

International Energy Agency

# IEA District Heating and Cooling

Programme of Research, Development and  
Demonstration on District Heating and Cooling

## A REVIEW OF EUROPEAN AND NORTH AMERICAN WATER TREATMENT PRACTICES

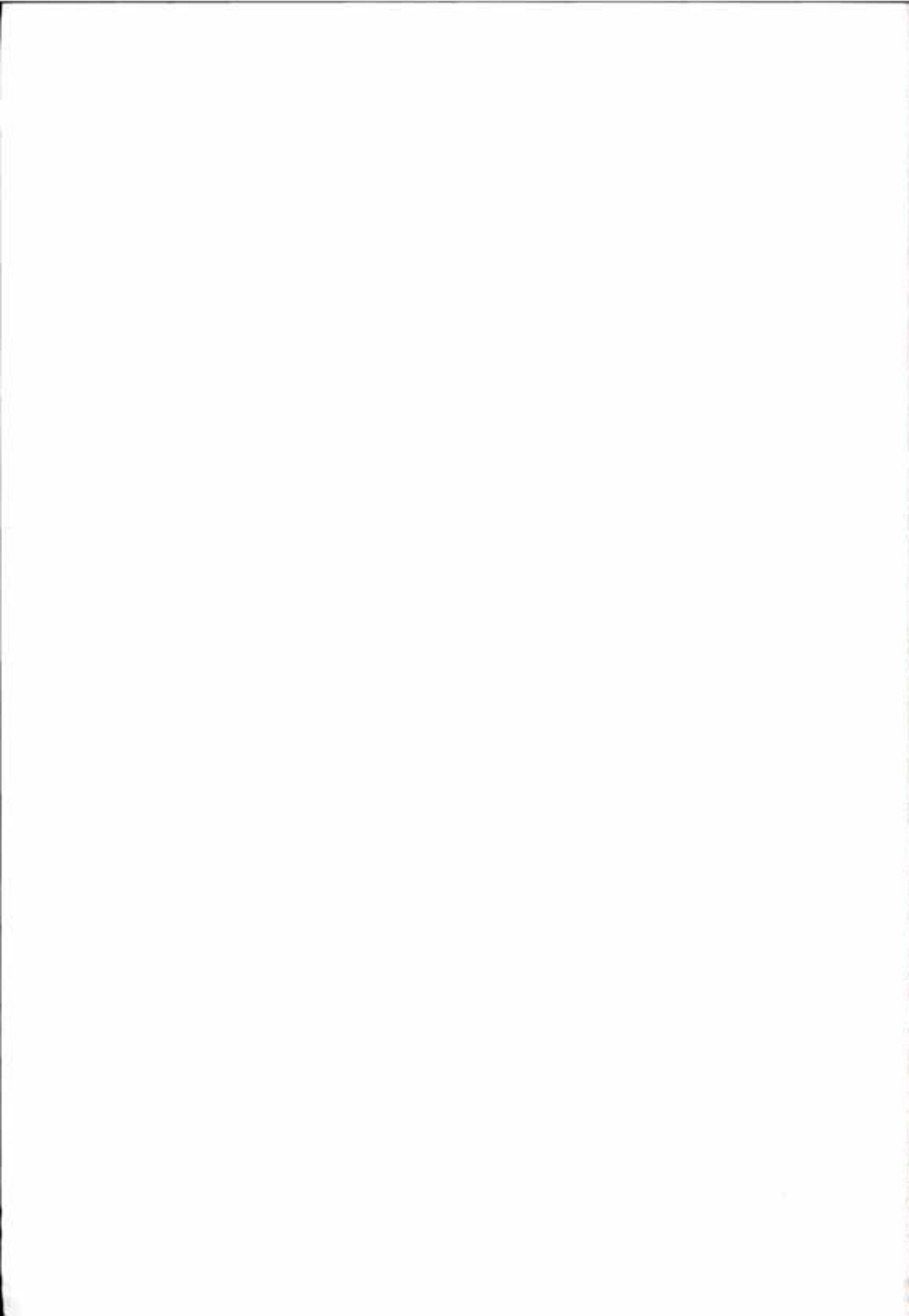
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# **INTERNATIONAL ENERGY AGENCY**

**Programme of Research, Development and  
Demonstration on District Heating and Cooling**

## **A Review of European and North American Water Treatment Practices**

**April 1996**

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## A REVIEW OF EUROPEAN AND NORTH AMERICAN WATER TREATMENT PRACTICES

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Abstract: This report is a collection of three papers on the subject of water treatment practices for corrosion prevention in hot water district heating systems. The first paper is a translation of a manual prepared by Nordvärme, the district heating association of Nordic countries in Europe. The second paper describes chemical additives which are commonly used to prevent corrosion in North American heating systems. The third paper describes two North American district heating systems which have adopted these different approaches and compares the water treatment programs in each on the basis of cost and effectiveness.

## PREFACE

The International Energy Agency (IEA) was established in order to strengthen the cooperation between member countries. As one element of the International Energy Program, the participating countries undertake cooperative activities in energy research, development and demonstration.

District Heating and Cooling is seen by the IEA as a means by which countries may reduce their dependence on oil and improve their energy efficiency. It involves the increased use of indigenous or abundant fuels, the utilisation of reject heat from industrial or other processes.

IEA's Program of Research, Development and Demonstration on District Heating was established at the end of 1983. Ten countries participated in the program.

In May 1993 a decision was made to proceed with Annex IV in which the participants will continue their cooperation for another three-year period. Projects in this phase include:

- (1) Design guide for integrating CHP and district cooling
- (2) Advanced transmission fluids
- (3) Heat distribution technology
- (4) Network supervision
- (5) Efficient substations and installations
- (6) District heating piping
- (7) Development of long term cooperation with East European countries

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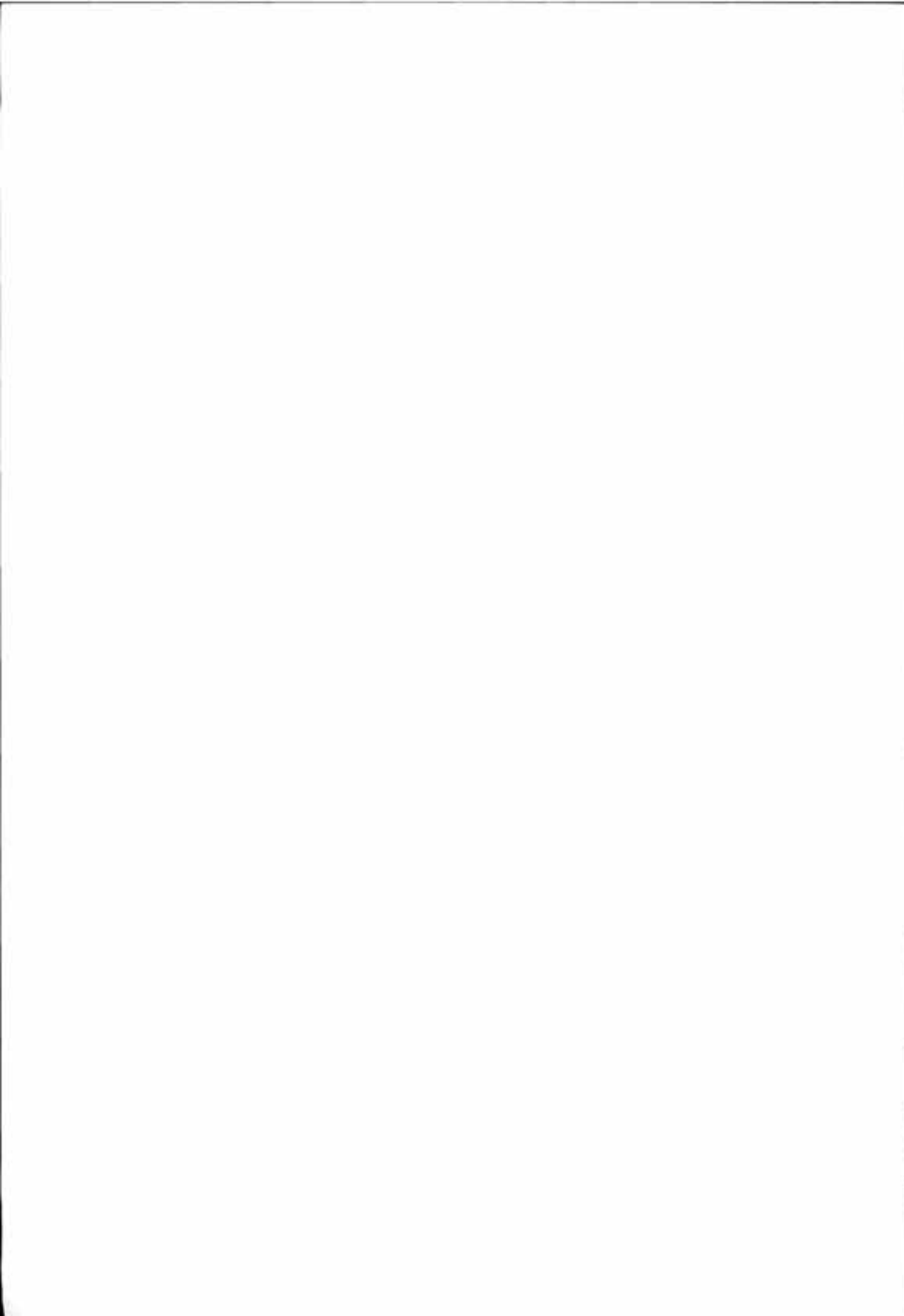
NOVEM has been the Operating Agent for the program since 1987.

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## SUMMARY

This report outlines the European approach to water treatment and corrosion prevention in hot water district heating systems, specifically the approach advocated by Nordvärme, the district heating association of Nordic countries in Europe. The intent of this report is to make information and operating experiences on the Nordvärme approach available to North American system operators as well as to describe common North American water treatment methods.

An interest in the European approach to water treatment has grown recently because of developments in advanced fluids for district heating and cooling systems. New additives are sometimes incompatible with chemicals traditionally added in North America to prevent corrosion in hot and cold water systems. In particular, some corrosion inhibitors have been shown to be incompatible with the use of friction reducing additives.

Friction or drag reducing additives reduce the frictional losses from water in turbulent flow by suppressing the formation of turbulent eddies. This results in lower pumping energy requirements and costs. Interest in these additives has grown over the last few years and the additives have been successfully demonstrated in several systems, including a transmission system in Herning, Denmark in which pumping energy requirements were reduced by 70% and overall operating costs were reduced by 40%.

In North America, corrosion of steel district heating pipes has traditionally been prevented by adding corrosion inhibitors which protect the pipe by forming a protective passivating film on the internal surfaces.

Most corrosion inhibitors are inorganic oxidizing substances which passivate the metal surface by forming an impervious film

which interferes with the anodic or cathodic corrosion reactions. These inhibitors work with metals that exhibit active-passive transitions such as iron, nickel, chromium and alloys containing these metals.

As well, chemicals are sometimes added which react with and remove dissolved oxygen. This limits corrosion by limiting the oxygen reducing cathodic reaction. Restricting either the cathodic or anodic reactions will limit the overall corrosion rate since these processes are dependent on one another. The electrochemical mechanisms of corrosion are explained in more detail in the first paper in this report, "Corrosion and Water Treatment in Nordic District Heating Systems, Experience and Practice".

The overall treatment strategy also includes filtering and demineralizing (or softening) system water and raising the pH. The second paper in this report describes chemical additives which are currently used to prevent corrosion in North American closed cold and hot water distribution systems and explains some of the advantages and disadvantages of each.

### Common chemical additives for corrosion prevention in North America

#### **Passivators:**

- chromate
- borate nitrite
- silicate
- molybdate

#### **Oxygen scavengers:**

- hydrazine morpholine
- sulphite caustic soda/soda ash

The strategy recommended by Nordvärme is simply to maintain high quality water in the system through continual filtering, deaeration and demineralization (or softening) and to maintain the pH between 9.5-10 by adding sodium hydroxide. The procedure requires careful monitoring of the chemistry of the

system water. The corrosion rate must also be monitored through the use of corrosion coupons or piping samples inserted in the flow. Demineralization is preferable to softening because it reduces the total ionic concentration.

#### Summary of Nordvärme water treatment method

- filter
- demineralize or soften
- deaerate
- raise pH to 9.5-10 by adding sodium hydroxide (NaOH)
- monitor corrosion rate and concentrations

The first paper in this report is an English translation of the Nordvärme water treatment manual for district heating system operators. This manual was prepared by expert representatives from five member countries of the Nordvärme working group on water treatment. In it, Nordvärme gives recommended ceiling concentrations for chemicals in the system water.

#### Summary of guideline values of dissolved species in district heating water

pH at 25°C	9.5-10.0
Oxygen concentration	< 0.02 mg O <sub>2</sub> /kg
Ammonia concentration	< 10 mg NH <sub>3</sub> /kg
Total iron concentration	< 0.1 mg Fe/kg
Total copper concentration	< 0.02 mg Cu/kg

The Nordvärme approach has been successfully applied in the two district heating systems in Prince Edward Island, Canada. In these systems raw water entering the network is filtered, softened and deaerated. Water in the system is continually filtered. The pH is maintained between 9 and 9.5 by adding sodium hydroxide.

In the St. Paul, Minnesota district heating system in the United States, water is pretreated by filtering and softening and a corrosion inhibitor is added to the system. The cost of this treatment is \$0.12 per gallon of makeup water compared with \$0.05 per gallon of makeup water in the P.E.I. systems. The cost of water treatment in the P.E.I. systems however, is dependent on the cost of laboratory analyses. In the St. Paul system, testing is included as a service with the purchase of the corrosion inhibitor.

The experiences in the P.E.I and St. Paul systems are outlined in the paper beginning on p. 44 of this report. This paper was presented at the annual conference of the International District Energy Association in Indianapolis in June 1995, and again at the IDEA's distribution workshop in St. Paul in November 1995.

Feedback from the audience at the IDEA conferences indicated that many North American operators were more comfortable contracting out water treatment activities. Even if there are savings to be made, operators prefer a complete treatment "service", where providing the chemicals and monitoring the system are both the responsibility of the chemical company. Water treatment activities sometimes require both time and a level of expertise that plant staff do not have.

Conversations with plant staff have indicated that in busy seasons, water treatment monitoring is sometimes the first activity put on hold although it is vital to the long-term health of the system. The assumption is sometimes made that if a given method has worked well in the past, it will continue to work. Stopping monitoring, however, can lead to unexpected problems. A number of conditions in the system can change such as the chemistry of the makeup water, and the operation of the deaeration and deionization equipment and chemical feed equipment.

### Comparison of Nordvärme approach and the use of corrosion inhibitors

#### Nordvärme approach (Carried out by plant staff)

##### Advantages

- avoids the need to add corrosion inhibitors
- if corrosion rate increases, corrosion inhibitors
  - can be added later
  - can be cheaper

##### Disadvantages

- requires careful monitoring

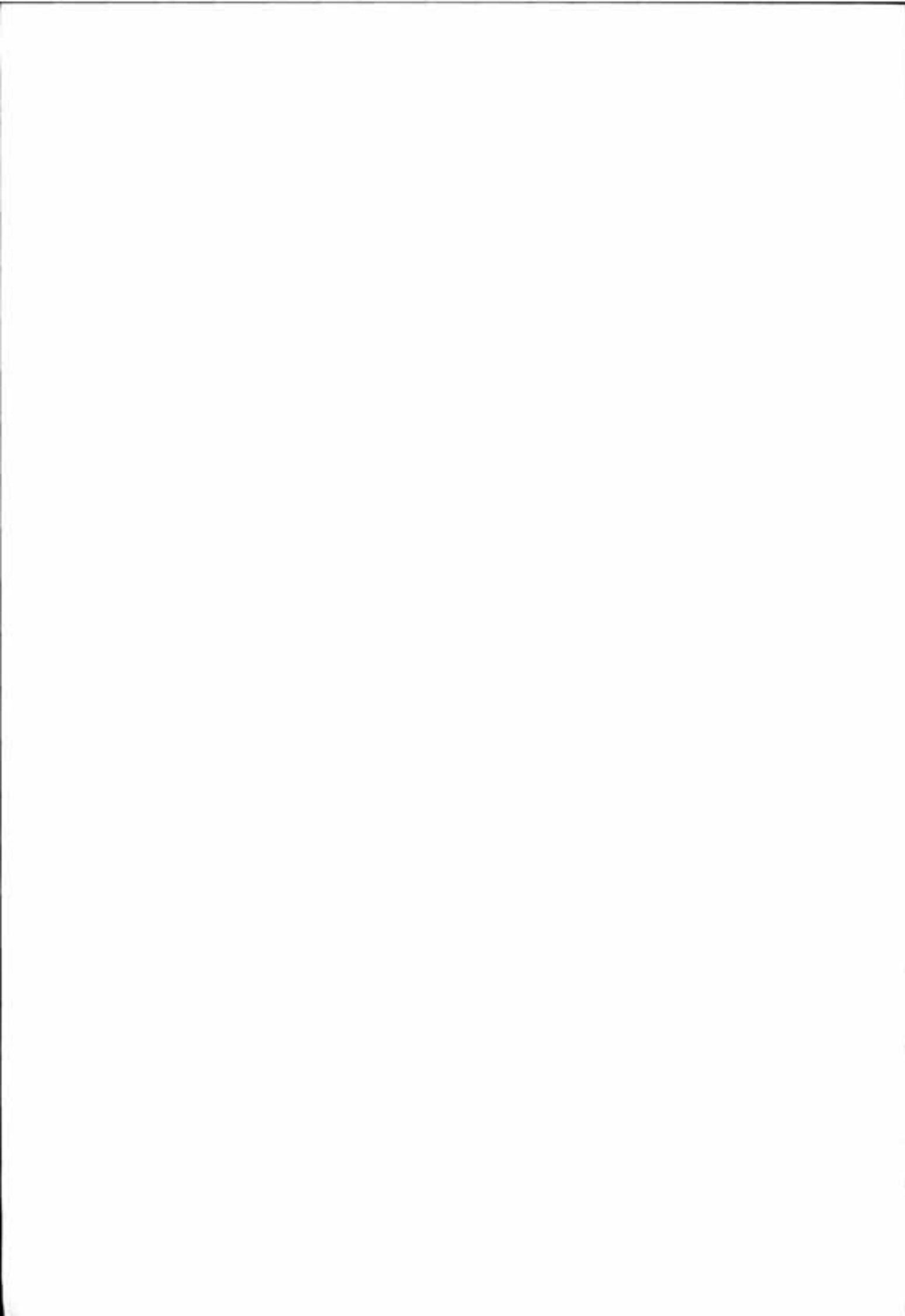
#### Corrosion inhibitors (chemical supply and monitoring by chemical company)

##### Advantages

- will protect pipe surfaces regardless of rate of oxygen infiltration
- addition and monitoring are the responsibility of the chemical company

##### Disadvantages

- once corrosion inhibitors are being used in a system it is difficult to stop
- in the future, use of some common corrosion inhibitors may be restricted because of environmental impact and regulations



## CORROSION AND WATER TREATMENT IN NORDIC DISTRICT HEATING SYSTEMS: EXPERIENCE AND PRACTICE

Nordvärme Association

### 1 FOREWORD

In its meeting on 8 June 1989 in Helsinki, the Board of Nordvärme decided to set up a working group for water treatment, which would produce a guide and coordinate Nordic experiences and practices in this area. The area is limited to water issues related to district heat distribution and substations.

