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Reagent approach for silicate deposits prevention in waste heat boilers

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Abstract. New reagent composition with optimal phosphate:thermal polymer ratio has been developed and studied for steam-and-condensate channel protection and its corrosion prevention as well as for on-line washing to remove old silicate deposits formations. Optimal dosage and water-chemistry conditions for a medium pressure steam boiler with specified quality of feed water have been selected. The causes of silicate deposits in medium pressure waste-heat boiler have been analyzed. The reagent efficiency has been evaluated while industrial applications.

Radiant surface of steam boilers are heated actively with flare system causing high local heating. So, even in case of a short decrease of heat-transfer between the boiler's wall and boiling water, the temperature of a steam-generating tube will exceed visibly the temperature of boiling water. The deposits formed on internal surfaces though being of low thickness but due to their low heat-conductivity can cause blisters, air leakage and explosions of water tubes enduring high heat-stress as a result of higher thermal resistance and significant local metal overheat. Besides, scale precipitation from the boiler unit can get into turbine together with steam, causing clogging of nozzle and paddle channels, making narrower their cross-section and resulting in pressure drop of the disks and diaphragm cascades. All these things cause low efficiency of the turbine, even the scale clogging being not severe.

Scale precipitation generally occurs due to deterioration of water environment of the unit, *i.e.* inefficient demineralization, low-quality condensate purification, condenser leakage and presence of non-boiled water as a result, omissions in boiler feed water inhibition *etc.* [1-2]

The most spread scales found in boilers and turbine flow channels are sulphates, calcium and magnesium carbonates, ferric & copper oxides, alumina and silicon oxide, the silicate deposits being the most challenging due to their low solubility and thermal conductivity. The scales of this kind are difficult to remove by chemical washing, the mechanical approach being usually in use. The most effective environment for silicate deposits cleaning is hydrofluoric acid, but its application is usually avoided by the reason of toxic properties. So, it was a challenge to find a solution for the "on-line" scale washing.

Silicate sediments found in a boiler have heat conductivity 50-500 times lower comparing to steel conductivity. Consequently, this scale sometimes promotes a 100 °C and even higher overheat of boiler' structure, so ductile properties of metal are affected adversely. Operating the boilers with scale being present leads to inevitable economic losses driven by fuel rate increase. Depending on deposits type, this unreasonable losses cause higher fuel consumption, making practically a several percentage increase per 1 mm of deposits (acc. to some literature data, this fuel increase amounts to 8-10% per 1



mm of deposits) due to higher heat losses along with exit gases. Table 1 gives data on thermal conductivity of some alloys and the most spread deposits [3-4].

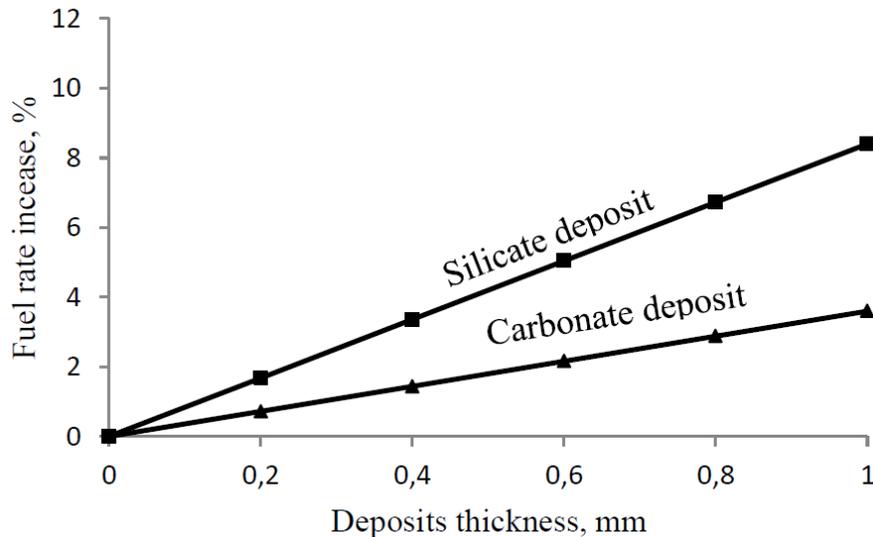


Fig. 1 – Comparative Analysis of Silicate & Carbonate Deposits.

