

## PROTECTIVE COATINGS IN THE POWER BOILERS WHICH ARE USED TO COMBUST WASTE – SURFACING ANTI-CORROSIVE LAYERS

General requirements and technological solutions of incinerating plants were presented. Heat processing of waste in fluidized and stoker-fired boilers were described. A problem of corrosion and the methods of preventing it in boilers used to combust waste were shown. Materials of increased resistance to corrosion used in power industry were characterised.

*Keywords:* surfacing by welding, surfacing layer, incinerator

### 1. Incinerating plant - general characteristics and technological solutions

Incinerating plant is a plant or its part designed for a thermal change of waste combined with an energy recovery or without it. The plant includes all installations, which belong to the system of waste transformation: a system of purifying waste gases, a supervising, a controlling and a monitoring system, and the systems required to gathering, initial processing and storing waste and the substances received in the process of combustion and purifying waste gases [1-7].

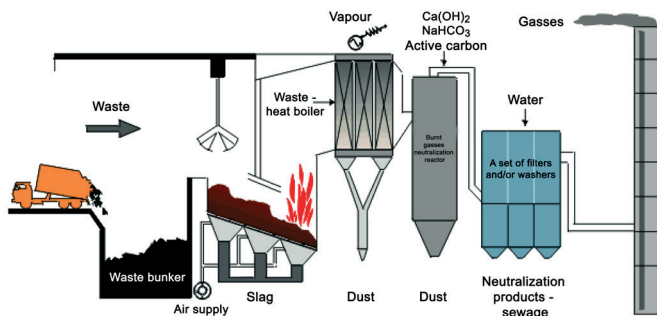


Fig. 1 A simplified draft of an incinerating plant

A history of incinerating waste in Europe has a long tradition – over one hundred years. The first incinerating plants were set up in the United Kingdom in the second part of the 19<sup>th</sup> century. Since then incinerating plants' capabilities, which reduced considerable amounts of waste, received much recognition in many countries. In the EU countries there are about 370 incinerating plants, which transferred thermally 43 million tonnes of waste, recovering electrical energy to meet the needs of 27 million people. For example Denmark combusts 54% of waste, Sweden 45%, the Netherlands 32%, France 34%, Germany about 22% [10].

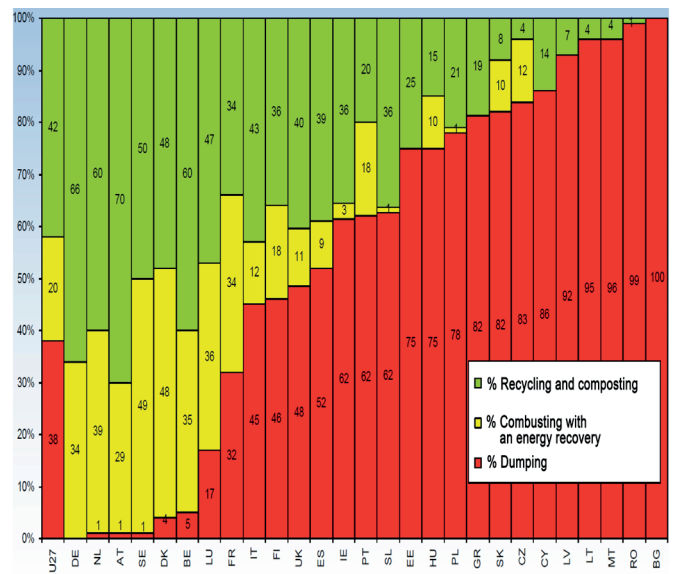


Fig. 2. Methods of municipal waste management in UE, source Eurostat 2007

An incinerating plant potential is systematically increased by building huge plants with a processing capacity of about 300-600 thousand tonnes per year, as well as installations with a processing capacity of about 40-80 thousand tonnes per year, which also use fuel obtained from waste to their production. It seems that the above trend will remain due to the fact that with an economic growth and increase of consumption, an amount of waste is rising. It is also worth mentioning that there are still worries about an environment pollution, but recently there has been a noticeable change in an attitude about the installations of heat processing of waste. They are not only the places to utilise waste, but also the places where waste is transformed into energy.

