYSTEM WATER

There are a number of basic parameters for defining the water quality in heating or cooling systems. Based on these basic parameters, an initial and reliable analysis can be made of the water quality. Basic knowledge of the different parameters is important to make an expert assessment of water quality in heating and cooling systems.

pH VALUE

The pH value, or acidity, is one of the most important parameters for the water quality. The value is defined as the negative logarithm of the hydrogen concentration ($pH = -\log [H+]$) and is used to describe the acid or basic character of a watery solution. Good knowledge of the effect of the pH value on the heating system offers an important advantage because certain chemical processes can only take place with a specific degree of acidity. The acidity of the system water can increase over the years, for example due to oxygen entering the system which influences the final corrosion susceptibility of a metal. Proper system deaeration can keep pH levels stable.

The pH value of the water is classified in a logarithmic scale of 0 to 14. This means that a difference of one unit on the pH scale leads to a substantial change in the acidity. With a pH value of 6.0, the acidity is 10 times higher (stronger) than with a pH value of 7.0. The pH value must therefore be measured with an accuracy of at least 0.1.

Solutions with a low pH value are acidic and have a high content of hydrogen ions (H^+). Solutions with a high pH value are basic (also called alkaline) and have a high content of hydroxide ions (OH^-). A pH value of 7 at room temperature indicates that a solution is neutral, like pure water. There are then as many H^+ as OH^- ions. However, the pH value is not a quantitative measure of the acidic or basic substances dissolved in the water.

The risk of corrosion at a particular pH value depends on the metal used. For ferrous metals, a pH value of more than 8.0 is ideal for reducing the risk of corrosion, while a pH of less than 9.0 is necessary for aluminium alloys. The higher the pH value, the greater the risk of calcium deposits. The recommended pH value is therefore a compromise.

ELECTRICAL CONDUCTIVITY (EC)

This parameter gives an indication of the purity of the water. Pure water has very low electrical conductivity (ion activity). Minerals (such as alkalis, chlorides, sulphides and carbonate compounds) dissolved in water increase the electrical conductivity value (EC). The electrical conductivity can be used as an indication of the likelihood of metal corrosion.

Corrosion in heating systems is caused by oxygen, acids, bases and dissolved salts. The higher the share of dissolved salts and minerals in the water (more ions), the higher the electrical conductivity and, therefore, the risk of corrosion. The higher the conductivity, the faster the corrosion process in untreated water. However, a low electrical conductivity value (fewer ions) causes higher potential formation, which leads to potential equalisation and earthing. As a result, crystallisation of certain salts occurs, leading to the formation of deposits.

Only an electrical conductivity measurement can determine the ions of these dissolved minerals in the measurement unit of microsiemens per centimeter (µS/cm).

CONDUCTIVITY VALUE IN µS/CM	CLASSIFICATION
0 - 100	Delayed corrosion
100 - 350	Very slow corrosion
350 - 500	Slow corrosion
500 – 1,000	Accelerated corrosion
1,000 - 2,000	Strongly accelerated corrosion
>2,000	Very strongly accelerated corrosion

A measurement of the conductivity shows the total concentration of the ions dissolved in water, but not the type and volume of minerals in the water. Because conductivity is easy to measure, it is often used to monitor water quality. However, conductivity is not suitable for monitoring the water composition. As long as the conductivity remains unchanged, the water composition remains stable (with softening, the conductivity remains the same but the Ca^{2+} and Mg^{2+} ions are replaced by Na^{+} ions). A change in the conductivity is an indication that the water composition has changed. The water must be reanalysed to determine which factors in the water have changed.

The electrical conductivity of the water depends on the water temperature: the higher the temperature, the higher the electrical conductivity, which is why the EC values measured must be compensated for temperature.

Demineralised water can act as an insulator due to its very low (if not negligible) conductivity and is therefore recommended for filling, refilling or treatment of the system water to reduce the conductive capacity.

Although there is a close relationship between electrical conductivity (EC) and the total volume of dissolved solids (TDS), these are not the same. EC is the capacity to conduct electricity and TDS is the total volume of solids dissolved in the water. Often, a conversion factor is used (e.g. 0.7). The total dissolved solids (ppm) = 0.7 x conductivity. (µS/cm).