Table 1. Thermal Conductivity Factor

Name	Thermal Conductivity Factor, Wt/(m·degree)	Note
Carbon Steel	48.0	-
12X18H9T	14.5	-
Brass	92-134	-
Hematite Fe ₂ O ₃ , porosity 0%	6.3	Scale is formed in high temperate and low pH conditions
Magnetite Fe ₃ O ₄ , porosity 0%	3.5	Main part of protection layer
Calcium Sulphate (gypsum) CaSO ₄ ·2H ₂ O	1.6	Firm and easy sticking scale
Calcium Carbonate CaCO ₃	1.2	Scale (the most spread composition)
Silicate scale (xonotlite): 5CaO·5SiO ₂ ·H ₂ O	0.8	Very firm scale

Deposits being formed in boilers and heated with waste nitrous gases employed by nitrogen fertilizer industries, can cause lower capacity of the unit or unscheduled shut-down meaning reduce of the principal product and a failure of a production plan.

Thus, one nitric acid factory faced some problems in the drums of nitrous-gases heat-waste boilers (KN 80/40) caused by lower heat removal related to scale precipitations on a heat-transfer surface.

Inspection of drums' internals in waste-heat boiler (boiler's separating drums of nitric acid Workshop KN-80/40) has detected both drums' and cyclones' inner surfaces of salt compartment to be covered with grey and beige deposits of 1 cm thickness; white deposits have been found in clean compartments of the boiler, predominantly on the surfaces below the line of liquid and vapour phase separation; as for the grids in clean compartments, 3 mm- thick deposits of grey and beige colour have been detected (Figure 2).

According to performed examinations, the scale has the following composition: silicates, being the main deposit and amounting to 33.4-50.0%; magnesium oxide - 2.9-36.9%; calcium oxide – 2.2-43.8%; iron oxide – 1.2 – 4.4% (Table 2).



Figure 2 –Picture of Waste-Heat Boiler KN-80/40 (Salt Compartment, 2nd Unit) at Nitric Acid Workshop

Table 2 – Analysis of Scale Samples

Sampling Point	Phase Composition (Matrix)	Main Chemical Components
Unit 1 Salt Compartment	$\text{Ca}_6\text{Si}_6\text{O}17(\text{OH})_2$	SiO_2 – 50% CaO – 43.8% MgO- 2.9%
Unit 1 Clean Compartment	$\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ $\text{Ca}_6\text{Si}_6\text{O}17(\text{OH})_2$ - admixture Fe_2O_3 – admixture	SiO_2 – 30.9% CaO – 4.9% MgO- 29.3% Fe_2O_3 – 8.6%
Unit 2 Salt Compartment	$\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$ $\text{Ca}_6\text{Si}_6\text{O}17(\text{OH})_2$ - примесь Fe_2O_3 – admixture	SiO_2 – 33.4% CaO – 6.8% MgO- 30.4% Fe_2O_3 – 3.6%
Unit 2 Clean Compartment	$\text{Ca}_6\text{Si}_6\text{O}17(\text{OH})_2$ $\text{Mg}_3(\text{Si}_2\text{O}_5)(\text{OH})_4$	SiO_2 – 42% CaO – 34.7% MgO- 20.7% Fe_2O_3 – 1.4%

The case being studied, it was found out that the main cause for the deposits of such kind was employment of partially demineralized (instead of completely demineralized) water as a feed water for the boiler. This water was determined to contain significant amount of silicon compounds entering the process along with natural water as well as non-reactive silicon. Sediments of such kind can be prevented by using demineralized water for feeding the boiler.

Due to inefficiency of the demineralizing unit failing to feed waste-heat boilers with absolutely minerals-free water, it was offered to use reagent complex, *i.e.* sediments dispersants, to minimize the deposits in the drums of nitrous gases waste-heat boilers.

A great number of laboratory experiments was carried out, the broad range of concentration and ratios of alkaline phosphates (ortho-, polyphosphates) and water soluble polymers were studied. The optimal phosphate:thermal polymer ratio and a new complex reagent MF-RSB-35 were developed as a result.

The aim of this work is to study AquaComplex MF-RSB-35 complex reagent for feed water treatment to improve boilers efficiency and reliability, and to minimize corrosion and/or scale and silicon sediments troubles. Optimal reagent dosage and chemistry conditions for medium pressure steam boiler fed with water of specified quality were determined by this study.

The reagent AquaComplex MF-RSB-35 is a balanced mixture of alkaline phosphates and

polymeric dispersants inhibiting scale precipitation and corrosion inside a boiler. MF-RSB-35 contains special dispersing polymer to reduce accumulation of silica and sodium silicate. Phosphates being a part of the composition are included to inhibit boiler corrosion and scales precipitation. As for the water-soluble polymer incorporated into the composition, it represents a carboxylic copolymer namely, a non-ionic thermal polymer with molecular weight of 5000 and the following structural formula (Figure 3).

