

IDENTIFICATION OF FOULING DEPOSITED ON THE HEAT TRANSFER SURFACES OF THE STEAM POWER PLANTS HEAT EXCHANGERS

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Abstract

The term “fouling” refers to a substance, which settles on the heat transfer surface and causes the rise of thermal resistance to the heat transfer process. Sometimes, fouling is regarded as deposit but that term should be only used to fouling in the form of solid. Taking the traditional division of matter states as a criterion for fouling classification, there are three sorts of fouling: the solid ones, e.g. boiler scale, metal oxides, mud; the liquid ones, e.g. lubricating turbine oil and the volatile ones, air as for example an inert gas. Despite maintaining the recommended methods of correction for the steam power plants working agents, such as: the feed water, the boiler water, the condensate and the water vapour, for example by using the phosphate-ammonia correction, both corrosion and deposition phenomena occur in the water and the steam sides of the heat exchanger. Recognition of the type and the amounts of deposits gathered on heat transfer surfaces of the steam power plants heat exchangers is used within the thermal-flow diagnostics and also supports the planning of overhaul and routine repair of these devices. The results of the author’s own experimental research based on the method of spectral analysis were presented in the paper. The study was carried out in order to identify the type of fouling settled on both the outer side (steam side) and the internal side (waterside) on the heat transfer surfaces.

Keywords: *steam power plants, heat exchangers, heat transfer surface deposits, spectral analysis*

1. Introduction

Adverse physicochemical processes, i.e. corrosion, formation of deposits on the heat transfer surfaces, occurring in the water–steam cycle of the steam power plants, could result in severe operating difficulties in proper running of these power plants [13]. It affects the determination of more stringent requirements, not only for water quality, but also for steam [9, 18, 20]. Filling the water circuit by means of proper chemically prepared working medium does not guarantee correct operation of the power plant equipment. High values of temperature and pressure, as well as large heat load of transfer surfaces are the cause of a number of complex physical and chemical changes of working medium. The phenomenon described above usually changes the properties of water and its reactivity to construction materials of the power plant equipment [3, 15].

During power plant units operation, while maintaining the suitable method of correction for feedwater, boiler water, condensate and water vapour, e.g. by applying the phosphate-ammonia correction, the deposition phenomenon and corrosion process occur simultaneously in the water and steam circuit [22]. As a result of these processes, the heat exchange surfaces of the heat exchangers are coated by the fouling on both the water side, and the steam side. These deposits also constitute an additional resistance to heat transfer process, leading to the degradation of the heat exchanger. As a consequence, reduction in the values of the convective heat-transfer coefficients for steam, water, condensate, distillate and cooling water are noticed. In addition, these impurities contribute to shortening the technical life of a given power unit for both the marine and the stationary power plants [1, 3, 4, 7, 11, 10, 17, 23].

The chemical composition of deposits formed on the waterside of heat exchangers for the stationary and the marine steam power plants depend largely on the type of heat exchanger design as well as the heat exchanger duty, i.e. the purpose of a condenser or a low-pressure and a high-pressure heat recovery exchanger [21]. There are plenty of different contaminants present in water such as the following chemical compounds: water-soluble salts, gases and certain organic materials, namely, calcium salts ($\text{Ca}(\text{HCO}_3)_2$, CaCO_3), calcium sulfates (CaSO_4 , $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), calcium chloride (CaCl_2), magnesium salts ($\text{Mg}(\text{HCO}_3)_2$, MgCO_3 , MgSO_4 , MgCl_2), iron and manganese salts ($\text{Fe}(\text{HCO}_3)_2$, $\text{Mn}(\text{HCO}_3)_2$, FeSO_4 , MnSO_4), sodium and potassium salts (NaCl , KCl , K_2SO_4), silica (SiO_2) and silicates and the so-called water glass (Na_2SiO_3 , K_2SiO_3). Moreover, impurities may be present in the liquid phase e.g. as turbine oil and in the gaseous phase, the so-called inert gases or non-condensable gases e.g. as air [8, 16, 18].

Taking into account the low-pressure and the high-pressure heat recovery exchangers of domestic power plants, most of chemical analyses of the deposits accumulated on the waterside of these kind of heat exchangers, indicate that the deposit composition consists mainly of iron oxides, in the forms of iron (II) oxide, iron (III) oxide and magnetite as well as copper compounds. [3, 5].

