

ELECTROCHEMICAL PROTECTION AGAINST CORROSION PROCESSES IN HOT TAP WATER INSTALLATIONS

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Summary

This report is a part of Phase 1 of the Project. Mapping the existing hot tap water production patterns with focus on problems related to it is the main objective of Phase 1. Task 2 focuses on quality of water and water treatment, particularly in the City of Gdansk. Its main objective is to specify all problems related to bad water quality and corrosion.

Introduction

The corrosion problem was unknown in Gdansk up to mid- nineties. After the start of the new surface water intake in Straszyn near Gdansk in 1993, from 1995 the „rust water” has appeared in newly built houses. At first, district housing administrators failed to notice that the phenomenon was a result of galvanized steel pipes corrosion. Appearance of rust water was regarded to be a result of incorrect operating the water supply systems and SAUR NEPTUN S.A.- the municipal water supply company - was blamed. The presence of corrosion product buildups inside pipes was a proof for poor pipe material resistance in the hot tap water environment. In 1996 the District Heating Enterprise (Gdańskie Przedsiębiorstwo Energetyki Ciepłej - GPEC), as a direct public hot tap water supplier, commissioned the Research and Development Company (Centrum Badawczo-Wdrożeniowe) UNITEX Ltd. in Gdansk to work out an expertise, which would find reasons of speed-up corrosion of HTW pipes in Gdansk. The expertise presented the problem of corrosion, its reasons and possible remedial methods. Housing Department of Gdansk City Hall popularized the installation protection idea.

R. Juchniewicz PhD and K. Darowski PhD from the Corrosion Department, the Technical University of Gdansk, proposed a technical solution to the problem. The research group pointed an electrochemical dissolution of metallic aluminum method as an optimal method for hot water installations protection against corrosion.

The theoretical basis for corrosion and incrustation processes in hot tap water installations

Corrosion of hot tap water installation

In the end of sixties, first in Warsaw and then in other regions of Poland, the new corrosion problem of major importance appeared - corrosion of galvanized steel HTW pipes [1]. The problem proved out to be a serious one and created an urgent need to exchange 75% of pipes in buildings in Warsaw by 1974 [2].

C.O.W. UNITEX, due to co-operation with the Technical University of Gdansk, created a data base complying of research results, literature and practical experience within the scope of design and application of relevant anticorrosive. It allows active participation in applying relevant technical solutions in hot water installations. Many hot tap water substations in Dabrowa Górnicza, Sosnowiec, Czeladź and Gdańsk were protected against corrosion in this way. Anticorrosive protection measures in hot water- systems and substations were taken on the grounds of previous research. The research

results enabled finding the reasons for corrosion, its mechanisms and appropriate anticorrosion prophylactics.

Material aspects

Hot Tap water installations in Poland were constructed mostly of galvanized steel. Corrosion resistance of zinc cover, which protects steel pipelines depends on thickness and uniformity of the outer layer η , i.e. the layer made of almost pure zinc [4,5]. The layer corrodes intensively until the layer of corrosion products arises on the pipe surface. In microscopic cover discontinuities the steel base corrodes.

Speed and character of water installation corrosion depends mostly on thickness and quality of zinc cover. Requirements concerning HTW installation are included in standard ZN-72/0640-01 and in the guidelines: "General guidelines of HTW installation design in residential buildings" [11]. The standard determines minimum thickness of zinc cover to be 85 μm , and it does not admit presence of blisters, chips and local damages of cover (TWT-2 technology). Drinking water installations can be constructed of galvanized pipes with thinner zinc cover no exceeding 50 μm , in accordance with standard PN-74/H/74200. **ONLY GALVANIZED STEEL PIPES SHOULD BE USED AS HTW PIPES IN ACCORDANCE WITH THE TECHNOLOGY ACCORDING TO STANDARD NZ-72/0640-01.**

In Poland, Huta im. Sendzimira is a steel zinc-covered pipe producer. It manufactures zinc -covered pipes with strengthened zinc cover according to the manufacturer's norm NZ-91/0640-01. The results of research lead at the Technical University of Gdansk [12] proved that even goods manufactures according to the norms, show a number of defects that are reason to a lower corrosion resistance. The defects are, f. ex. microfractures in the zinc cover, various inclusions and alloy interlayer. During the operation, galvanic cells are created between various zinc alloy layers and the steel base in microfractures.

Environmental factors

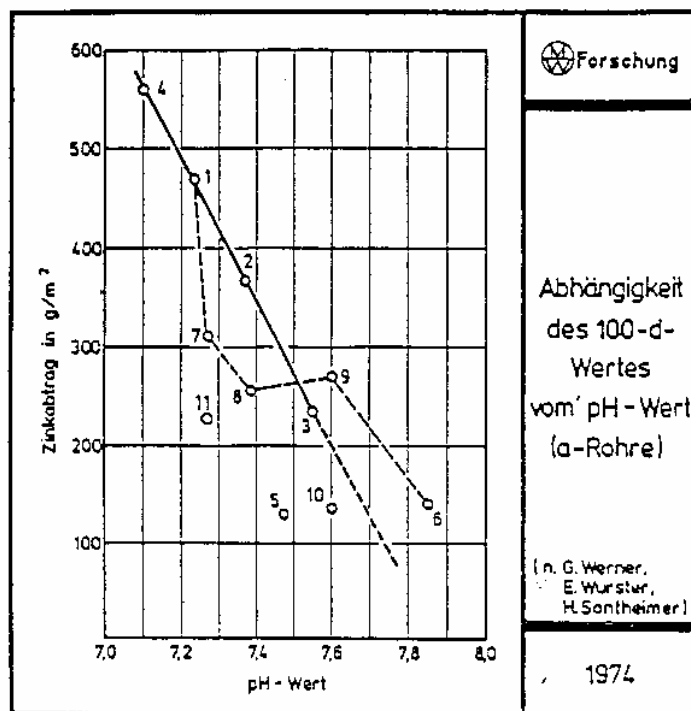
Water supplying hot water installations must meet the requirements of the sanitary regulations "Ministry of Health and Social Welfare Decree", issued on the 4th September 2000. The decree designates terms for the quality of drinking water and for household use. Water may contain neither any substances harmful to human health or showing its pollution, nor ingredients influencing negatively its taste, smell or colour as well as ingredients causing turbidity of water. Some parameters are described by chemical and corrosion limits. (n. d.z.)

The limits (n.d.z.) are as follows:

- reaction	-	6,5- 9,5 pH
- available chlorine	-	0,3 mg/dm ³
- zinc	-	1,5 mg/dm ³
- manganese	-	0,05 mg/dm ³
- copper	-	1,0 mg/dm ³
- sulphates	-	250 mg/dm ³
- chlorides	-	250 mg/dm ³
- total hardness CaCO ₃	-	60÷500 mg/dm ³
- iron	-	0,2 mg/dm ³
- aluminium	-	0,2 mg/dm ³
- electricity conductivity	-	2500 $\mu\text{S/cm}$

The norms, although favourable from the sanitary point of view, do not specify requirements for the scope of acceptable parameters and ingredients responsible for corrosion. The parameters and ingredients are, f. ex. oxygen, aggressive CO₂ and so on. Broad scope of pH factor of water, particularly

below 7, as well as high salt and dissolved gases content cause the situation when **DRINKING WATER AND WATER FOR HOUSEHOLD USE MAY INTENSELY CORRODE METALS.**



Rys. 1. Ubytek korozyjny powłoki cynkowej w funkcji pH wody

Pic.1. Corrosion loss of zinc cover in function of water pH

The presented data prove that increasing the pH reaction within the range 7,1-7,9 causes slowing down the rate of zinc covered steel corrosion several times.

Long term professional experience of Mr. Marjanowski and Mr Jankowski show that increased pH indicator (within the range 7,4-7,8) always produce a positive effect, diminishing the rate of corrosion.

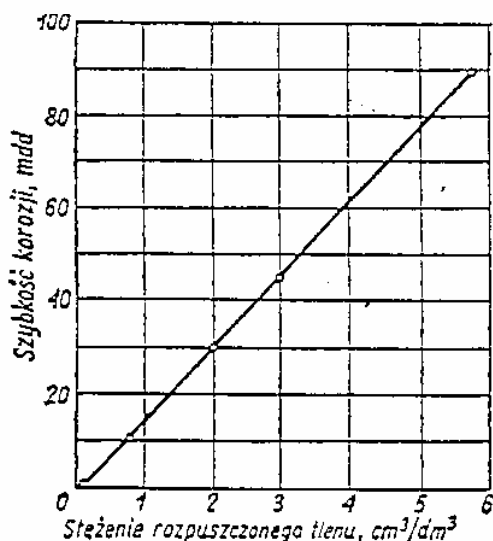
Water oxygenation

Oxygen dissolved in water is responsible for cathode depolarisation presented in p. 1.1.1. Oxygen strongly accelerates corrosion. Data available in the literature show that the rate of metal corrosion is directly proportional do oxygen concentration in water [20]. This interdependence is presented in picture 2.

Tap water, with high oxygen content (6-10 mg O₂/dm³), corrosion is usually intensive. It refers also to surface water intakes, where, in winter-spring periods, the oxygen content in water goes up to 10-20 mg/dm³ and achieves the saturation level (due to low temperatures).