The Working Group, which had its first meeting in Uppsala on 5 October 1989, consisted of the following members:

Bjarne Aastrup	Herning Municipal Works (Denmark)
Egil Evensen	Trondheim Electricity Plant (Norway)
Einar Gunnlaugsson	Reykjavik Heating Plant (Iceland)
Trygve Strandell	Vantaa Electricity Plant (Finland)
Haakan Westas	Uppsala Energy Ltd (Sweden), Chairman

The Working Group has had five meetings.

The present report is intended primarily for minor and medium-sized plants with general knowledge of corrosion and water treatment issues. The Working Group hopes that the report will be used as a practical manual in the plants. The report was presented at the Third Nordic District Heating Symposium in Reykjavik on 5-8 June 1990.

### 2 SUMMARY

In a district heating system, water quality depends on the quality of the raw water and varies from non-deaerated raw water to de-aerated, totally desalinated water. Water quality plays a big role in the corrosion of district heating systems. Corrosion risks are further increased by the leaking in of raw water and air. The degree of the corrosion is influenced by the selection and combination of

materials. A system is subject to corrosion attack during both operational and in operational periods. Corrosion attacks are electrochemical in nature, and they are mostly characterized as oxygen-reducing or hydrogen-generating corrosion.

Oxygen-reducing corrosion is caused by oxygen in the water, while hydrogen-generating corrosion is caused by a low pH, that is, by acid water. Therefore, the water must be oxygen-free and the pH value sufficiently high. Low conductivity reduces the corrosion risk as well.

Problems are caused also if the water contains salts and solid particles, which form corrosion films. This refers to hardness-causing agents such as calcium and magnesium and corrosion products in the form of ferric and copper oxides.

To achieve a good water quality, different purification methods are used. Salts are removed through ion exchange by means of water softeners, cation filters and anion filters. Oxygen is removed by thermal or chemical deaeration of the water, while solid particles are removed with mechanical filters.

Analytical guideline values have been developed with the intent to make trouble-free operation possible, primarily in view of corrosion and deposition, and to provide a foundation for a good operating economy. The recommended values that are presented are based on experiences with different types of modern plants.

The present report discusses sampling and analyses as well and provides recommendations for analyses and the intervals at which they should be performed.

Current statistics on damages in district heating systems show that leakage from the network generally increases with increasing age. Therefore, it is important to find leaks quickly, before water losses become excessive. The report discusses the most common leak detection methods.

In recent years, environmental issues have received increasing attention. Environmental issues and protective equipment to be used with chemical inhibitors are discussed in the report as well.

District heating plants in Iceland are mostly different, because Iceland uses geothermic water which goes directly to consumers.

### 3 INTRODUCTION

The Nordic countries practise extensive distribution of district heat, which contributes to a flexible energy management in heating and hot water heating. A district heating system has three main components: production plant, district heating network, and substations, all connected to each other.

Building a district heating system has very high investment costs, and accidents/ breakdowns in the system may have serious economic consequences. Therefore, its operation has to be systematically monitored to maintain a satisfactory quality of its components, especially in the case of direct connection. It is important that the quality of the district heating water is monitored carefully, as corrosion may otherwise develop in the pipe network and the components and result in the long term in high costs and serious interruptions in service.

Several types of corrosion can attack district heating pipes. Satisfactory monitoring and operation require that the quality of materials and service conditions are correctly selected, and not least, that the quality of the water is good. Most district heating plants have experienced corrosion and/or water leakage in their network. To reduce service interruptions to a minimum, several methods are applied to prevent corrosion and to control and detect leakage.

The present report describes corrosion conditions and provides recommendations for reducing problems and maintaining an acceptable monitoring of the system.

## 4 CORROSION AND DEPOSITION

### 4.1 Materials and corrosion types

#### 4.1.1 General

Depending on the quality of the raw water, water quality varies in district heating systems from non deaerated raw water to de-aerated, totally desalinated water. Corrosion risks are increased by the leaking in of raw water and air (Ref. 10.5.1 and 10.5.2). The corrosion degree is influenced by the selection and combination of materials. The materials most commonly used in district heating systems are:

##### Carbon steel

Used in piping, valves and condensing tubes

##### Copper

Used in piping and heat exchangers

##### Acidproof steel

Used in heat exchangers and pump impellers

##### Stainless steel

Used in compensators and heat exchangers

##### Brass

Used in valves and meters

##### Red brass

Used in valves and pump impellers

##### Cast steel

Used in pump housings, pump impellers and valves

##### Nodular graphite cast steel

Used in pump housings, pump impellers and valves

##### Plastic and rubber

Used in pipes and seals

##### Enamel

Used in water heaters

Corrosion damage occurs during both operational and in operational periods. Corrosion attacks are of electrochemical origin, and they consist mostly of oxygen-reducing or hydrogen-generating attacks taking the following forms:

- General corrosion
- Crevice corrosion
- Galvanic corrosion
- Stress corrosion cracking
- Pitting corrosion
- Erosion corrosion
- Drop corrosion

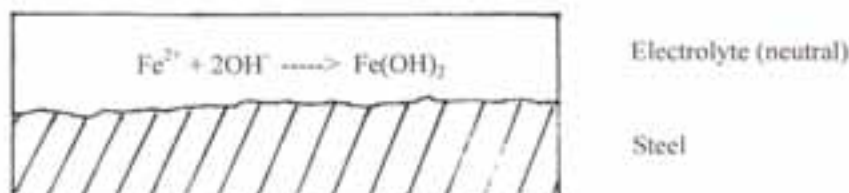


Fig. 4.1.1 General corrosion. Fluctuating anodic and cathodic surfaces distribute corrosion products uniformly over metal surface. Ferrous (II) hydroxide ( $\text{Fe}(\text{OH})_2$ ) dissolves in the electrolyte.

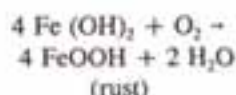
- Sulphide corrosion
- Deposit corrosion
- Selective corrosion

Several of these corrosion types frequently result in point corrosion of the material and in some cases in a more extensive, even loss of material. The corrosion types listed above are discussed briefly in the following.

#### 4.1.2 General corrosion and magnetite formation

General corrosion means that a metal surface is attacked uniformly over all parts covered by the electrolyte. The corrosion rate is expressed either as weight loss per surface and time unit, or more commonly, by practical evaluation of thickness loss per time unit, such as  $\mu\text{m}/\text{year}$  or  $\text{mm}/\text{year}$ . Thus, general corrosion is characterized by that the entire surface in question is uniformly eroded, which is due to fluctuating anodic and cathodic surfaces. See Fig. 4.1.1.

Under continuing effect of oxygen, the ferrous hydroxide is oxidized further to ferric (III) hydroxide. This oxide is the well-known reddish rust:



Hydrogen-generating corrosion takes place in low pH water, for example on steel, in accordance with the anode process formula



The metal goes into solution, that is, it corrodes while hydrogen ( $\text{H}_2$ ) forms. The corrosion accelerates with declining pH values and increasing temperatures. At a pH exceeding 9.0, corrosion can be considered negligible. Hydrogen-generating corrosion occurs mostly in the form of general corrosion. If the water is calcium-precipitating, the precipitant may prevent corrosion by forming a film on the metal.

Thus, rusting of steel requires a simultaneous presence of water and oxygen on the steel surface.

The cathodic and anodic surfaces that are formed are dependent on the composition and structure of the steel. Steel is a combination of iron and carbon, and its manufacturing process does not allow a homogeneous mixture. Therefore, some parts of the surface are richer in carbon than others and form cathodic surfaces, while the more iron-containing parts become anodes and go into solution as ions.

At a temperature exceeding  $200^\circ\text{C}$ , for example in a boiler, carbon steel oxidizes according to the following simplified formula and forms magnetite ( $\text{Fe}_3\text{O}_4$ ):



Magnetite is a black oxide with magnetic properties and very low solubility at pH 9.5. Magnetite forms a very dense film on a steel surface, preventing

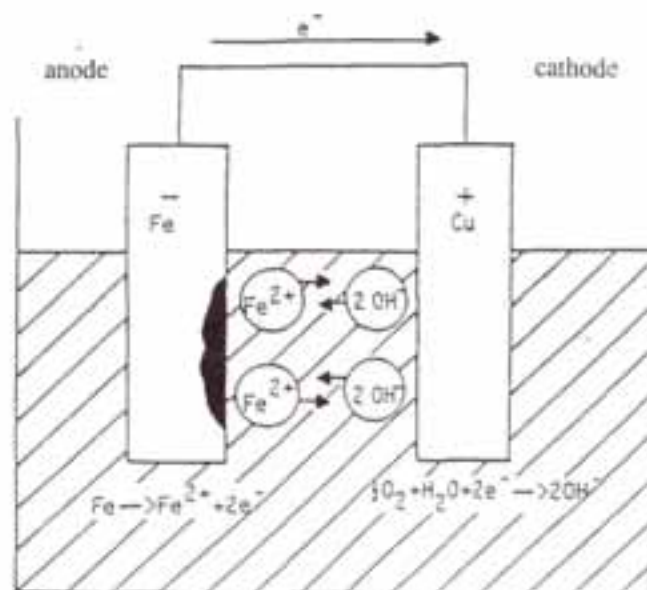


Fig. 4.1.2 Example bi-metallic cell

further oxide formation and protecting the steel against further corrosion.

Magnetite is formed also at lower temperatures, based on the formula



The magnetite that forms in this manner does not constitute a protective film as good as and as dense as the one formed at higher temperatures, that is, directly by oxidation of steel. Also, it does not attach as well to the steel surface, and lots of oxide is transported around in the system, where it fastens to heat-loaded surfaces.

General corrosion of copper is relatively minor even at high oxygen contents such as those occurring in faucet warm water (approx. 10  $\mu\text{m}/\text{year}$ ), and thus, it is insignificant in this context. The prerequisite is, however, that the pH lies between 8 and 9.5. This leads to precipitation of corrosion products such as copper oxides and copper hydroxides of the carbonate type, which protect the metal against further corrosion. The corrosion increases again at pH 9.5.

#### 4.1.3 Galvanic corrosion

Galvanic corrosion occurs in bi-metallic cells. An example is illustrated in Fig. 4.1.2. The cell consists of an electrolyte, in which a piece of steel (Fe) and a piece of copper (Cu) are immersed. Table 4.1 shows that Fe has a negative electrode potential (0.44 V) and Cu a positive one (+ 0.34 V), which means that the steel piece becomes anodic in the cell and corrodes, while Cu becomes cathodic and develops reduced corrosion rate or becomes fully protected, which is what cathodic protection is in principle based on.

These examples show that different metals cannot be combined arbitrarily. Corrosion attacks may be highly localized, and they may lead to perforation of the less noble material. Also galvanic microcells originating from settling out of metallic copper on steel may lead to corrosion. Corrosion increases with increasing conductivity of water, which is generally assumed to be valid for most corrosion types. Galvanic corrosion requires the presence of oxygen.



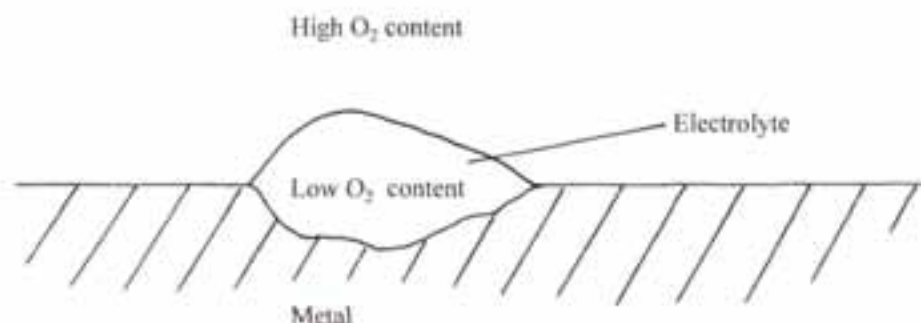


Fig. 4.1.3 Example of drop corrosion. Concentration differences in oxygen provide sufficient driving force to make the metal under a drop become anodic and corrode. Cathodic surface develops at the margin of the drop against the metal, where  $O_2$  content is higher.

Table 4.1 Example of electrode potentials, listed in the order of an electromotive force series

Li	-	$Li^+$	-3,045 V
K	-	$K^+$	-2,925 V
Al	-	$Al^{3+}$	-1,660 V
Zn	-	$Zn^{2+}$	-0,763 V
Fe	-	$Fe^{2+}$	-0,440 V
Cd	-	$Cd^{2+}$	-0,403 V
Ni	-	$Ni^{2+}$	-0,250 V
Sn	-	$Sn^{2+}$	-0,136 V
$1/2H_2$	-	$H^+$	-0,000 V
Cu	-	$Cu^{2+}$	+0,337 V
Cl	-	$1/2Cl_2$	+1,360 V
Au	-	$Au^{3+}$	+1,500 V
F	-	$1/2F_2$	+2,870 V

#### 4.1.4 Pitting

Some specific corrosive media, for example chlorides, are capable of contributing to local perforations of the protective film (passive film) which occurs naturally on certain materials, e.g., stainless steel. A microanodic area and a relatively large cathodic area are formed in each perforation, current density becomes high, and this results in point corrosion which forms a cavity in the material. The corroded area is very limited, with the corrosion acting depth-wise and eating into the

metal - a phenomenon that can have serious practical consequences. Pitting is seen in certain materials frequently also under different deposit films, where aeration cells with dissolved oxygen in the electrolyte occur.

Dissolved oxygen in water contributes so that the metal in the system is attacked and goes into solution. This is known as oxygen-consuming corrosion, and it is frequently localized. The attack usually results in pitting of the material, in the form of either pit or point corrosion.

The corrosion rate accelerates with rising temperatures in closed systems. In open systems, the corrosion rate accelerates but reaches its maximum at  $80^\circ C$ , because the solubility of oxygen decreases with a rise in temperature.

Low pH value (usually  $< 7.0$ ) and a low bicarbonate/sulphate ratio ( $HCO_3^-/SO_4^{2-}$  usually  $< 1$  calculated by mg/L) in the water can result in pit-type corrosion on copper materials.

#### 4.1.5 Drop corrosion

Moisture stays on metal surfaces in pressurized or open systems that have been drained and exposed to the atmosphere. Aeration cells are formed, and the metal begins to corrode. See Fig. 4.1.3.

Electrolyte, High  $O_2$  content



Fig. 4.1.4 Example of deposit corrosion. Concentration differences in oxygen contents provide sufficient force to make the metal under the deposit form an anodic surface and corrode. The higher  $O_2$  content in the electrolyte functions as a cathodic surface.