In the subject literature, referring to deposits formed at the steam side (the outer surface of the tube) on the heat transfer surface of the power plants heat exchangers, i.e. condensers, the low-pressure heat recovery exchangers as well as the high-pressure ones, it is stated that this type of sediments consist mainly of iron oxides, in the form of $\text{FeO} \cdot \text{Fe}_2\text{O}_3$, Fe_2O_3 i FeO and FeO and copper compounds. The percentage of these compounds in the sediment varies, and is dependent on the material of the heat exchanger [12].

Exemplary results of deposits at the steam side are taken from the publication [13]. The study of the composition and the amounts of sediments was carried out for two turbine condensers, the one of power unit No. 6 and the second of power unit No. 8 in Turow power plant. The condenser pipes of power unit No. 6 were made of copper-nickel alloy (MNŻ51) whereas the condenser tubes of power unit No. 8 were made of brass (MC70). Studies have shown, that the main component of the deposits settled on the vapour side of the examined exchangers, are iron compounds – magnetite in particular. The magnetite ratio is accordingly 71.26% for the copper-nickel tubes and 59.84% for the brass tubes. Another important component of such deposits is copper compounds, whose share in terms of pure Cu is: 24.34% for the copper-nickel pipes and 26.8% for the brass pipes. In addition, there were insignificant quantities of zinc and nickel compounds, whose share in relation to zinc oxide and pure nickel has gained the following values 1.99% pure Ni and 10.86% zinc oxide for the pipes made of copper-nickel alloy.

It is worth mentioning, that other interesting issue concerning fouling formation on the heat transfer surfaces of the steam power plant's heat exchangers is the presence of micro- and macroorganisms forming biological contaminants (more often known as biofouling). The most important microorganisms responsible for the corrosion phenomena include, among others, bacteria oxidizing iron and manganese compounds, i.e. *Thiobacillus ferrooxidans*, *Ferrobacillus ferrooxidans*, *Galionella*, *Metalogenium symbioticum*. Furthermore, *a contrario*, some of the biological fouling, in relevant conditions, can cause the desired effects on heat exchanger running, such as slowing down the heat exchange surface corrosion process [6].

2. Research methodology

The spectral analysis was used in the author's own research as an essential method to identify the chemical composition of deposits formed on the heat transfer surfaces of the heat exchangers of steam power plants. It is a kind of visual analysis and is based on X-ray spectra, and these spectra images are the so-called spectrograms, which have the distinctive lines of emission or absorption spectrum of electromagnetic radiation absorbed or emitted by the tested substance. The

main purpose of the analysis is the detection of elements or compounds of the test samples (the qualitative part) and the quantitative determination of the composition of a sample by measuring the intensity of radiation of a specific wavelength (the quantitative part) [2, 19].

2.1. Measuring method

Spectral analysis of the chemical composition of deposits formed on the inner and outer surfaces of heat exchangers tubes from the steam power plants was carried out by analyzing the emission of the characteristic EDS radiation using the semi-quantitative method with no pattern [19, 24]. To identify the elemental composition of the tested samples and determining their quantitative composition, highly advanced class of the scientific and research equipment has been used i.e. the environmental scanning microscope manufactured by Philips, FEI XL 30 ESEM type which belongs to the Chair of Materials Science of the Faculty of Mechanical Engineering of Gdansk Technical University. Basic features of that microscope were shown in Tab. 1 [24].

Tab. 1. The nominal characteristics of the environmental scanning electron microscope, manufactured by Philips, FEI XL 30 ESEM type, according to [24]

Item	Feature	Description
1	Accuracy	< 1% of the measured value
2	Operating mode	1) High vacuum for conductive preparations, 2) Low vacuum for non-conductive preparations, 3) Environmental ESEM in the atmosphere of gases or water vapor for the hydrated and moist samples which eliminates the need to prepare preparations
3	Control	Computer software running on Windows® NT
4	The electron gun	Tungsten cathode with auto saturation and tuning mode
5	Resolution	1) 3.5 nm at 30 kV for low and high vacuum, 2) 15 nm at 3 kV for low vacuum
6	Detectors	Built-in spectrometer detector EDX
7	Magnification	1) 6×1 200 000 at high vacuum, 2) 250×400 000 at environmental mode
8	Vacuum system	Turbomolecular pumps, time to achieve vacuum: 1) high 3.5 min, 2) low 2.5 min
9	The mounting of samples	Computer-controlled four axis motorized centric table (X, Y, R, Z), Offset sample X, Y, Z = 50 mm, 360° rotation, 15°/75° inclination, sevenfold positioned small sample holder and the holder for large sample, inner diameter of the chamber of 284 mm, max. sample weight of 1 kg, max. sample height of 25 mm
10	Preview of chamber's interior	IR CCD camera for observing the interior of the chamber and the sample in a high vacuum or under environmental mode
11	Presentation and description of the image	Two 15-inch LCD colour monitors, an 7-inch high-resolution fotomonitor with AF SLR camera, recording of digital images on the HDD, FDD, CDR ROM, a videoprinter and an inkjet printer for printing photos

