ECO-INNOVATIVE METHOD OF CLEANING HEAT EXCHANGERS FROM BOILER SCALE

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Abstract
The operation of thermal devices and installations, in particular heat exchangers, is associated with the formation of various deposits of sediments, forming the boiler scale. The amount of precipitate depends on the quality of the flowing liquids treatment, as well as the intensity of the use of devices. There are both mechanical and chemical treatment methods to remove these deposits. The chemical methods of boiler scale treatment include the cleaning method consisting in dissolving boiler scale inside heat devices. Worked out descaling concentrate contains phosphoric acid (V) and the components that inhibit corrosion, anti-foam substances, as well as anti-microbial substances as formalin, ammonium chloride, copper sulphate and zinc sulfate. Dissolution of the boiler scale results in the formation of wastewater which can be totally utilized as raw materials in phosphoric fertilizer production. As a result, both the preparation produced and its use are entirely free from waste.

Keywords
Heat exchanger, chemical treatment method, eco-innovative, boiler.

Introduction

The corrosion protection of heating systems is connected with great difficulties caused by their complex geometry, large capacity and the presence of various metals. It is necessary to treat water for using in such systems, which is not easy due to changing factors or ingredients, such as salt and oxygen content, flow rate, temperature and volume of water to be treated. In addition, the occurrence of algae and bacterial mucus in the water should also be taken into account.

The accumulated sediments reduce the efficiency of equipment operation, as well as transmission capacities, which cause an increase in energy needed for pumping water. The fundamental factors associated with the formation of accretions can be \([1–3]\):

- speed; the higher the speed the lower the chance of creating sediment,
- pH, liquid temperature, the surface temperature of heat exchange,
- surface material; the higher the heat transfer coefficient of the material, the greater the susceptibility to buildup (copper > aluminum > brass > stainless steel) \([4]\),
- surface roughness; increasing surface roughness increases deposition \([4]\),
- type of the heat exchanger.

The problem of stone deposition forces the selection of adequately oversized heat exchangers at the design stage because one must take into account the decrease in heat exchange efficiency in the course of time. The purchase and installation of enlarged devices result in costs during the investment phase but does not exempt from additional costs at the stage of use \([5]\). Oversized devices also cause an increase in heat loss to the environment as well as thermal inertia \([5]\).
The methods of getting rid of the stone include chemical, biological and physical methods, differing in the degree of efficiency of removing boiler scale. Alternative methods are also methods such as magnetic, electronic and electrolytic [6]. In addition, this work also lists the method of eluting settled compounds in flow channels using clean water with the right high jet pressure, used for fresh sediments (work on the so-called fresh deposit) [6]. The use of these methods requires the proper construction of exchangers. The hydrodynamic cleaning method is also used for sanitary purposes. The high-pressure stream increases the effects, and at the same time shortens its time [1].

Scaling in boilers

Common feed water contaminants that can form boiler deposits include calcium, magnesium, iron, aluminum, and silica. Scaling is mainly due to the presence of calcium and magnesium salts (carbonates or sulfates), which are less soluble hot than cold, or to the presence of too high concentration of silica in relation to the alkalinity of the water in the boiler. These salts reach the deposit site in a soluble form and precipitate. The deposition of crystalline precipitates on the walls of the boiler interferes with heat transfer and may cause hot spots, leading to local overheating. The less heat they conduct, the more dangerous they are. The values corresponding to their thermal conductivity are \[\text{kcal/m}^2 \text{h} \circ \text{C}^{-1}\]: steel – 15; \(\text{CaSO}_4\) 1–2; \(\text{CaCO}_3\) 0.5–1; \(\text{SiO}_2\) 0.2–0.5 [7].

A carbonate deposit is usually granular and sometimes of a very porous nature. The crystals of calcium carbonate are large but usually are matted together with finely divided particles of other materials so that the scale looks dense and uniform. Dropping it in a solution of acid can easily identify a carbonate deposit.

A sulfate deposit is much harder and denser than a carbonate deposit because the crystals are smaller and cement together tighter. A sulfate deposit is brittle, does not pulverize easily, and does not effervesce when dropped into acid.

A high silica deposit is very hard, resembling porcelain. The crystal of silica is extremely small, forming a very dense and impervious scale. This scale is extremely brittle and very difficult to pulverize. It is not soluble in hydrochloric acid and is usually very light colored.

Iron deposits, due either to corrosion or iron contamination in the water, are very dark colored. Iron deposits in boilers are most often magnetic. They are soluble in hot acid giving a dark brown colored solution.

