Are the chemicals the solution or part of the problem in relation to corrosion?

There are attitudes both for and against, but the Danish District Heating's recommendations to limit the use of chemicals correspond to the recommendations of the German standard for district heating water: AGFW FW 510.

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WATER TREATMENT In general, the Danish District Heating Association's guide "Water Treatment and Corrosion Prevention" from September 2015 has been well received by both the association's members and suppliers of equipment for the district heating industry, and there was great attendance at a theme day on the topic, which was held in May 2016.

However, there have been critical voices in relation to the guide's more pronounced recommendation to use only demineralized, degassed make-up water and minimize the use of chemicals in addition to lye (NaOH) for pH-adjustment. The criticism comes not least from the chemical suppliers, who naturally are not interested in the whole industry following the recommendations too closely.

Against this background, Kate Wieck-Hansen (chemistry expert at Dansk Fjernvame) and the undersigned had a meeting with one of the suppliers, where we exchanged views on the recommendations in the guide and presented arguments for and against the use of chemicals for oxygen binding, corrosion inhibition and dispersion of calcium and corrosion products. It became an interesting discussion, where each party weighted the different properties of the chemicals differently, and thus also the use of them. It is an area where there is no conclusion beforehand and where the justification of the chemicals must be assessed for each individual plant. Nevertheless, it may be interesting for district heating professionals to have the arguments for and against the chemicals outlined, so that you can better assess whether your own plant leans towards one side or the other.

<table>
<tr><th>Arguments put forward by the suppliers</th><th>Arguments of the Danish District Heating Association and COWI:</th></tr>
<tr><td>In real life, the recommendation to use only demineralized water conditioned with NaOH falls too often to the ground when oxygen and drinking water penetrate the district heating network because there is nothing in the water to counteract that oxygen is used for corrosion and that lime deposits on surfaces.</td><td rowspan="2">Oxygen will, due to the lower conductivity of demineralized water, be used for surface corrosion rather than localized corrosion, thus changing its character from harmful to relatively harmless. Even the most effective oxygen scavenger removes only a fraction of the oxygen, since the best oxygen scavenger in the system is the steel surfaces themselves. A certain amount of corrosion products will still be formed which can be transported with the water and removed by partial flow filtration.</td></tr>
<tr><td>If chemicals are dosed, the oxygen scavenger will ensure that the oxygen is not used for corrosion. When a suitable excess of oxygen scavenger is maintained, this will be present all around in the system and can take care of oxygen from penetrating drinking water in water heaters or from old floor heating tubes without oxygen barrier.</td></tr>
<tr><td>Calcium is prevented from forming precipitations and is bound by the dispersant so that it can be transported by flow and eventually end up in a partial flow filter. Especially precipitations in heat exchangers can reduce the efficiency and almost clog a heat exchanger in some cases.</td><td rowspan="2">Demineralized water can dissolve considerably more calcium than softened water because of the lower carbonate content. Thus, there is no immediate precipitation of calcium, i.e. there is time to detect the problem based on the analyses and to intervene with correction in the form of partial flow treatment (using ion exchange or reverse osmosis). Partial flow filtration with cartridge filters or bag filters is also a good idea with demineralized water, and it works well without dispersants. The best long-term tactic against penetrating drinking water is to find the sources, i.e. the leakages. This can be done with campaigns, through addition of colouring agents to the water, by continuously conducting leakage checks at the consumers, through cooperation with the water supply, so that consumers with extraordinary water consumption are located.</td></tr>
<tr><td>Corrosion products are also kept in suspension by the dispersant so that they too can be trapped by partial flow filtration and do not precipitate in locations where calm flow conditions reside. Deposits at such locations can cause localized corrosion (pitting) which, due to its local character, can quickly cause serious damage such as e.g. pores through the bottom of the accumulator tank.</td></tr>
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Table 1. Outline of arguments regarding the use of oxygen absorbents and dispersants.