Therefore, the Authors, on the grounds of long-term experiences, maintain that corrosion of cold and hot tap water installations is usually higher when the **INSTALLATIONS ARE SUPPLIED WITH WATER FROM SURFACE WATER INTAKES.**

However, we have to remember that oxygen concentration in water lower than 2 mg/dm^3 may cause putrescibility of water, which manifests itself by hydrogen sulphide presence in water. Oxygenation processes run in the water intake in Straszyn are also contributing to increasing the oxygen concentration in water.



Rys.2. Szybkość korozji stali w wodzie w funkcji stężenia tlenu

Pic.2. The rate of steel corrosion in water in function of oxygen concentration in water

Oxygen dioxide

CO_2 presence in water may influence corrosion directly (due to its acidic character) and indirectly by limiting creating protection layers of calcium carbonate [3]. Details analysis of water stability will be described further on in the paper. Since presence of aggressive CO_2 in water counteracts creation of protection layers, particularly in water with low hardness, where calcium carbonate barely layers, it is not desired. From the point of view of corrosion defects, **PRESENCE OF AGGRESSIVE CO_2 IN WATER IS CONDUCTIVE WITH CORROSION PROCESSES** [3,21].

Dissolved salts

Among the dissociated salts, present in water, chloride ions are the most aggressive. They cause an increase in electricity conductivity of water, facilitate the flow of corrosion current and, simultaneously, hinder creation of protection layers. they destroy the passive state, contributing to nucleation and propagation of corrosion pits. Additionally, Cl^- ion creates dissolving salts with most of metals and therefore, protection layers made of corrosion products are not created.

A new sanitary norm for drinking water (issued on the 4th September 2000) extended the limit for copper compounds in water from $0,5 \text{ mg/dm}^3$ to 1 mg/dm^3 .

Operational factors

Operational factors that should be taken into consideration, are, as follows:

- the temperature of water and its variability,

- character and rate of flow,
- hot water production method,
- installation pipe joining method,
- circulation method,
- presence of other metals.

Operational recommendations were prepared by the construction resort as “General guidelines for designing hot water installations in housing” [11].

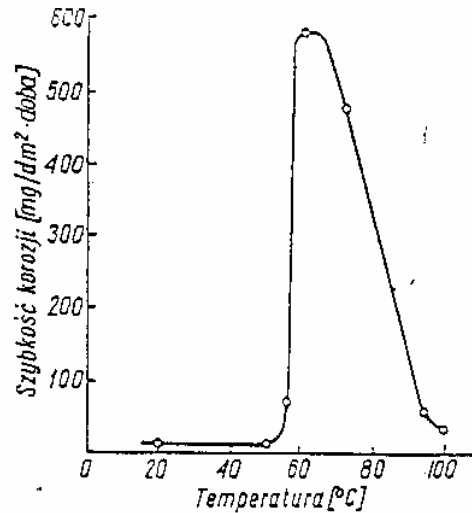
The basic settlements relate to:

- applying hot tap water installations made of homogenous materials, that is zinc covered steel, excluding elements made of copper and its copper alloys, but including materials not influencing zinc covered steel negatively,
- use of zinc covered pipes according to the technology TWT-2 (norm NZ-91/0640-01); the pipes are characterised by thicker zinc cover, removed internal seam flash; the pipes are subject to specific collection at the manufacturer's and the receiver,
- joining pipes by zinc covered steel joints or by joints made of malleable cast iron, excluding welding of conduits and joining them with cooper joints or joints made of copper compounds,
- ensuring the right water circulation in the periods of lower - or no water intake ; pump circulation is recommended, a gravity circulation use should be limited,
- providing the vertical conduits and their branches in apartments with cutting-off fittings,
- providing the installation with automatic vents ,
- installing heat accumulator behind the flow heat exchanger, also zinc covered, or additionally protected by magnesium anode.

Introducing the above recommendations reduce corrosion in installations supplied with water, which content can be influenced neither by its operator nor user. Below, influence of more important factors on the process of corrosion was described.

Temperature influence. Pole reversal phenomenon

Practical experience shows that zinc covered hot water pipelines corrode a lot faster than similar cold water installations. The influence of temperature on the rate of zinc corrosion is presented in picture 3, published by Cox for the first time. [25].



Rys.3. Wpływ temperatury wody na szybkość korozji cynku

Pic.3. Influence of temperature on the corrosion rate of zinc

With further water temperature increase up to ca. 60°C, particularly with presence of oxygen, bicarbonates, nitrates, copper ions, pole reversal of the iron-zinc set. [2,12,20].

Many hot tap water installations in Warsaw and Gdansk are exchanged after 3-5 years operation time [26]. Research conducted by the Authors in Silesian region and in the south of Poland (for ex. in Katowice, Sosnowiec, Dąbrowa Górnicza, Czeladz, Cieszyn, Stalowa Wola) in 1986- 1992 shows that the problem of corrosion isn't less significant than in Warsaw.

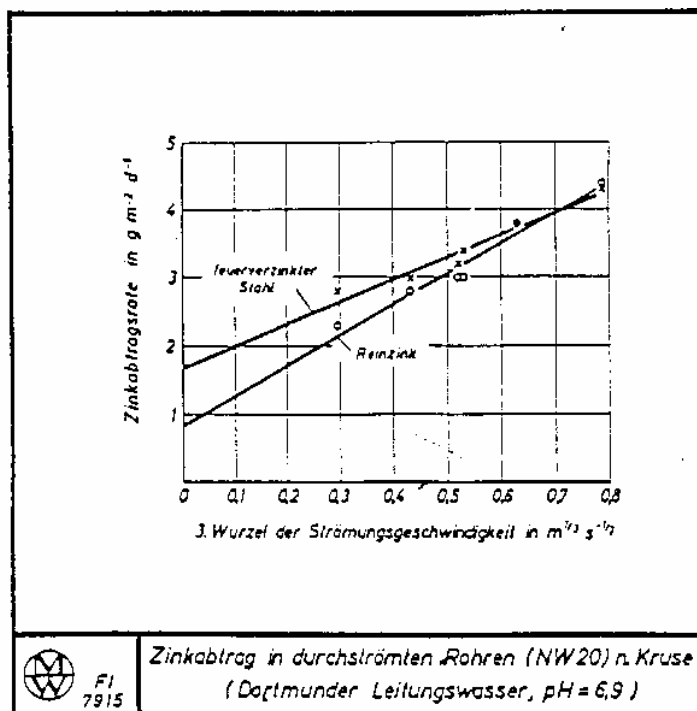
Corrosion defects in hot tap water installations in Gdansk Wrzeszcz are similar to the above mentioned. The zinc cover is completely destroyed within 3-4 years. According to the calculations, a pit, 3 mm deep (pipe's wall) and 0,1 cm² surface is caused by a 23 μA current flow during 1 year's time [2].

This order of value was also measured in laboratory examination, while destroying pipes with defected zinc cover may last 1-3 years. Transitory changes of temperature are as important as the temperature itself since they are conducive with cracking and spattering created layers of products of corrosion.

KEEPING STEADY TEMPERATURE BELOW 55°C, MOST PREFERABLY 45-50 °C, IS THEREFORE MOST FAVOURABLE.

Flow speed

Increase in the flow speed usually fastens processes of steel and zinc covered steel. Pic. 4 [27] presents how the flow of water with steady pH (ca. 6.9) influences the rate of corrosion processes in pure zinc and zinc covered steel.



Rys.4. Szybkość korozji cynku w funkcji prędkości przepływu wody

Pic. 4. The rate of zinc corrosion in a function of water flow speed

Hot tap water production method

Corrosion of hot tap water installations can be influenced in a various way by choosing various heat exchangers. It is observed that the more exchangers corrode, the less zinc covered installation corrodes[1]. Mr Marjanowski has observed that more corrosion resistant material causes increased durability of a given heat exchanger and increased rate of a zinc covered installation corrosion. This related to JAD heat exchangers. Oxygen, as a cathode depolariser is mostly responsible for the process of corrosion of heat exchangers. If the oxygen is used partly in the corrosion of heat exchangers at the beginning of the hot tap water installation, corrosion of the installation itself is smaller. It leads to a conclusion that it is necessary to removing or at least limiting the amount of oxygen in hot tap water [28]. Naturally, removing oxygen from water should be thoroughly reconsidered in case of cold water where presence of oxygen is essential to prevent water from putrescibility and is required by sanitary requirements.

Estimating the threat of corrosion

The corrosion rate in water installations may be variable. Classification of corrosion speed rates for steel and zinc covered steel was prepared to estimate the degree of corrosion threat.

Table 1. Classification of corrosion rates for steel and zinc covered steel

Estimation of corrosion rate	Corrosion rate (mm/year)	
	carbon steel	zinc covered steel
no corrosion	do 0,02	do 0,005
poor	0,02 ÷ 0,04	0,005 ÷ 0,010

acceptable	0,04 ÷ 0,05	0,010 ÷ 0,015
strong	0,05 ÷ 0,20	0,015 ÷ 0,035
emergency	above 0,20	above 0,035

There is a norm to estimate corrosiveness of water in Poland. It is a standard no PN-72/C-04609 "Initial estimation of corroding work of cold natural waters on cast iron, steel and zinc covered steel conduits". The norm presents limits for cold water at temperature 25°C; at this temperature water has smaller corrosive qualities. Although the norm is not suitable for water at higher temperatures, some parameters for zinc covered steel are presented below:

- saturation index I_L - above -0,5
- calcium hardness - above 0,7 mval/dm³,
- general alkalinity - above 0,7 mval/dm³,
- dissolved oxygen - not less than 2 mg/dm³,
- sulphates - less than 250 mg/dm³,
- chlorides - less than 150 mg/dm³,
- nitrates - less than 62 mg/dm³

The norm accepts slightly negative Langerier index, and therefore, presence of small amounts of aggressive CO₂ in water.