In addition to the removal methods, there are methods of prevention, e.g. by adding appropriate inhibitors, preparation of the surface of the heat exchanger [5]. Adding gum arabic to the surface reduces the amount of deposit, without harming the environment [2].

The current lack of cheap and at the same time safe due to the used chemical agents and the quick method of removing sediment causes that purification of the installation from sediments is not widely used, especially in cases of small thermal installations. Nevertheless, chemical cleaning is an extremely important element of equipment operation. Carrying out the chemical cleaning process correctly, while adhering to the relevant technological regimes, allows to minimize the risks associated with the cleaning process.

**Literature review**

Internal surfaces of steam generator systems are cleaned to remove contaminants that impair heat transfer and may ultimately cause tube failure. In the decision to clean chemically and the selection of the cleaning method, the following factors should be considered: the type of design, amount of flow, operating temperature, and pressure of the steam generator; the characteristics and quantity of deposit; the compatibility of the cleaning solvent with system metallurgy; the method of spent solvent disposal; cost [8].

Deposit characteristics are influenced by raw water characteristics, type of external treatment, feed water treatment methods and control, and the nature and degree of external contaminants which have entered the feed water during operation.

Environmental regulations must be considered in solvent selection. Plants with no waste treatment facilities must have spent cleaning solution trucked away, or they must use a process in which the spent solution can be evaporated.

The choice of solvent should be based on laboratory studies of the deposit sample found inside the tube. This will help ensure that the expected results of the chemical cleaning are achieved at minimum expense and risk to the system.

Inhibited hydrochloric acid is the most commonly used solvent. It is effective for removing most calcium and iron deposits. Hydrofluoric acid or ammonium bifluoride is often added to the hydrochloric acid to aid in the removal of silicate-containing scales. This mixture is also used to accelerate the removal of certain complex scales.

Chelating agents, such as EDTA and citric acid, are used to dissolve iron oxide deposits. They can
also be used to dissolve deposits containing copper oxides by the injection of an oxidizing agent through the boiler circuits [9].

The composition of the cleaning liquor is very important for efficient de-scaling. In [10] the scale from an industrial boiler is treated with four different acid solutions to study their dissolving effect on the scale/deposits in the tubes of the boilers. Results reveal that 5% solution of HCl is the most effective to dissolve the scale in a specified time at room temperature. Sulfuric acid shows very poor de-scaling properties under the test conditions. The order of effectiveness to dissolve the scale deposits is HCl > HNO₃ > HCOOH > H₂SO₄. Hydrochloric acid may provide 30–50% savings on the circulation time as compared to HNO₃ based on the rate of dissolution.

Proper chemical cleaning removes deposits from the inside of boiler tubes which improves the boiler heat rate, reduces tube failures and improves the stability of boiler chemistry. However, chemical cleaning is expensive. The need to chemically clean the boiler should be determined by the deposit loading of tube samples, not the amount of time since the last cleaning. Improving boiler and feed water chemistry and lay-up and start-up practices can extend the time between cleanings. Together, these techniques and practices also can save money and help reduce risk of forced shutdowns [8, 11].

The effect of different acids on the scale removal from heat exchanger are investigated in study [12]. Different concentrations of the acids resulting higher the concentration of acids higher the removal of the scale. The inhibition effect of different concentration the hexamine and glutamine were studied with weight loss method. The results show that inhibition efficiency increases by increasing the concentration of the inhibitors. Higher the time of dissolution higher will be the efficiency. Theoretical calculations result 2.5 M HCl solution with 0.80 grams of glutamine at 2.5 hr. time gives the best results of removal of scale.

Inhibited hydrochloric acid in strengths of 5 to 20% is very effective for removing calcium scale and iron oxide [13]. It can be used for removing scale consisting primarily of carbonates with lesser amounts of phosphates, sulfates, and silicates. This type of scale is typically found in a steam boiler system containing copper alloys that has been treated with a phosphate-based program. Depending on the specific descaling application, some of these ingredients can be omitted from the formulation. For example, diethylthiourea is not needed if there is no copper in the system. It should be noted that if diethylthiourea is used, the waste material should be treated as a hazardous waste. Where there is only carbonate scale to be removed, ammonium bifluoride, which is used to remove silica-based scales, may be omitted.