The set of research material was comprised of the deposits formed on the outer and inner surfaces of the heat exchangers' tubes derived from the heat exchangers of the domestic steam power and heat plants. Research material was coded by the following symbols: KR02, KR07, KR09 and AG12, because the donors reserved the rights to disclose their data. Basic information about this research material is shown in Tab. 2.

2.2. Preparing the research samples


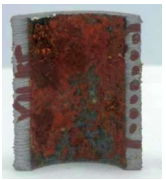

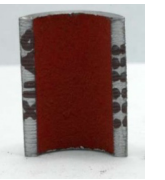




The relevant samples of the research material i.e. for the tubes covered with the deposits on the waterside and the steam side, were prepared. Subsequently, spectral analysis for the samples was carried out. The accuracy of spectral analysis is a function of experimental measurements accuracy

Tab. 2. The research material – the heat exchangers tubes derived from the domestic steam power plants or heat and power plants [the author's own research material]

Item	Code of tube	Pipe dimensions [mm]		Origin of the research material
		outer diameter	inner diameter	
1	KR02	17.5	13.5	High-pressure heat recovery exchanger, EC1 heating unit 100 MW, Donor – KR Energoremont
2	KR07	17.5	13.5	Low-pressure heat recovery exchanger, E1 power unit 200 MW, Donor – KR Energoremont
3	KR09	17.5	13.5	Starting exchanger of the steam boiler OP230, EC1 heating unit 100 MW, Donor – KR Energoremont
4	AG12	16.0	12.0	Low-pressure heat recovery exchanger, Donor – AG IMPPAN

and applied methods of correction [2, 19]. Therefore, test samples were prepared in accordance with the appropriate procedure in quantitative X-ray microanalysis, e.g. taking into account constraints resulting from the geometry of the research microscope chamber [2, 19, 24]. Photos of samples KR02, KR07, KR09 and AG12 are shown in Tab. 3.

Tab. 3. Photos of the research samples prepared to spectral analysis examination. Photos of research samples were taken with a tripod by Nikon D70S camera equipped with MicroNikkor 105mm-1:2.8D lens, settings: white balance – the user, ISO – 200, diaphragm – 32, time – 1s, according to [the author's own work]

Fouling	Research samples			
	KR02	KR07	KR09	AG12
inner side (the water side)				
outer side (the steam side)				

2.3. Research results

The exemplary spectrogram of deposits settled on the inner heat transfer surface of the KR02 heat exchanger tube coming from the domestic steam power plant is presented in Fig. 1.

Other research results of spectral analysis for the examined samples of fouling KR02, KR07, KR09, AG12 in were shown in Tab. 4.

2.4. Interpretation of research results

The identification of the internal and external fouling for the analysed samples was carried out based on the method of the stoichiometric analysis. At the beginning, the number of moles of the sample individual elements was determined. Then, the comparison analysis was performed. The comparison was conducted on the received results of examined samples and the theoretical values of quantitative molar ratios that exist in the theoretical chemical compounds, which, according to the literature reports, can potentially constitute the deposits on the inner and outer heat transfer surfaces of the heat exchangers in the steam power plants [14, 25].