Estimating hot tap water corrosiveness

In Poland, there are no norms for estimating hot tap water corrosiveness that could fulfil requirements for cold drinking water, although hot tap water corrosiveness is a lot higher than cold water corrosiveness.

The estimation method is presented in table 2. It is assumed that water with a positive saturation index I_L and total chlorides and sulphates content more than 50 mg/dm³ is highly corrosive water. Marjanowski thinks that it is possible to refer the norm to zinc covered steel as well.

Table 2. Classification of corrosiveness of water at 60°C temperature with reference to steel pipes

Water type	Hot water saturation index I_L	Concentration in cold water [mg/dm ³]		Hot water corrosive characteristics	Need to protection against corrosion
		O ₂	Cl + SO ₄ ²⁻		
surface water	$I_L < -1,0$	10 ÷ 14	< 50	strongly corrosive	protection against corrosion needed
	$-1,0 < I_L < 0$	10 ÷ 14	> 50		
surface water	$-1,0 < I_L < 0$	10 ÷ 14	< 50	corrosive	protection against corrosion needed
	$I_L > 0$	10 ÷ 14	> 50		
surface water	$I_L > 0$	2 ÷ 4	> 50	barely corrosive	no protection allowed
	$I_L > 0$	10 ÷ 14	< 50		
artesian water	$I_L > 0$	2 ÷ 5	< 50	not corrosive	no protection required

Measurement of water corrosiveness

Contrary to water corrosiveness estimation on the grounds of either physical-chemical analyses or corrosiveness factor calculations (as above), direct measurements of corrosion rates in installations taken during their operation time are the most reliable. Apart from a classical technique of estimating

type and rate of corrosion on the grounds of corrosimetrics, modern measurement techniques using electrical resistance [30] - and electrochemical measurements [31-33].

Resistance corrosimetrics consists of putting a relevant metal sensor in a corrosive environment, which corrosion rate is to be controlled; periodical measurements of the environment's electrical resistance will be taken by a variable current bridge. As corrosion progresses, the sensor's resistance increases. Next, resistance rise is calculated into corrosion rate with help of relevant tables or monograms. The method resembles an automated gravimetric technique but, in this case, instead of weighing a sample, a corrosive defect is estimated on the grounds of electric measurements taken. It gives very good results in case of uniform corrosion.

Polarisation techniques consist of determining polarisation characteristics of examined metals in an electrolytic environment in a potential-current system. Depending on a degree of technical quality of instruments, the characteristics cover 1, 2 or more measuring points. Their electronic analysis using theory of kinetics in electrode processes allows determining the density of corrosion current; according to the Faraday law, the corrosion current is equivalent to the corrosion rate expressed in mm/year. High sensibility, preserving character and short measuring time are the greatest advantages of electrochemical techniques.

Apart from a rich instrument offer of foreign device, complete corrosimetric sets consisting of relevant sensors and measuring device are produced in Poland as well [34]. It is possible to buy resistance corrosimeters, PMK series as well as polarisation corrometers, type MOP, f. ex. microprocessor meter MOP-7, produced by "Micron" from Warsaw.

Incrusting device and hot tap water installations

Overgrowing device and hot tap water installations, defined as "incrustation" and it is caused by:

- calcium and magnesium precipitation due to exceeding the salt solubility product in water,
- zinc covered conduit - and heat exchangers corrosion as well as deposition of corrosion products in installations.

Corrosion products may cover several times larger metal volume than the metal that they were made of. It causes increasing volume of corrosion products and blocking the pipes.

Precipitation of calcium carbonate sediments

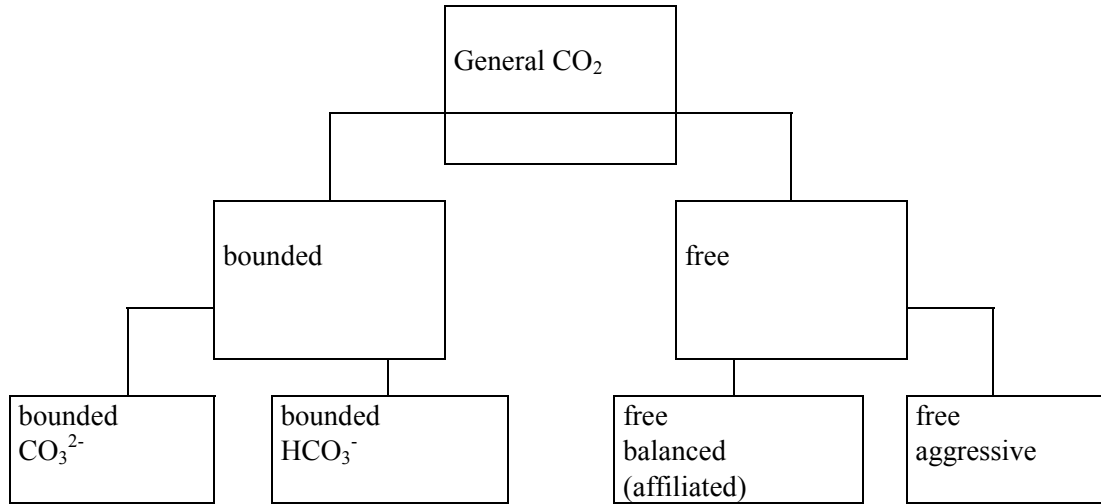
According to the point 3.1.3., it was assumed that in case of precipitation of tight calcium carbonate sediments layer in internal surfaces of hot tap water installations is slowed down by corrosion in pipes. Therefore, it is extremely important to understand the phenomena related to the carbonate balance in hot tap water. Understanding the processes will enable estimating possibilities of calcium carbonate sediments precipitation. It is generally considered boiler scale precipitates only in hard waters. It is not completely true but this opinion is often confirmed by practical experience. **MUTUAL BALANCE CALCIUM CARBONATE-CARBON DIOXIDE IS RESPONSIBLE FOR POSSIBILITIES OF CaCO_3 (BOILER SCALE) PRECIPITATION.**

The following graph presents the timing for CaCO_3 sedimentation in a hot tap water production device according to its operation [22] depending on temperature at water hardness ca. 5 mval/dm³:

temp. 30°C	-	120 h
temp. 40°C	-	24 h
temp. 50°C	-	1 h
temp. 60°C	-	at once

Carbon dioxide

Carbon dioxide is present in water as:



Since CO₂ solubility in cold water is particularly high, it is extremely important to know the given form of CO₂ in water. Free balanced carbon dioxide, which is stoichiometrically affiliated by carbonate and bicarbonate, does not influence water corrosiveness and its precipitation abilities.

Free aggressive CO₂ is in excess and it is responsible for:

- environment's acidification (lowering pH factor),
- corrosion processes,
- dissolving existing CaCO₃ sediments from the protection layer with no ability to rebuild the layer and protecting metal surface.

CO₂ excess or shortage causes boiler scale dissolving or precipitation. For waters with high carbonate hardness at low noncarbonate hardness, even small unbalancing (by venting, preheating, flow change) causes CaCO₃ precipitation.

Identifying precipitation and corrosion properties of water on the grounds of saturation indexes.

Mutual connection of precipitating and dissolving calcium sediments in water caused by presence or absence of aggressive CO₂ was the reason to preparing so called water saturation indexes (water stability indexes).

At present, electronic methods of calculating water saturation indexes are more and more popular. [35, 36].

Additionally, a so-called Ryznar stability index, described by the equation:

$$I_R = 2pH_s - pH$$

is used for identifying properties of water.

Identifying precipitation and corrosion properties of water on the grounds of I_L and I_R indexes is done as follows:

- I_L < 0 - water is unsaturated in relation to calcium carbonate, it contains aggressive carbon dioxide, it is corrosive and it has no inclinations for precipitating calcium carbonate sediment,
- I_L = 0 - water is stable, it has no inclinations for either precipitating or dissolving calcium carbonate sediment,
- I_L > 0 - water is unstable, it does not contain aggressive carbon dioxide it is non-corrosive and it has inclinations for precipitating calcium carbonate sediments.

for I_R:

- I_R < 5 - water has strong tendencies to precipitating calcium carbonate sediments,

- $5 < I_R < 6$ - water has weak tendencies to precipitating calcium carbonate sediments,
- $6 < I_R < 7$ - water does not create sediments,
- $7 < I_R < 7,5$ - water with noticeable corrosive power,
- $I_R > 7,5$ - water with significant corrosive power.

CCPP (Calcium Carbonate Precipitation Potential) indicator prepared and used in the USA has been the most adequate indicator of carbonate balance in water [37]. The indicator is calculated with use of an iterative technique and it enables direct estimation of the amounts of calcium carbonate that can be dissolved or precipitated in water after its reaching the state of balance. Precipitation and corrosion diffuse and are difficult for univocal estimation.

Ways of protecting hot tap water installations against corrosion

Zinc covered steel and particularly carbon steel, corrodes in hot tap water environment. It has already been largely described in the theoretical section and proved with research results in the practical section of the paper. However, changing installation material into:

- stainless steel,
- aluminium alloy,
- plastics,

were omitted in the paper, although plastics and copper are more and more significant in anticorrosive prevention.