#### 4.1.6 Deposit attack and crevice corrosion

Aeration cells may form in areas with restricted liquid flow and lead to attack on the material. The corrosion is intensified by accumulation of nonflowing liquid (electrolyte) under deposits. In this case, the attack originates at deposits. See Fig. 4.1.4. or in narrow cracks, which is known as crevice corrosion. See Fig. 4.1.5. Even chloride concentrations, e.g., in crevices in stainless steel lead to corrosion. The pH of the trapped liquid frequently drops below the pH of the surrounding medium.

Anodic and cathodic surfaces, caused by concentration differences in  $O_2$  content, appear in structures with narrow crevices. The prerequisite is, however, that an electrolyte can enter the crevice. See Fig. 4.1.5. Frequently the pH of the trapped electrolyte drops, which contributes to an

acceleration of corrosion.

#### 4.1.7 Stress corrosion

Risk of cracking appears in an alloyed material in the presence of interaction between internal and/or external static tensile stresses and a specific corrosive medium. This attack is known as stress corrosion cracking, and it frequently leads to brittle fractures in the alloyed material. Chloride ions and ammonia are among the specific ions that can result in stress corrosion cracking, e.g., in stainless steel (potentiometers and heat exchangers) and copper alloys. **Stress corrosion cracking in stainless steel is induced, however, by relatively high chloride concentrations, and generally, evaporation of water must first take place on the surface, before the corrosion process begins. Temperature affects the corrosion rate as well.**

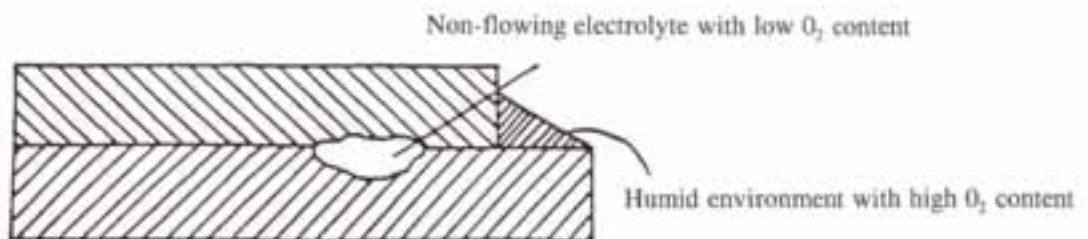


Fig. 4.1.5 Example of crevice corrosion. Concentration differences in oxygen content provide sufficient force for the formation of anodic and cathodic surfaces. The metal in the crevice corrodes.

#### 4.1.8 Erosion corrosion

Damages caused by interaction between erosion and corrosion appear primarily on copper and copper-alloyed material. Known as erosion or turbulence corrosion, this type of corrosion occurs in the presence of oxygenated water and high flow velocities (or disturbed flow) and results in erosion of the protective copper-oxide film and exposure of the copper to water. The attack is aggravated by the presence of gas bubbles and/or solid particles in the water. The corrosion rate increases with aggressive water, that is, with dropping pH values and rising carbon dioxide content. If the water has high ammonia content and dissolved oxygen, the copper becomes subject to damages which, to some degree, resemble erosion corrosion attacks. Erosion corrosion has proven to be the main cause of damage on copper materials in district heating systems.

#### 4.1.9 Sulphide corrosion

When the water contains hydrogen sulphide ( $H_2S$ ), like, e.g., geothermic water does, or when sodium sulphite ( $Na_2SO_3$ ) is used to bind oxygen, sulphide may form and react with copper and copper alloys in piping and valves. This leads to formation of copper sulphide ( $CuS$ ), which is loosely bound to the metal and therefore easily separates under the effect of changes in pressure or flow. This means that the water will contain solid particles.

If geothermic water contains hydrogen sulphide or has been treated with sodium sulphite to remove oxygen, copper pipes must not be used.

#### 4.1.10 Selective corrosion

In selective corrosion, the less noble component of a binary alloy becomes dissolved. Dezincification of brass is an example of this. The process is initiated because of local variations in the composition. According to whether the more noble metal is preserved or dissolves, the corrosion process itself creates a galvanic element. In the dezincification of brass in water solution, zinc goes into solution and dissolves out as zinc carbonate, while the copper attains a porous form with poor

resistance properties. Corrosion resistance of alloys depends on their composition and usually increases with decreasing concentration of the less noble metal in the alloy.

#### 4.2 Measurement of corrosion

Corrosion can be measured simply and reliably with corrosion coupons placed in the flowing medium. The coupons are made of the same material as the system to be examined. A coupon holder and measuring station are shown in Fig. 4.2.1. Normally, four coupons are used simultaneously. They are removed, cleaned, weighed and examined visually after 1, 4, 8, and 12 weeks, for example. The method has been standardized in the USA (ASTM D 2688-75 Method B). The Standard describes in detail both the equipment and the evaluation method (Ref. 1.5.7 and 10.5.8).

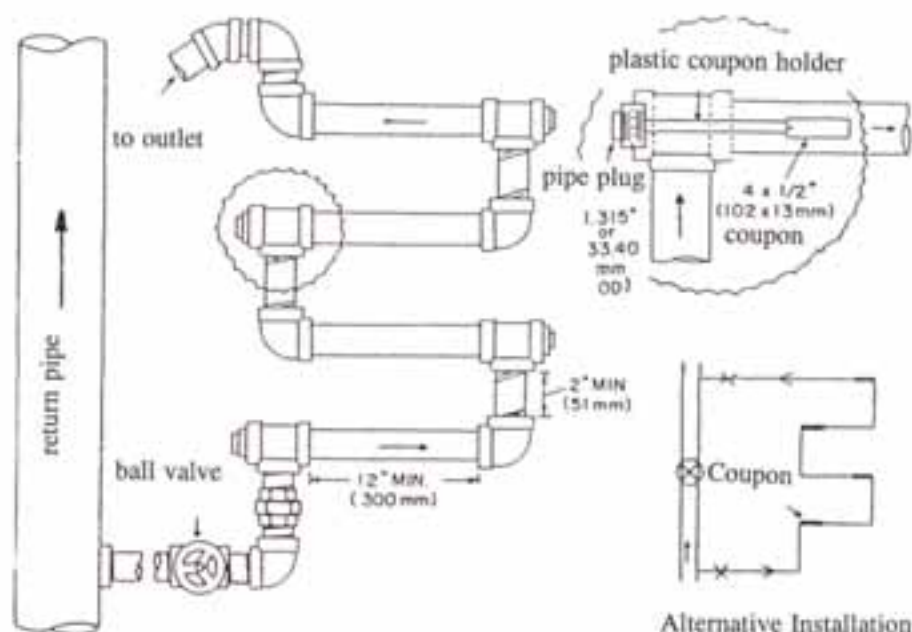


Fig. 4.2.1 Station for corrosion measurement

Electronic instruments for corrosion measurement can be found on the market. These are coupled to probes, which are placed in the pipe system. A joint Nordic research project (Ref. 10.1.3) contained a sub-project titled "Corrosion Measurements in Hot-Water Systems", in which measurements were performed with "Corratersond", "Corrometersond" [sond = probe] and corrosion coupons. The project showed that electronic measurements did not provide reliable results for district heating systems. The experiments carried out within this project with a reconstructed probe for measuring crevice corrosion gave ambiguous results.

In many cases, it may be better to place the coupons in the main current instead of a by-pass. This way, the results reflect the service conditions and the process itself.

Coupon holders are used to avoid closing the system when coupons are inspected. The holders pass through a stuffed 1-4 in. stop valve. See Fig. 4.2.2. If compared with the ASTM Standard, the only difference here is that the coupons are inserted in the main current. Such equipment has been tried by district heating plants in Iceland with favorable results for major periods.

### 4.3 Corrosion films and deposits

Corrosion films form on pipe surfaces and heat exchangers because of the dissolution or decrystallization of one or several compounds, which requires that the water-solubility of these compounds is exceeded. In district heating systems, this usually involves the hardness-inducers calcium and magnesium, which dissolve out as carbonates, sulphates or silicates. This is because these compounds have negative solubility coefficient, that is, their solubility decreases with increasing temperatures.

District heating water contains almost always larger or smaller amounts of suspended material, which may become deposited in undesirable locations. This refers to rust, welding slag, sand, corrosion products, etc.

Corrosion films and deposits possess a high heat resistance and therefore a poor heat transfer capability. Also, they lead to an increasing pressure drop, which results in poor business economy. In the presence of oxygen, corrosion may start under the corrosion films and deposits as well.

## 5 WATER TREATMENT TECHNOLOGY

Treatment of dilution water for district heating plants

Definitions/explanations for terms used in this guide:

### Ion exchange:

A process by which positive ions and negative ions are replaced by desirable ions. Positive ions are called cations, negative ions, anions.

### Softener:

A filter for softening water, containing a cation mass in sodium form. Regenerated with sodium chloride (NaCl).

### Softened water:

Water that has passed through a softening filter, where calcium (Ca) and magnesium (Mg) ions have been exchanged against sodium (Na) ions. Anions are not replaced.

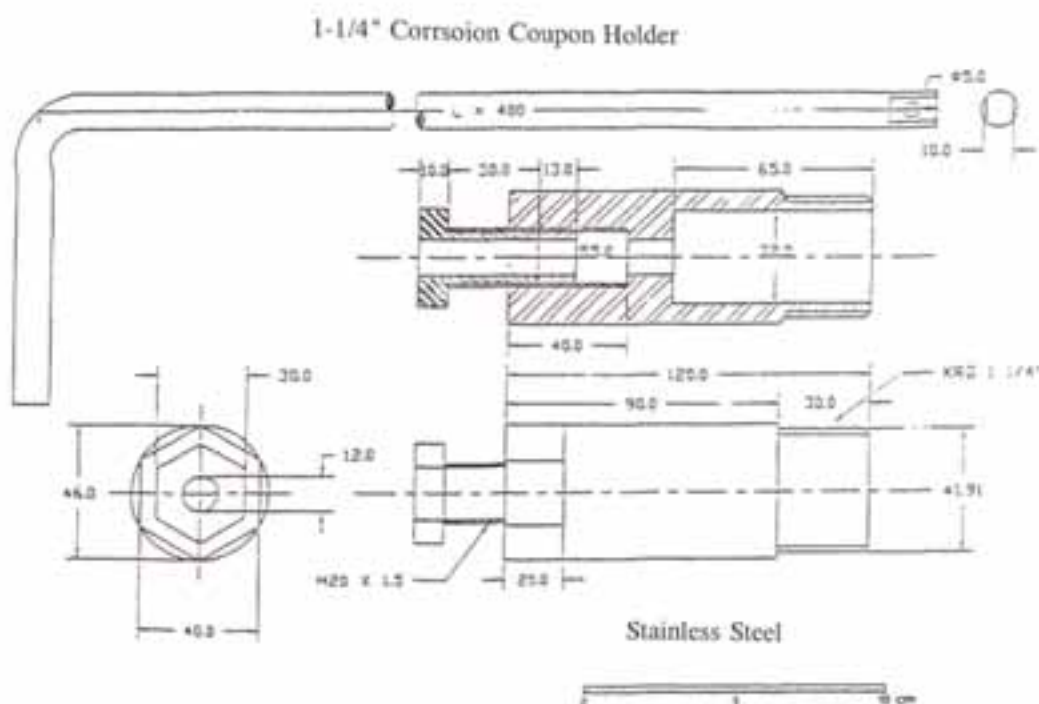


Fig. 4.2.2 Measuring station for corrosion measuring

**Cation filter:**

A filter that removes cations by means of cation mass in hydrogen form. Regenerated with a strong acid such as hydrochloric acid (HCl).

**Anion filter:**

A filter that removes anions by means of anion mass in hydroxide form. Regenerated with sodium hydrate (NaOH).

**Reverse osmosis:**

RO is an environmentally friendly process used for example for desalination and removal of organic substances from raw water. The process is based on the use of semipermeable membranes. These let pure water through but bar substances exceeding a given molecular size (ion size); that is, they perform separation at the molecular level.

**Desalinated water:**

Water from which salts have been removed by passing it through a cation and an anion filter. All ions are thus replaced by hydrogen and hydroxide ions, meaning that the salts of the raw water are transformed to water. Salts can be removed in a reverse osmosis facility as well. Desalinated water is also called deionized, totally desalinated, or demineralized water.

**Mechanical filtration I:**

Mechanical filtration of raw water before it goes to a softening facility.

**Mechanical filtration II:**

Mechanical filtration by partial flow cleaning of circulating water in a district heating system.

Examples of different treatment methods for district heating water are described in the Appendix.

## 5.1 Softened water

Softening of water removes calcium and magnesium ions which would otherwise form films and sludge in the district heating system. The ions are replaced by sodium ions by passage through a filter with cation mass in sodium form. As softening does not reduce the salt content, the risk of oxygen-caused corrosion will not be reduced either (cf. desalinated water).

The design of a facility depends on the raw water composition and the capacity desired, and therefore, dimensioning the facility requires expertise. Sodium chloride (NaCl) is used as a regeneration agent, and the consumption amounts to about 300% of the theoretical quantity.

### 5.1.1 Description of facility

Figure 5.1.1 is a diagram of a softener. Calcium and magnesium are replaced by sodium from the salt-regenerated mass, while anions pass through unhindered.

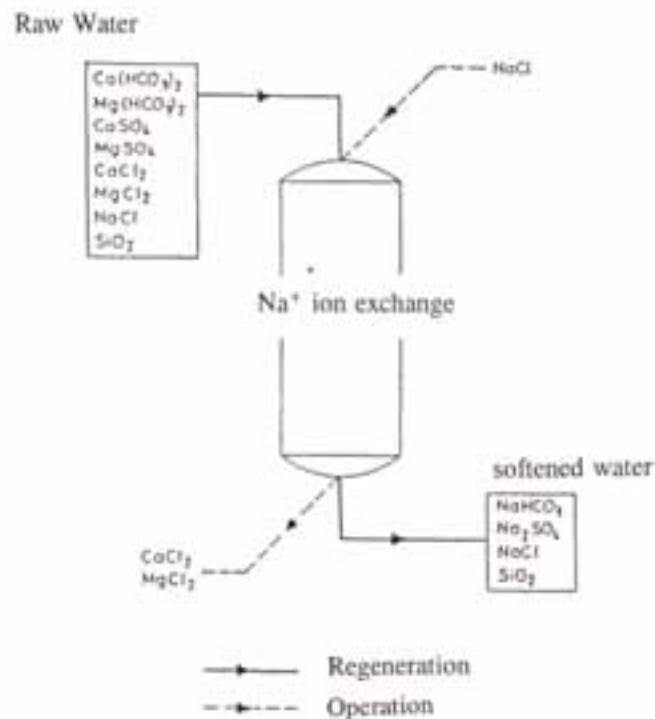


Fig. 5.1.1 Softener

### 5.1.2 Water quality

Quality of treated water is expressed in hardness degrees [°d]. In softened water, hardness degree is  $< 0.1^\circ\text{d}$ . The remaining salts consist mainly of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{NaHCO}_3$ .

Conductivity of softened water is of the same order as that of raw water, namely  $300 - 1000 \mu\text{S}/\text{cm}$  in Norway and  $25-800 \mu\text{m}/\text{cm}$  in Sweden. The conductivity of the geothermic water used in Iceland ranges from 200 to  $5000 \mu\text{S}/\text{cm}$ .

### 5.1.3 Advantages and disadvantages

Examples of the advantages of softened dilution water:

- boiler scale formation is noticeably reduced
- sludge formation is noticeably reduced
- initial expenses are low
- operating costs are low

Examples of disadvantages:

- if raw water has a high content of bicarbonate ions, which are not removed by softening, insufficient alkalization of circulating water will promote corrosion
- water has a high total salt content, which promotes corrosion and results in salt accumulations at leaks
- higher expenses for chemical additives (pH adjustment)
- chloride content of water increases risk of point corrosion, e.g., in radiators (refers to direct connection)
- chloride ion content of water favors stress corrosion cracking in stainless steel

### 5.2 Desalinated water - ion exchange

Desalination of water removes almost all salts, which makes its conductivity drop to  $1-10 \mu\text{S}/\text{cm}$ , as against the conductivity of softened water, which ranges from 25 to  $1000 \mu\text{S}/\text{cm}$ .

As conductivity is a prerequisite for the formation of corrosion processes in district heating systems,

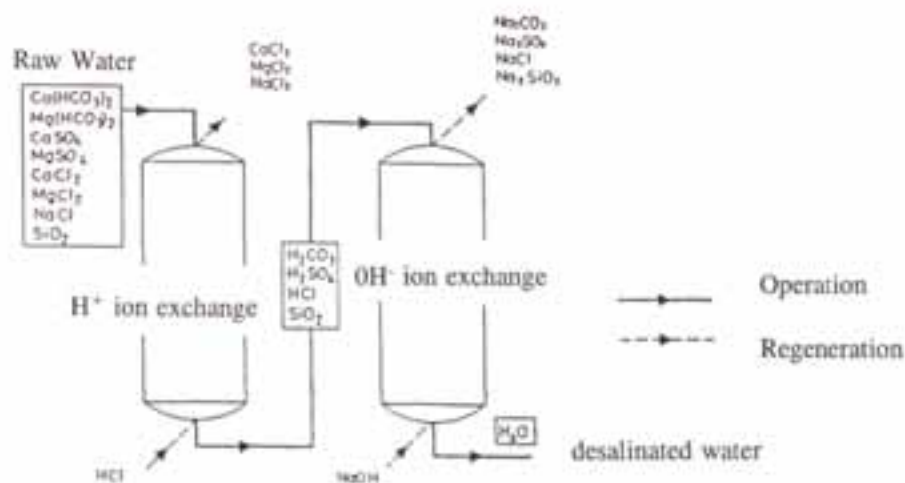


Fig. 5.2.1 Demineralization facility

desalination essentially reduces the rate of oxygen corrosion.