According to [14] cleaning agent for removing scale from the surface of internal heat exchangers contains in its composition 75% phosphoric acid solution, 31% hydrochloric acid solution, EDTA, glycol, glycerol and water. The selected individual components of the composition also provide surface protection against damage during the descaling process. The operating temperature and applying pressure according to the recommendations are 45–65°C and 2–6 bar, respectively. In order to increase the effectiveness of active agents, the flow of the preparation should be 25–50 dm³/min. The authors assume the possibility of repeated use of the mixture, which remains active until reaching pH = 3.5. This composition requires a high concentration of strong acid (hydrochloric acid). It does not contain any corrosion inhibitors, which would significantly reduce damage to cleaned surfaces, or substances with antimicrobial activity removing biofilms. Disadvantage of the solution use is the requirement of high temperature, which significantly increases the energy consumption of the cleaning process.

Patents [15, 16] proposed cleaning method with use of phosphoric acid. The chemical composition of the preparation was selected on the basis of laboratory tests. The main component is phosphoric acid containing 8–10% H₃PO₄. The addition of Na₂H₂P₂O₇ increases the dissolution rate and supports formation of complex compounds of salts sparingly soluble in phosphoric acid. Zinc oxide intensifies the dissolution of iron compounds that are part of the scale deposits. A 1:1 mixture of formalin and ammonium chloride acts as a corrosion inhibitor. The addition of formalin also prevents the formation of foams when dissolving carbonate deposits. Copper sulfate and zinc sulfate act as corrosion inhibitors and antimicrobial agents.

The proposed method enables non-invasive cleaning, prevents the formation of mineral and biological deposits in heating and cooling installations, does not cause damage to the surface of plates, pipes, valves and gaskets, reduces the risk of failure due to damage to the surface of the installation. The cleaning agent used is cheap, non-toxic and non-aggressive towards the materials used for apparatus, thermal devices and installations.

A characteristic feature of the preparation and the technology used is the high rate of boiler scale at room temperature with no foaming during dissolution. The product after full dissolution of scale deposits does not attack the metal surfaces from which heat exchangers are made.
The aim of this work is to present an innovative chemical method for cleaning heat exchangers and pipes using preparation DoroFos.

**Research method**

**Characteristics of the preparation and its use**

The analyzed method of cleaning is a chemical method of dissolving the boiler scale accumulated inside heat devices by means descaling concentrate contains phosphoric acid (V) at a concentration of 75 to 85% H₃PO₄, and a corrosion preventive agent selected from the group consisting of formalin, ammonium chloride, copper sulphate and zinc sulfate. The descaling composition DoroFos consists of a concentrate and water in the ratio of 1:7 up to 1:11, preferably 1:9 (v/v). It is an innovative, biodegradable preparation, in which, in addition to the main descaling component (phosphoric acid solution), there are corrosion inhibitors, anti-foam substances as well as anti-microbial substances. The enrichment of the composition with anti-microbial properties has been achieved by introducing copper and zinc ions into its composition. The base of the composition has anti-corrosive properties [9], which, combined with anti-microbial properties, make it intentional to use it in circulating water systems. The use of copper and zinc as preservatives in the circulating liquid allowed to obtain a simultaneous, constantly active biocidal activity against bacteria and algae. In this way, the product also limits the physiological activity of microorganisms and thus eliminates the growth of problematic biomass.

The chemical composition of the preparation was selected based on laboratory tests. The main ingredient is phosphoric acid, which at a concentration of 8–10% H₃PO₄ (about 6–7.5 P₂O₅) best dissolves scale deposits. The addition of Na₂H₂P₂O₇ sodium acid pyrophosphate increases the dissolution rate and facilitates the formation of complex compounds of insoluble or sparingly soluble salts in phosphoric acid. In turn, zinc oxide intensifies the dissolution of iron compounds contained in the boiler scale, and accelerates the rust removal of the metal surface. A mixture of 1:1 formalin and ammonium chloride as corrosion inhibitors. The addition of formalin at the same time prevents the formation of foams when dissolving carbonate deposits.

The preparation of the preparation is carried out by periodic method. The first stage of production consists in diluting the concentrated phosphoric acid (75% H₃PO₄) with water in the proportion of 1 part of concentrated preparation to 9 parts of water (by volume), which results in obtaining the working concentration of 10% H₃PO₄. The zinc oxide is then dissolved first; followed by acid sodium pyrophosphate, copper sulphate and zinc sulfate followed by the addition of formalin and ammonium chloride. As a result, a blue liquid is obtained.

The preparation is delivered to the place of operation in a liquid form with the help of specialized transport. It does not require additional preparation before cleaning. This transport is carried out in a standard horizontal tank with a capacity of 5 m³ (diameter 1.6 m), with a submersible pump installed, all placed on the trailer. This tank will also serve as a circulating tank during cleaning and a sewage tank from boiler scale treatment.