Therefore, more attention was put to changing corrosive environment with reference to zinc covered steel. Modification should be done according to previously described sanitary norms in force in Poland. In theory, it is possible to protect installations by changing the physical-chemical properties of water and precipitation of protection layers on the zinc surface; these methods are:

- adding corrosion inhibitors, such as silenals (silicates), polyphosphates,
- physical and chemical modification methods (deoxidisation, regulating pH factor),
- protecting hot tap water installations with use of magnesium anodes,
- electrochemical protection with use of aluminium anodes fed from an external power source.

Corrosion inhibitors

Among inhibitors used in hot tap water installations, silicates and polyphosphates are the most significant. Silenales are strongly promoted at the beginning of the 70-ties because silenales for hot tap water were produced in Poland in Chemical Factories in Rudniki near Czestochowa. It is necessary to keep the required inhibitor dose, usually ca. $10\text{--}100 \text{ mg SiO}_2/\text{dm}^3$ [21,38] to maintain the required protection level.

Use of those inhibitors for drinking waters are not binding anymore due to a norm issued by the State Sanitary Institute accepting only low active silica content in drinking water - $8 \text{ mg SiO}_2/\text{dm}^3$. Sodium tri- and sixphosphates (Polifos is its commercial name) are among the most known polyphosphates. Both polyphosphates and silenales behave in a similar way- together with calcium ions, they create a barrier layer on metal surface. The layer has protective properties. However, inhibitor protection is not popular in Poland since there are problems regarding dosing inhibitors on the flow basis [39] and there is a possibility of an overdose.

Water deoxygenating

Water deoxygenating is the main physical method of modifying corrosion properties of water. It is commonly done in degasifiers in water tube boilers for energy purposes. Regarding the experiences in this field, it is theoretically possible to degasify hot tap water and remove corrosive oxygen from water.

However, effective degasifying does not take place at temperatures lower than 100°C and at the atmospheric pressure. Therefore it is necessary to install a vacuum degasifier that degasifies water effectively but needs some investments and a place in the hot tap water production station. Due to limiting corrosion processes, the return of the invested capital is quick and, according to some sources, takes only 1-2 years [28]. UNITEX owns a series of types of vacuum degasifiers produced by a Danish company SILHORKO-EUROWATER A/S. Their efficiency is 3 to 22 m³/h. In case of using vacuum degasifiers, problems with CaCO₃ precipitation due to carrying away not only oxygen but also free and aggressive CO₂, which unbalances the carbonate amount in water. In this case, calcium carbonate will systematically precipitate in the device.

Regulating pH

Regulating pH factor in drinking water and hot tap water to limiting their corrosiveness is commonly known and used in many countries. Lime, caustic soda and carbon dioxide are most often used in the process. Good liming results are also described in Polish literature [41,42].

Liming of soft, acidic and aggressive waters was commonly used in Norway in the 80-ties [44]. To lowering corrosive properties of water, it should be described by the following:

- pH above 8,0
- alkalinity above 0,65 mmol/dm³
- Ca content above 18 mg/dm³.

Electrochemical protection

Two types of electrochemical protection in water installations are used: using galvanic anodes (known as galvanic cathodic protection) and anodes supplied with external power source (cathodic protection) [45]. Electrochemical machining of water with digestive aluminium anodes is another type of the method; it is called- Guldager method.

Galvanic cathodic protection

Galvanic cathodic protection of internal surfaces in water tanks against corrosion has been known for a few tens of years. It is applied directly for protection of not painted, painted or zinc covered internal water tank surfaces and capacitive heat exchangers. The method consists of galvanic anodes (sacrificial anodes) made of magnesium, zinc or aluminium alloy inside tanks. The galvanic anodes do not require external energy sources. Due to differences in potentials between tank metal (steel, zinc covered steel) and the anode, electricity begins to flow since the anode is connected to the tank's construction. As a result of electricity flow, anode material is dissolved and the tank construction is protected galvanically. [7,20,22,40].

Galvanic anodes are produced in Poland by the Casting House in Trzebinia. They are made mostly of Mg, Al and Zn alloys as rollers, 55 mm diameter and 500 mm length with metal cores for welding. Anodes are installed along the walls creating tanks. Hot tap water tank that are not zinc covered according to rules in force [11], should be protected against corrosion in this way. Calcium hydroxide sludge, which is a result of electrochemical processes in the tank, has protective properties. The sludge increases alkalinity and pH factor of water and that slows down corrosion processes effectively. The sludge disperses with water and causes increasing pH factor in the whole water environment. It makes bounding aggressive CO₂ and unbalancing carbonate amount in water easier because it precipitates CaCO₂ protection layer. There is no quantitative research on galvanic protection layer influence on hot tap water installation's life although the literature confirms that the influence is profitable since it leads to limiting steel corrosion rate [22,45].

Electrochemical treatment of water by aluminium methods dissolving

This method of electrochemical protection of hot tap water installations secures high level of protection hot tap water installations made of steel, zinc covered steel and copper against corrosion. There are aluminium anodes installed either in hot water storage bins or in tanks installed particularly for this reason. The tanks are installed in the hot tap water installations. Anodes are electrically insulated from the tankers walls and they are connected to the red pole of the direct current source. The tank's construction is connected to the blue pole. The tank and the electrodes set is called a (an electrochemical) reactor. Current flow is forced by connecting appropriate voltage. It is done to digesting and introducing a desired amount of aluminium into the solution. Moreover, the reactor itself has its own cathodic protection, described in other articles [22,45,47].

Specialists got interested in the method in the 70-ties when the heating sector was extensively developed in Poland. The Technical University of Gdansk was the leading research centre in this field [2,12,46,48,49,50]. The research results, obtained by the University, were introduced in OPEC Gdynia by Mr. Marjanowski and, later, by made specialist companies in the Warsaw region, f. ex. nearly all the new hot tap water installations in buildings belonging to the Housing Co-operative "Ursynów" are protected against corrosion with this method. Several hundred installations in Poland, 90% of which in Warsaw and Upper Silesia as well as in the Tri-City area (from 1999 in the Housing Co-operative "Południe" and "Szadółki", among others), are installed on the grounds of research made by the Technical University of Gdansk.

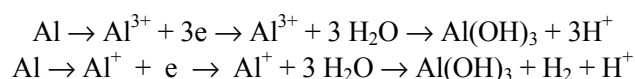
Electrochemical protection according to the patent no. 142 844

A method with a patent no. 142 844, prepared by the Technical University of Gdansk Research Group and OPEC Gdynia is one of the electrochemical methods. It was elaborated at the end of 70-ties and Mr Marjanowski is its co-author.

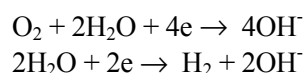
Applying electrically insulated aluminium anode sets inside cold water tanks, before preheaters and inside hot water tanks is the main idea behind the method. The anodes are electrically insulated from tanks- and storage tanks constructions and connected to the red pole of the direct current source. (Electrochemical) reactors constructions are connected to the blue pole. The set is connected to an external current source with an intensity that allows to introduce 0,1- 0,2 g Al/m³ products of anodic aluminium digesting to water depending on properties of treated water and the size of corrosion threat.

The following chemical reactions proceed during the process:

- anodic:



- cathodic:



Colloidal aluminium hydrocomplexes are created as a results of the above reactions in water. Moreover, oxidation level lowers slightly (oxygen is bounded in the cathode), water alkalinity increases and electrolytic conductivity is limited due to bounding active ions with colloidal aluminium compounds. Increase in water alkalinity contributes to bounding aggressive carbon dioxide. The mechanism of creating the protective layer in metal surface is of colloidal-chemical nature. Oxygen presence in water and 6,0-8,5 pH factor is necessary for obtaining positive results.

To sum up, due to using an electrochemical method : water oxidation level, CO₂ content and electrolytic conductivity are lowered,. It causes lowering its corrosion aggressiveness. Moreover, water is prone to creating a thin aluminium rich protection layer on metal surface. This layer should not be

mistaken for a CaCO₂ protection layer or corrosion products layer. This layer is of limited thickness (up to 0,3 mm) and has a polyfunctional protective working. It works as a barrier, separating metal from corrosive environment (in a similar way as carbonate layer but it has a lot higher resistance). Moreover, it hampers the molecular cathodic process and, in case of zinc covered steel, it prevents the Zn-steel cell from pole reversal and contributes to the right functioning of the galvanic ground protection of the zinc coating. Water electrochemical treatment effectiveness with regards to multiple water flow through storage tanks and heat exchangers of the second degree caused by circulation loading pumps. Digestive aluminium anodes are applied at hot water storage tanks and in additional reactors installed in cold water conduit before the exchangers battery of the first degree. Anodes and reactors constructions are connected to blue and red pole of the direct current source by electric conduits.

ELECTROCHEMICAL PROTECTION GIVES THE BEST ECONOMIC RESULTS ALREADY BEFORE TWO YEARS OPERATION PROVIDED IT IS APPLIED NOT LATER THAN 1-2 YEARS AFTER THE INSTALLATION OPENING.