TOTAL HARDNESS

The total hardness is the sum of all alkaline earth ions dissolved in the water and is expressed in ppm $CaCO_3$ or in degrees of German hardness (°dH), or in degrees of French hardness (°fH). The water hardness is primarily determined by dissolved minerals such as calcium and magnesium salts. Calcium bound to m-alkalinity is called temporary hardness, this hardness spontaneously converts to boiler scale as soon as the water reaches a temperature above 60°C.

The harder the water, the greater the risk of deposits of calcium and magnesium salts. On the other hand, too soft water is aggressive and corrosive.

When hard water is heated, calcium (calcium carbonate) deposits can form in the parts of the heating system with the highest temperatures. This can substantially reduce the service life and the yield of the appliance. Heating boilers, heat exchangers and heating pipes are insulated from the inside out, as it were, and the energy costs rise. Calcium deposits in appliances, pumps, vents and water meters lead to wear and tear of moving parts.

A high hardness can lead to substantial calcium deposits. Thermal stress caused by calcium deposits is the biggest problem for stainless steel heat exchangers. However, water that is too soft can be corrosive and more aggressive.

Calcium deposits in a heating system and, therefore, the total hardness can be reduced by:

- Softening, through ion exchange (exchanging $Ca2^+$ and $Mg2^+$ ions for Na^+ ions
- Demineralisation or reverse osmosis of the filling or refilling water.

Demineralisation removes all ions, including magnesium and calcium, so that good pH buffering is not possible. An inhibitor should be added to fully softened water to stabilised the pH-value.

There are two ways to measure water hardness at the location: test strips or titration (adding drops). Titration is more accurate, while test strips are simpler and faster.

TURBIDITY

Turbidity is a measure of the relative clarity of a fluid. Turbidity is primarily caused by the presence of floating particles, including sludge, corrosion products and bacteria, referred to as ‘suspended solids’. The Total amount of Suspended Solids (TSS) in the water has a major impact on the normal functioning of a system. These particles may come from the installation work or contact with the external environment, or may result from chemical reactions (corrosion) in the system water. The solids in the water also lead to erosion of soft metals such as copper, aluminium and zinc.

Regardless of their origins, suspended solids can block the pipes, control vents, pumps and heat exchangers. The measurement of the total volume of suspended solids can therefore be of great importance for the functioning of the installation and can be performed together with the determination of the dissolved salts.

The water is regarded as turbid when the presence of these floating particles reaches a certain value or concentration. The turbidity or lack of clarity of the water is one of the most difficult parameters to measure because it is a subjective measurement. Turbidity measurements are not measurements of the concentration, type or size of the particles present.

The amount of light diffused by the floating particles in the water sample is measured by the optical characteristic of the water. The higher the intensity of the diffused light, the greater the turbidity. This enables the user to determine how turbid the water in the system is.

MAGNETITE

In essence, the solid corrosion products contain poorly solvable black particles (magnetite) or orange particles (hematite). These particles are deposited at points in a heating system where the flow is weak.

Magnetite (Fe_3O_4) is a black substance (sludge) that is formed through wear and tear and corrosion when air and water react with ferrous metals in heating systems. It has a tendency to accumulate in pipes and radiators and in time, to heap up, ultimately restricting or completely blocking the water flow. Hematite is deposited and heaps up, causing a gradual reduction in the pipe diameter, until at the certain point, the pipe becomes blocked.

Deposits of suspended particles can lead to moving parts (such as in pumps, vents and measurement devices) seizing up. This effect can be reinforced by the magnetic properties of magnetite particles. This is possible in, for example, high-yield circulation pumps, electric vents and measuring instruments based on magnets. If the magnetite in the system water is not removed, this inevitably leads to faster wear and tear of pumps, loss of boiler yield and loss of capacity of the entire installation.

Magnetite consists of black iron particles that are magnetic. If the particles attach themselves to a magnet, this indicates that they are the product of iron corrosion. This is a very good visual indication of how contaminated or clean the system is and whether magnetite is present.