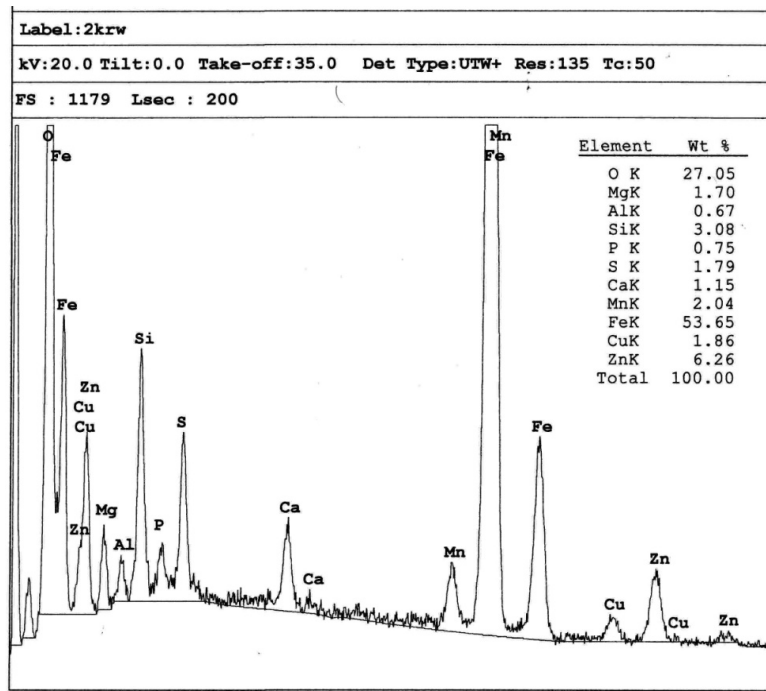


Fig. 1. The spectrogram of inner deposits of KR02 sample, obtained by means of the environmental scanning electron Philips microscope XL 30 ESEM EI type, according to [author's own study]

Tab. 4. Results of spectral analysis for deposit samples of the examined heat exchangers [author's own study]

Fouling (deposit)	Research samples							
	KR02		KR07		KR09		AG12	
	Element	Wt %	Element	Wt %	Element	Wt %	Element	Wt %
inner side (water side)	O K	27.05	O K	21.08	O K	22.97	O K	20.20
	Mg K	1.70	Mg K	2.29	Na K	6.70	Si K	0.30
	Al K	0.67	Si K	1.45	Mg K	1.19	Sn L	1.00
	Si K	3.08	Ca K	0.53	Si K	1.45	Cr K	0.55
	P K	0.75	Mn K	0.92	S K	3.08	Fe K	76.11
	S K	1.79	Fe K	73.73	Ca K	0.97	Cu K	1.83
	Ca K	1.15	Total	100.00	Mn K	1.56	Total	100.00
	Mn K	2.04			Fe K	50.29		
	Fe K	53.65			Ni K	0.47		
	Cu K	1.86			Cu K	3.36		
	Zn K	6.26			Zn K	7.95		
Total	100.00			Total	100.00			
outer side (steam side)	Element	Wt %	Element	Wt %	Element	Wt %	Element	Wt %
	O K	21.92	O K	20.21	O K	21.53	O K	18.57
	Si K	0.34	Si K	0.72	Fe K	78.47	Fe K	79.30
	P K	0.53	Mn K	0.62	Total	100.00	Co K	2.12
	S K	0.38	Fe K	64.84			Total	100.00
	Mn K	1.38	Cu K	13.61				
	Fe K	75.45	Total	100.00				
Total	100.00							

Thus, the number of moles n_{SP} of an element P in the sample was obtained by the following formula:

$$n_{SP_i} = \frac{m_{P_i}}{M_{P_i}} \quad (1)$$

The molar ratio $mr_{P_i:P_j}$ of two elements i -th and j -th in the sample was expressed as:

$$mr_{P_i:P_j} = \frac{ns_{P_i}}{ns_{P_j}}, \quad (2)$$

where:

ns – number of moles of an element in the sample [mol],

m – mass of an element in the sample [g],

M – molar mass of an element [g/mol].

The values of the theoretical stoichiometric proportion sr_T of the chemical compounds forming deposits on the heat transfer surfaces of the heat exchangers in the steam power stations are presented in Tab. 5 [14].

Tab. 5. The values of theoretical stoichiometric proportion sr_T for compounds forming deposits on heat transfer surfaces of the steam power plants heat exchangers, according to [14]

Compound	FeO	Fe ₂ O ₃	Fe ₃ O ₄	CuO	Cu ₂ O	SiO ₂	ZnO
Ratio sr_T	Fe:O = 1:1	Fe:O = 2:3	Fe:O = 3:4	Cu:O = 1:1	Cu:O = 2:1	Si:O = 1:2	Zn:O = 1:1
Value of sr_T	1.00	0.67	0.75	1.00	2.00	0.50	1.00

A detailed analysis was performed to identify deposits which were formed on the outer surface of the heat transfer (of the water vapour side) for the KR07 sample, as an exemplary calculation. Thus, taking into account both the data of Tab. 5 and the notation of the formula 1, the number of moles ns for the received elements in the KR07 research sample was calculated as follows:

$$ns_{\text{O}} = \frac{m_{\text{O}}}{M_{\text{O}}} = \frac{20.21}{16.00} = 1.263,$$

$$ns_{\text{Si}} = \frac{m_{\text{Si}}}{M_{\text{Si}}} = \frac{0.72}{28.08} = 0.026,$$

$$ns_{\text{Mn}} = \frac{m_{\text{Mn}}}{M_{\text{Mn}}} = \frac{0.62}{54.93} = 0.011,$$

$$ns_{\text{Fe}} = \frac{m_{\text{Fe}}}{M_{\text{Fe}}} = \frac{64.84}{55.85} = 1.161,$$

$$ns_{\text{Cu}} = \frac{m_{\text{Cu}}}{M_{\text{Cu}}} = \frac{13.61}{63.55} = 0.214.$$