At present, in Europe, 50 million tonnes of waste per year is being processed in incinerating plants, generating energy,

\* CZĘSTOCHOWA UNIVERSITY OF TECHNOLOGY, 69 J.H. DĄBROWSKIEGO STR., 42-200 CZĘSTOCHOWA, POLAND

\*\* BOILER FACTORY SEFAKO SA, 9 PRZEMYSŁOWA STR., 28-340 SĘDZISZÓW, POLAND

# Corresponding author:jacek\_slania@poczta.onet.pl

which can deliver electricity to 27 million people, or heat to 13 million people. An average, one tonne of waste gives 0,67 MWh of electrical energy, or 7,0 -9,0 GJ heat energy [10]. Two tonnes of waste equals one tonne of coal.

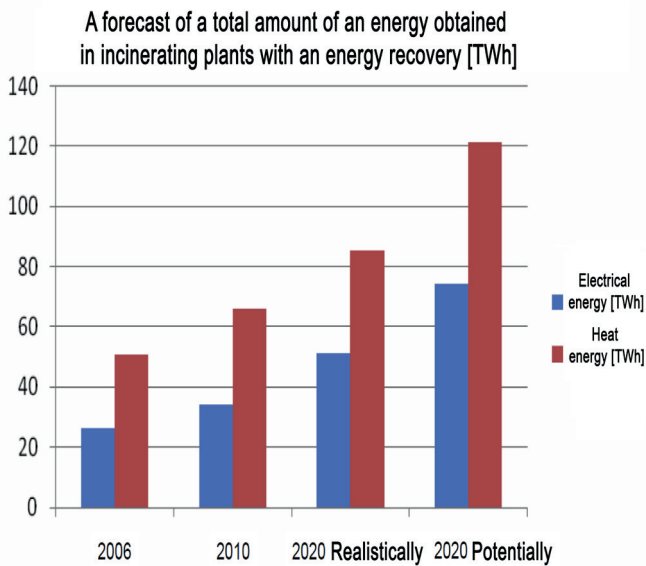


Fig. 3. A forecast of a total amount of energy made in incinerating plants with an energy recovery [TWh]

Boilers used to combust waste are usually based on the projects of water-tube boilers, which mostly consist of 3 vertical radiation draughts and a convection draught. The radiation draught is an integral part of a combustion chamber. The convection draught, where are evaporators, heaters, and economizers, can be either vertical or horizontal. Installations to combust waste, which are existing now, or were built in the last century, are mostly based on the grate and fluidized furnace. Waste is sometimes initially processed in order to get high calorific fractions.

**2. Heat treatment of waste in fluidized boilers**

Fluidized boilers are the most modern boilers and are the best to combust different types of waste fractions. They are particularly good to combust very moisture and liquid waste, sludge, and fragmented solid waste. There are fluidized furnaces with a bladderly or stationary deposit. They are characterised by a high efficiency of combustion despite a low combustion temperature of about 850°C in the combustion chamber, a low NOx emission, a possibility to reduce sulphur oxide directly in the combustion chamber. Heat treatment of municipal waste in the fluidized boilers as well as heat treatment in the grate furnace is a technology based on the use of oxygen in the process of combustion.

Fluidized boilers have a shape of a vertical cylinder. In the bottom part of the boiler there is a deposit of a solid inertial material (sand, ash), which is fluidized by air delivered by a nozzle bottom. Waste is provided directly into the volume of the deposit, from the top or from the side of the furnace, depending on the boiler’s structure. Heated air is delivered by nozzles, making fluidized deposit by the mixture of the deposit

and waste in the combustion chamber. Due to a considerable heat capacity of the deposit, combustion process is not very sensitive to changes of the waste flux and its flammable properties.