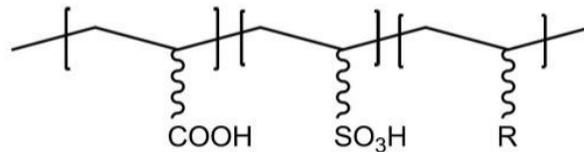


Figure 3 – Thermal Polymer Structural Formula

The performance range of the reagent under study is assumed to be within 10-100 mg/dm³ depending on feed water quality and the boiler operating conditions. To monitor the dependency of major feed water specifications on reagent dosing rate correctly, it was decided to keep the purging volume the same. To achieve maximum “on-line” purging of the boiler, it was settled to perform pilot testing at maximum possible purging, *i.e.* 6 % of the units capacity. Besides, a maximum concentration was added while initial feeding, namely 100 mg/dm³, each further dosage making up 10 mg/dm³ proportionally to the feed water volume.

As it is shown in Fig. 4, pH values of feed and boiler water are relatively stable while treatment procedure, although being along the lower limit and slightly below target values.

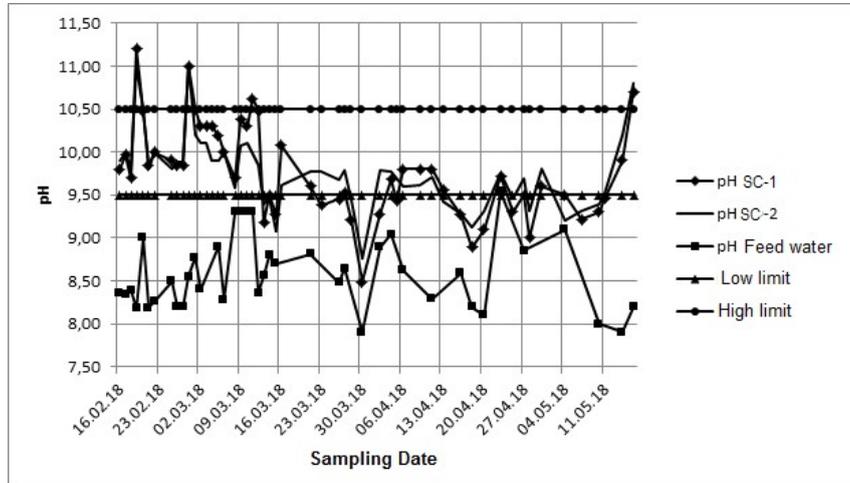


Figure 4 – Feed and Boiler Water pH Values of while Testing

The level of orthophosphate within the boiler water is a main criterion characterizing the concentration of the inhibitor. Water soluble polymer is contained in a certain ratio towards orthophosphate, so knowing phosphates concentration, the content of polymer in a boiler water can be calculated accordingly. As it is shown by the diagram of Fig. 5, this value was above the normal getting stable within specification limits afterwards. As for the reagent dosage, it was adjusted depending on boiler water exponents during the test.

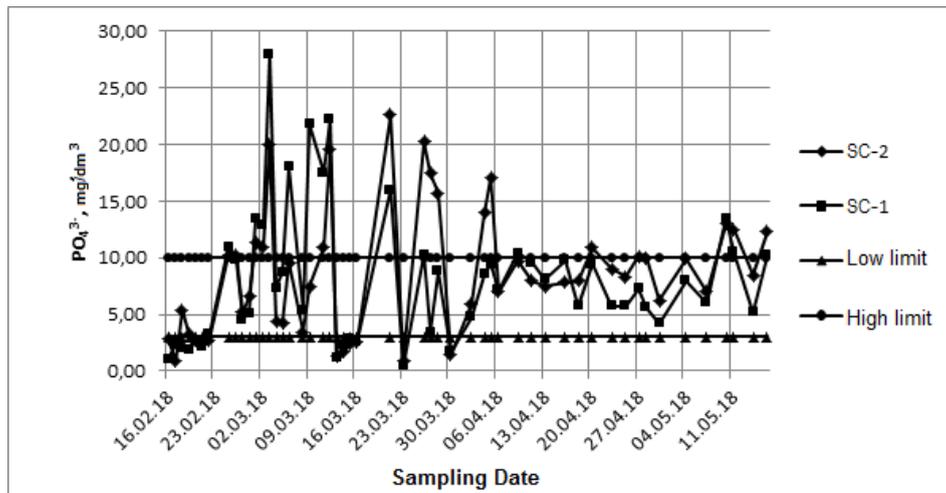


Figure 5 – Orthophosphate Fluctuations in Feed and Boiler Water while Testing.