It has been shown that 1000 dm³ of DoroFos working solution dissolves about 50 kg of boiler scale (5000 dm³ of solution diluted with ca. 250 kg of boiler scale). However, because virtually every installation has a different composition of accretions, the above data may differ. Therefore, before each cleaning, it is necessary to carry out tests to dissolve deposits in the device.

The preparation of the cleaning technology includes taking samples from devices and performing analyzes of boiler scale deposits as well as performing the above-mentioned solubility tests. In addition, the potential consumption of the cleaning solution and the required rinse time is pre-estimated. In addition, the method of connecting to the devices, may sometimes require additional nozzles or it may need dismantling some devices.

The removal of boiler scale from thermal devices occurs as a result of dissolving it in a circulating DoroFos solution that is passed through the device. Circulation is forced by the circulation pump. The solution, after passing through the device, returns to the output tank forming a closed circuit. Such a system allows for multiple circulation of the solution and maximum use of all active ingredients in the preparation in the process.

**Results and discussion**

Three types of sediments were tested [17] from heat exchangers marked as K1, K2, and H. To determine the elemental composition of sediments, they were subjected to XRF tests. The results obtained are summarized in Table 1.

X-ray examinations (XRD) were performed to determine the phase composition of the sediments. The results of analyzes are presented in Fig. 1.
On the basis of the obtained results, it can be concluded that K1 precipitate is a carbonate stone, K2 a carbonate stone with iron compounds, and H a precipitate formed by iron compounds, which in most cases may be a derivative of corrosion processes of water supply and heating installations.

**Corrosion tests**

Corrosion laboratory tests of the preparation were carried out to determine the rate of corrosion of metals and metal alloys, protective properties of coatings, environmental impact on changes in mechanical properties of materials.

The tests are carried out on specially prepared samples, in natural liquids, industrial solutions or solutions prepared in the laboratory in accordance with the standard [18]. According to this standard, the apparatus used for testing in liquids and solutions should make it possible to maintain the assumed temperature. The samples must be completely immersed. The ratio of the volume of liquid or solution (in cm$^3$) to the surface of the test samples (in cm$^2$) should be 10:1. The total test time is determined depending on the corrosion rate. For example, for samples whose corrosion velocity at elevated temperature (calculated after 24 h) exceeds 0.3 mm/year, the testing time should be at least 168 h, and at a speed below 0.3 mm/year – at least 769 h. Tests of the preparation in accordance with the standard [19] used the weight method, which is the most popular method of tracking the progress of uniform corrosion. It results in determining the loss or increase in sample mass. Gravimetric determinations are also carried out on isolated (mechanically or chemically) layers of corrosion products, to determine their thickness. This method is particularly useful in the selection of materials for constructions. It allows for the expression of the rate of change of the cross-section of the metal structure due to the progress of corrosion and the assessment of the corrosion resistance group based on the scale of resistance [20, 21].

**Performing tests**

1. Before testing, samples of steel sheets should be cleaned from corrosion and degreased according to standard [19] and their areas should be measured and calculated.

2. Place the plates in a beaker and pour over the test preparation so that they are completely covered. The ratio of the volume of the tested liquid or solution (in cm$^3$) to the surface of the test samples (in cm$^2$) should be 10:1. Leave the system for 24 hours, noting the mass changes of samples every 4 h.
each time the plates must be rinsed with water and dried with tissue paper).

3. After the scheduled time has elapsed remove the plates from the beaker, rinse with water and dry with a tissue and weigh them.

Corrosion rate $V_c$ and the linear corrosion rate $V_p$ were calculated according to Eqs (1) and (2):

$$V_c = \frac{\Delta m}{S \cdot t},$$

where $V_c$ – corrosion rate [g m\(^{-2}\) day\(^{-1}\)], $\Delta m$ – weight loss [g], $t$ – duration of the process [day], $S$ – active surface of the sample [m\(^2\)];

$$V_p = \frac{365}{1000 \cdot d} V_c,$$

where $V_c$ – corrosion rate [g m\(^{-2}\) day\(^{-1}\)], $V_p$ – linear corrosion rate [mm year\(^{-1}\)], $d$ – specific gravity of material [g cm\(^{-3}\)] = 7.8.

The correlation of the corrosion rate over time was tested [22]. The Pearson linear correlation coefficient for all tests obtained was $-0.12$. This is a relatively low dependence on the corrosion rate on time. In individual samples (Fig. 2) for which measurements were made every 4 hours, the correlation coefficient reached values from $-0.49$ to $0.61$. As a result of regression analysis, the following results were obtained: intercept value: 27 and regression coefficients for time: $-0.022$, coefficient $R^2$ equals only 0.016 and $p$-value 0.49 (very high).

The product meets the requirements of the standard [23].