TEMPERATURE

The temperature, or degree of heat, is the most important physical value of the system water that, as a carrier, transfers the heat to other materials. Heat can only go from a high temperature to a low temperature. Physically, it is a measure of the average chaotic kinetic energy of the constituent particles, i.e. of the movement of the molecules plus the movement of the atoms in the molecules. In addition, the temperature also causes variations in the macroscopic parameters such as volume and pressure. Under the influence of temperature gradients, the salts dissolved in the water can deposit on the walls of components and in pipes.

In installations with high water temperatures, the system water must cool down before measuring pH or electrical conductivity (EC) or requiring the use of a meter with temperature compensation. Although temperature is not necessary for the analysis of the water quality of a heating system, it is nevertheless an important parameter.

INHIBITOR (PROTECTOR)

An inhibitor or corrosion protector is a substance that sharply slows the speed of chemical reactions such as calcium deposits and corrosion. By adding an inhibitor to system water, the corrosion reaction will slow down and the water will stabilise. In some cases, the chemical reaction can even be halted completely.

An inhibitor is added to the system water in order to protect the heating system and so increase its energy efficiency. It prevents corrosion of all metals that are normally found in a heating system, such as carbonated steel, stainless steel, copper alloys and aluminium. It ensures that no corrosion sludge develops and protects vents, pipes and radiators against blockages. It also prevents calcium deposits in the heating boiler and heat exchangers, which increases the yield and has an energy-saving effect. As a result, the maintenance and repair costs are reduced and the service life of the system is increased.

The SpiroPlus Protector consists of specially selected stabilising and crystal structure-destroying polymers, organic corrosion inhibitors and a penetration agent. The pH-neutral effect destroys the crystal structure of the mineral salts and ensures that these continue to float in the system water. They can then easily be removed without forming deposits. Through its pH buffering capacity, the pH value remains stable.

The inhibitors form a film on the metal surfaces to be protected. For all products, including for Protector, it is important that the recommended concentration is respected. This is why it is so important to closely monitor the inhibitor concentration.

GASES AND OXYGEN

Every water system contains a certain amount of dissolved gases. These gases may be of a natural origin. They may be air (oxygen, carbonic acid, carbon dioxide and nitrogen) or other gases resulting from chemical reactions, such as gaseous hydrogen, hydrogen sulphide or ammonia.

Dissolved gases may be released in the form of microbubbles if the water temperature rises or the system pressure falls (Henry's law). Air bubbles are poor carriers of heat, as a result of which heat transfer diminishes and energy consumption rises, for example in heat exchangers and radiators, and which can lead to the boiler overheating. At higher flow speeds, they can also lead to noises throughout the system or even cause cavitation and erosion. Air also makes it more difficult to set up the installation, causes early wear and tear phenomena to components and promotes corrosion and, therefore, the formation of dirt and magnetite. Air pockets (accumulated gases) can even cause a complete restriction of the water flow.

Oxygen causes strong, accelerated corrosion of pipes, (aluminium/iron) boilers, radiators, etc., particularly in systems with a raised water temperature. Oxygen corrosion is also problematic in closed cold water applications. Under the influence of oxygen, iron oxide (rust water) is formed first, followed by the formation of magnetite (Fe_3O_4). Oxygen corrosion of materials containing iron first leads to an increase in the pH value (formation of OH-). However, with further strong oxygen input, the corrosion will cause a reduction in the pH value. In alkaline system water (pH >8.2) with limited oxygen, an oxide layer (passivation layer) will form that protects the metal surface.

Fully air-tight heating installations have no corrosion problems. However, this is not realistic, as gases will enter the system water in different ways, including through the filling and refilling water, insufficient bleeding, local negative pressure, gas diffusion through plastic pipes or membranes in expansion vats and via chemical and/or microbiological reactions.

The standards contain no guidelines for oxygen because special, costly in-line measuring equipment is necessary to measure the correct oxygen value and an oxygen value is only important for the location where corrosion can arise, not for the entire system.

Limiting the continual input of gases (oxygen) into the system water, and removing the released gases and air pockets as soon as possible are recommended measures. Automated systems (quick vents, air separators or vacuum degassers) can be installed in for this purpose, to remove the gases and air bubbles from the system water.