In its simplest form, a desalination facility consists of a cation filter and an anion filter for removal of cations and anions. In principle, this facility is sufficient for producing desalinated water, and it is used by smaller plants.

If the raw water has a high bicarbonate content, a carbon dioxide ( $CO_2$ ) expeller is needed, to improve chemical economy.

Major plants build their desalination facilities with a view to an optimal economical solution with both weak and strong ion exchange masses.

The design of the facility is based on raw water composition, on requirements concerning quality of the water produced, and on the plant's capacity. This requires cooperation with suppliers or advisors.

### 5.2.1 Description of facility

Figure 5.2.1 shows the typical structure of a small facility. This is a counterflow-regenerated facility. Addition of chemicals during regeneration takes place in a direction reverse to that during operation. This saves chemicals and results in cleaner water.

Regeneration chemicals include, e.g.,  $HCl$  for the cation mass and  $NaOH$  for the anion mass.

The advantage of a counterflow-regenerated facility is that the chemicals are utilized better, and therefore, fresh chemicals are obtained in the least loaded part of the ion exchange mass, which results in a higher regeneration level (g of chemical/L of ion exchange mass) and a smaller salt leakage.

Counterflow-regenerated facilities have proven to be almost always the most economical. Even at  $1 \text{ m}^3/\text{h}$  ( $3600 \text{ m}^3/\text{year}$ ; operating time being about  $10 \text{ h/d}$ ), the counterflow facility is more advantageous.

A concurrent facility, where regeneration takes place in the same direction as during operation, uses 300 - 350% of the theoretical quantity of chemicals, while a counterflow facility uses 100 - 170% of the theoretical quantity.

### 5.2.2 Water quality

After desalination, the quality of the water is characterized by low conductivity.

The conductivity must be  $< 10 \mu\text{S/cm}$  and carbon dioxide content  $< 10 \text{ mg/L}$  (cf. requirements concerning dilution water and circulating water).



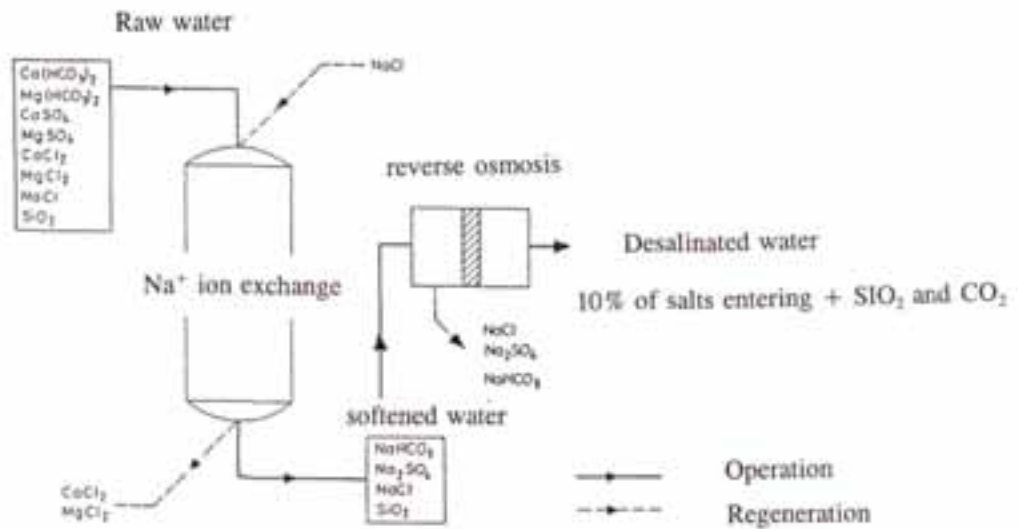


Fig. 5.3.1 Softening and reverse osmosis

### 5.2.3 Advantages and disadvantages

Examples of the advantages of desalinated dilution water:

- oxygen-related corrosion is essentially reduced due to the removal of all salts, whereby the corrosion flow also diminishes and the oxygen content becomes less critical
- boiler scale formation is prevented
- sludge formation is prevented
- smaller risk exists of point corrosion and stress corrosion cracking on stainless steel
- low chemical inhibitor expenses

Examples of disadvantages:

- initial expenses higher than those of a softening facility
- operating costs for regeneration higher than at a softening facility

### 5.3 Desalinated water - reverse osmosis

A reverse osmosis facility is where water is passed under high pressure through a sufficiently fine-pored membrane that the majority, about 90%, of salts in the raw water is retained.

#### 5.3.1 Description of facility

Figure 5.3.1 shows a softener followed by a reverse osmosis facility.

### 5.3.2 Water quality

About 10% of the salts remaining in the water after it has gone through a softener is estimated to pass through the reverse osmosis facility, together with 25% of the silica ( $\text{SiO}_2$ ) contained by the water and all free carbon dioxide ( $\text{CO}_2$ ). Thus, the quality of the cleaned water will depend on the quality of the raw water.

### 5.3.3 Advantages and disadvantages

The advantages of using reverse osmosis are similar to those mentioned in section 5.2.3 for desalinated water, with the following additional features:

- low operating costs
- more environmentally friendly

Examples of disadvantages:

- higher initial expenses than with softening and desalination with ion exchange (depends on dimensions as well)
- membranes are expensive, with limited service life
- water losses amount to 25%, compared with the 10% in ion exchange facilities

## 5.4 Deaeration (O<sub>2</sub>) methods

### 5.4.1 Thermal deaeration

Boiling expels oxygen and other gases from water. Boiling can be performed either by steam injection, that is, with slight overpressure and a temperature > 100°C, or with vacuum and lower temperatures, which is more common in district heating plants.

### 5.4.2 Chemical deaeration

Chemical deaeration is performed by adding agents which react with oxygen.

#### 5.4.2.1 Sodium sulphite (Na<sub>2</sub>SO<sub>3</sub>)

As sodium sulphite reacts with oxygen, it transforms to sodium sulphate. The dosage is about 8 g of sodium sulphite per gram of oxygen, Na<sub>2</sub>SO<sub>3</sub> + 1/2 O<sub>2</sub> → Na<sub>2</sub>SO<sub>4</sub>. Normally, an excess of 30-50 mg/L, calculated as Na<sub>2</sub>SO<sub>3</sub>, is needed. Sodium sulphite counteracts oxygen corrosion on steel but is accompanied by increased risk of sulphide attack on copper and some solder metals. Salt content increases as well. Sodium sulphite must not be used at temperatures exceeding 250°C (40 bar).

#### 5.4.2.2 Hydrazine (N<sub>2</sub>H<sub>4</sub>)

Hydrazine is a deoxidizing additive, which reduces oxygen dissolved in the water and therefore, provided that the reduction is thorough, renders oxygen-reducing corrosion impossible. In the temperature range 25°C- 75°C, reaction between dissolved oxygen and hydrazine is stoichiometric according to the formula



The final products are nitrogen (N<sub>2</sub>) and water (H<sub>2</sub>O). At higher temperatures, hydrazine decomposes to form ammonia according to the formula



Decomposition of hydrazine to form ammonia and nitrogen can take place even at temperatures below

100°C, if oxygen is not present. The degree of the decomposition depends on the time factor, temperature and possible catalytic forces. For example, the presence of copper ions has a catalyzing effect on the reaction. The reaction rate depends on the pH. Higher pH values lead to increased reaction rates.

At the same time, pH-adjusting agents (for example sodium hydroxide) and deoxidizing agents can be added to district heating water to achieve a fully satisfactory corrosion protection. These will prevent both the hydrogen-generating and the oxygen-reducing corrosion.

In Denmark, hydrazine may be used in the primary circuit, which interchanges heat with the secondary circuit, which then delivers the heat to individual consumers (Ref. 10.1.2).

In Sweden, the maximum permissible hydrazine concentration is 0.5 mg N<sub>2</sub>H<sub>4</sub>/L.

#### 5.4.2.3 Tannins

Tannins are complex organic compounds of vegetable origin, with a molecular weight between 600 and 2000. Thus, great differences may exist between different tannin products. Tannins are active in an alkaline environment. They are capable of absorbing oxygen dissolved in water in a manner similar to that of sodium sulphite. In alkaline form, some tannins occur as salts, and for example sodium tannate is used for similar purposes as hydrazine. Complete reduction of 1 g of oxygen requires 2 g of sodium tannate, and the reaction rate for oxygen binding is similar to that of catalyzed sodium sulphite. The oxygen absorption capacity of natural tannins is difficult to express directly by reaction formulae. Considering the properties of hydrolyzable tannins, 40 mg of tannin should bind 1 mg of O<sub>2</sub>.

Tannins are believed to be stable up to 2.8 MPa (the information found in the literature varies). Its decomposition products are partly volatile (CO<sub>2</sub>). Tannins are used also as corrosion inhibitors due to their capability to form a protective film of ferric tannate complex on a metal surface. Tannins are

considered environmentally-friendly (Ref. 10.5.11 and 10.5.12).

#### 5.4.2.4 Organic oxygen-reducing agents (Ref. 10.5.4)

In recent years several new organic oxygen-reducing agents have been put on the market as substitutes for hydrazine. It is recommended that when these chemicals are used, the supplier be responsible for documentation concerning their effectiveness, content, and toxicity, and this applies to reaction products as well. Dosing and control must be performed in accordance with the supplier's instructions. Follow up consists of oxygen and iron analyses. In Denmark, reference is made to the Environmental Protection Agency's Announcement No. 144 of 14 April 1982, concerning prohibition against using poisons in certain heating systems.

#### 5.4.2.5 Catalytic reduction of oxygen

Catalytic reduction is carried out by adding hydrogen. Hydrogen and oxygen react with each other in a container holding a catalyst, and form water. Excess hydrogen is blown off with nitrogen. Experience with this method is still very limited (Ref. 10.4.4).

### 5.5 Corrosion protection

#### 5.5.1 Chemical inhibitors

Desalinated water is dosed with sodium hydroxide. The dose shall be approximately 2 g of NaOH/m<sup>3</sup>, to obtain a pH of about 9.8. Reverse osmosis does not remove free carbon dioxide, and therefore, larger quantities of sodium hydroxide have to be used to raise the pH.

Deaeration removes 95% of carbon dioxide, which saves some chemicals.

Additionally, softened water requires NaOH for binding (neutralizing) carbon dioxide. The inhibitor dose is therefore dependent on bicarbonate content. For example, softened water with a content of

HCO<sub>3</sub> = 2.95 val/m<sup>3</sup> requires 50 g of NaOH/m<sup>3</sup> for a year to attain a pH between 9.5-9.7, compared with desalinated water which requires about 2 g/m<sup>3</sup>. A higher content of bicarbonate requires a larger dose of sodium hydroxide.

Both ammonia and hydrazine raise the pH value. If desalinated water is used, it may be sufficient to use only one of these.

#### 5.5.2 Ready chemical mixes

Sometimes heating plants purchase ready chemical mixes. If a plant uses ready mixes, it has to investigate first whether the mix contains only substances permissible for use in district heating water.

Also, the plant has to consider whether the ready mix is suitable for the facility in question under different operating conditions.

For example, if a mix of sodium phosphate and sodium sulphite is used, the mixing conditions may be such that normal dilution with softened water results in the correct surplus in the circulating water. If raw water is leaking into the system, sodium phosphate consumption increases, and the dosage must be increased as well. This will then lead to an overdose of sodium sulphite.

### 5.6 Mechanical filtration I - Raw water treatment

When raw water is pretreated with a mechanical filter, contaminants are removed from the water as solid particles.

Mechanical filtration is usually applied when surface water from the city water supply is used as dilution water for the district heating system.

#### 5.6.1 Description of facility

Figure 5.6.1 shows the placement of a mechanical filter in a softening facility, where raw water

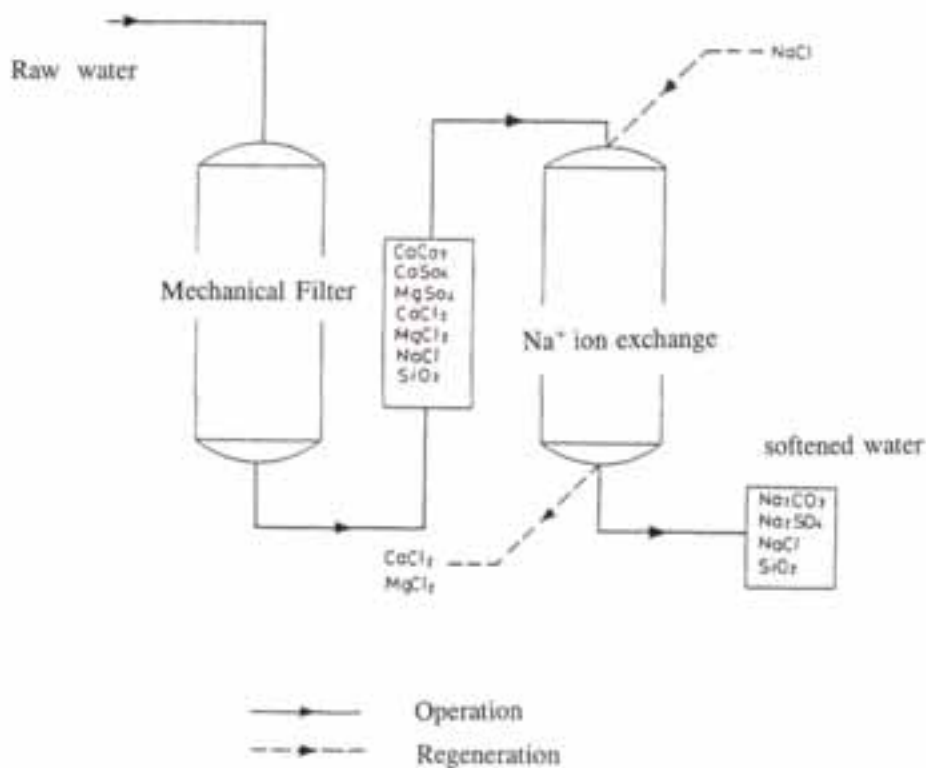


Fig. 5.6.1 Mechanical filter in series with softening filter

always passes through the filter before entering the softening facility.

Usually, a fraction corresponding to 1-3 % of the circulating water quantity is drawn from the bottom of the main return pipe after the water has passed horizontally for at least 5 pipe diameters, preferably over a longer distance.

The mechanical filter may be a sand filter or a cartridge-type filter. The pore size of a cartridge filter is determined by the filtration requirement in question and varies between 2 and 50  $\mu\text{m}$ .

### 5.7.1 Description of facility

#### 5.7 Mechanical filtration II - Partial flow cleaning

A partial flow cleaning facility is an installation used for cleaning sludge and possibly salts from circulating district heating water.

Sludge is removed by a mechanical filter as mentioned above. The composition of the sludge may vary depending on whether the plant is recently established or the operation is normal. Therefore, it is important to choose the correct cartridge pore size. If, for example, operation is just starting, it may be necessary to have a filter pore size of 20-40  $\mu\text{m}$  and change it to < 2  $\mu\text{m}$  after a time. The smaller the pore size the greater the possibility of removing magnetite, which may create problems for some flow measurements.

Chemical cleaning can be set up in series with the mechanical filter by installing a softener or a desalination facility, depending on water quality specifications of the system in question. If ion exchange filters are used, some of the fine-particled sludge is reduced.

A magnetic filter removes magnetic corrosion products from the circulating water, such as magnetite. If the filterable substances are limited, a mechanical filter must follow the magnetic filter.

After passing the mechanical filter, the return water must have a temperature  $< 60^{\circ}\text{C}$ , if a desalination facility is to be installed. However, some types of ion exchange masses tolerate only  $50^{\circ}\text{C}$ .

Partial flow cleaning:

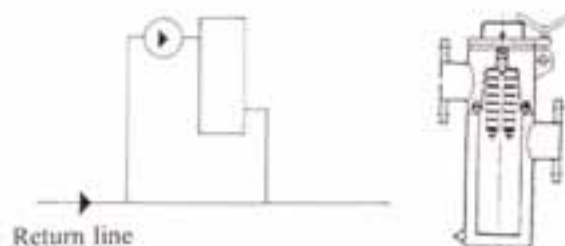


Fig. 5.7 Mechanical filter in combination with magnetic filter

## 6 WATER QUALITY

The causes of internal damages in a district heating system can in most cases be attributed to insufficient treatment of dilution water and/or circulating water. Correct treatment of the water is important in view of both corrosion and film deposition.

