



SYSTEM PROBLEMS – METALS/WATER

ALUMINIUM ALLOY

For the production of die-cast aluminium radiators, the material used is the **GD - To Si 12 Cu 2 Fe** (international abbreviation) alloy, which is equivalent to UNI EN AC 46100.

The use of such an alloy is important to manufacture radiators because of the physical and mechanical features and percentage chemical composition of the metals contained therein.

The alloy is composed of different percentages of several metals, such as: aluminium (85%), silicon (Si 12%), iron ($Fe \leq 1.1\%$), copper ($Cu 1.75 \div 2.5\%$). All the other metal elements have very low percentages (*).

(*) By varying such an alloy, as some manufacturers do, i.e. by increasing **zinc from 0.9 to 1.3 ÷ 1.8 %**, the alloy becomes "non-titrated". While this is an advantage for manufacturers because the cost of the alloy decreases, users may experience problems in their systems resulting from the high percentage of zinc, which, when activated by "some" hot waters, at a temperature higher than 55°C, forms gases (hydrogen bacteria) that are corrosive and damaging to the whole circuit.

WATER

Even though it is used everywhere as a heat carrier in residential heating, water and its fundamental properties have often been given little attention by designers, manufacturers and installers of systems.

In too many cases, this attitude involved little or no prevention of the problems associated with primary circuit water.

On the other hand, modern boilers are increasingly compact in size, with increasingly smaller exchangers that are a true "bottleneck" in the circuit and act as a filter for the whole system.

This explains why attention to these issues by manufacturers and, in general, by those operating in this sector is finally on the increase.

The knowledge of problems that water may cause and a professional approach towards their solution can only entail advantages: in particular, we shall see that chemical water analysis can provide a lot of information about the state of health of the system.

WATER MOLECULES

Among all molecules, both natural and man-made, that of water is unique.

It is present in nature in all three physical states: solid, liquid and gas. Because of its special structure, the amount of energy required to vaporise water, as to freeze it, is greater than that required for other simple molecules. Therefore, the amount of heat absorbed or released when temperature changes is greater, i.e. water has a very high thermal capacity, which makes it an excellent means of heat transmission.

Furthermore, water is often defined as a "universal solvent", because it tends to melt everything it comes in contact with.

Water with low concentration of dissolved solids is corrosive and behaves in a more aggressive manner compared to water with a higher concentration of dissolved elements, which tend to increase its solid content. In Italy, water with such characteristics is found in some areas of Novara and Vercelli.

We shall now see the consequences of different water qualities for heating systems.

SCALE IN THE SYSTEM AND ITS CONSEQUENCES

Many people are aware of the scale that forms on some element of the sanitary water circuit, such as boilers, exchangers and pipes, in some areas where there is especially hard water (hard water is defined as a water with a low concentration of dissolved substances).

However, scale formation in the main heating circuit is rarely taken into consideration.

In heating circuits, scale is mostly caused by two phenomena:

- lime scale deposit;
- the formation of iron oxide resulting from corrosive phenomena.

Lime scale (**calcium carbonate**) is often present together with low percentages of other calcium salts, such as sulphates.

Unlike other salts, calcium salts become less soluble as temperature increases (inverse solubility).

Being obviously present in a lot of aqueduct water, all systems where these waters are warmed are likely to be subject to scale formation. Let us consider a type of filling water having a hardness equal to 30°Fr, i.e. containing 300 mg/l of calcium hardness. The potential lime scale weight produced in 100 litres of water is equal to 30 g, just taking into account the first filling.

Once formed, lime scale tends not to dissolve. This leads to big problems in case of system restoration, as the water discharged from the system is not able to bring away scale, while the new filling water will contribute additional calcium salts to the system, further increasing the scale thickness in the system. Being a direct consequence of the increase in temperature, lime scale will always form in the hottest areas of the system, i.e. the boiler exchanger. Moreover, at times, scale can also trap corrosion residues, thus further aggravating the problem.

On the contrary, iron oxide firstly deposits as a sediment in the area where corrosion has occurred, and then changes into true scale when it is transported by water to the exchanger, where it undergoes a hardening process by heating.