Figure 6 contains diagram of silicates fluctuations in feed and boiler water (Salt Compartments 1 and 2). The silicate content in feed water varies within 3.5-5.5 mg/dm^3 , being practically 180-800 mg/dm^3 in boiler water which is two orders of magnitude higher. The second salt compartment (SC-2) has the concentration several times higher, comparing to the first one (SC-1). As for the boiler's vaporization coefficient, it is about 10-20 (judging by the iron salts contained in feed and boiler water). Consequently, the silicate content in purging boiler water is to be within 35-110 mg/dm^3 at relevant vaporization coefficient. Taking into consideration much higher silicate concentrations present in boiler water (not proportional to the mentioned vaporization coefficient), we supposed these silicates come from the older boiler deposits while washing. Higher silicates content in boiler purging water at enhanced purging is an evident of scale dissolving and deposits removal from the boiler. This idea is proved by the fact of better heat removal, the temperature difference showed a 6-12°C increase thus, reaching the normal values. The test being completed, the equipment was opened and inspected, and we didn't find any sediments that had been previously present.

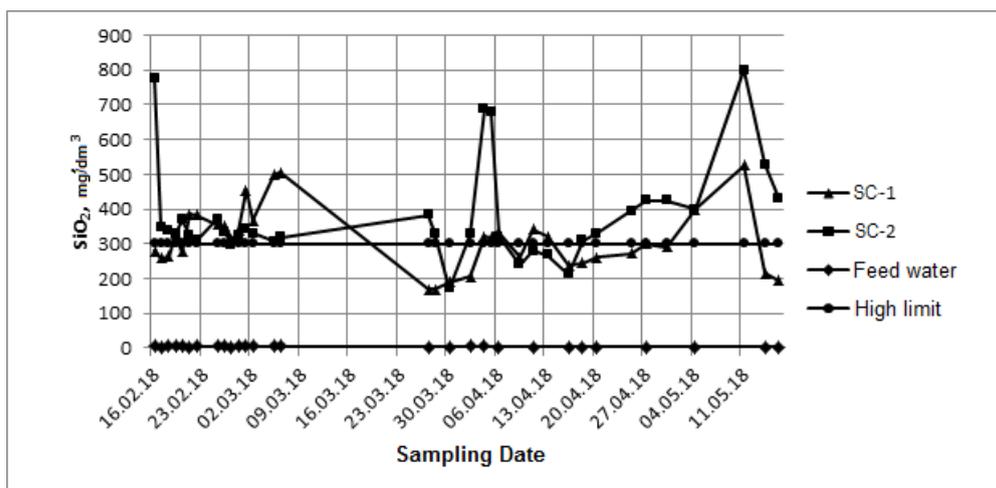


Figure 6 – Silicates Fluctuations in Feed and Boiler Water while Testing.

Basing on the quality indices of water in salt compartment, we decreased the reagent supply while washing. Actually, the optimal reagent content was 2.5-3 times lower comparing to theoretically

calculated dosage. It should be noticed, that the more old deposits were removed, the less reagent was needed. So, according to our speculations, the efficient performance dosage for an operated boiler following to its cleaning is 3 mg/dm^3 , as for orthophosphate concentration in salts compartments, it makes up $5\text{-}6 \text{ mg/dm}^3$.

Speaking about the dissolving mechanism of old deposits, it is probably governed by the carboxylic groups being present in the polymer and preventing the formation of water-insoluble compounds of calcium phosphates and iron phosphates. The sulfonic acid group supports dissolving of the existing silicate sediments and inhibits formation of new crystals, and non-ionic groups facilitate steric repulsion of the solids being already formed. Nevertheless, the chemistry of the reaction needs further detailed study and some additional research.

Thus, the minimum level of iron-based sediments in medium and high pressure boilers is achieved by the special polymers making a part of the inhibitor, as well as dispersing and suspending oxides, that can be easily removed via draining. The polymers that control deposits formation, are adsorbed on metal oxide entities, changing the growth and surface charge of the crystal, and alkaline phosphates diminish corrosion activity of boiler water.

Employment of reagent complex MF-RSB-35 for internal boiler water treatment provides sediments control and their minimization reduces the areas of hydroxide concentrations, thus ensuring the heat-exchange at maximal efficiency and eliminating the problems of tubes overheating enduring high temperature impact.

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