### 6.1 Guideline values for circulating water

Table 6.1 indicates the values customarily applied in order to avoid internal corrosion and deposits in district heating networks and boilers.

#### 6.1.1 Analytical guideline values; comments

##### pH value

The corrosion rate of steel is at its lowest at pH 9.5-10. This pH is also sufficiently low to keep the rate of dezincification of brass low.

**When copper alloys are used, pH should not exceed 10. Therefore, the pH interval 9.5-10 has been chosen as the optimal range. Aluminium must not be used at these pH values.**

##### Hardness

The hardness-causing ions in water are calcium ( $\text{Ca}^{2+}$ ) and magnesium ( $\text{Mg}^{2+}$ ). For example calcium carbonate ( $\text{CaCO}_3$ ) dissolves out together with bicarbonate and settles on tube surfaces. The dissolution depends on the concentration of different salts and the temperature. The hardness-causing agents have negative solubility coefficient, that is, their solubility decreases with rising temperatures. This is the reason for choosing different guideline values for direct and indirect system connection. Water analyses indicate at what temperature dissolution takes place.

##### Oxygen

Dissolved oxygen in water leads to corrosion of steel. As the corrosion rate is dependent on the oxygen concentration, the oxygen content must be as low as possible. Iceland has a guideline value of  $< 0.01 \text{ mg O}_2/\text{L}$ . See also section 4.1, on materials and corrosion types.

##### Ammonia

High contents of ammonia may cause stress corrosion cracking in copper and copper alloys. If the content is  $< 10 \text{ mg NH}_3/\text{kg}$ , this is avoided.

##### Iron and copper

Iron and copper concentrations in district heating water provide an indication of the level of

corrosion. At the pH values in question, most iron and copper ions occur in oxide and hydroxide form, which results in solid particles and sludge in the system. The majority of the ferric oxide occurs as magnetite ( $Fe_3O_4$ ), which fastens to flow meters and causes erroneous readings. Magnetite may also cause erosion in pipe elbows and controls.

#### Oil and fat

Oil and fat in the network water may cause deposits on boiler tubes and stalling in flow meters.

#### Conductivity

Conductivity is a measure of the salt content of water and varies therefore relatively strongly in raw water, depending on soil conditions and on whether the water is surface or groundwater.

The conductivity of softened water does not differ appreciably from that of the raw water, while desalinated water has a very low conductivity due to the removal of its salts.

Guideline values for conductivity have not been issued, but it can be generally stated that the lower the conductivity, the lower the corrosion rate. Due to corrosion, some plants have changed over to using desalinated water as dilution water for the district heating network.

Inductive flowmeters require  $> 25 \mu S/cm$ .

#### Solid particles

Solid particles in the circulating water are partly corrosion products and partly slag, gravel, etc, from the installation phase. To avoid seizures and erosion, solid particle content must be kept as low as possible.

#### 6.2 Guideline values for dilution water

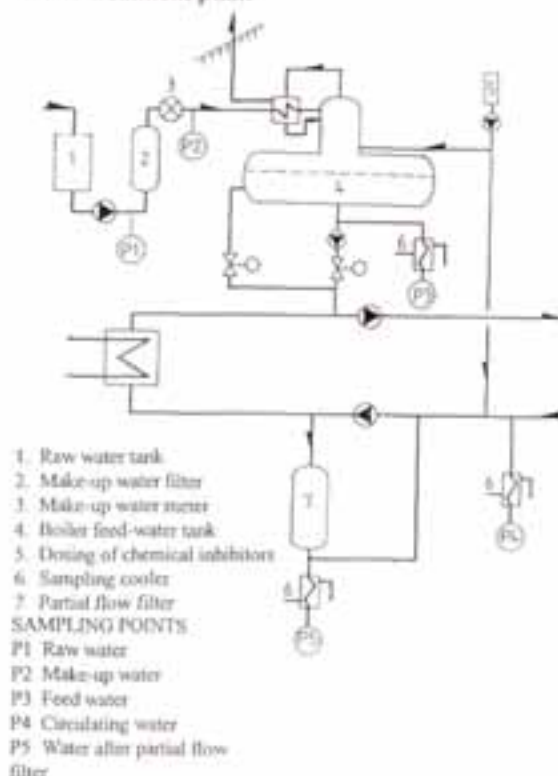
If the dilution water has the following qualities, it should be possible to maintain the guideline values mentioned previously in connection with circulating water (Table 6.1).

TABLE 6.1 ANALYTICAL GUIDELINE VALUES

Plant size: System connection:	> 100 MW		10-100 MW		< 10 MW	
	syst. conn. 1)		syst. conn. 1)		syst. conn. 1)	
	INDIRECT	DIRECT	INDIRECT	DIRECT	INDIRECT	DIRECT
pH-value (25°C)	9.5 - 10	9.5 - 10	9.5 - 10	9.5 - 10	9.5 - 10	9.5 - 10
Hardness mmol (Ca+Mg)/kg 2)	< 0.178	< 0.018	< 0.178	< 0.018	< 0.178	< 0.089
Hardness °d	< 1.0	< 0.1	< 1.0	< 0.1	< 1.0	< 0.5
Oxygen mg O <sub>2</sub> /kg	< 0.02	< 0.02	< 0.02	< 0.02	See comments	See comm.
Ammonia mg NH <sub>3</sub> /kg	< 10	< 10	< 10	< 10	-	-
Iron, tot. mg Fe/kg	< 0.1	< 0.1	< 0.1	< 0.1	-	-
Copper, tot. mg Cu/kg	< 0.02	< 0.02	< 0.02	< 0.02	-	-
Oil, fat mg/kg	< 1	< 1	< 1	< 1	-	-
Conductivity (25°C) mS/cm	See comm.	See comm.	See comm.	See comm.	-	-
Solid particles	See comm.	See comm.	See comm.	See comm.	-	-

1) Indirect connection means that boiler and district heat network are separated by heat exchangers. In direct connection, network water is heated directly in the boiler. Temperature of boiler cycle is as a rule higher (120-180°C) than that of network.

Fig 7.1 Placement of sampling points in a water treatment plant



Transition problems may occur in a district heating system in connection with a change-over from softened water to desalinated water, because desalinated water dissolves deposits accumulated during the softened water period. Similar problems may arise by a transition from raw water to softened or desalinated water. The dissolution gives rise to a higher content of sludge, which has to be removed by mechanical filters to avoid stalling of flowmeters and heat exchangers.

## 7 SAMPLING AND ANALYSES

### 7.1 General

District heating water must have a continuous acceptable quality conforming with the guideline values for dilution water; see 6.2. Both the frequency and the number of analyses vary depending on operating conditions and the need for dilution water.

Table 7.1 Frequency of analyses at sampling points

To be analysed	P1 Raw water	P2 Make up water	P3 Boiler feed water	P4 Circulating water	P5 Water after partial flow filter
pH	D		B	B	
Ca	D	A	B	B	B
O <sub>2</sub>			B		
NH <sub>4</sub> <sup>+</sup>				C	
Fe	D			C	C
Cu				C	C
Oil				C	
Conductivity	D		B <sup>1)</sup>	B <sup>2)</sup>	
Solid particles	D			B	B
Chemical inhibitors				B/C	

A = every weekday

B = once a week

C = once a month

D = once a year or when needed

1) if ammonium or hydrazine is used

2) continuous monitoring is recommended if oil is preheated with district heating water

3) continuous monitoring is recommended if makeup water is demineralized

### 7.2 Sampling locations

Figure 7.1 shows placement of sampling points in a water treatment plant.

### 7.3 Analyses

Table 7.1 indicates proposed sampling points, frequency of analyses and substances to be analyzed.

As a general rule, the analytical results must be filed, so that they can be subsequently compared with each other to detect possible changes.

The analyses must be performed according to standardized analytical methods.

### 7.4 Sampling and analyses in Iceland

As Iceland is in a special position, being able to use geothermic water in its district heating

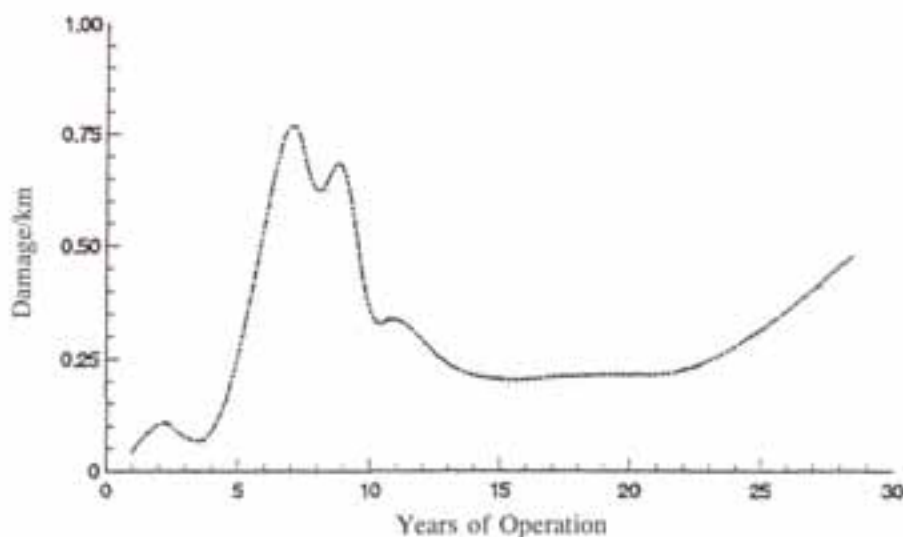


Fig. 8.1 Damage frequency; Swedish registrations covering all culvert types

networks, sampling and chemical analyses take a different form. Regular chemical analyses of geothermic water may facilitate detection of changes in the geothermic reservoirs, for example, in connection with overexploitation. Chemical follow-up of geothermic water reservoirs is therefore very important. Sampling is recommended at least once a year and even several times a year, if water analyses show changes. However, the substances indicating changes are different under different conditions. Reduction in the concentration of silica ( $\text{SiO}_2$ ) and fluorine is usually indicative of overexploitation (overloading of geothermic reservoirs). It is caused by the flowing of cold groundwater into the reservoir.

## 8 LEAKAGE CONTROL

### 8.1 General

Some damage statistics have been prepared for district heating networks in the Nordic countries. Figure 8.1 shows a damage frequency curve for Swedish plants (Ref. 10.5.9).

The pronounced peak seen at years 5-10 is characteristic of the corrosion attack and leakage caused by installation errors. Most of the damages

relate to the leaking in of rain or groundwater from outside through the pipe jacket, which leads to attack on the pipes and also reduced insulating properties.

### 8.2 Leakage control

Leakage control is always performed by measuring the consumption of makeup water. An increased makeup water consumption indicates that there are leaks from the system, while a reduced consumption may be due to leaks into the system, for example, from an indirectly connected boiler or from a substation.

Makeup water control:

- Major plants are frequently equipped with an increased consumption warning system.
- Minor plants carry out daily manual reading of consumption.

Measuring of the makeup water for leakage control purposes is frequently performed in combination with several of the methods mentioned in the following.



### 8.3 Leak detection methods

Several leak detection methods exist for locating a damaged place:

- District heating pipes with built-in electric moisture alarm: The system consists of an electric circuit registering changes in moisture content of insulation. The alarm is set off by high moisture content, and the damaged place can be found by means of localized measurements at connection points
- Thermography: Thermography of stretches of culverts helps to detect points that have higher temperatures indicating reduced insulation capacity. A number of plants thermograph yearly the entire stretch of culverts to detect possible external leakage/damage (Ref. 10.5.5 and 10.5.6)
- Temperature measurement: Detection of elevated temperatures at points exposed (chambers, sub-stations, etc) may indicate leakage from the district heating network
- Pressure measurement: If increased makeup water consumption is registered, the leakage point can be located by shutting off and pressure-testing parts of the district heating network
- Tracers: Tracers (e.g. the dye pyranine, which has been tested in Sweden) can be added for visual observation of leakage (Ref. 10.5.3)
- Analysis of characteristic chemicals in district heating network
- Acoustic methods: Methods based on the use of listening control equipment for locating the water sounds of leakage
- Visual observation: Visual observations of stretches of district heating piping route,

with attention to melting snow or steam development

Several leak detection methods can be used simultaneously to locate damage.

## 9 ENVIRONMENT

### 9.1 General

District heating water is alkaline, having typically a pH-value of 9.5-10. Depending on what chemicals are added to the water, it may be harmful for the environment if it is discharged in large quantities. Hydrazine-containing water may be harmful even in small quantities if it is consumed as drinking water or splashed on skin.

Specifications concerning the internal environment are drawn up by industrial safety authorities, while those for the external environment are drawn up by environmental protection authorities. The specifications and the authorities responsible for them vary from country to country. The safety measures discussed here are therefore those commonly accepted.

The owner of a plant is responsible for seeing to it that valid regulations are observed.

### 9.2 Chemical inhibitors

Safety regulation brochures regarding handling and transport have been issued for all chemicals considered to constitute a risk for health or the environment. They are available from the supplier.

Table 9.1 indicates the area of application and protective equipment for the chemicals most commonly used in the district heating field. As the use of hydrazine is permitted and at the same time subject to debate, it is discussed in more detail in the following section.

## 9.2.1 Information about hydrazine

### 9.2.1.1 General

In accordance with the instructions of the Swedish Industrial Safety Board (AFS 1987:12), hydrazine is included in the limit-value list, because:

- it can be absorbed through skin
- it has cancer-inducing properties
- it has sensitizing (allergy-inducing) properties

The hygienic limit value for hydrazine concentration in air, that is, for hydrazine as an air pollutant, is set at 0.1 ppm or 0.13 mg/m<sup>3</sup>. The concentration can be thus given either in litres of gas (vapor) per million litres of air (ppm) or in mg per m<sup>3</sup> of air.

### 9.2.1.2 Toxicological effects

The limit value indicated above is not based on any absolute or sharp limit set by medicine between harmful and harmless concentrations. Even if a hydrazine air concentration that is equal to the limit value poses, as a rule, no health risk or only an insignificant health risk, an effort must be made to keep hydrazine content as much as possible **below** the limit value.

### 9.2.1.3 Absorption through skin

Hydrazine is a substance that easily penetrates the skin. Therefore, special measures have to be taken to prevent intake through skin, particularly when working with concentrated solutions. For example, chemical protective clothing must be worn whenever hydrazine is handled.

### 9.2.1.4 Handling

The plants normally use a 15% hydrazine solution (24% hydrazine hydrate), which is diluted further for normal application doses. Thus, the work involves very diluted water solutions of hydrazine, which allows the assumption that the limit value is not reached in premises where for example

handling and dosing of hydrazine take place. This is apparent also from the measurements conducted. Should small quantities of hydrazine be spilled on the floor, the hydrazine in the air naturally increases, and the floor should be rinsed as soon as possible with lots of water.

TABLE 9.1 CHEMICAL ADDITIVES

Chemical	Formula	Reaction	Area of use	Protective equipment
Sodium hydroxide	NaOH	Strongly alkaline	Raising pH and conductivity in district heating water and boiler water	Rubber gloves, rubber apron and goggles or visor
Trisodium phosphate	Na <sub>3</sub> PO <sub>3</sub>	Strongly alkaline	Raising pH and conductivity in electric boilers. Reducing hardness and raising pH in boiler water	Goggles
Disodium phosphate	Na <sub>2</sub> HPO <sub>4</sub>	Weakly alkaline	Raising pH and conductivity in electric boilers. Lowering hardness in boiler water.	None required
Sodium sulphite (activated)	Na <sub>2</sub> SO <sub>3</sub>	Neutral	Binding oxygen in boiler water and feed water at low pressures (< 40 bar)	None required
Hydrazine hydrate	N <sub>2</sub> H <sub>4</sub> · H <sub>2</sub> O	Alkaline	Binding oxygen and raising pH in feed water and district heating water	Closed handling. In open handling, gas mask and chem. protect. suit
Tannin (Heatreat 600)	See ch. 3.4.3	Alkaline	Binding oxygen and inhibiting corrosion in district heating water	Protective gloves and goggles
(DM 4-1)	See ch. 3.4.3	Slightly acid	Binding oxygen and inhibiting corrosion in boiler water. Used together with sodium hydroxide.	Protective gloves and goggles
Ammonia 25 %	NH <sub>3</sub> OH	Strongly alkaline	Raising pH in feed water and district heating water	Protective gloves

### 9.3 Water treatment plants

When softening or desalination facilities are regenerated, a surplus of regeneration chemicals stays in the wastewater. They may be harmful and therefore need to be treated before discharge. Among other things, the pH of the water from a desalination facility must be adjusted. It is recommended that the specifications of local authorities be followed.