The presence of scale in a heating system causes three important effects:

- 1) **Boiler noise.** Proper boiler operation mostly depends on the uniform removal of the heat produced in the exchanger, so that the skin temperature of the metal in contact with circulating water always remains below the boiling point. Boiler noise is really caused by localised overheating of circulating water, which leads to steam formation.
- 2) **Reduced efficiency.** The reduction in efficiency caused by the decreased thermal exchange coefficient, although not easily quantifiable, is a problem in modern heating systems. The extent of reduction depends on the thermal conductivity of scale: since a porous lime scale deposit conducts heat 100 times worse than the metal in the exchanger, the insulation created by a lime scale as thick as an egg shell will lead to an increase in the consumption of fuel up to 10%.
- 3) **Increased thermal stress in metal.** In extreme cases, scale can increase to a point where thermal flow restriction can overheat the insulated metal surface, causing the part to break.

INTERNAL AND EXTERNAL TREATMENT

To prevent scale formation, water can be treated both internally and externally.

The internal treatment includes the addition of a **scale inhibitor**. The inhibitor can be part of a more complex product, or a specific substance, generally a polymer. Today, the best products on the market contain substances that change the scale crystal form from cubic, as in the natural state (calcite), to spherical (valerite), so that packing of layers is prevented. Also, the polymer is able to react with scale to form soluble complex substances even at high temperatures. These properties give exceptional characteristics to scale removers.

Instead, the only external water treatment that has been proven to be really valid is **softening with ionic exchange resins**.

However, it is necessary to consider that the softener used makes the resulting water more corrosive. Therefore, it has always to be treated with a suitable corrosion inhibitor

for softened water.

A widely believed but incorrect idea is that softeners reduce the concentration of dissolved solids in water, while their function is actually just to exchange calcium ions for sodium ions.

However, the use of softened water in the main circuit is superfluous if an inhibitor is present, and is never recommended in the presence of aluminium.

Corrosive phenomena always take place, in various forms and speeds, in all heating systems.

The extent of such phenomena depends on many factors:

- the type of metals in the system;
- the amount of air that may enter the system;
- the filling water quality.

OXYGEN INPUT AND HYDROGEN FORMATION

Among all corrosive phenomena that can attack a heating system, oxygen is probably the most important.

It is wrong, although commonly said, to think that the amount of oxygen injected during the first filling is quickly consumed due to the reaction with metal surfaces, and that corrosion does not proceed any further.

That is denied by the fact that, in practice, there are no systems that are completely without oxygen. Even though dissolved oxygen is depleted, corrosion continues due to the reaction of the oxygen present in the various system components, which slowly continue their self-destruction process.

In its simplest form, the chemical reaction between iron (or steel or cast iron) and oxygen in water produces iron oxide, as well as hydrogen gas.

The effect of hydrogen formation is to lower the water level in radiators, thus producing a gas (hydrogen) pocket that does not allow a proper exchange with the heat carrier and causes the formation of cool areas, which are usually up high. A combined factor is pressure rising in the radiator, which now has to manage local pressures even up to 10 times greater.

In extreme cases, pressure is such that it literally breaks radiators.

Most of the times, the gas (hydrogen) ends up accumulating in a radiator in the lowest pressure point, which is furthest from the circulator.

The pressure caused by **hydrogen** is often noticed in the form of hissing or other noise.

When the pressure in the system causes you to suspect a gas formation, it is firstly necessary to check the actual presence of hydrogen: the gas can also simply be air. To do this, bleed the radiator into a glass or other glass container held upside down. Being lighter than air, hydrogen will occupy the place of air in the container. At this point, remove the container from the radiator and light a match: if hydrogen is present, the match will burn with a light and non-hazardous detonation and you can conclude that a corrosive process is occurring in the system.

pH FEATURES

pH is a numeric indication of a solution acidity or alkalinity.

The pH scale ranges from 0 to 14, where 7 corresponding to neutral: values < 7

indicate acidity, values > 7 indicate alkalinity. The scale is logarithmic; therefore, a solution of pH 5 is 10 times more acidic than a solution of pH 4, and a solution of pH 3 is 100 times more acidic.

Metals are affected in different ways by pH: for instance, carbon steel is more stable between pH 10.5 and 11.5, while aluminium is attacked above pH 8.7 due to the destruction of its naturally formed layer of alumina oxide. Copper can corrode at a pH higher than 9.5.

The ideal pH range for heating systems is between 6.5 ÷ 8, within which the corrosion speed of all metals is acceptable.

CONTACT BETWEEN VARIOUS METALS

When two different metals come in contact through water, a galvanic cell (electrochemical) is created.

According to the relative position in the electrochemical series, one of the two metals will go into solution.

Copper is the most noble of the metals used in heating systems and all the other metals are "sacrificed" in its presence.

Metals that corrode more easily in a heating system are those in radiators: steel, cast iron, aluminium, even though for the latter the protective factor, activated by the alumina oxide, extends its life with a ratio > 5 times than that of cast iron and steel.