The arguments for and against the use of chemicals

The arguments for and against the use of oxygen absorbents and dispersing chemicals are briefly summarized in table 1.

The supplier's arguments are not wrong, but overall this treatment is symptomatic treatment of a poor water chemistry in general. This may be appropriate in special cases, but it is not the best long-term strategy to operate a district heating network. If you want to get at the root of the evil, the water chemistry must be improved by using demineralized make-up water and thus running the system with (partially) demineralized water.

The disadvantages of using the chemicals are:

- These are mostly organic chemicals, so by adding them to the water, a food basis for the growth of bacteria is created and thus the formation of biofilm. Biofilm can also give rise to local corrosion under the film, and biofilm isolates so well that reduced heat transmission over heat exchangers is a consequence often disregarded.
- The best oxygen scavenger in the system is the steel faces per se. An added oxygen absorbent can manage to react with some of the penetrating oxygen, but a great deal will still be consumed by corrosion. The higher the conductivity in the water, the more local and harmful the corrosion becomes.
- The chemicals are expensive, even a small district heating plant often buys chemicals for DKK 40-50,000 a year. By comparison, the required amount of NaOH to condition the water would cost a few thousand Danish kroner at most.

The German standard for district heating water quality

In our discussion with the supplier, reference was also made to international standards which, according to the supplier's statements, recommended the use of chemicals. Specifically, the supplier referred to a TÜV standard from Germany, which I have subsequently found. Contact with colleagues in the power plant industry in Germany has given an updated impression of the recommendations for quality and conditioning of district heating water in the large district heating land to the south of us.

The contact with Germany showed that the latest and current standard for the quality of district heating water is the AGFW-Arbeitsblatt FW 510. The AGFW means "Der Energieeffizienzverband für Wärme, Kälte und KWK, e.V.", i.e. a trade association in the field of technical heating and cooling. TÜV, a member of this association, has abandoned its own standard in the field and now recommends following the FW 150 when treating district heating water. It is therefore interesting to compare the recommendations of the FW 150 (which I have translated) with the Danish District Heating Association's guide.

The recommended German limit values for the chemical quality parameters are shown in table 2.

Parameter	Unit	Low-salt water (~ demineralized)	(~ partially demineralized)	Saline water (~ softened)
Conductivity at 25 °C	µS/cm	10-30	>30-100	≥100-1500
Appearance		Clear, free of suspended matter		
pH at 25 °C		9.0-10.0	9.0-10.5	9.0-10.5
Oxygen	mg/l	<0.1	<0.05	<0.02
Hardness	mmol/l	< 0.02	< 0.02	< 0.02

Table 2. The table from the FW 510 shows the indicative German values for circuit water in directly or indirectly heated systems.

There is a great deal of correspondence between the guiding values in the German FW 510 and the more detailed quality criteria in the Danish District Heating Association's guide. Where we aim at a pH of 9.8 ± 0.2 as the best compromise between considerations for steel and copper/brass materials, the Germans allow a wider pH-range. The attitude towards oxygen in the low-salt water of the German standard is also more relaxed with up to 100 µg/l in the demineralized and up to 50 µg/l in the partially demineralized water. The requirements for hardness (0.02 mmol/l ~ 0.1 ºdH) are as in the previous version of the Danish guide. The Germans have not recognized that the value can be reduced in demineralized and partially demineralized water without risking lime formation.

The central elements of the German FW 510 standard, which says something about conditioning and the use of chemicals, are summarized in table 3.