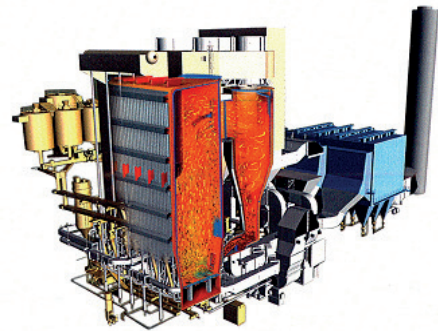


Fig. 4. A structure of a fluidized boiler

**3. Heat treatment of waste in the stoker-fired boilers**

The most common technological installations used to heat treating municipal waste are installations with a grate furnace. Nowadays, this solution is the most often used in EU countries. Grate technology is well known from the technological and exploiting point of view. It allows to process all kind of solid municipal waste, including high calorific fractions of waste. Its beginnings are in the solutions of boiler – rooms and heat power stations adapted to incinerating low calorific sorts of coal. Among many different structures of grate, these used to incinerate waste should have a considerable size and allow to mix waste in the process of combustion. Due to the quality of combustion, an organisation of flow of burnt gases in the furnace over grate is very important (a parallel, counter, mixed flow of burnt gasses). On the grate furnace, waste is moving into three temperature zones. It is being dried in the first zone, degassed in the second, and after-burnt in the third one. Waste which is aimed to be heat treated in the grate furnace does not have to be initially prepared and can be directly delivered into the grate. A full integration of the grate, furnace and boiler is a key element of an installation to work efficiently and safely for the environment.

Stoker-fired boilers can have two types of a structure:

- vertical draught boilers, which have up to 3 radiant draughts, and up to two convective draughts – fig 5. One of the advantage of above boilers is that heating surfaces can be cleaned by so called system of reflecting devices, which unlike the traditional soot blower, does not use vapour. Pollution which is caused during a cleaning process is getting into the chute without passing other heating surfaces, which in turn enables to reduce a risk of setting dust on the bank of tubes.
- or boilers with vertical radiant draughts and a horizontal convective draught – fig. 6. Banks in the convective draught are usually cleaned by soot blowers, which are very effective and reduce a risk of setting pollution on the banks. To avoid erosion caused by inter alia such a system of cleaning, protective straps made of stainless steel are used on the pipes of superheaters

and evaporators. Vertical boilers are a compact type of boilers, which require much smaller space to be built into than horizontal boilers. They have one common ash chute, which may reduce the costs of manufacturing and purchasing necessary materials.

The most common solutions are mainly boilers with empty vertical draughts and a horizontal draught with built-up convective surfaces. They are also characterised by a relatively fast and easy change of a heating surface when corrosive processes cause great losses in the pipes' structure.

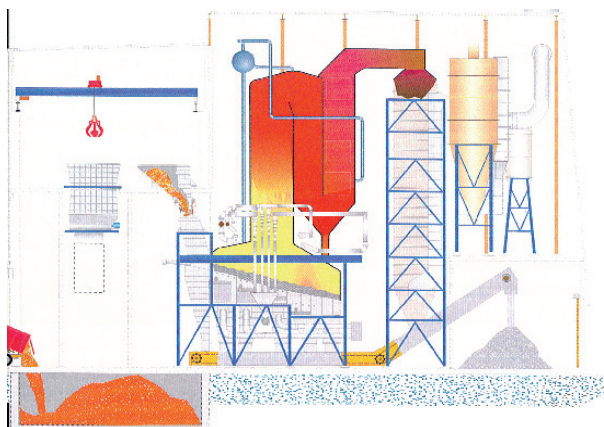


Fig. 5. Stoker-fired boiler of a vertical construction

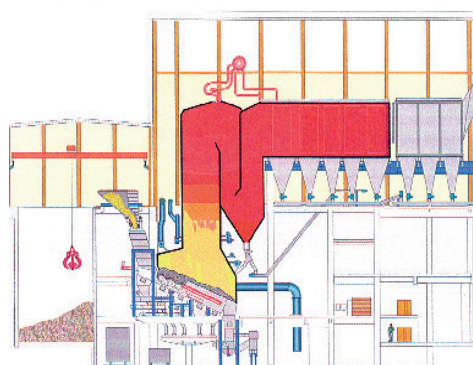


Fig. 6. Stoker-fired boiler of a horizontal construction

There are new or advanced projects of the following installations, which in most cases base a thermal process on a movable mechanical grate (in Poland projects Białystok, Bydgoszcz-Toruń, Konin or Kraków).

Bearing in mind an experience of many European countries, it can be claimed, that combustion technologies will be mainly based on those mentioned above. A decision will be made under a certain condition i.e. an implemented advanced waste management in a particular country. Cities which have already had neutralising and segregation plants according to the required standards, will mainly base their technologies on fluidized boilers. They will guarantee a high standard of combustion with lower costs of burnt gases processing. Cities without implemented system of waste segregation, which waste is a mixture of organic and inorganic waste, will base on stoker-fired boilers.