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## APPENDIX

### Examples of different treatment methods for district heating water

The following examples illustrate treatment of district heating water at plants representing different sizes

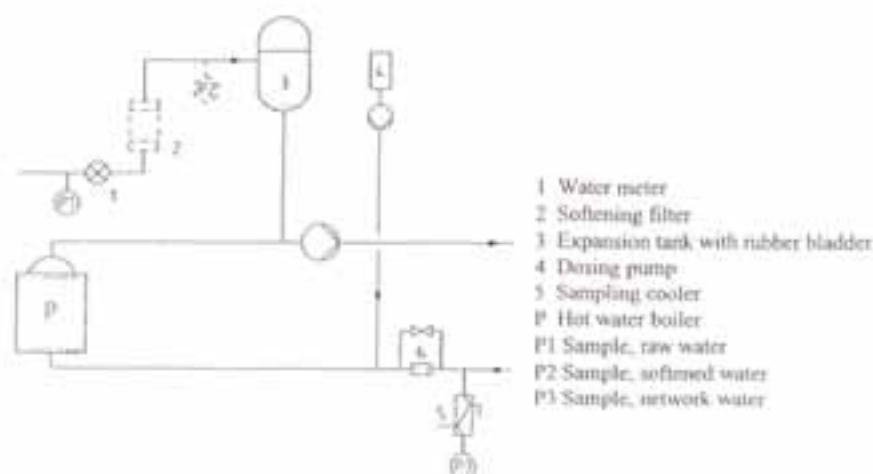
#### Example 1 (<5 MW)

This example refers to small and auxiliary networks with plants of up to 5 MW with expansion tank equipped with rubber bladder. Normally, plants of this size have small volumes of makeup water and water in the network. The makeup water can consist of raw water, provided that leaks are not too large and that hardness level is not too high. The water can be deaerated chemically, that is, by applying some oxygen-reducing chemical.

The pH is adjusted to  $>9.5$  by applying sodium hydroxide.

Control of makeup water quantity is important. Increased volume of makeup water is accompanied by a risk of film formation and corrosion. If hardness exceeds  $1\text{ }^\circ\text{d}$ , doses of oxygen-reducing chemicals must be increased and softening with manual regeneration must be carried out.

Control analyses shall include the analyses indicated in Table 6.1.



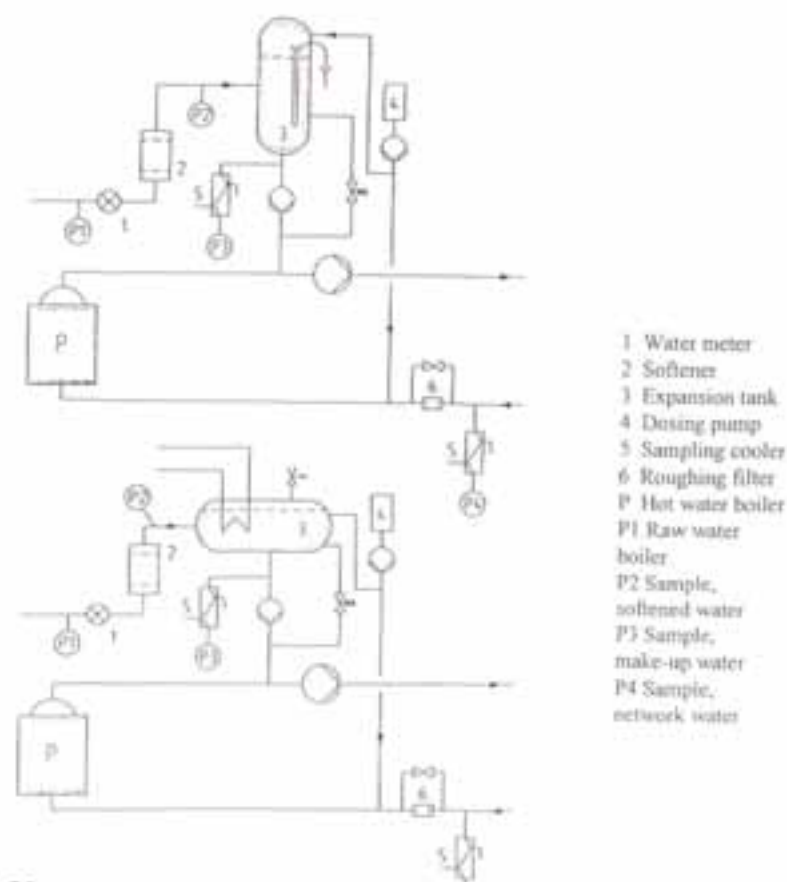
### Examples 2 and 3 (5-10 MW)

Examples 2 and 3 refer to permanent plants ranging from 5 to 10 MW with expansion tanks equipped with one-way valves and steam cushions. Makeup water quantities are normally relatively small, and deaeration is done chemically. If the hardness of raw water exceeds 1 °d, it is recommended that the water be softened by means of filtering, with automatic regeneration.

Control of makeup water quantity is important. Increased volume of makeup water is accompanied by a risk of film formation and corrosion. If this happens, softening and increased dosing with oxygen-reducing chemicals or thermal deaeration must be performed.

The pH is adjusted to >9.5 with sodium hydroxide treatment.

Analytical control must include the analyses indicated in Table 6.1.



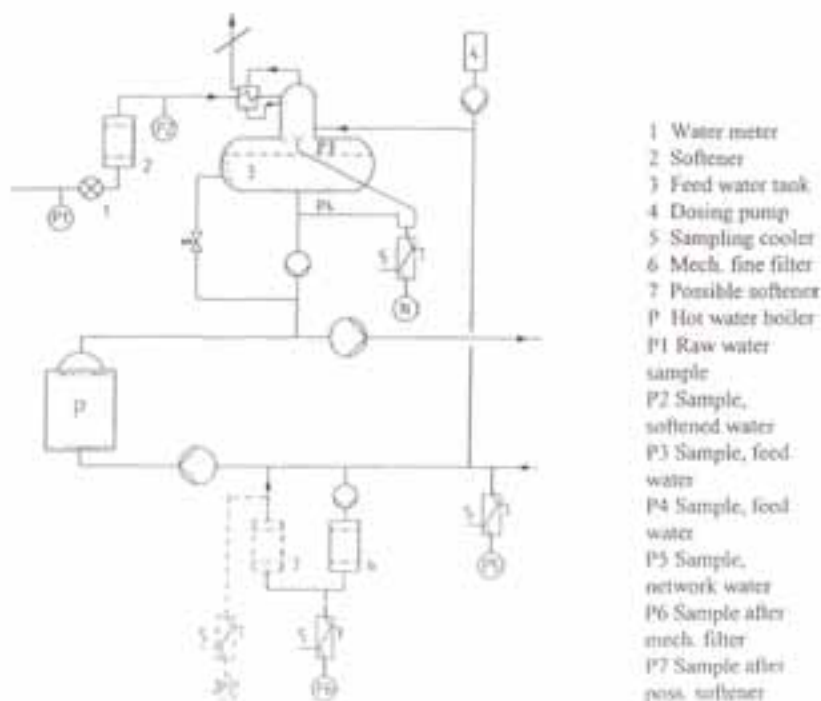
#### Example 4 (10-50 MW)

Example 4 illustrates permanent plants from 10 to 50 MW, with feed water tank and thermal deaeration. Make up water is softened and network water is cleaned mechanically in bypass filter. Partial flow through a filter is adjusted in accordance with circulation flow; recommended percentage is 1-3. If raw water leaks in, it is recommended that partial flow be equipped with a softener in series with mechanical filter.

Control of makeup water quantity is important for leakage detection.

pH is adjusted to  $>9.5$  with sodium hydroxide treatment.

Analytical control must include the analyses indicated in Table 6.1.



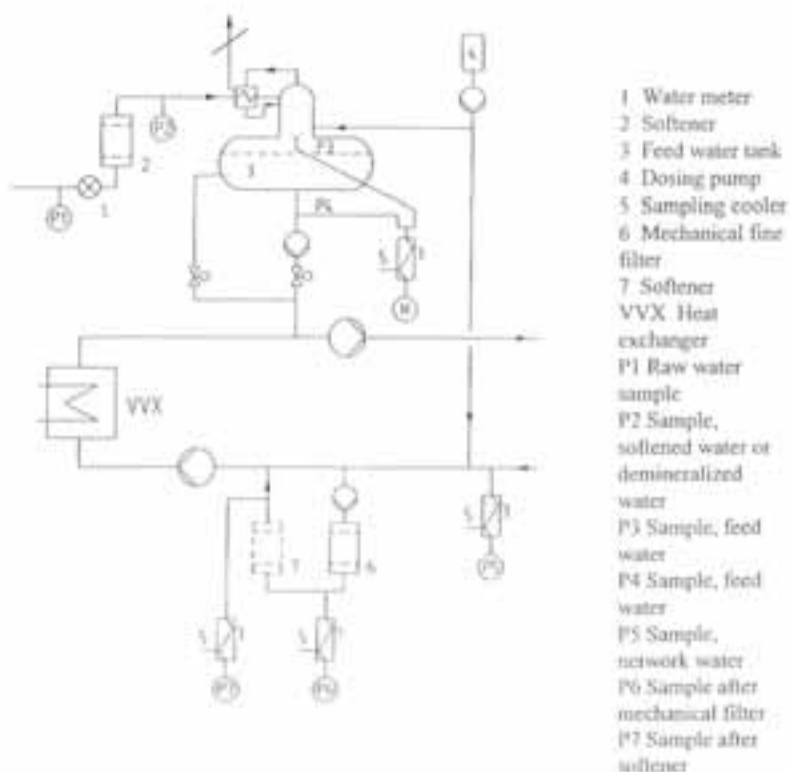
### Example 5 (> 50 MW)

Example 5 illustrates permanent plants above 50 MW, with feed water tank and thermal deaeration. Makeup water is softened or desalinated, and network is cleaned mechanically and by ion exchange in bypass filter. Partial flow through filters is adapted to circulation flow; recommended percentage is 1-3.

Control of makeup water quantity is important for leak detection.

pH is adjusted to >9.5 with sodium hydroxide treatment.

Analytical control must include the analyses indicated in Table 6.1.





NORDVÄRME :

DDF [Association of Danish District Heating Plants]

LLY [Registered Association of Heating Plants, Finland]

FNE [District Heating Association, Union of Norwegian Energy Plants]

SIH [Association of Icelandic Heating Plants]

VVF [Swedish District Heating Organization]

**EVALUATION OF CLOSED WATER  
CORROSION INHIBITORS AND IN SERVICE  
REMOVAL OF CHROMATE DEPOSITS IN  
CLOSED WATER SYSTEMS**

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**Holiday Inn Crown Plaza  
New York City, New York  
19-Jul-94**

Technological advances in closed hot and chilled water systems have made necessary the assessment of the available types of closed water treatments.

The ideal closed water inhibitor that will meet today's ten major water conditioning requirements should have the following properties:

- I. Effective corrosion inhibitor for both flowing and static operating conditions.
  - I. High temperature - hot water heating system.
  - II. Low temperature - chilled water system.
- II. Effective scale and sludge inhibitor.
  - I. High temperature - hot water heating system.
- III. Non-nutrient for biological growth.
- IV. Will not break down to form undesirable type of products.

- V. Low inorganic solids - will not affect recirculating pumps, seals and glands.
- VI. Buffers pH so that it will not be corrosive to amphoteric metals or alloys.
- VII. Non-polluting.
- VIII. Non-toxic.
- IX. Colourless, non-staining.
- X. Simple and accurate test method.

There are three potential major water conditioning problems that must be effectively controlled in order to maintain a successful water conditioning program.

- I. Corrosion.
- II. Scale and sludge deposits.
- III. Microbiological growth.

1. CORROSION

Corrosion attack in a closed water system results in the loss of metal and the formation of insoluble corrosion products. Metal loss will result in costly repairs, possibly including replacement of equipment and piping.

The various types of corrosion that may occur in a closed water system are:

I. Oxygen

Increasing the temperature of a closed water system releases nascent oxygen and results in an accelerated increase in corrosion (Figure 1, page 28).

## II. Alkaline pH

Alkaline pH values above 9.5 will attack amphoteric metals and alloys such as aluminum, brass, etc. The addition of silicates will prevent this alkaline attack up to a pH of about 11.

## III. Acidic pH

As the pH value decreases from 8.5 to 4.5 the corrosion rate increases. At a pH of 4.5 or below, free mineral acidity (FMA) is present and regardless of the corrosion inhibitor present or its concentration, a serious corrosion attack will occur.

## IV. Under Deposit Cell Type

The accumulation of suspended solids on a metal surface may result in under-deposit cell type corrosion attack.

## V. Anaerobic Bacteria

Anaerobic sulphate reducing bacteria may develop in the absence of oxygen on the metal surface beneath deposits. This type of anaerobic bacteria is very corrosive and regardless of the type of corrosion inhibitor being used or its concentration, this serious corrosion attack will continue.

However, this anaerobic bacteria can be destroyed by:

1. Removing the deposit buildup from the metal surface.
2. Applying a suitable biocide that can effectively penetrate through the deposit.

## VI. High Inorganic Dissolved Solids

As the conductivity or the ionized inorganic total dissolved solids, and in particular the sulphate and chloride ions increases, the corrosion rate is accelerated. The application of sodium sulphite in a closed system that has a high air (oxygen) ingress could accelerate in this type of corrosion attack.

## VII. Galvanic (Dissimilar Metals)

Connecting two dissimilar metals that are not close together in the electromotive series without proper insulators will cause a serious corrosion attack on the more reactive metal. This corrosion attack will occur regardless of the corrosion inhibitor present or its concentration. (Figure II, page 29).

## 2. SCALE AND SLUDGE DEPOSITS

The accumulation of objectionable scale and sludge deposits interfere with the normal operation of a chilled water system by:

- I. Plugging or reducing flow rates through heat exchanger tubes, orifices, valves, strainers and feed lines to automatic sensing instruments.
- II. Impeding heat transfer rates in heat exchange equipment.
- III. Retarding the formation of a strong protective corrosion inhibitor film on the metal surface.
- IV. Providing an insulating environment for the formation of corrosive types of anaerobic bacteria such as the sulphate reducing species.
- V. Producing under deposit type corrosion cells on the metal surface.

## I. Calcium and Magnesium

The temporary hardness content of makeup water, which is composed of calcium and magnesium bicarbonate, will break down to form scale and sludge deposits under the following conditions:

High alkaline pH values, high metal skin temperatures at the heat exchanger and high hot water temperatures (above 160°F) can produce objectionable calcium carbonate and magnesium hydroxide deposits.

The use of softened or dealkalized makeup water is recommended whenever the makeup water has a high temporary hardness content and/or a large volume of makeup water is continually being required by a system.

## II. Corrosion Products

The reaction products of corrosion in a ferrous and non-ferrous closed water system are normally the insoluble oxides of iron and copper.

## III. Chromate Reduction

The presence of organic contaminants, glycol, oil, grease, etc. in a chromate treated system will result in the reduction of chromate which will form insoluble chromic hydroxide deposits.

## IV. Silicate Treatment

The use of unsoftened makeup water in a silicate treated system will result in the formation of very objectionable crystalline deposits of calcium silicate.

## MICROBIOLOGICAL GROWTH

Microbiological growth (aerobic and/or anaerobic) is objectionable in a closed water system since it:

- I. Plugs or reduces flow rates through heat exchanger tubes, orifices, valves, strainers and feed lines to automatic sensing instruments.
- II. Impedes heat transfer rates in heat exchange equipment.
- III. Retards the formation of a strong protective corrosion inhibitor film on the metal surface.
- IV. Provides an insulating environment for the formation of corrosive types of anaerobic bacteria such as the sulphate reducing species.

## REVIEW OF CLOSED WATER CORROSION INHIBITORS

In assessing what closed water corrosion inhibitor is the most cost efficient and effective, for a particular system, it is necessary that their specific advantages and disadvantages be evaluated.

### I. CHROMATE INHIBITOR

Chromate was the first widely accepted corrosion inhibitor that has and still sets the standard for corrosion prevention. However, the pollution aspects of chromate and their attack on the seals and glands of recirculating pumps has resulted in many systems being changed to more acceptable type of inhibitors.

### CHROMATE ADVANTAGES

- I. Excellent corrosion inhibitor for ferrous and non-ferrous metals in both flowing and static conditions.
- II. The pH of the closed water can be effectively buffered by a blended alkaline

product to the desired pH range of 9.0 to 9.5. (Figure III, page 30).

- III. Bacteria may develop at chromate concentrations below 700 ppm, while at chromate levels higher than 700 ppm, bacteria will not normally grow.
- IV. Quick and accurate colourimetric titration test method.

#### CHROMATE DISADVANTAGES

- I. Considered to be a pollutant at the level normally maintained in a closed system.
- II. The yellow colour of chromate will stain carpets, drapes, etc.
- III. May cause skin dermatitis reactions.
- IV. Will damage glands and seals of circulating pumps when the chromate concentration is over 500 ppm as  $\text{CrO}_4^{2-}$ .
- V. Requires a high level of treatment that results in the formation of objectionable deposits wherever there is a leak in a system.
- VI. Not compatible with organic compounds, such as ethylene glycol, oil, grease, etc. and will form objectionable chromic hydroxide deposits.

\* NACE Task Group T-7G-1

#### 2. BORATE-NITRITE INHIBITOR

Borate-nitrite inhibitors replaced chromate products in many systems. They are also excellent corrosion inhibitors in both hot and chilled water systems. Unfortunately, borate-nitrite treatment has gained disfavor as a result of the nitrite inhibitor being a nutrient for bacteria. The growth of bacteria has

caused objectionable deposits and odours. Frequent shock dosages of biocide have not really been completely successful in preventing the growth of bacteria.