Life of old installations, which zinc cover was removed, is prolonged by the electrochemical protection, but the general effect is smaller than in case of complete zinc cover (average destruction of 50% zinc cover takes 2-3 years in Warsaw, Upper Silesia and Gdansk) . Practical experience shows that new installations can be kept with complete zinc layer (without defects) for more than 10 years by protecting water systems with use of this method.[51]. Mr Marjanowski's and Mr Kukielko's practical experience shows that in case of heavily defected installations at the beginning of electrochemical protection operation problems occur. After starting electrochemical protection, higher sediment precipitation in a given system takes place, comparing to the previous situation. The sediments consist of corrosion products, which fall from pipe surfaces due to rebuilding the structure and chemical content of the sediment. This problematic situation may last over a year and be a reason to recipients disappointment (because of water colour given to water by iron compounds). The new layer, that is built instead of corrosion products, is just fragile and tight. The tighter it is, the newer installation was subject to protection. The final results of incrustation and corrosion processes are very difficult to foresee in case of changing one or more ingredients or temperature since waters composition is very complicated.

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Corrosion state research

Hot tap water installation supplied by GPEC from a hot water production station at Podleśna street in Gdansk Wrzeszcz was chosen for corrosion state research. The installation supplies blocks of flats (belonging to a housing cooperative "Zakonieczyn") and single houses with hot tap water produced in the hot tap water production station.

C.B.W. UNITEX examined the buildings to which it has access due to an agreement with GPEC in Gdansk.

The whole hot tap water installation is supplied from the municipal water supply network and the surface water intake in Straszyn.

The following tests were made:

- physical-chemical water analysis,
- macroscopic examination - there were pictures of corrosion defects in hot tap water pipes taken,
- chemical analyses of sediments in zinc covered hot tap water pipes,
- microphotographs of metallographic specimen of zinc covered pipes,
- measuring the corrosion rate in laboratory conditions with electrochemical methods use,
- measuring the corrosion rate in hot tap water production station at Podleśna street during operation (so called site examination) with use of the electrochemical method (polarisation method).

Results of physical-chemical analysis of water

According to the markings (see below), marked points were analysed

- 1 - cold supply system water supplying the tap water station at Podleśna street,
- 2 - hot tap water- supplying the district,
- 3 - hot circulation water (returning from the district),
- 4 - building at Gotycka street,
- 5 - building at Renesansowa street.

The analytical research results were presented in Table 3.

Iron content research results in many water intake points in the hot tap water supply system were presented in Table 4.

Table 3 Results of extended research at the hot tap water production station at Podleśna street in Gdansk Wrzeszcz, according to intake dates and water type

No.	Marknig	Unit	19.06.96			25.06.			01.07.				05.07.				12.07.		
			1.	2.	3.	1.	2.	3.	1.	2.	3.	5.	1.	2.	3.	4.	1.	2.	3.
1	Turbidity	mg/dm ³	n.b.	n.b.	n.b.	0	n.b.	0	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.
2	Colour	mg Pt/dm ³	5	10	10	10	10	5	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	5	5	10
3	Smell	-	n.b.	n.b.	n.b.	g 0	n.b.	g 0	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	g 0	g 0	g 0
4	Reaction	pH	7,0	7,1	7,1	6,9	7,1	6,9	7,1.	7,2	7,1	7,1	7,1	7,2	7,2	7,2	7,0	7,1	7,1
5	Oxygen consumption	mg O ₂ /dm ³	n.b.	n.b.	n.b.	2,4	n.b.	1,8	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	2,2	2,0	1,8
6	Ammonia	mg/dm ³	n.w.	n.w.	n.w.	n.w.	n.b.	n.w.	n.w.	n.w.	n.w.	n.w.	n.w.	n.w.	n.w.	n.w.	n.b.	n.b.	n.b.
7	CO ₂ free	mg/dm ³	8,4	8,4	8,8	9,9	n.b.	10,4	12,4	12,2	12,4	12,5	n.b.	n.b.	n.b.	n.b.	8,7	8,7	8,2
8	CO ₂ aggressive	mg/dm ³	6,4	6,5	4,3	7,9	n.b.	5,7	8,5	8,0	4,2	3,7	n.b.	n.b.	n.b.	n.b.	7,3	5,1	4,8
9	Dissolved oxygen	mg/dm ³	8,2	7,1	5,2	6,6	5,8	3,8	5,1	5,0	3,4	3,8	4,3	3,1	2,1	3,4	7,2	5,2	4,7
10	Hydrogen sulfide	mg/dm ³	śląd	n.w.	n.w.	śląd	śląd	n.w.	n.w.	n.w.	n.w.	śląd	śląd	śląd	śląd	śląd	n.w.	n.w.	n.w.
11	General hardness	mval/dm ³	3,68	3,65	3,58	3,60	3,60	3,57	3,7	3,7	3,6	3,6	3,8	3,8	4,0	3,8	3,6	3,6	3,6
12	carbonate hardness	mval/dm ³	2,4	2,4	2,4	2,5	2,5	2,6	2,5	2,4	2,4	2,4	2,3	2,4	2,5	2,5	2,4	2,4	2,6
13	„m” Alcalicity	mval/dm ³	2,4	2,4	2,5	2,5	2,5	2,6	2,5	2,4	2,4	2,4	2,3	2,4	2,5	2,5	2,4	2,4	2,6
14	„p” alcalicity	mval/dm ³	6,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0	0,0
15	Potassium	mg/dm ³	n.b.	n.b.	n.b.	2,4	n.b.	2,4	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.
16	Sodium	mg/dm ³	6,8	6,8	6,8	7,0	7,4	7,0	7,9	7,9	7,9	7,9	n.b.	n.b.	n.b.	n.b.	7,5	7,5	7,5
17	Calcium	mg/dm ³	56,9	56,9	56,9	57,3	57,3	57,3	59,3	59,3	59,0	59,4	55,1	55,1	60,1	55,1	56,8	56,7	56,7
18	Magnesium	mg/dm ³	9,0	8,8	8,5	9,1	9,0	8,5	9,1	8,8	8,4	8,4	9,7	12,7	12,1	12,7	9,4	9,1	8,8
19	Iron	mg/dm ³	0,5	0,6	1,1	0,2	0,4	0,4	0,9	0,2	0,6	0,8	0,5	1,3	0,4	10,7	0,3	0,4	0,9
20	Manganese	mg/dm ³	0,05	0,08	0,05	0,05	0,05	n.w.	n.b.	n.b.	n.b.	n.b.	0,05	0,05	0,05	0,10	0,10	0,10	0,08
21	Copper	mg/dm ³	0,015	0,015	0,020	0,006	0,005	0,011	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	0,005	0,010	0,014
22	Zinc	mg/dm ³	0,37	0,37	0,62	0,22	0,37	0,88	0,35	0,35	0,95	0,82	n.b.	n.b.	n.b.	n.b.	0,18	0,62	0,94
23	Sulfates	mg/dm ³	51,5	51,5	51,5	49,8	49,4	42,4	48,2	48,2	47,8	47,8	52,5	51,7	52,5	52,7	50,5	51,4	48,4
24	Chlorides	mg/dm ³	19,7	19,7	19,7	19,3	19,3	19,4	19,5	19,5	19,5	19,5	19,5	19,5	19,5	19,5	19,6	19,6	19,7
25	Fluorides	mg/dm ³	n.b.	n.b.	n.b.	n.w.	n.b.	n.w.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.
26	Phosphates	mg/dm ³	0,10	0,10	0,10	0,05	n.b.	0,05	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	n.b.	0,10	0,10	0,12
27	Organic silica	mg/dm ³	11,4	11,0	9,7	8,4	n.b.	5,4	10,3	10,1	8,8	9,3	n.b.	n.b.	n.b.	n.b.	9,3	9,2	8,1

Key:

- 1 – cold water (supplying) 2 – hot water supply 3 – hot water return (circulation-station)
 4 – hot water circulation 5 – building at Renesansowa str. 3
 n.w. – not detected n.b. – not examined

Table 4. Iron content complied Fe (mg/dm³) in district hot tap water in installations supplied with water by the hot tap water station at Podleśna street.

No.	Water intake point	Complied iron w mg/dm ³ according the intake date									
		19.06	21.06	22.06	25.06	01.07	03.07	05.07	08.07	10.07	12.07
1.	cold water-station	0,5	0,3	0,3	0,2	0,3	0,4	0,5	0,2	0,3	0,3
2.	hot water station	0,6	0,4	0,6	0,4	0,7	0,5	1,3	0,5	0,4	0,4
3.	circulation water-station	1,1	1,3	1,1	0,4	1,5	0,5	0,4	0,8	0,8	0,9
4.	circulation water-Gotycka str.	0,8	3,2	0,8	1,2	0,7	0,5	10,7	0,7	1,7	1,8
5.	detached house-Renesansowa str	1,4	0,8	0,9	-	0,9	0,5	0,6	2,8	1,1	4,5
6.	detached house-Renesansowa str	1,8	1,5	1,2	-	0,9	0,5	0,8	1,2	0,9	0,6
7.	detached house-Renesansowa str	1,3	1,1	0,9	-	3,5	0,9	1,4	0,9	0,8	9,7
8.	detached house-Renesansowa str	1,2	0,9	0,9	-	1,7	0,7	2,7	0,9	1,1	0,6
9.	a flat- Gotycka str.	0,7	2,1	0,8	-	0,8	0,7	0,8	0,8	1,2	5,2
10.	a flat- Gotycka str.	0,5	2,2	0,9	-	0,7	0,5	0,7	0,9	0,9	0,7
11.	a flat- Gotycka str.	0,5	1,9	1,1	-	0,8	0,8	1,8	0,9	1,4	0,5

COMMENTS:

Water was taken from accessible detached houses at Renesansowa street and accessible apartments in the building at Gotycka street after ca. 5 minutes after opening the tap. The differences in results are big. Measurement results from the same source are different and do not stabilise themselves in time. Stable iron content in cold and hot water in intake points in station at Podleśna street.