#### 4. Corrosion of the boilers used to combust waste and the methods of preventing it

Generally speaking a process of corrosion is a process of a continuous deterioration of materials. According to PN-EN ISO 8044:2002 standard corrosion is a physical-chemical reaction between a metal and an environment, as a result, there are changes in the properties of metal, environment or a technical system, which is a part of [12]. Corrosion processes and corrosion damages of boilers used to combust waste have usually many causes. They are as follows: properties of fuel (a content of fuel), a type of a boiler, a temperature of operating pipe material and a temperature of burnt gasses, conditions of combustion and a localisation of elements in the boiler. Corrosive damages are characterised mainly as a degradation of pipes in the heat side. Corrosion on the surfaces of a heat exchange does not cover vast areas, rather shallow cavities, notches and holes, and does not spread easily without a possibility to foresee it. There are all kind of known types of corrosion in the elements of the power installation. Due to the range of the following article, corrosion processes, which occur the most common in the boilers to combust waste, will be described.

#### 5. Corrosion of boiler heating surfaces used to combust waste

A process of combustion such an inhomogeneous material as waste, no matter if it is municipal, industrial, medical or sewage sludge is a source of emission of many chemical and toxic substances. The following factors have a considerable influence on the corrosive properties of fuel: a content of chemical substances, a type of chemical bonds, a proportion of a specific chemical substances to other substances, moisture, a shape and a size of fuel and a calorific value [13]. A content of dangerous substances in waste is several dozen per cent higher than in mineral fuel. Waste, which is thermally utilised, is full of dangerous substances. Depending on the type of combustion and purifying, it contains:

- organic compounds (e.g. carbon, hydrogen), in case of an incomplete combustion there is an emission of carbon dioxide, vapour, or carbon monoxide.
- inorganic compounds (e.g. sulphur, nitrogen, chlorine or fluorine), which cause an emission of sulphur dioxide, nitrogen monoxide, hydrogen chloride or hydrogen fluoride.
- heavy metals (e.g. zinc, lead, cadmium)
- additionally there are solid combustion products: ash, slag and dust from filters.

Substances may cause new toxic compounds, so called dioxane during a combustion process. Dioxane is made when there is an organic substance and chlorine in the combustion process. An unfavourable factor is a dynamic and continuous change of a waste content, both by means of a calorific value and its physical-chemical properties. An instability of combustion is a reason of an increasing corrosion.

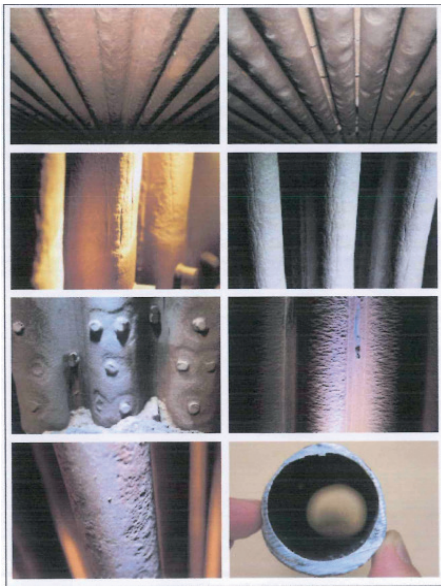


Fig. 7. Examples of possible damages caused by corrosion in boilers used to combust waste [13]

Moreover, corrosive properties due to the area of combustion depend on the following: a decomposition of an air in the first combustion zone, a coefficient of an air excess and a precise mix in the combustion zone, burning out burnt gasses, solved or solid/liquid substances in the burnt gasses, a position and a length of flame, a release of energy in the combustion zone, a geometry of a combustion chamber and the flows. In case of a heat exchange in burnt gasses, corrosive properties are as follow: pressure, a temperature of heaters, a range of burnt gasses temperature in the radiant and convective zones, a speed of burnt gasses, a time of burnt gasses retention before a convective part [13].

A problem of corrosion is very complex, as it includes an influence of different factors on metal and its behaviour. Corrosive processes in boilers can be divided into many ways. One of the division is made according to the place of their appearance i.e.