#### BORATE-NITRITE ADVANTAGES

- I. Excellent corrosion inhibitor for ferrous and non-ferrous metals in both flowing and static conditions.
- II. Considered to be non-polluting.
- III. Compatible with ethylene glycol treated system.
- IV. The pH of closed water is buffered to the desirable range of 9.0 to 9.5 or about 10.5 if a silicate inhibitor is present.
- V. Colourless and therefore is non-staining to carpets, drapes, etc.
- VI. Quick and accurate colourimetric titration test method.

#### BORATE-NITRITE DISADVANTAGES

- I. Promotes bacteria growth as a nutrient that results in the formation of objectionable deposits and odours.
- II. Requires a high level of treatment that results in the formation of objectionable deposits wherever there is a leak in a system.

#### 3. HYDRAZINE MORPHOLINE INHIBITOR

A hydrazine morpholine inhibitor was introduced as a "non-solids" type treatment that would not affect the seals and glands of recirculating pumps. However, since

hydrazine has been reported as a suspected carcinogenic compound, this product is being replaced in many systems with non-toxic type treatments.

#### HYDRAZINE MORPHOLINE ADVANTAGES

- I. Good corrosion inhibitor for both ferrous and non-ferrous metals in both flowing and static conditions.
- II. Since hydrazine and morpholine are organic compounds they will not affect the seals and glands or circulating pumps.
- III. Will not form objectionable deposits wherever there is a leak in the system since both hydrazine and morpholine are organic compounds.
- IV. The pH of the closed water is buffered to the desirable pH range of 9.0 to 9.5.
- V. Non-nutrient for bacteria growth.
- VI. Considered to be non-polluting.
- VII. Colourless and therefore is non-staining to carpets, drapes, etc.
- VIII. Quick and accurate colourimetric titration test method.

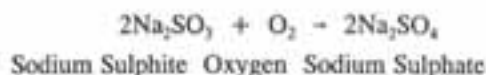
#### HYDRAZINE MORPHOLINE DISADVANTAGES

- I. Hydrazine is a suspected carcinogenic compound.
- II. Hydrazine, under certain catalytic conditions, will break down to form ammonia. Ammonia will in the presence of oxygen, aggressively attack copper and/or copper bearing alloys.

- III. Ethylene glycol contamination breaks down over a period of time to form acetic acid (Table I, Page 31). Acetic acid will neutralize this alkaline inhibitor and depending upon the amount of acetic acid produced, it could lower the pH to a corrosive level. Additional morpholine would therefore be required to maintain the pH value in the desired range of 9.0 to 9.5.

#### 4. SULPHITE-CAUSTIC SODA OR SODA ASH INHIBITOR

Sodium sulphite-caustic soda or sodium sulphite-soda ash type treatment's main advantage is its low toxicity and non-polluting properties. However, if a system has air (oxygen) ingress problems, the sodium sulphite dosage requirements can become excessive. The sodium sulphite chemical reaction with oxygen is as follows:



#### SULPHITE-CAUSTIC SODA OR SODA ASH ADVANTAGES

- I. Good corrosion inhibitor for ferrous and non-ferrous metals in both flowing and static conditions.
- II. Colourless and therefore is non-staining to carpets, drapes, etc.
- III. Considered to be a non-pollutant and also non-toxic.
- IV. Non-nutrient for bacteria growth.
- V. Compatible with ethylene glycol treated system.
- VI. Quick and accurate colourimetric titration test method.

SULPHITE-CAUSTIC SODA OR SODA  
ASH DISADVANTAGES

- I. Air (oxygen) ingress in a system will result in the formation of high sulphate concentrations. Excessive sulphate levels may result in:
  - A. Damage to glands and seals of circulating pumps.
  - B. Formation of objectionable deposits wherever there is a leak in a system.
  - C. Corrosion potential increased.
- II. The addition of either caustic soda or soda ash must be carefully controlled, so that the pH of the closed water system is not allowed to rise above 9.5. If the pH exceeds 9.5, a serious corrosion attack could occur on any amphoteric metal or alloy in the system regardless of the sulphite content present.
- III. Sulphite can be contributing factor in cracking the mechanism of stainless steel expansion bellows.

5. SILICATE INHIBITOR

A silicate based treatments main advantage is that it is non-toxic, and a non-pollutant type product. Unfortunately, unsoftened makeup water cannot be tolerated due to the formation of objectionable crystalline silicate type deposits. Also, under prolonged "static" conditions, a silicate inhibitor cannot provide effective corrosion protection.

SILICATE  
ADVANTAGES

- I. Good corrosion inhibitor for ferrous and non-ferrous metals under flowing conditions.

- II. Non-nutrient for bacteria growth.
- III. Colourless and therefore is non-staining to carpets, drapes, etc.
- IV. Considered to be a non-pollutant, and also non-toxic.
- V. Compatible with ethylene-glycol treated system.
- VI. Most economical of all corrosion inhibitors.
- VII. Quick and accurate colourimetric comparator method.

SILICATE  
DISADVANTAGES

- I. Not suitable as a corrosion inhibitor for "static" operating conditions for extended periods of time.
- II. Softened (no hardness) makeup water is required to prevent the formation of an objectionable crystalline calcium silicate type deposits.

MOLYBDATE INHIBITOR

A patented molybdate based, neutralizing amine, azole, polymer type product, was introduced to provide a treatment that would eliminate the objections of the previously described closed water inhibitors.

The only problem observed with this treatment is that acetic acid, which is the decomposition product of ethylene glycol, will neutralize the amine present in the molybdate formula. Therefore, additional neutralizing amine is required to raise the pH of the closed water to 9.0 - 9.5 in order to prevent corrosion from occurring in the system.

### MOLYBDATE ADVANTAGES

- I. Excellent corrosion inhibitor for ferrous and non-ferrous metals in both flowing and static conditions.
- II. Colourless and therefore non-staining to carpets, drapes, etc. Quick and accurate colourimetric comparator method.
- III. Considered to be a non-pollutant and also non-toxic.
- IV. Non-nutrient for bacteria growth.
- V. The pH of the closed water is buffered to the desirable pH range of 9.0 to 9.5.
- VI. Compatible with ethylene-glycol treated systems.
- VII. Low inorganic solids present in this inhibitor and therefore, will not damage seals and glands of circulating pumps.
- VIII. Will not form objectionable deposits wherever there is a leak in the system due to the low inorganic solids present in the product.

### MOLYBDATE DISADVANTAGES

- I. Ethylene-glycol contamination can cause break down over a period of time to form acetic acid. Acetic acid will neutralize the alkaline buffer. Depending upon the amount of acetic acid produced it will lower the pH to a corrosive level. Additional neutralizing amine buffer must be added to maintain the pH value in the desired range of 9.0 to 9.5 in order to protect the system from corrosion.

### IN-SERVICE REMOVAL OF CHROMATE DEPOSITS FROM CLOSED WATER SYSTEMS

Closed water systems treated with a chromate inhibitor has resulted over the years in the accumulation of a considerable amount of objectionable deposits.

These deposits can cause the following operational problems:

- I. Plugs or reduces the flow through orifices, valves, strainers and feed lines to automatic sensing control instruments.
- II. Impede or prevent flow through heat exchange equipment and/or piping.
- III. Retards heat transfer rates through heat exchange equipment.
- IV. Increases the opportunity for under deposit cell type corrosion.
- V. Interferes with the formation of a strong corrosion inhibitor film on the metal surface.
- VI. Provides an environment for the growth of corrosive anaerobic type bacteria.

Chemical analysis of these deposits show that they are about 1/3 chromous oxide, 1/3 iron oxide and 1/3 organic matter.

The chromate inhibitor has been reduced to the insoluble chromic hydroxide by ethylene glycol contamination in the closed water system. This contaminant has entered the system from the chilled water coils. When the cooling season is over these coils are "winterized" with ethylene glycol antifreeze, to protect them from freezing and rupturing the coils.

Before these coils are put back into service they are drained and flushed. However, our experience has



shown that all the ethylene glycol is not always completely removed from these coils and unfortunately it enters the closed water system when they are put back into service. Analyses of various chilled water systems has shown the presence of up to 1500 ppm of ethylene glycol present which has resulted in the formation of objectional chromic hydroxide deposits.

McMaster University, Hamilton, Ontario have developed a unique method in which they have modified their supply fan ducts so that a flexible air duct can be connected to the chilled water coil. The coil is disconnected, drained and the supply air duct is attached. This procedure allows the coils to be laid up dry and therefore not require any ethylene glycol.

Our research department tried various types of cleaners to dissolve this deposit such as:

- I. Chelating, complexing and sequestering compounds.
- II. Detergents, dispersants and wetting agents.
- III. Polymeric compounds.
- IV. Inhibited sulphamic acid.
- V. Inhibited muriatic acid.

The above cleaners were evaluated to determine which one or a combination of them was most effective in dissolving this deposit. It was found that a 8 to 10% solution of inhibited muriatic acid at ambient temperature for six hours, was the most effective and suitable type cleaner.

Unfortunately, inhibited muriatic acid will aggressively attack any amphoteric metal or alloy such as magnesium or brass. Since these types of metals or alloys are normally present in closed water systems, therefore inhibited muriatic acid could not be used.

Our research laboratory reasoned that since this deposit was formed from a "reduction" reaction, could it not be reversed by introducing an "oxidization" reaction?

Hydrogen peroxide was selected as the most ideal and effective oxidizing agent for the following reasons:

- I. It would oxidize and redissolve the chromic hydroxide deposit into soluble sodium chromate, which would again act as an effective corrosion inhibitor.
- II. The strong oxidizing properties of hydrogen peroxide would destroy any living biomass and also burn up any dead microbiological matter.
- III. Hydrogen peroxide is non-corrosive to the metals and alloys in a closed system and it has no effect on the protective chromate inhibitor film.
- IV. Rubber and synthetic type rubber products, are unaffected by hydrogen peroxide.
- V. Any insoluble matter that is released by this redox reaction can be effectively removed from the closed system by the in-line filters or a sand filter.
- VI. When the cleaning operation has been completed, it would not be necessary to drain, flush and refill the system with fresh makeup water and a chemical inhibitor.

This unique cleaning procedure was performed at three Southern Ontario Universities. All of these universities had used a chromate inhibitor for many years and had experienced ethylene glycol contamination in their chilled water systems. Objectionable chromic oxide based deposits were present and therefore they all agreed to using hydrogen peroxide as an in service cleaner.

Hydrogen peroxide at a pH of 9.5 to 10 will redissolve chromic hydroxide by the following redox chemical equation.



102 lbs.	206 lbs.	160 lbs.	324 lbs.	144 lbs.
Hydrogen Peroxide	Chromic Hydroxide	Caustic Soda	Sodium Chromate	Water

Therefore, 306 lbs. of 35% reactive hydrogen peroxide will redissolve 206 lbs. of chromic hydroxide.

Sufficient 35% hydrogen peroxide should be added to provide 1000 ppm of 100% reactive hydrogen peroxide concentration in the closed water system.

The hydrogen peroxide oxidizing reaction with the chromic hydroxide deposit results in a lowering of the pH of the chilled water. It is essential that for this redox reaction to stoichiometrically go to completion, the pH must be maintained between 9.5 to 10. Caustic soda or soda ash should therefore be applied when required, to maintain the pH value in this desired range.

A 150,000 I.G. capacity chilled water system was cleaned with hydrogen peroxide while it was in service.

The hydrogen peroxide was pumped directly from the drum into the chilled water expansion tank, which had been partially drained prior to the addition of the oxidizing cleaner.

Approximately 5,000 lbs. of 35% reactive hydrogen peroxide was added in two stages, in order to obtain 1,000 ppm of 100% reactive hydrogen peroxide in the system.

The in service cleaning operation was continued for 4½ months. During the cleaning period about 592 lbs. of insoluble chromic hydroxide as  $Na_2CrO_4$  was redissolved from the system. Caustic soda was also added when required throughout the cleaning, to maintain the pH of the chilled water in the required range of 9.5 to 10.

In addition to redissolving 592 lbs. of chromic hydroxide deposit as  $Na_2CrO_4$ , the system was also sterilized and both dead and alive bacteria were

destroyed. The total biomass of the chilled water system was reduced from 2.8 nanograms/mL to 0.017 nanograms/mL, which clearly indicates the effective disinfecting properties of hydrogen peroxide.

Corrosion rates obtained during this 4½ month cleaning operation showed only 0.20 MPY and 0.29 MPY on steel and copper strip type corrosion test coupons respectively. (TABLE II, Page 32). These corrosion rates clearly show the effectiveness of the redissolved chromate in providing excellent corrosion protection during the cleaning period. During the cleaning period 45,000 I.G. of makeup water was added to the system and the chromate level as  $Na_2CrO_4$  averaged about 450 ppm. The chromate content as  $Na_2CrO_4$  prior to the addition of hydrogen peroxide was 300 ppm and it increased during the cleaning operation to 460 ppm, which is an increase of 260 ppm as  $Na_2CrO_4$ . Therefore, a chromate inhibitor treatment was not required during the 4½ month cleaning period, since the hydrogen peroxide oxidized the insoluble chromic hydroxide deposit back to the soluble chromate (corrosion inhibitor) state.

No operational problems were encountered as a result of the in service cleaning operation. It was also not necessary to drain and flush the system after the cleaning was completed since no objectionable reaction products were produced. The in-line filters were able to effectively remove any suspended solids that were released by the hydrogen peroxide and therefore the chilled water remained clear.

**CAUTION** - All the required precautions for handling a strong oxidizing chemical like hydrogen peroxide should be carefully followed.

The author would personally like to thank John Daly of our Research Department for developing the in service cleaning concept. We also greatly appreciated the excellent co-operation and assistance by the management and staff of the physical plant department at the universities at the universities which performed the cleaning of their closed systems.

## CORROSION PROTECTION STRATEGIES FOR HOT WATER DISTRICT HEATING SYSTEMS: TWO CASE STUDIES

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### ABSTRACT

Corrosion of steel district heating pipes can cause premature failure of what is often the largest investment of a new district heating system. Two general strategies exist for preventing corrosion in distribution pipes. The first, and most common in North America, involves the ongoing addition of chemicals to pretreated system water that act as corrosion inhibitors by forming passivating films on pipe surfaces.

The second method involves pretreating feed water before it enters the system to remove dissolved minerals and oxygen and maintaining this water quality carefully. The only chemical added to the system is NaOH in order to maintain a pH of 9.5-10. Because of leakage from the system and the need for ongoing makeup, many systems have continuous treatment of a partial stream. This approach is widely employed in European systems.

The application of the two different strategies is examined in two existing North American systems and the two strategies are compared on the basis of effectiveness and cost.

### INTRODUCTION

Water treatment programs are important for district energy system operators in order to prevent shutdowns and replacement costs associated with corrosion of district heating pipes and other metallic components in the system. A related problem is the buildup of scale on pipe and heat exchange surfaces which can lead to both poor heat transfer and high return temperatures as well as increasing the pressure drop and hence the operating costs in the distribution system.

Although the objective of this paper is to look at the engineering approaches for preventing corrosion rather than examining in detail the chemistry involved in the corrosion processes, it is important to understand the conditions which lead to destruction of steel distribution pipes.

Corrosion can be defined as any chemical or electrochemical reaction which leads to the degradation of a metal. However, in the context of district heating pipes, it has been described as oxygen-reducing and hydrogen-generating attacks that result in both uniform and localized degradation of the inner and outer pipe surfaces.

The Nordvärme Association Working Group on Water Treatment proposes the following strategy [1]:

1. **Filter raw water to remove suspended particulates.** Ongoing filtration of a partial stream is also recommended to remove corrosion products and to minimize the occurrence of erosion.
2. **Soften water to remove the Ca and Mg ions** responsible for the formation of deposits and scale through ion exchange. Alternatively, the water can be (more completely) deionized through sequential ion exchange or through reverse osmosis, to remove Ca, Mg and other ions which contribute to deposition, pitting and stress corrosion. The conductivity of the water will also be reduced in this way.

It should be noted that most inductive flowmeters require a conductivity of  $>25 \mu\text{S}/\text{cm}$  [1]. Demineralization is more effective than softening but has higher associated capital and operating costs. Recommended hardness levels [(mmol (Ca + Mg)/kg water)] are  $<0.178$  for indirect systems and  $<0.018$  for direct systems 10-100 MW in size [1].

3. **Remove oxygen** through thermal deaeration or chemical deactivation. Deaeration distills off oxygen as well as some dissolved carbon dioxide and is usually accomplished by flowing water over a large heat exchange surface,

countercurrent to steam. In chemical deactivation the removal of dissolved oxygen is achieved by reacting the oxygen with chemicals such as sodium sulphite or other oxygen reducing agents (including tannins).

Reaction of sodium sulphite with oxygen:



The recommended level of oxygen in district heating water is <0.02 mg O<sub>2</sub>/kg water [1]

4. **Raise the pH to 9.5-10 by adding NaOH** to assist in preventing corrosion. Less NaOH will be required for systems which employ deaeration in the system makeup water since this process removes most of the CO<sub>2</sub> in addition to O<sub>2</sub> present in feed water.
5. **Monitor the system during operation.** It is recommended that samples of the pipe material be placed in continuous contact with the circulating system water and extracted and weighed after various periods to determine the extent of degradation.