Results of macroscopic examination of pipe slices - photographic documentation

Pictures Phot. 1 - Phot. 7 present macroscopic pictures of pipe slices with pipe's front uncovered (for presenting sediments). These photos are enclosed as **Appendix 1**.

Results of chemical analysis of sediments collected from zinc covered pipes in hot tap water installations

There was a chemical analysis of zinc covered pipes sediments done on the following pipe slices:

- segment supplying the district with hot tap water, pipe ϕ 80 mm after five years operation,
- segment returning water from the district (circulation), pipe ϕ 65 mm after five years operation,
- circulation segment in the building at Gotycka street after 1 year operation (the segment had been exchanged due to strong corrosion).

Sediments similar to steel corrosion products are visible in all the pipe segments.

Detailed analysis is presented in Tables 5, 6, 7.

Table 5. Chemical analysis of the zinc covered pipe sediment- supplying the district with hot tap water

<p>Research and development centre „UNITEX” Ltd.</p>	<p>Results of chemical analysis of the sediment</p>	<p>Address: Hot Tap Water Production Station. Gdańsk, Podleśna street</p>
<p>Sediment collection point:</p> <p>Type of the sample and its physical features:</p> <p>Water supply source</p> <p>Loss of precipitates ignition at 800°C</p> <p>Elements insoluble in HCl 1:1</p> <p>Ingredients:</p> <ul style="list-style-type: none"> - Calcium as CaO - magnesium as MgO - Aluminium as Al₂O₃ - Complete iron as Fe₂O₃ - Complete copper as CuO - Zinc as Zn - Silicates as SiO₂ - Carbonates as CO₂ - Sulphates SO₃ - Others up to 100 % 	<p>Zinc covered pipe ϕ 80 supplying the district with hot tap water - hot tap water production station output Podlesna street (after ca. 5 years operation)</p> <p>Brown sediment with light spots, adhered to the pipe, the sediment is hard and fragile</p> <p>Intake in Straszyn</p> <p>4,1%</p> <p>8,7%</p> <p>2,1%</p> <p>1,8%</p> <p>2,3%</p> <p>82,5%</p> <p>trace</p> <p>1,5%</p> <p>3,4%</p> <p>2,4%</p> <p>1,8%</p> <p>2,2%</p>	

Table 6. Chemical analysis of the zinc covered pipe sediment - hot tap water circulation

Research and Development Centre „UNITEX” Ltd.	Results of chemical analysis of the sediment	Address: Hot Tap Water Production Station. Gdańsk, Podleśna street
Sediment collection point:	Zinc covered pipe ϕ 65 - hot tap water - return from the district to the hot tap water production station at Podleśna street (after 5 years operation)	
Type of the sample and its physical features:	Brown sediment, without spots, medium strongly adhered to the pipe, the sediment is hard and	
Water supply source	Intake in Straszyn	
Loss of precipitates ignition at 800°C	2,9%	
Elements insoluble in HCl 1:1	3,0%	
Ingredients:		
- Calcium as CaO	1,5%	
- Magnesium as MgO	1,2%	
- Aluminium as Al ₂ O ₃	2,7%	
- Complete iron as Fe ₂ O ₃	92,1%	
- Complete copper as CuO	trace	
- Zinc as Zn	trace	
- Silicates as SiO ₂	0,8%	
- carbonates as CO ₂	1,2%	
- Sulphates as SO ₃	0,5%	
- Others up to 100 %	1,5%	

Table 7. Chemical analysis of the zinc covered pipe sediment - hot tap water circulation in a building

Research and Development Centre „UNITEX” Ltd.	Results of chemical analysis of the sediment	Address: Hot Tap Water Production Station. Gdańsk, Podleśna street
Sediment collection point:	Zinc covered pipe ϕ 32 - hot tap water circulation in a building at Zabytkowa 4 street (after one year operation)	
Type of the sample and its physical features:	Sediment adhere strongly to the pipe, white-cream colour at the bottom, light brown at the top, the sediment is hard and medium fragile	
Water supply source	Intake in Straszyn	
Loss of precipitates ignition at 800°C	5,1%	
Elements insoluble in HCl 1:1	7,2%	
Ingredients:		
- Calcium as CaO	12,4%	
- Magnesium as MgO	2,5%	
- Aluminium as Al ₂ O ₃	3,9%	
- Complete as Fe ₂ O ₃	57,9%	
- Complete copper as CuO	lack	
- Zinc as Zn	12,4%	
- Silicates as SiO ₂	4,3%	
- Carbonates as CO ₂	4,2%	
- Sulphates as SO ₃	1,1%	
- Others as 100 %	1,3%	

Microphotographing metallographic specimen

Metallographic specimen on the cut-set of the (inner) surface of the pipe was done to check the reactions of the (zinc) galvanic layer on the pipe surface and the size of corrosion defects of the layer.

Pipe samples, after preparation, that is grinding, polishing and etching causing visualisation of the galvanic layer structure adhering directly to the steel pipe, were observed with use of a microscope.

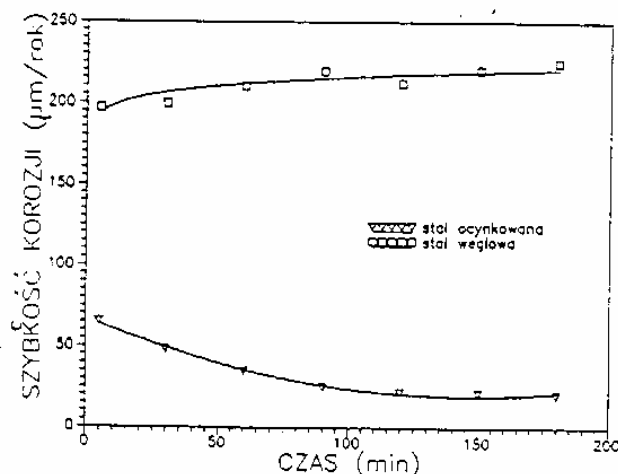
Analysed pipe segments were the same as the pipe samples analysed in point 4.3.

Metallographic specimen were observed with use of the metallographic microscope; the researcher tried to choose the characteristic pictures of the observed surface. Pictures of the observed zoom were taken 200 times bigger than in reality. they are presented in photographs 8, 9, 10, 11. The photos 8, 9, 10 and 11 are enclosed as **Appendix 2**.

Results of testing corrosion rates in laboratory conditions

Measurements of corrosion rate were done in case of zinc covered steel and steel without galvanic (Zn) layer in water from the water intake in Straszyn.

First, sample measurements of polarisation curves of steel and zinc covered steel were taken every half an hour 5 hours after putting the samples in hot water environment. It was found that corrosion current values stabilise and are repeatable after some 2 hours. Therefore, all the further measurements of polarisation curves were taken comparatively after that period. Examples of the measurements with connection with the calculation results are presented in pictures 7 and 8 and relationships between the corrosion rate in steel and zinc covered steel and time were presented at picture 6.



Rysunek 6. Zależność szybkości korozji metali od czasu ekspozycji w środowisku c.w.u. ($t=50^{\circ}\text{C}$, $\text{pH}=7,0$)

Picture 6. Relationship between metals corrosion rate to the time of their exposition in hot tap water environment ($t=50^{\circ}\text{C}$, $\text{pH}=7,0$)

Average calculation results of corrosion rate determined after 2 hours exposition together with standard deviations are presented in Table 8.

Table 8. Average metals corrosion rates in unmodified water (t=50°C, pH=7,0)

Installation material	Corrosion current density $\mu\text{A}/\text{cm}^2$	Corrosion rate $\mu\text{m}/\text{year}$	Corrosion threat estimation
zinc covered steel	$1,44 \pm 0,37$	$21,6 \pm 5,5$	strong
carbon steel	$18,25 \pm 6,85$	$212,1 \pm 79,6$	emergency