- on the side of burnt gasses
- water
- and vapour of different pressure and temperature

Another division is made according to a precise appearance of corrosion in the boiler [14]:

- in the combustion chamber, which is strictly connected with the process of combustion and a type of fuel
- low temperature corrosion, which occurs on the heating surfaces in the steam boilers especially on the surfaces of evaporators and heaters' pipes. Depending on the local conditions of a temperature above 260°C can cause high temperature corrosion.

Corrosive processes can have a following character [15]:

- oxidising, connected with a presence of nitric and chromium acid, iron and copper salt, nitrates, chromates, carbamide.
- reducing, related to an influence of sulphur, hydrochloric, and phosphoric acid, organic acids, alkaline salt solutions, halide solutions.

- and oxidising-reducing, related to the influence of all above compounds.

Both a presence of mentioned compounds and a higher temperature may cause a local corrosion i.e. crevice or pitting corrosion on the surface of the boilers' elements.

The main reason of crevice corrosion is an unsteady access of oxygen. A process of crevice corrosion starts after use of oxygen in a highly difficult soluble compounds in the mouth of the crevice, and easily soluble salts inside it, acidifying the corroding medium of the crevice.

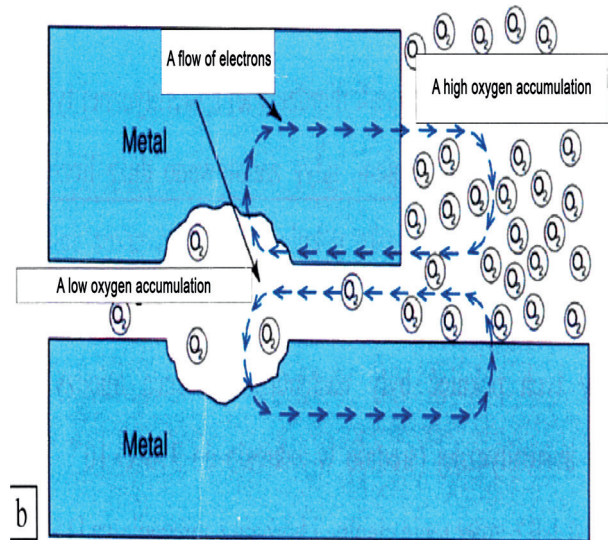


Fig. 8. Crevice corrosion which appears due to a different accumulation of oxygen inside and outside crevices

On the other hand, pitting corrosion mostly appears on the surfaces of metals which are passive to chloride, bromine and oxygen ions, in the acid or neutral reaction. Additionally, a presence of  $Fe^{3+}$  and  $Cu^{2+}$  oxidants makes the process of corrosion faster. Corrosion pits are usually invisible at the beginning, but progressive local damages may lead to a destruction due to the punching of the element. Pitting corrosion appears both on the alloyed steel resistant to corrosion, and unalloyed structural steel.

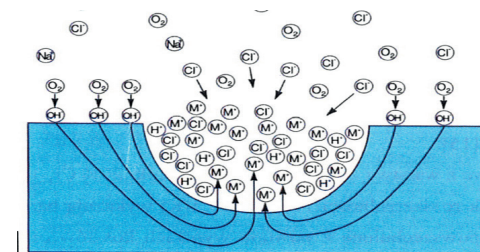


Fig. 9. Pitting corrosion as a result of an increase of  $Cl^-$  and  $H^+$  ions

The most significant for the boilers used to combust solid fuel (including waste and biomass) are two high-temperature types of corrosion caused by the presence of chlorine or sulphur, so called chlorine corrosion and sulphate-sulphur corrosion. Heaters and evaporators are endangered. A problem of high-temperature corrosion grew due to:

- the use of low emission combustion techniques, which

aim is to reduce NOX. They cause an appearance of a reducing atmosphere and a growth of a flame in the area of a combustion chamber, which in turn increase a possibility of a contact between non-burnt elements of fuel and the surfaces of walls [16].

- combusting fuel which includes a higher amount of chlorine > 0,2% and alkalies (waste, biomass, some sorts of coal)
- rising an operating temperature in order to obtain a better efficiency of power units.