6.2 Operating conditions with low-salt water
"In low-salt water, the risk of oxygen corrosion is lower, the lower the conductivity. Therefore, limit values for oxygen of 0.05 and 0.10 mg/l, respectively, can usually be tolerated. The prerequisite is a reduction of the conductivity to <100 µS/cm. Only demineralized water can be used as make-up water”.
6.3 Operating conditions with saline water
“District heating systems can be operated with saline, circulating water when admission of oxygen and other gases can be excluded to a great extent. As far as the limit values for oxygen, pH, and conductivity in normal operation can be safely met, the use of oxygen absorbents and corrosion inhibitors can be omitted. Conditioning with oxygen absorbent or corrosion inhibitor may make sense to reduce the risk of corrosion by e.g. penetration of raw water or use of oxygen-containing make-up water. In addition, there must be attention to maintaining a low hardness in the circulating water”.
6.5 Conditioning
6.5.3 Stabilization of hardness
”In circulating water, the limit values of table 6.1 can be observed through application of the stated water treatment methods (ref. note: softening or demineralization through ion exchange or reverse osmosis). Minor increases in hardness from penetrating raw water that cannot be avoided can be countered by the addition of hardness stabilizers and inhibitors of lime formation. In practice, phosphate-based chemicals, polyphosphate as well as polyacrylate, have been found to be useful. In addition to preventing precipitations, they have a dispersing effect and thus also prevent deposits of corrosion products and suspended solids. Complexing agents such as EDTA and NTA are today considered to be problematic for wastewater”.
6.5.4 Oxygen removal
“In the district heating network, penetration of oxygen cannot be completely avoided. In an extensively (ref. note: read technically) closed district heating network without (ref. note: abnormally) high make-up water consumption, the oxygen penetration at undisturbed (ref. note: normal) operation is so low that there is no reason to fear corrosion damage. Oxygen removal is technically unnecessary here. On the other hand, oxygen removal makes sense when increased oxygen penetration due to special operating conditions cannot be ruled out. The removal can be done using partial flow degassing plants, by catalytic and electrochemical oxygen removal, and by addition of oxygen scavengers. In the case of operational disturbances with massive oxygen penetration, it must be assumed that the reaction rate of the corrosion processes is greater than the reaction rate of the oxygen absorbent (ref. note: Thus, the oxygen absorbent has limited/no effect in that situation)”.

Table 3. Translation of key sections of the FW 510 which deals with conditioning and use of chemicals.

Danish and German recommendations agree with each other

The sections on conditioning in the German standard show a clear and evident correspondence with the recommendations in the Danish District Heating Association’s guide: Both systems with demineralized water and systems with soft water can in normal cases (without major penetration of oxygen and contaminants) be operated alone by conditioning with NaOH to a pH-value over 9 and tempering with degassed water. The application of oxygen absorbents and dispersants can be used in special cases where there is a (temporary) need.

The observations of the German standard that, in the event of oxygen penetration, the oxygen absorbent has not time to prevent the oxygen reaction with the steel surfaces, i.e. consumption of oxygen for corrosion, fits very well with our perception. Already more than 15 years ago, this was clearly demonstrated in a study conducted by the Fælleskemikerne at the then Elsam organization on behalf of the Danish District Heating Association (Karsten Thomsen, Erik F. Smitshuysen, "The operation of chemical oxygen absorbents and impact on the corrosion environment in district heating systems", DFF-F&U report 2001-02, the editors).

Of course, monitoring of the quality parameters is also mentioned in FW 510. In addition to the quality parameters in table 2, the German standard recommends analysing for additional parameters, all of which are covered by the recommendations in the Danish District Heating Association’s guide.

Summary

In addition to an exchange of views and attitudes to the use of oxygen absorbents and dispersants in district heating systems, the discussion with the supplier led to a check of the Danish District Heating Association's guide on water treatment and corrosion prevention in relation to the current German standard in the field: AGFW FW 510. The review of this standard has clearly shown that there is substantial agreement with the Danish guide on recommending the use of demineralized water in district heating systems. Furthermore, to minimize the use of the organic conditioning agents to the few cases where there really is a need caused by unsatisfactory water chemistry. The use of chemicals will then be symptomatic treatment that does not eliminate the cause of the poor water chemistry and which has adverse side effects. The real cure for the problem is detection and repairs of the leakages. This can be difficult, nevertheless using the various methods available can bring progress.