Taking into account the above set of values of elements moles and notation of the formula 2 as well as the theoretical stoichiometric proportion values presented in Tab. 5, the following elements, which constituted deposits of KR07 sample, were evaluated as:

- iron compounds (where Fe:O = 1:1 = 1.00 is the theoretical ratio value reference)

$$mr_{\text{Fe:O}} = \frac{ns_{\text{Fe}}}{ns_{\text{O}}} = \frac{1.161}{1.161} = 1.$$

It was estimated that iron (II) oxide was one of the deposit constituents. For further analysis 0.102 mole of oxygen was taken, as a result of operation 1.263-1.161.

- copper compounds (where Cu:O = 2:1 = 2.00 is the theoretical ratio value reference)

$$mr_{\text{Cu:O}} = \frac{ns_{\text{Cu}}}{ns_{\text{O}}} = \frac{0.214}{0.102} = 2.09.$$

It was estimated that copper (I) oxide was also one of the deposit constituent.

Other elements were present in trace amounts. These elements could presumably be extracted from the pipe material. The results of the identification of chemical compounds that constitute deposits on heat transfer surfaces for the remaining samples KR02, KR07, KR09 and AG12 were summarized in Tab. 6.

Tab. 6. Identification of compounds that constitute deposits on heat transfer surfaces for samples KR02, KR07, KR09 and AG12 [author's own study]

Sample	Heat transfer surface	Number of moles in the sample	Identified compounds of the deposit
KR02	outer side	$n_{SO} = 1.370$, $n_{Fe} = 1.351$, other elements in trace amounts	FeO
	inner side	$n_{SO} = 1.691$, $n_{Fe} = 0.961$, $n_{Si} = 0.110$, $n_{Zn} = 0.096$, $n_{Mg} = 0.070$, $n_{S} = 0.056$, other elements in trace amounts	FeO, ZnO, SiO ₂ , MgSO ₄
KR07	outer side	$n_{SO} = 1.263$, $n_{Fe} = 1.161$, $n_{Cu} = 0.214$, other elements in trace amounts	FeO, Cu ₂ O
	inner side	$n_{SO} = 1.318$, $n_{Fe} = 1.320$, other elements in trace amounts	FeO
KR09	outer side	$n_{SO} = 1.346$, $n_{Fe} = 1.405$, other elements in trace amounts	not determined
	inner side	$n_{SO} = 1.436$, $n_{Fe} = 0.900$, $n_{Si} = 0.052$, $n_{Zn} = 0.122$, other elements in trace amounts	Fe ₃ O ₄ (FeO · Fe ₂ O ₃), ZnO, SiO ₂
AG12	outer side	$n_{SO} = 1.160$, $n_{Fe} = 1.420$, other elements in trace amounts	not determined
	inner side	$n_{SO} = 1.263$, $n_{Fe} = 1.362$, other elements in trace amounts	FeO

3. Conclusions

The conducted research aiming to identify the chemical composition of the fouling formed on the heat transfer surfaces of steam power plants heat exchangers has shown that the elements most frequently occurring in the deposits were the following ones: oxygen, iron, zinc, silicon, copper, magnesium as well as sulphur. The results of spectral analysis have also shown the presence of trace elements such as chromium, tin, cobalt, manganese and nickel. A possible reason for the presence of these elements on the spectrograms could be their dislocation from the pipes material. Based on the author's own study results of chemical composition of the deposits, the attempt to identify chemical compounds forming deposits has been made by the author of the paper. The most common occurring compound within the examined deposits was iron (II) oxide. Moreover, during the research the following compounds have been identified: zinc oxide, silicon (IV) oxide, magnesium sulphate, copper (I) oxide and as well iron (II, III) oxide. It should be noted that the shape of spectral analysis results was dependent on the sort of method applied, i.e. semi-quantitative method with no reference pattern. This method is considered less accurate than a full quantitative method with the reference pattern. However, the results obtained from the empirical studies largely confirmed the compatibility with the results presented in the literature concerning the fouling which is formed on heat transfer surfaces of the steam power plants heat exchangers.

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