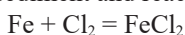
Chlorine has a corrosive influence on steel in high temperature, mostly by an active oxidizing of metal, which destroys the layer of oxides, changing it into a loose and unprotected sediment. Hydrogen chloride (HCl), which is present in the burnt gasses, can be a source of molecule chlorine (Cl<sub>2</sub>) by the surface of a metal, and also alkaline metal chlorides (K i Na). Chemical reaction is as following:

- during oxidizing  

$$2\text{HCl} + 1/2\text{O}_2 = \text{Cl}_2 + \text{H}_2\text{O}$$
- during condensation reaction on the pipes of potassium and sodium chloride with iron oxides in the deposit:  

$$2(\text{K}, \text{Na})\text{Cl} + \text{FeO} + 1/2\text{O} = (\text{K}, \text{Na})\text{FeO} + \text{Cl}$$

Molecular chlorine released from the reaction diffuses by the sediment and reacts with it:



Chlorides diffusing by the magnetite layer destroy it, and in the areas reach in oxygen, iron oxides appear:

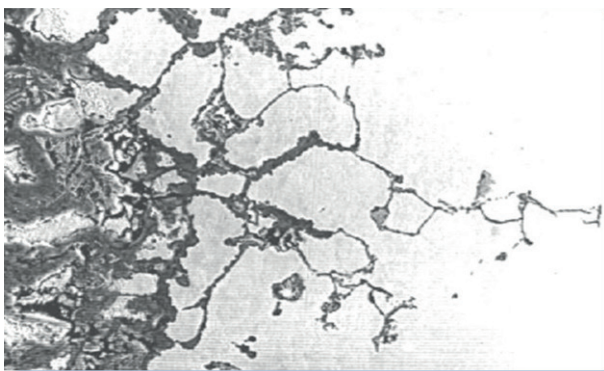


Fig. 10. Chlorine corrosion outside ferrite grains boundaries of radiant tubes [17]

It is considered that sulphates and pyrosulphates of alkaline metals have the most aggressive influence from all kinds of sediments and ashes of solid fuel [18]. Sulphate corrosion is connected with a presence of alkaline metals K and Na in a mineral substance, which together with sulphur make sulphates Na<sub>2</sub>SO<sub>4</sub> and K<sub>2</sub>SO<sub>4</sub> in the furnace. Sulphates accumulate on the surface of tubes. They are not directly corrosive due to a high temperature of melting, but in the presence of SO<sub>3</sub> pyrosulphates appear near the surface of tubes:



and trisulphides sodium-ferrite 2Na<sub>3</sub>Fe(SO<sub>4</sub>)<sub>3</sub> and potassium-ferrite 2K<sub>3</sub>Fe(SO<sub>4</sub>)<sub>3</sub> with a lower melting temperature:



The issue of a corrosive influence of pyrosulphates and trisulphides is that due to a low melting temperature they can appear on the surface of tubes, respectively an evaporator and a heater, in a liquid state. Pyrosulphates are aggressive in relation to metal, and also they destroy a protective oxides layer of evaporator tubes. Trisulphides can directly attract metal of tubes, or they unveil metal to oxidise by an ability to solve ferric oxide.

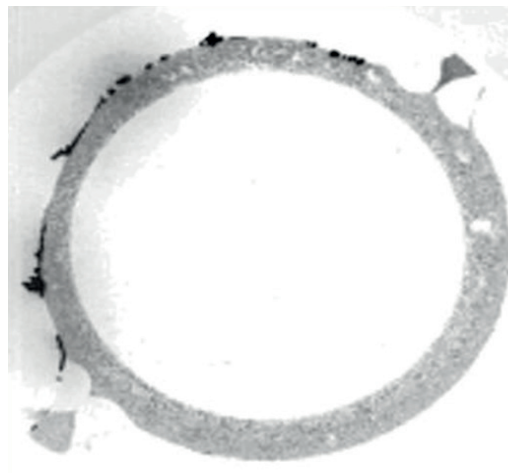


Fig.11 An arrangement of sulphides on the boiler's tubes on the burnt gasses side – Baumann printing – sulphur in sediment [17]

Methods, which can efficiently prevent corrosion, are mainly focused to the modifications of the combustion process. They lead to a reduction of corrosive properties of burnt gasses and boiler's sediments. Corrosion can also be reduced by using high-alloyed tubes, as well as by protecting tubes by a layer of brickwork and by using protective coatings such as Inconel.