Waste from boiler scale treatment

After cleaning, the slurry remaining in the tank suitable for transport is transported to the producer. The slurry is treated there, which results in obtaining of filtrate and a filtration sediment.

The filtrate corresponds to the quality of technical water and is stored in a storage tank from which it is returned to the production of DoroFos. The filtration sediment is dried on trays, and after 24 hours its moisture reaches about 2%. After sieving, grinding and packing, it can be sold as a finished product used in production of fertilizers.

Comparative assessment of preparation DoroFos and preparation based on hydrochloric acid using the BATNEEC option methods

Two preparation used for chemical dissolution of boiler scale were compared. The first one is DoroFos containing phosphoric acid with proper inhibitors and complexors. The second one is the most widely used solvent a 5% hydrochloric acid solution HA with inhibitor and complexors. The BATNEEC (Best Available Technologies not Entailing Excessive Costs) method allowed assessing two basic elements. The first of them is the compliance of the tested technology with the BAT (Best Available Techniques) standard, containing solutions that guarantee a minimum of threats to the natural environment, with simultaneous economic profitability of production. The second is to ensure a balance between environmental benefits and costs (NEEC) [24, 25].

For the BATNEEC option evaluation for the evaluated two preparations DoroFos and HA, the option evaluations and the criteria for their evaluation are presented in Table 2. The assessed options were scored by four experts on a scale of 0 to 10 points within a given criterion. The sum of the average rating of criteria makes up the option rating [26]. The
ranking assessment indicate a 27.5% advantage of the DoroFos over 5% HCl (Table 4). This results mainly from the utilization and production of fertilizer components from waste from dissolution of boiler scale with DoroFos.

Table 3
Options, criteria for their evaluation and assessment of the various options of using boiler scale solvents DoroFos and 5% HCl.

<table>
<thead>
<tr>
<th>No</th>
<th>Options criteria</th>
<th>Option assessment</th>
<th>DoroFos</th>
<th>5% HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Consistency with the goals of sustainable development</td>
<td>7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Coherence with national and EU programs</td>
<td>8</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>The degree of adaptation to local conditions</td>
<td>7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Improving relations with consumers</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Legal permits required</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Technology availability</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Degree of difficulty and implementation time</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Investment costs</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Technology efficiency</td>
<td>8</td>
<td>7</td>
<td></td>
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<tr>
<td>10</td>
<td>Implementation risk</td>
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<td>8</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Product quality and stability</td>
<td>9</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Waste formation</td>
<td>10</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>By-products (waste) management</td>
<td>10</td>
<td>1</td>
<td></td>
</tr>
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<td>14</td>
<td>Substitution of natural resources with waste</td>
<td>10</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Ecological assessment of releases volume and quality</td>
<td>10</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Material consumption</td>
<td>8</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>The degree of modernity related to the world level</td>
<td>7</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Total score [point]</td>
<td>146</td>
<td>106</td>
<td></td>
</tr>
</tbody>
</table>

Table 4
Ranking of the assessment of the various options of using boiler scale solvents DoRofos and 5% HCl with BATNEEC method.

<table>
<thead>
<tr>
<th>Options</th>
<th>Score [points]</th>
<th>Maximum M</th>
<th>Reached R</th>
<th>% [R/M]</th>
</tr>
</thead>
<tbody>
<tr>
<td>DoroFos</td>
<td>170</td>
<td>146</td>
<td>85.9</td>
<td></td>
</tr>
<tr>
<td>5% HCl</td>
<td>170</td>
<td>106</td>
<td>62.4</td>
<td></td>
</tr>
</tbody>
</table>

Conclusions

Presented chemical method of boiler descaling effectively removes deposits, in particular from thermal devices.

The corrosion inhibitors used are adsorbed on the protected surface. As a result, corrosion processes are slowed down or completely inhibited. Due to the presence of copper and oxygen ions, it is possible to create a passive oxide layer that provides effective protection against corrosion. The use of copper and zinc also prevents microbial corrosion in a successful way, as the salts and oxides of these metals are characterized by effective antimicrobial activity.

The prepared concentrate also provides a high degree of protection against electrochemical corrosion, regulating the pH level, effective operation in acidic and alkaline environments, preventing contamination, microbial corrosion, galvanic corrosion and creating a protective layer as well as durability. The composition simultaneously protects carbon steel, stainless steel, zinc, cast iron, aluminum alloys, brass, copper, tin and other metals.

The proposed method of boiler scale removal is waste-free due to the slurry obtained from dissolving boiler scale can be, after appropriate processing, processed into product used in production of fertilizers.

References