Here, according to the amount of copper, corrosion can take two forms.

1. Where a vast radiator area is covered with copper there will inevitably be uncoated areas: galvanic corrosion takes place here with the current concentrated in the point where the sacrificial metal is in contact with water. The current is intense; corrosion due to metal perforation is very quick, and a passing-through hole is formed in a very short time. The dimension of the hole on the outside of the radiator is about the same as that on the inside, as if the metal had been drilled. This corrosive form is called "**pinhole**" corrosion.
2. Unlike this situation, small copper pieces can stick to the inner radiator surface. Galvanic corrosion will still take place, but this time the current will concentrate on the part of the non-sacrificial metal (copper). The result is a loss of metal through its entire surface. This form is called "**generalised corrosion**" and is always slower than the previous one.

Usually, chemical reactions proceed more quickly as temperature increases. For this reason, a heating system will corrode much more quickly than other circuits run on lower temperatures.



MECHANICAL STRESSES

Points of mechanical stress such as welding, elbows, etc., are always most subject to corrosion.

Some salts, like chlorides, attack stressed areas along the edges of metal grains.

The greatest sources of chlorides are faulty softeners, residues of acids used by mistake to remove boiler noise, as well as residues of welding fluxing agents.

DIRT

Dirt means the presence of contaminants on the surface of metal heating systems: they can be of an organic (bacteria or other micro-organisms) or inorganic type (metal sludge resulting from corrosion).

Whatever the nature, contaminants create a local gradient of oxygen concentration, which causes corrosion deposits and takes the form of pin-holes.

SYSTEM CLEANING

To effectively clean a new system from the various contaminants, effective, non-acidic products are available.

These products contain detergents and surfactants that remove residues resulting from welding fluxing agents, manufacturing residues (metal shavings, foundry sand, and paint fragments), and residues of greases and cutting oils, if any. Our products, as already stated, are properly treated in the pre-painting process, which ensures the removal of such pollutants.

Vice versa, to clean a system which has been operating for some time, other non-acidic products have been made to remove magnetite sludge that forms over time in order to restore full water circulation to partially blocked radiators.

Moreover, this operation avoids dirtying a new boiler just installed in an old system.

CORROSION INHIBITION

The most effective corrosion inhibitors act by reacting with the metal surface to produce a protective, monomolecular film made of a stable complex. The effectiveness of an inhibitor also obviously depends on its concentration.

In a multi-metal system, the product to be used should contain various inhibitors in its formulation, each suitable to protect a specific system metal.

WATER ANALYSIS

A chemical water analysis enables a quick diagnosis of the problems listed up to now so that appropriate corrective actions can be promptly taken.

It is important to note that for such purposes, in practice a precise laboratory analysis is not required.

The following crucial parameters to be taken into account when inspecting a system can be obtained with readily available simple analytical kits contained in small, portable cases:

- **Conductivity:** the capacity of water to conduct electricity is directly proportional to the concentration of dissolved solids. It is usually expressed in γ s/cm (microSiemens/cm) and can be measured with a conductivity meter.

In general, where hardness salts are present, the concentration of dissolved solids in the system water (and therefore its conductivity) is lower than that of filling water.

The addition of an inhibitor increases conductivity and that makes it possible to determine the inhibitor concentration from the conductivity reading.

- **pH:** a pH lower than 5 or higher than 8.5 is harmful to the aluminium parts in the system.

A pH beyond these limits results from some kind of alteration.

If the pH is lower than 5, then an acid is present in the water; if the pH is higher than 8.5, then the water is alkaline. Alternatively, an alkaline treatment is taking place, for example with phosphates or glycols as antifreeze, or in certain cases owing to the natural generation of alkalis in the system.

- **Chlorides:** they are contained to a greater or lower extent in all types of water. Even though the level of chlorides in the network waters is subject to fluctuations, when a substantial increase (higher than 50%) is noted between their level in the system compared to that in the network water, it is

likely that contaminants are present in the system.

- **Hardness:** network water can be classified as shown in the below table:

Network water classification

Denomination	Hardness (mg/l CaCO_3)
Almost soft	0 – 100
Moderately hard	100 – 200
Hard	200 – 300
Very hard	Over 300

A comparison between the hardness of the network and system waters shows if scale has formed.

A decrease in hardness equal to 100 mg/l means that around 10 g of scale has formed for every 100 litres of system water.

In case of scale formation, almost all the scale is very likely to be in the boiler exchanger.