## 6. Materials which have an increased resistance to corrosion used in the power industry

Corrosion belongs to phenomena which cannot be fully eliminated, but considerably reduced. A corrosive use causes non-destruction of many elements of power unit installations. Depending on the range of aggressiveness, specified by the content of fuel and combustion conditions, a temperature of a material operation or properties of the material, a corrosive use in some areas of a combustion chamber (around the burner area) on the heaters and economizers tubes, feeding fuel and air units as well as ash removal units takes place [19]. Degradation of materials and the environment due to corrosion can be effectively reduced by an efficient prevention, mostly by using anti-corrosive protection methods and a proper choice of materials.

There are many types of steel used in the power industry. Energy devices such as pressure boilers, operate in a variable exploiting conditions, which are characterised by high temperatures ranging from 400 to 700°C, as well as high pressure between 1,2 ÷ 30 MPa. Moreover, the directions of the power industry development are more often focusing on building power units with supercritical parameters, and what was emphasized many times, on building units, which

use alternative fuel (including waste). The above conditions require the use of strictly defined and fulfilling high standards materials to build boilers.

Depending on the operating temperature different structural materials are used, such as low-carbon, low-alloyed, martensite, austenite types of steel, nickel alloys [20-26]. All mentioned types of steel are characterised by a proper chemical content and mechanical properties i.e. resistance to stretching, yield point, ductility, impact strength and hardness. Introducing new ferrite and austenite types of steel allowed a usage of higher supercritical vapour parameters in the power industry, which caused an increase of power units efficiency and a decrease of an emission of pollution into the atmosphere. Therefore, these types of steel is characterised by the heat resistance i.e. enough resistance to oxidising, so an increasing layer of oxides inside tubes and pipes does not cause an excessive rise of temperature their walls (sheet pile walls, heaters, and reheaters). It may lead to damages due to creeping and/or an excessive chipping of hard elements of scale. The second characteristics is a creep resistance i.e. such mechanical properties which allow a long operation in high temperature (resistance to creeping) taking into account a cycling loading (resistance to low cycling thermal fatigue) [21].

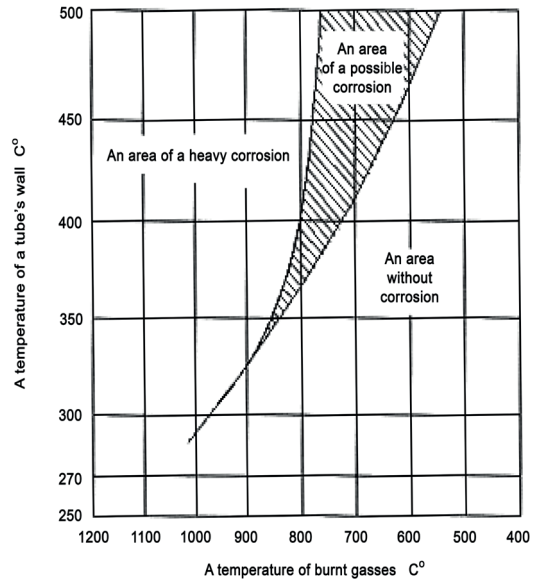


Fig. 13. A diagram of corrosion [14]

Assuring proper conditions to protect against aggressive medium takes place by the modification of a composition of main elements. A supplement of chromium guarantees a resistance to corrosion. Chromium, in the conditions of oxidising medium, makes oxide layers on the surfaces of steel. Moreover, it makes a change from an active state (soluble state) into passive (insoluble) in which steel is resistant to an influence of a corrosive medium. Furthermore, the major alloy additions in steel devoted to operate in increased temperatures except of Cr are Ni, Mo, Nb and W.

As it was mentioned before, in the production process of power units different types of steel are used, but in this paragraph only chosen structural materials, which have an increased resistance to corrosion, are described.

There are four main types of steel resistant to corrosion (described such as stainless steel, resistant to rusting, steel chemically resistant to rusting): austenite steel, ferrite steel, martensite steel, ferrite-austenite steel (duplex type of steel). By means of a proper content of chromium and nickel, stainless steel is resistant to an atmospheric, chemical and electrochemical corrosion in the acids, bases and salts [22]. Each type consists of many sorts of steel. Austenite steel is about 70% of production of stainless steel.