ALKALINITY

The total alkalinity shows the concentration of carbonates, bicarbonates, and hydroxide in the water, eliminate H+ ions, and is a measure of the capacity of the system water to neutralize acids. Alkalinity indicates the acid-buffering capacity of the system water, which is its ability to keep the pH value stable. The higher the alkalinity value, the less the pH value of the system water can vary. System water with low alkalinity, such as from the addition of demineralized fill water, can have a decrease in pH with only a small addition of an acid or base.

The relationship between the pH value, carbon dioxide (CO_2) and alkalinity describe the general condition of system water. The total alkalinity value is expressed in mg/l $CaCO_3$.

IRON

Iron is a metal found in nature in the form of oxides, or in combination with silicon or sulphur. In system water, iron occurs mainly in two forms: soluble and insoluble ferric particles. Water with fully dissolved iron is clear and colourless. When the iron is oxidised under the influence of oxygen, it turns into iron particles. Water with ferrous particles has a reddish-brown colour and possibly a sediment that does not dissolve.

Iron determinations can provide information on the degree of corrosion taking place in the heating system. It can accumulate in pipes, cause damage or reduced flow and reduced heat transfer or exchange.

A regular analysis can help determine if the iron content is increasing, which could indicate ongoing corrosion. This analysis should also determine whether the iron is soluble or insoluble. Insoluble iron can be removed with magnetic dirt separators or filtration. Soluble iron must be converted into insoluble iron to be removed. If this conversion is not possible, flushing and subsequent cleaning is required to remove the iron. Suitable corrosion inhibitors should be maintained to help prevent ongoing corrosion.

CHLORIDE AND SULPHATES

Chlorides and sulphates are salts present in the system water that increase the electrical conductivity and the speed of corrosion.

In systems with permanent or intermittent oxygen input, no corrosion damage usually occurs to stainless steel. However, unfavourable conditions, usually based on high chloride or sulphate concentrations, can lead to corrosion and leaks, particularly in system water with low alkalinity. Chloride is extremely damaging to the passivation layer (oxide layer) of materials, especially in the case of stainless steel whose protective chromium oxide layer can be affected. Consequently, tension, tear or pitting corrosion can occur in weak oxide layers. The risk of pitting corrosion increases with the chloride content and temperature of the water. It is therefore advisable to have low chloride and sulphate concentrations in the system water.

ATP (MICRO-ORGANISMS)

Adenosine Tri-Phosphate (ATP) is the most important molecule for the transfer and storage of energy in all living cells, from human and animal cells to microbes such as aerobic and anaerobic bacteria, algae and fungi. If water contains a high concentration of living organisms, large volumes of ATP will be detected.

All open and closed water systems form an environment in which micro-organisms can develop. Uncontrolled microbiological activity can lead to biofilms (slime layers) on surfaces of the cooling or heating system. As a result, the heat transfer deteriorates and favourable conditions arise for corrosion caused by air and scale formation. This can reduce the efficiency and service life of the installation and may cause unforeseen system failures.

An ATP measurement is used to quickly check the microbial activity. The result of this provides a general picture of the microbiological status of the installation.

FILLING AND REFILL WATER

Filling a heating system is preferably done with water that complies with the guidelines for the quality of system water. Refill water is the water needed to top up the water lost through evaporation, leaks and flushing.

Modern heating boilers and the accompanying installation components require that filling and refill water complies with certain quality requirements, so that problem-free functioning is assured. Even a small amount of oxygen or calcium deposit can partially overload the surfaces of heat exchangers through heat accumulation, and cause damage and tears through thermo-mechanical tensions. To avoid this risk, different water quality parameters should be measured 8 to 12 weeks after the first filling and then once a year, in accordance with the regulations.

In large installations, it is best to use conditioned tap water as filling or refilling water, for which softening (de-salting) and degassing are the simplest methods. In order to reduce the hardness of the water and prevent problems with calcium deposits, the filling and refilling water should be softened. In order to comply with the local guidelines or the guidelines of the boiler manufacturer, it is best to degas and soften or demineralise the tap water, or to treat it with a reverse osmosis unit.

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