- **Total alkalinity:** this test gives a measurement of bicarbonate in the water. High total alkalinity values, especially when combined with high hardness values, cause water scaling tendency to increase.
- **Aluminium:** a difference of concentration equal or higher than 0.3 mg/l between system water and topping-up water indicates that there is corrosion. If the pH is between 5 and 8.5, then aluminium surfaces are passivated and protected against any corrosive attack.
- **Copper:** a difference in concentration between the system and network levels higher than 0.2 mg/l is already significant. If the difference is higher than 0.3 mg/l, then the presence of galvanic copper deposits is probable on steel or aluminium surfaces.
- **Iron:** as we have already seen, as a heating system corrodes, the iron dissolves and then re-deposits to form sludge, which entails the development of **hydrogen**.

The amount of particles present (visible as suspended solids) is a way of determining the extent of corrosion.

In terms of dissolved iron, an increase above 0.5 mg/l of the iron present in the system compared to the network is already significant, while an increase above 3 mg/l is a symptom of active corrosion.

If the sample contains suspended iron oxide particles, they will dissolve during the analysis.

Therefore, it is always necessary to make sure that the suspended solids found are representative of the conditions of the whole system.

- **Deposit analysis:** calcium carbonate (lime scale) is effervescent when in contact with acid, since carbon dioxide is released.

The degree of effervescence does not only depend on the lime scale percentage in the deposit, but also on its hardness and porosity.

You must therefore be careful in estimating this percentage.

The attraction of solid particles to a magnet does not necessarily mean that the entire deposit is magnetite, because non-magnetic salts can also be mixed in.

CONCLUSIONS

The thermal fluid (water) is the factor that affects a heating system durability and corrosion. For this reason, the heating system water used must have features suitable for such use, to avoid triggering corrosion.

In some countries, including Italy, the physicochemical features of water are specified by suitable laws. In our case the reference standard is UNI 8065.

This standard lays down the features of filling and topping-up water for heating systems, including circuit water.

Filling and topping-up water features (Standard UNI 8065)

Aspect Limpid Total Hardness	< 0.5° Fr
Fixed residues (at 180°C)	< 1000 mg/kg
Electrical conductivity	< 1500 μ s/cm
Iron (as Fe)	< 0.2 mg/kg
Copper (as Cu)	< 0.05 mg/kg.

Circuit water features (Standard UNI 8065)

Aspect	Possibly limpid
pH	7.0 to 11.5
P alkalinity (as C_aCO_3)	< 800 mg/kg
Fixed residues (at 180°C)	< 2000 mg/kg
Electrical conductivity	< 3500 μ s/cm
Iron (as Fe)	< 0.5 mg/kg
Copper (as Cu)	< 0.2 mg/kg

SOLUTIONS TO PROTECT SYSTEMS FROM GASEOUS AND NON-GASEOUS CORROSION

Among the various chemical treatments available to protect systems from corrosive attacks, we shall mention the two most widely used:

- Protection with protective film formation;
- Protection from freezing.

Protection with protective film formation: in any new system composed of multiple metals (e.g.: steel or **copper pipes**, brass valves, aluminium, cast iron or steel radiators, boiler with exchangers in cast iron, **copper**, steel, etc.), it is advisable to treat water with a protective film based on film-forming aliphatic polyamines, such as **CILLIT-HS 23 Combi**, which is a corrosion inhibitor and acts by protecting metal surface parts through the formation of a compact passivated layer (protective film). Such a treatment isolates water from dielectric contact with the multiple metals that compose the system.

In any old system, before installing new components, such as the aluminium radiator, system balancing is advisable with a suitable product, such as **CILLIT-HS 23 RS**; the recommended product has a formulation capable of removing corrosion residues and lime scale from the circuit, thus restoring proper water circulation. After this treatment, and the relevant rinses, the radiator can be installed adding the aforementioned **CILLIT-HS 23 Combi** to the heating circuit water.

Protection from freezing: to prevent water from freezing inside the system, it is necessary to treat the circuit chemically with organic compounds based on passivating non-toxic glycol. One of the following two solutions can be chosen:

- Glycol: widely used as antifreeze in car cooling circuits, suitably inhibited with special additives for use in heating circuits. The glycol-water ratio must be determined according to the minimum outdoor temperature.
- Non-toxic propylene glycol with additives and inhibitors, such as **CILLIT-CC 45 S**: a complete antiscaling, anticorrosion and antifreezing product. With a dosage of 65% in the circuit, a resistance to outdoor temperatures up to -50°C can be guaranteed.

PASOTTI INDUSTRIES

S.p.A. Technical Management