The limitation for this five step approach is that the system must be tight, that is, the leakage of air or oxygenated water into and treated water from the system must be minimal. In such systems the initial corrosion of the steel uses up most of the dissolved oxygen and the system then stabilizes.

This paper outlines for hot water system operators the advantages of each approach - as well as limitations. CANMET also has an interest in developing a water treatment procedure that is compatible with the use of drag reducing additives. We believe that the European strategy might be a good way of doing this as certain corrosion inhibitors have been found to inhibit the effectiveness of these new additives.

## CHARLOTTETOWN AND UNIVERSITY OF PEI SYSTEMS - An example of the European approach

Two separate district heating systems are owned and operated by the PEI Energy Corporation, (recently purchased by Trigen Canada), one in downtown Charlottetown and one at the University of Prince Edward Island in Prince Edward Island, Canada. Both systems are hot water based and provide heat year round at supply temperatures ranging from 80°C-120°C through a total of 18 km of steel distribution piping. Currently the combined systems have 72 buildings connected with a peak load of approximately 21 MW.

When the systems were constructed, staff at the PEI Energy Corporation decided to adopt the same principles of the European strategy for corrosion protection. The objective was to keep the treatment as simple as possible; they felt that it would always be possible to add inhibitors later if required. They knew that the systems would be closed, and expected that they would be fairly tight and so would be suitable candidates for this type of treatment approach. It was also felt that municipal building inspectors would be more comfortable with the use of domestic hot water single wall heat exchangers if the use of chemical additives was minimal.

The PEI systems use the following water treatment strategy.

During the initial filling of the systems the only pretreatment is to soften the feed water to reduce the total hardness to zero. Oxygen present in the water is depleted rapidly through initial corrosion reactions. The pH is raised to 9 by adding sodium hydroxide.

The strategy for ongoing treatment is to:

1. Maintain pH at 9 by adding sodium hydroxide to raise the pH, or sulfamic acid to lower it.

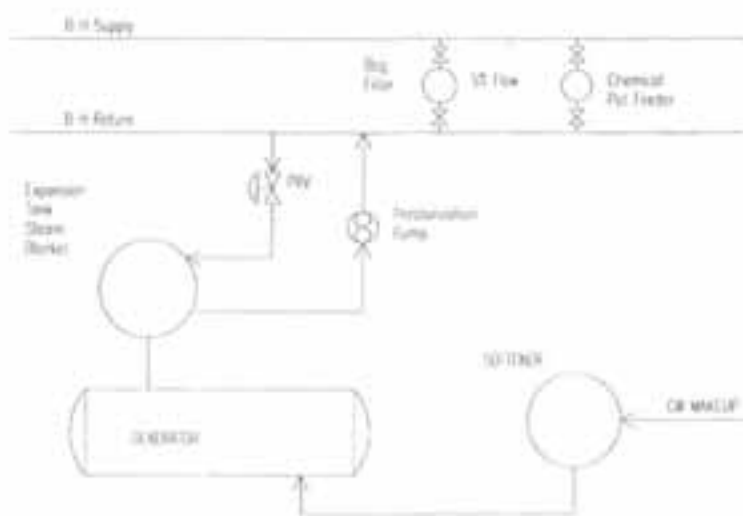


Fig. 1 - Water treatment in the University of PEI district heating system

2. Filter the system water through a bag filter to remove magnetite (5% of the flow is filtered per pass).
3. In the UPEI system, deaerated makeup water is supplied to an expansion tank that has a steam blanket to prevent oxygen pickup.

The treatment for makeup water is:

1. In both systems, to soften the water through sodium zeolite ion exchange.
2. In the Charlottetown system dissolved gases in the makeup water ( $\text{CO}_2$  and  $\text{O}_2$ ) are removed by steam deaeration from the boiler makeup system.

The pH is held at 9 to prevent damage to copper pipes in the system's ELGE heat exchangers which might occur at high pHs and to prevent damage to steel pipes that occurs below this. Both systems operate at a pH of 9-9.5 rather than 9.5-10 because of the proportions of copper and iron in the systems. Magnetite allowed to accumulate in the system can cause erosion in tube bends and in regulating valves and can cause incorrect metering in induction flowmeters. A schematic of the water treatment process in the university system is shown in Fig. 1.

Because the practice of using a simple water treatment approach was unusual at the time of construction of the system, the corrosion rate was monitored fairly carefully through the use of corrosion coupons inserted in the system and laboratory tests of the system water. The steel coupons were removed after 30-day and 12-month periods and indicated that a negligible amount of corrosion took place (Table 1). Laboratory analyses of the water in the system confirmed this by not showing an increase in metal products.

The use of coupons was felt to be a low cost method of monitoring the health of the system. Monitoring was contracted to a water treatment company on the premise that they would be examining the test results very carefully. The results showed an increase in corrosion products when the system was extended in 1990. The cause was traced back to excessive use of a boiler plant softener system during initial charging of a system expansion at the PEI Home resulting in unsoftened water getting into the system.

**Table 1:** Results of corrosion tests in the Charlottetown and UPEI systems

Date	Coupon metallurgy	Days of exposure	Corrosion rate
11 July/89	Mild steel	30	0.02 mpy
6 June/90	Mild steel	338	0.108 mpy
13 June/91	Mild steel	365	0.18 mpy
22 July/92	Mild steel	376	0.13 mpy

[mpy = mils per year. General corrosion rates of <0.5 mpy are considered moderate, <0.1 mpy are considered good and <0.01 mpy are considered excellent.]

The systems have been operating for 10 years and no failures have resulted due to corrosion, with the exception of a small leak due to external corrosion at a joint muff where water had leaked into the insulation.

After six years the monitoring by using corrosion coupons was scaled back as the results did not change. This summer, staff at the Energy Corporation will start the monitoring process again when the system is extended.

#### DISTRICT ENERGY ST. PAUL DISTRICT HEATING SYSTEM - Corrosion prevention through use of corrosion inhibitors

The St. Paul district heating system provides heat to approximately 75% of the downtown St. Paul area through 47 km of steel and copper distribution piping in two separate networks. The peak load is 131 MW. The customers' internal piping systems are connected to the hot water distribution system through customer-owned heat exchangers. The system is hot water based with supply temperatures ranging from 88°C-120°C.

Initially the system was filled with unsoftened city water to which a corrosion inhibitor was added. Makeup water is now softened before it is added to the system. The system fluid is monitored every other day by the plant operator to ensure that the corrosion inhibitor concentration, conductivity,

hardness, iron concentration and pH levels are at the recommended levels.

Laboratory testing and water treatment are contracted out to a chemical treatment company. To confirm the effectiveness of this treatment procedure corrosion coupons are used to monitor the rate of corrosion of a steel sample which is in constant contact with the system fluid. A schematic of the treatment process is given in Fig. 2.

This treatment procedure has been very effective in the St. Paul system. Recent inspection of distribution pipes during a system expansion indicated no visible occurrence of corrosion. The results of corrosion coupon testing shown in Table 2 below indicate the treatment's effectiveness.

**Table 2:** Results of corrosion tests in the St. Paul system

Date	Coupon metallurgy	Days of exposure	Corrosion rate
18 Feb/94	Copper	112	0.4 mpy
20 May/94	Copper	99	0.1 mpy
14 Dec/94	Copper	91	0.1 mpy
11 Jan/95	Copper	446	0.2 mpy
18 Feb/94	Mild steel - pretreated	112	< 0.1 mpy
25 May/94	Mild steel - pretreated	99	< 0.1 mpy
11 Jan/95	Mild steel - pretreated	446	< 0.1 mpy
11 Jan/95	Mild steel - pretreated	41	0.1 mpy

mpy = mils per year

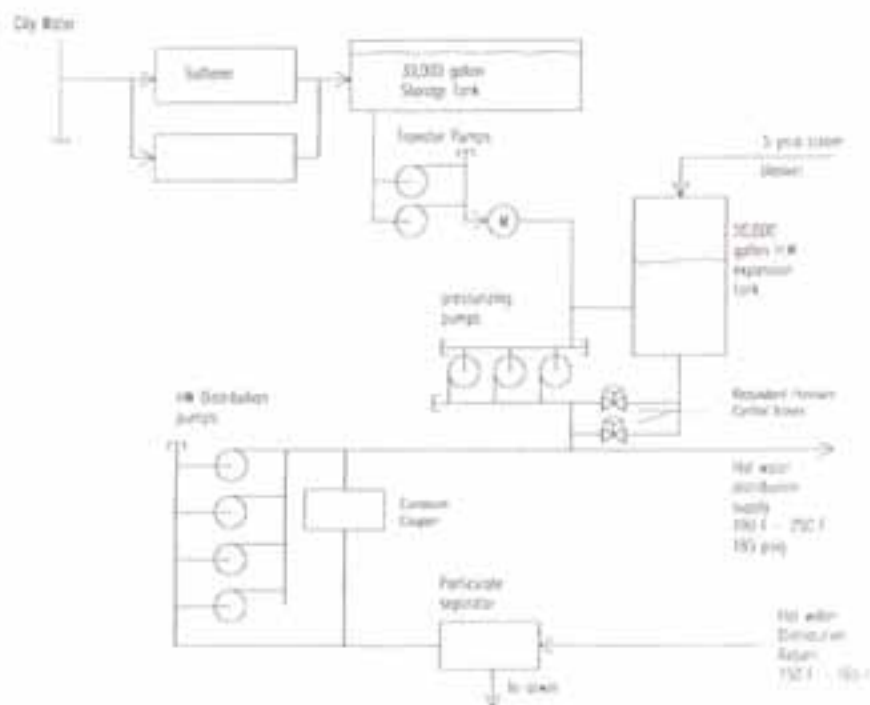


Fig. 2 - Schematic of District Energy St. Paul district heating plant

**COMPARISON BASED ON ANNUAL COST**

**Charlottetown (expressed in terms of \$US)**

Cost of caustic	\$19.25/a
Cost of sulfamic acid	\$77.00/a
Cost of monitoring	
corrosion coupon tests	\$55.50/test(/a)
chemical analyses	\$144.00/test(/a)

Annual makeup volume is approximately 6500 gallons

Cost of water treatment is 0.05 \$/gallon makeup water added

**St. Paul (\$US)**

Cost of chemical treatment (corrosion inhibitors, etc.)	\$19,000/a (avg)
Cost of monitoring	
corrosion coupon costs	\$6/coupon
corrosion coupon analysis	free

Annual makeup volume is approximately 165,000 gallons (due to maintenance, losses during system expansions, and leakage)

Cost of water treatment is 0.12 \$/gallon makeup water added

The simpler water treatment process has lower costs per gallon of makeup water. Given the low cost of a regular monitoring program it is felt that this should be a continuous process.

## CONCLUSIONS

The low corrosion rates seen in the PEI systems indicate that the European approach for water treatment in hot water systems as described in reference 1 can be effective in North American situations. In this treatment strategy the risk of corrosion is minimized by removing oxygen from the feed water through chemical or thermal deaeration, by raising the pH to at least 9 and by decreasing the hardness by softening. Good water quality monitoring and leak detection systems are important elements of this type of water treatment program.

Operators of new hot water systems might want to consider simple pH control as an alternative to the more common North American approaches. The treatment strategy is suitable when there is a slow rate of makeup and when leakage into or from the system is small. This strategy might be especially suitable for systems considering the use of friction reducing additives, since some corrosion inhibitors have been shown to lower their drag reducing capabilities [4].

For the cases examined, the simpler approach to water treatment is less expensive. The cost of maintaining corrosion inhibitors in the St. Paul system exceeded the cost of the simpler approach in the Charlottetown system. Other considerations which should be taken into account include the amount of makeup required in the system, availability of steam for deaeration, and the availability of staff to operate the equipment and monitor the water quality.

The authors would like to thank John Davey and John te Raa of the PEI Energy Corporation and Ron Cackoski of District Energy St. Paul for their help in preparing this paper.

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Addendum to Paper 3: Evaluation of Closed Water Corrosion Inhibitors and In Service Removal of Chromate Deposits in Closed Water Systems

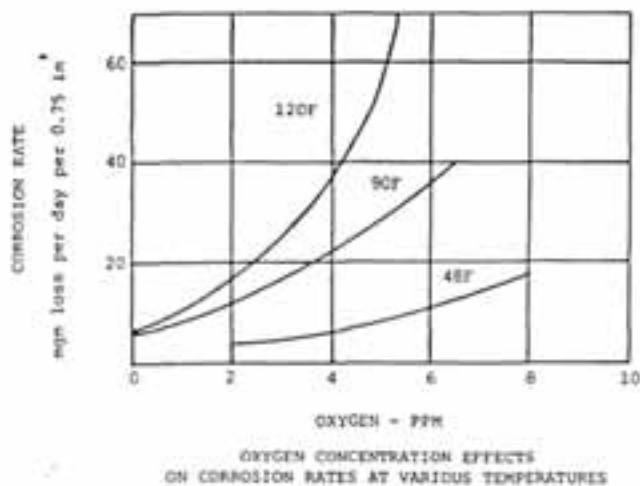
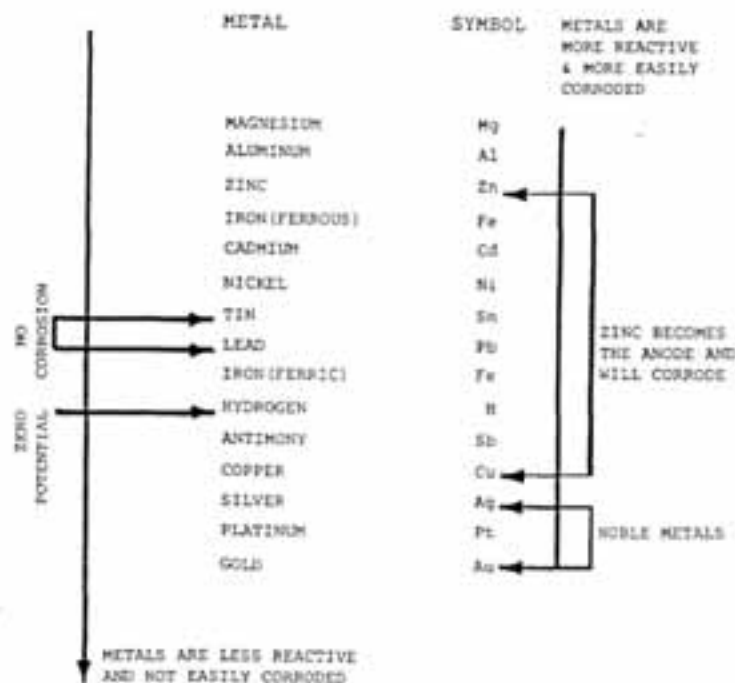


FIGURE 1



ELECTROMOTIVE SERIES OF METALS

FIGURE 11

EFFECT OF pH ON CORROSION RATE  
FOR COPPER AND IRON

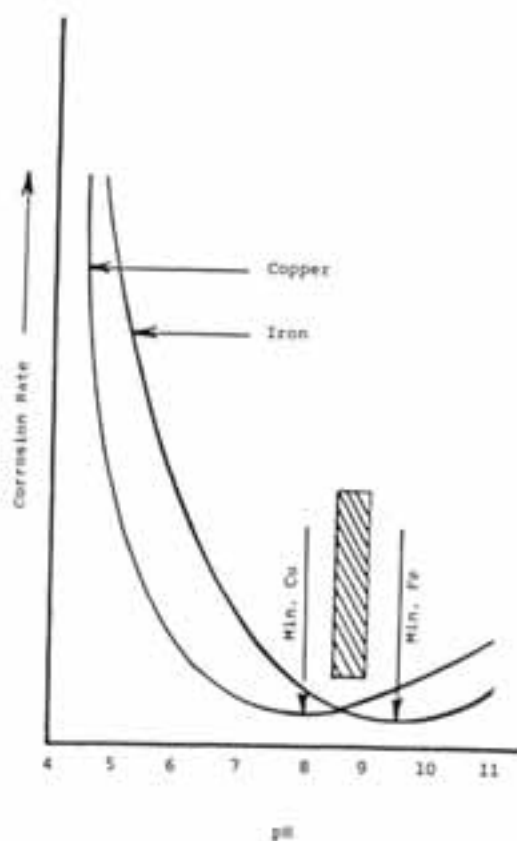


FIGURE III

TABLE I

CONTAMINATED ETHYLENE GLYCOL BREAKDOWN PRODUCTS  
IN  
CLOSED WATER SYSTEMS

- I. Acetaldehyde
- II. Acetic acid
- III. Ethanol

TABLE II

INTERPRETATION OF CORROSION RATES

0 - 1	MPY	Excellent corrosion rates
1 - 2	MPY	Good corrosion rates
2 - 5	MPY	Poor corrosion rates
5 - 10	MPY	Serious corrosion rates
10 - 20	MPY	Unprotected system

# IEA District Heating and Cooling

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