Traditional austenite steel used in the power industry includes about 0,1% C, 18–25% Cr and 8-16% Ni [23]. A content of 18% chromium decides that austenite and chromium-nickel steel are well resistant to corrosion which make them universal in the production processes. An increase of chromium (30% - maximum value) or other elements of a similar influence cause an appearance of ferrite in austenite, which in turn have a negative influence on its creep resistance. In order to get an austenite structure the following alloy elements are used Mo, Ti, Nb. A corrosive resistance to austenite steel directly results from passive oxide layers, which are made on their surfaces. They include chromium and iron oxide. Materials with an increased content of chromium have a tendency to make Cr<sub>2</sub>O<sub>3</sub>. Such an iron scale is characterized by a lower susceptibility to damages and porosity in comparison to oxide layers of

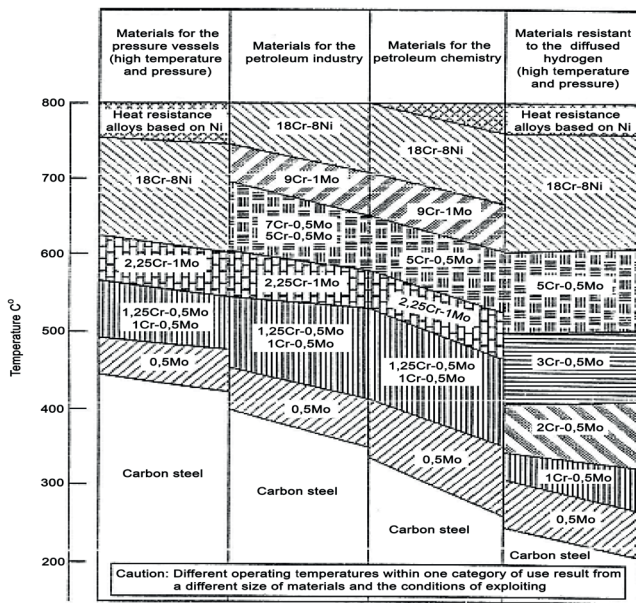


Fig. 12. A range of an exploiting temperature of different materials used in operating in increased temperatures [20].

Many examinations related to the corrosive phenomena showed a direct relationship between an intensity of corrosive processes in the aggressive medium, and the temperatures of burnt gasses and walls of the tubes. This relationship is shown in the diagram of corrosion underneath. It allows to chose appropriate parameters, which can guarantee a safe operation of the machine.

materials with a lower content of chromium. Austenite steel should have an addition of titanium or niobium (stabilized steel) [18] or an addition of carbon should be lower than 0,03% to be resistant to transcrystalline corrosion. Titanium and niobium bind carbon, and in this way prevent releasing chromium carbides. Introducing an addition of molybdenum has a positive influence on reducing crevice and pitting corrosion, and an increase of nickel favours a resistance to an austenite structure on the stress corrosion.

Ferrite steel is usually a highly-chromium type of steel (so called superferrite steel of 25% Cr content), and a low content of carbon. It is characterised by a low creep resistance, and in the same time high heat resistance. Adding alloy elements such as molybdenum, titanium and niobium to steel causes a favourable increase of mechanical properties. Superferrite steel, which was mentioned before, is featured as high resistance to pitting corrosion and to stress corrosion.

In case of martensite type of steel with a chromium content between 9÷12% Cr, steel changes into a passive state, which influences on an increase of resistance to corrosion in the oxidizing medium.

Austenite–ferrite steel is often described as a double type of steel so called Duplex. Recently, it becomes more and more important due to some of its properties: a high yield point, a low coefficient of thermal expansion, and a high resistance to stress, crystalline and pitting corrosion mostly by increasing a content of alloyed elements such as chromium, molybdenum, and nitrogen. Steel possess these favourable properties due to its dual microstructure, which consists of ferrite and austenite. A disadvantage of given steel is a tendency to release fragile phases of increased temperature, which in turn decreases their resistance to corrosion and have an influence on fall down of plastic properties. It has numerous applications, mostly in the chemical devices, environment protection and technology connected with marine.

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