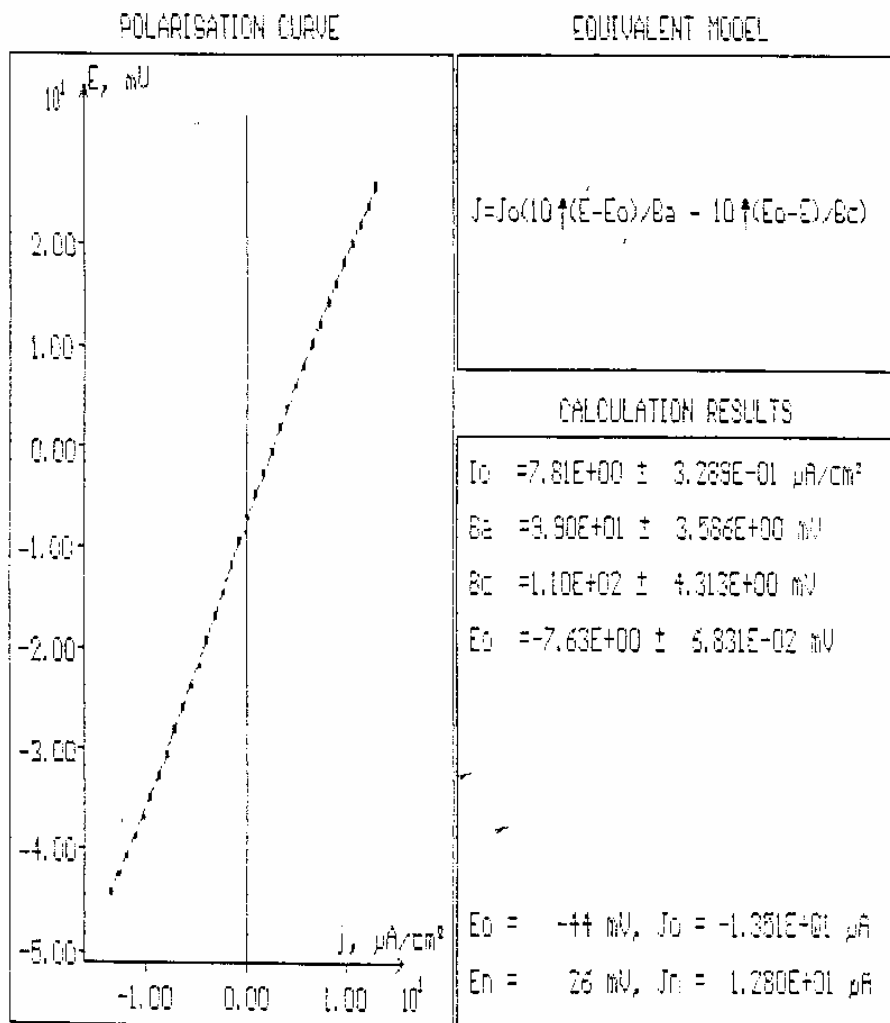
Corrosive environment was also modified by adding $\text{Ca}(\text{OH})_2$ as limewater to the supply system water from Straszyn to bounding aggressive CO_2 in water. Metals corrosion rate measurements were taken in water with pH between 7,0 and 8,2 by adding, respectively 0 - 1,0 cm^3/dm^3 saturated limewater. The measurements results are presented in Table 9 and Picture 9.

Table 9. Results of metal corrosion rate measurements in hot tap water (t=50°C) with various pH factor

Water reaction	Installation material	Corrosion current density $\mu\text{A}/\text{cm}^2$	Corrosion rate $\mu\text{m}/\text{year}$	Corrosion threat estimation
7,0	zinc covered steel	$1,44 \pm 0,37$	$21,6 \pm 5,5$	strong
	carbon steel	$18,25 \pm 6,85$	$212,1 \pm 79,6$	emergency
7,4	zinc covered steel	$1,13 \pm 0,57$	$16,9 \pm 8,6$	strong
	carbon steel	$16,39 \pm 4,65$	$190,5 \pm 54,0$	strong
7,8	zinc covered steel	$1,07 \pm 0,25$	$16,1 \pm 3,8$	strong
	carbon steel	$16,47 \pm 3,85$	$181,4 \pm 44,7$	strong
8,2	zinc covered steel	$0,93 \pm 0,45$	$13,9 \pm 6,8$	admissible
	carbon steel	$12,85 \pm 3,18$	$149,3 \pm 37,0$	strong

POLARISATION MEASUREMENTS

Date: 1996-08-02 Material of sample: stal węglowa
 Exposed area: 6.60 cm² Environment: c.w.u. z Podleśnej
 Temperature: 50.00°C pH value: 7.00
 Rest potential: -18 mV
 Notes: po 2h, G, 1µA/s

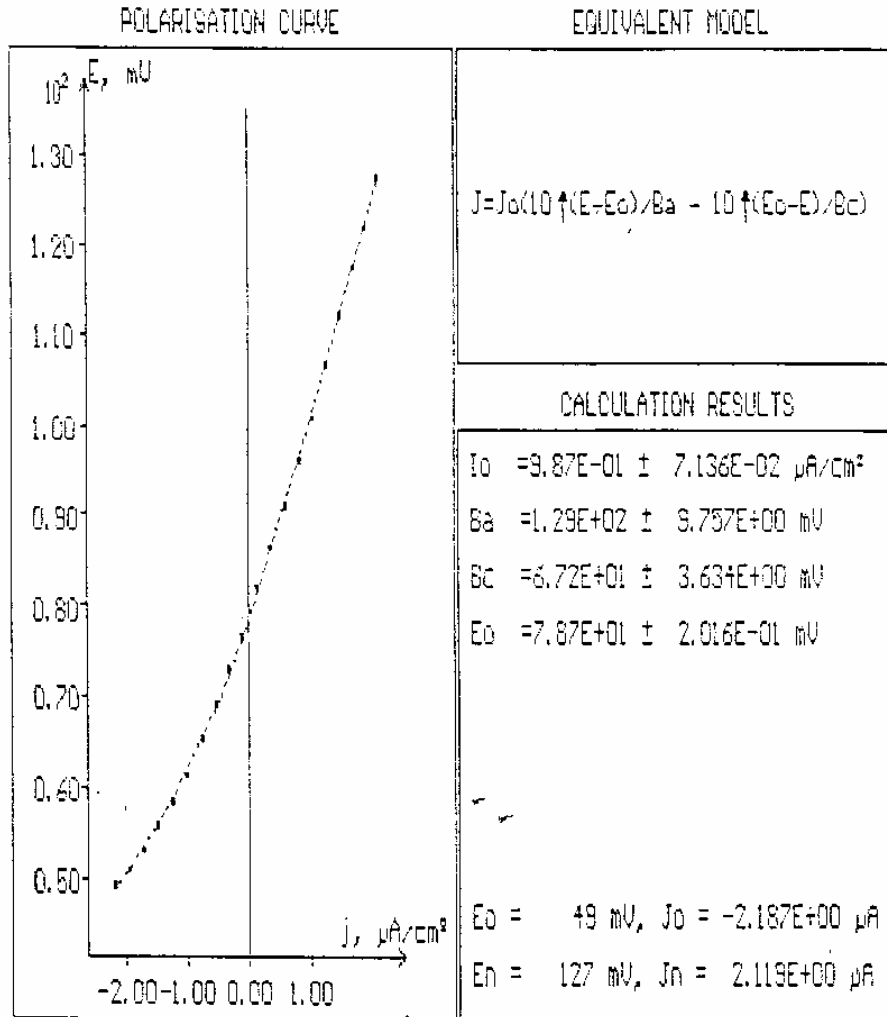


Rysunek 7. Krzywa polaryzacji stali w środowisku c.w.u. z os. Podleśna – wydruk komputerowy łącznie z wynikami obliczeń

Picture 7. Curve of metal polarisation in hot tap water environment in Podleśna district - computer outpost and calculation results

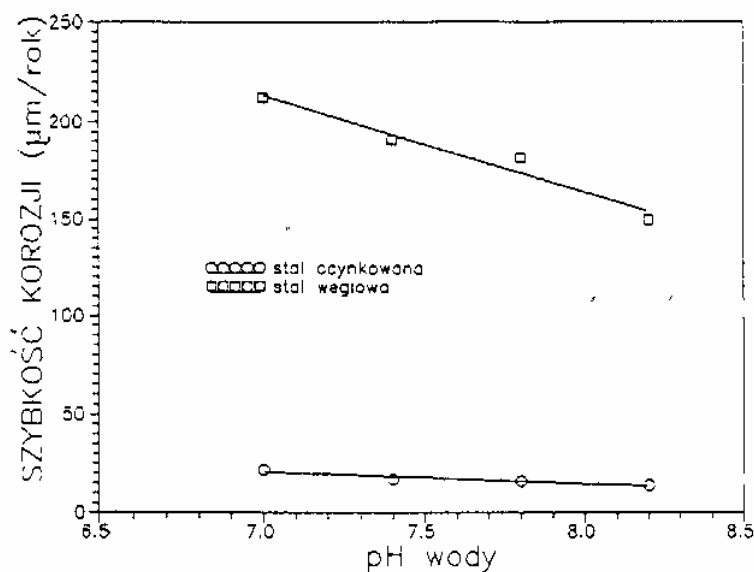
POLARISATION MEASUREMENTS

Date: 1996-08-02 Material of sample: stal ocynkowana
 Exposed area: 6.60 cm² Environment: c.w.u. z Podleśnej
 Temperature: 50.00°C pH value: 8.20
 Rest potential: 98 mV
 Notes: po 2h, G, 1µA/s



Rysunek 8. Krzywa polaryzacji stali ocynkowanej w środowisku c.w.u. z os. Podleśna - wydruk komputerowy łącznie z wynikami obliczeń

Picture 8. Curve of metal polarisation in hot tap water environment in Podlesna district - computer outpost and calculation results



Rysunek 9. Zależność szybkości korozji metali od pH ciepłej wody użytkowej

Picture 9. Relationship between metal corrosion rate to pH factor in hot tap water

On-the-site measurements of corrosion rate with linear polarisation method with use of a corrosimeter

Linear polarisation method was used for measuring corrosion rate on the site in the hot tap water installation directly in the hot tap water production station at Podleśna street.

Polarisation sensors were installed directly in pipes: in the pipe supplying the district with hot tap water and the return pipe from the district (circulation pipe). The sensors were made of R35 carbon steel and were supposed to estimate the corrosion rate in pipes without the galvanized zinc cover.

Calculating corrosion rate was based on the Stern-Geary method. The research results are presented in tables 10 and 11.

Table 10. Polarisation measurements of hot tap water installation corrosion rate

Collection point: Gdańsk, Zakoniczyn District, „Podleśna” exchanger station

Installation type: HTW installation, circulation pipe, return from the district

Material: R35 carbon steel (pipes without zinc layers were assumed)

Temperature of water: 45±40°C

No.	Operation time [24 h]	Polarisation current [μA]				Corrosion rate [mm/year]
		I ₁	I ₂	I ₃	I ₄	
1.	1	-	32,3	-	32,3	0,101
2.	14	-	69,0	-	69,0	0,215
3.	20	-	77,6	-	77,6	0,242
4.	27	-	54,4	-	54,4	0,170
5.	42	-	41,3	-	41,3	0,129

Table 11. Polarisation measurements of hot tap water installation rates

Collection point: Gdańsk, Zakoniczyn District, „Poldeśna” exchanger station
 Installation type: hot tap water installation, supplying water from the district
 Material: R35 carbon steel (pipes without zinc cover were assumed)
 Temperature of water: 52÷47°C

No.	Operation time [24 h]	Polarisation current [µA]				Corrosion rate [mm/year]
		I ₁	I ₂	I ₃	I ₄	
1.	1	86,2	47,1	62,8	65,4	0,204
2.	4	95,8	-	-	95,8	0,299
3.	7	65,9	-	-	65,9	0,205
4.	20	90,9	-	-	90,9	0,283
5.	27	84,2	-	-	84,2	0,262

Discussion on the results

Discussing estimation of corrosion- and sediment threats in hot tap water installation supplied with water from water intake in Straszyn on the grounds of measurements taken in the hot tap water installation in exchanger station at Podleśna street in Gdansk

Supplying and installation water

The cold water content (water supplying the hot tap water installation) was presented in Tab. 3.

COLD WATER SUPPLYING HOT TAP WATER PRODUCTION STATION IN PODLEŚNA STREET BASICALLY MEETS ALL THE SANITARY REQUIREMENTS REGARDING ITS QUALITY AS HOUSEHOLD WATER AND DRINKING WATER, EXCEPT PERIODICAL H₂S PRESENCE AND HIGHER Fe CONTENT IN WATER. The water has good sanitary quality regarding Polish conditions and medium-good quality with regards to western European norms.

THE WATER IS CORROSIVE, PARTICULARLY AFTER INCREASING ITS TEMPERATURE. Water, which total chlorides and sulphates content is higher than 50 mg/dm³ and oxygen content 2 ÷ 4 mg/dm³, is corrosive even if the Langelier index is positive. Installations needs therefore additional protection. In this case Langelier index is negative due to aggressive CO₂ presence in water. Higher theoretical relation was confirmed by empirical results presented in table 3.

Zinc content in hot water supplying the district, and particularly in circulation water, is higher (even four times higher - up to 0,88 mg/dm³) in relation to cold (supplying) water. The dissolved iron content in water is also a few times higher in hot water than in the cold water. Simultaneously, there is ca. 50% less oxygen and ca. 30-40% less aggressive CO₂ in circulation waters. This situation leads to a simple conclusion. **OXYGEN AND AGGRESSIVE CO₂ PARTICIPATE IN ZINC - AND STEEL CORROSION PROCESSES DUE TO A KNOWN CLASSICAL ELECTROCHEMICAL REACTION.**

Limiting the amount of oxygen in water supplying the hot tap water installation is not possible in practice. At first, during this research, heated water was degassified with a vacuum method in a laboratory. Aggressive and free CO₂, together with oxygen was being removed from water and boiler scale started to precipitate rapidly on the filling of the degassifying column. The

experiment was stopped at the beginning since the result was easy to foresee: the degassification process was successful and the column was filled with sediments. Due to water degassification, both oxygen and aggressive carbon dioxide as well as balancing “CaCO₃ sediments- dissolved free balancing CO₂” are being removed from water. Removing oxygen and aggressive carbon dioxide is profitable but due to removing balancing CO₂, boiler scale starts to precipitate rapidly. Complete oxygen removal is not possible also because of water putrescibility and possibility of hydrogen sulphide bacteria development (low redox potential).

Table 4 presents results of measurements of iron concentration in water in various points in the hot tap water installation supplied from the exchanger station at Podleśna street.

Measured iron contents over 0,5 mg/dm³, only sometimes 10 mg/dm³, are present mostly as free sediments moving in the installation. The sediments move in the installation and cause single high measurement results in case of momentary measurements. The measurements done confirm that the hot water is of low quality, which is a common opinion of the district dwellers. **THE QUALITY OF HOT TAP WATER, PARTICULARLY, OF CIRCULATION WATER, DOES NOT MEET THE STANDARD NORM FOR DRINKING WATER IN POLAND DUE TO HIGHER THAN USUALLY Fe BOUNDS CONTENT.**

With regard to the above statement, it is necessary to say that there is no possibility of removing oxygen from water to limit the corrosion without any side effects. However, there is also the other corrosive factor - aggressive CO₂. Removing it from water will contribute to increasing the Langelier index and will decrease the corrosion rate. It will create possibilities of creating a protection layer either on the zinc covered steel or on the surface without the galvanic layer. The protection layer will separate metal from water environment. At present, due to presence of aggressive CO₂ in water there are no such possibilities.

Discussing the results of measuring corrosion rate

Laboratory research on corrosion rate

The obtained results should not be analysed as absolute corrosion rate values but rather as comparative values, allowing to estimate the influence of the factors in question and observing the trends. Short time of the experiment, lack of possibility to mapping real operating conditions in the laboratory and clean, metallic surfaces of measuring electrodes made of steel and zinc covered steel (in relation to installation conduits covered with sediments and corrosion products) suggest choosing this approach. Nevertheless, the experiments confirmed literature assumptions and proved the positive influence of water deoxygenating on slowing down corrosion rate both in case of steel and zinc covered steel as well as increasing pH factor by water liming. It is believed that in the real hot tap water installation the influence of liming will be more visible at longer water treatment period since protection layers on the metal surface are created within a few months time. It is necessary to say that deoxygenating water contributes to slowing down corrosion rate several times for zinc and more than ten times for steel in relation to oxygenated water, at temperature 50° C and pH = 7,0.

Influence of the pH factor on the supply system water is the following: the biggest decrease in corrosion rate at temperature 50 degrees takes place while changing pH of water to pH = 8,2. Corrosion rate for zinc covered steel equal 13,9 µm/year in this case. This leads to 36% drop of corrosion rate in relation to water with a pH factor equal pH = 7,0. A similar drop in corrosion rate (that is ca. 30%) is obtained for steel after changing the pH factor from pH = 7,0 to pH = 8,2.

The Authors emphasise that it is necessary to focus on tendencies in corrosion rate changes, not on their values.

On the site research on corrosion rate in unmodified water

Steel corrosion rate measurements taken on the site in the hot tap water installation at “Podleśna” district confirmed comparatively high corrosion threat regarding the installation. Final measurement results from the six-week research period should rather be considered as the most adequate. At first,

probe corrosion rates in the installation were very high due to high reactivity of their metal surfaces. After ca. 2 weeks, the probes covered with sediments and corrosion products and their measurement results were more adequate to the operation conditions of the examined installation. Despite this fact, measured corrosion rate may be still too high due to long time of protection layers formation, depending on electrochemical water treatment which may last even a year.

The obtained results suggest emergency or high corrosion threat for steel. Corrosion rate values are ca. $0,10 \pm 0,24$ mm/year for circulating water and ca. $0,10 \pm 0,26$ mm/year for supplying water (Tables 10 and 11).

The above is dependent on high level of water oxygenation ($3, - 7,1$ mg/dm³), presence of aggressive CO₂, and high total content of chlorides and phosphates. Despite lower corrosion rate values for circulation water in comparison to supplying water, the circulation water should also be classified as water with strong or emergency corrosion threat. Lower corrosion threat with regards to supplying water is caused first of all, by lower oxygen ($2,1 - 5,2$ mg/dm³) and aggressive CO₂ content in circulation water, because oxygen and carbon dioxide were partly consumed in the process of installation corrosion.

THE ON THE SITE CORROSION MEASUREMENTS SHOW THAT STEEL CORROSION RATE AT TEMPERATURE 50°C IN HOT TAP WATER INSTALLATION ENVIRONMENT AT THE STATION AT PODLEŚNA STREET SHOULD BE CLASSIFIED AS STRONG OR EMERGENCY LEVEL.

Conclusions

1. Hot tap water installation made of steel pipes, supplied with water from the hot tap water production station at Podleśna street corrodes strongly in the environment of water supplied from the municipal supply system (that is from the water intake in Straszyn).
2. Zinc covered steel corrodes strongly even before heating and it corrodes very strongly after heating; corrosion of steel without galvanic layer is on an emergency level.
3. Content of water supplying the station is mostly responsible for higher corrosion of the hot tap water installation material.
4. High water oxygenation level and presence of aggressive CO₂ in water are the main corrosive factors. Chloride and sulphate ions content in total amount 50 mg/dm³ classifies the water as strongly corrosive and therefore protection against corrosion is necessary.
5. Cold water supplying hot tap water installation periodically does not meet sanitary requirements included in the norm according to the Decree of the ministry of Health and Social Welfare issued on the 4 September 2000 r. concerning standards for household and drinking water with regard to Fe and rarely H₂S (unacceptable smell) content.
6. Hot tap water installation material - zinc covered steel pipes have either strongly defected zinc cover (ca. 50%), or have no zinc cover at all which causes increased steel corrosion.
7. Presence of "dirty water" effect in the hot tap water system within the area supplied by the hot tap water production station at Podleśna street is caused, mostly by presence of too high amount of iron compounds from steel corrosion processes in the system water.