Study of the Efficiency of a New Reagent Composition Hydro-Phos to Decrease Water Hardness and Scale Formation

I. I. BRAZOVSKIY, G. I. KATIBNIKOVA, I. A. SALNIKOVA and V. V. SAMOYLENKO

United Institute of Energetic and Nucler Research – Sosny, Belarus National Academy of Sciences, Ul. Akademika A. K. Krasina 99, Minsk 220109 (Belarus)

E-mail: radchem@tut.by

(Received December 12, 2004; in revised form March 1, 2005)

Abstract

Investigations have been conducted on the development of the "Hydro-Phos" reagent composition, which prevents formation of scale in the boilers of heat power units and in the networks of heat and water supply. Chemical, technological, and service properties of the "Hydro-Phos" reagent composition have been studied. It has been demonstrated that the employment of this composition ensures an effective protection against corrosion and scale formation on the internal walls of heating elements; water hardness tangibly drops, and previously accumulated corrosion products dissolve.

INTRODUCTION

The quality of circulating water is one of the major factors, which have an influence on the reliability and efficiency of functioning of the boiler and heat exchange equipment in the district water supply systems. Growth of a content of dissolved and suspended particles in water causes their deposition on a heating surface of the heat extraction equipment, a decrease in the efficiency of heat transfer and in the efficiency factor of the heat exchange equipment, and a significantly excessive demand of combustible.

The application advisability of chemical admixtures as inhibitors of scale (antiscale agents), the use of which considerably simplifies the maintenance of heat extraction systems and raises their reliability in general, is now a received fact. Their distinctive feature lies in the fact that even trace contents (2–5 mg/l) of them are capable to stabilise water solutions, preventing crystallization of sparingly soluble compounds. By now, several organic antiscale agents have been produced that contain anionic, cationic, or nonionic active groups like sulphonic, hydroxyl, phosphonic, and the similar ones [1–4].

Currently Danish reagent composition Hydro-X [5] has found an increased use in Russia for the most widespread types of steam and water-heating boilers in carrying out the additional water reclamation. With its help, the necessary correctional treatment of water is performed for steam and water-heating boilers up to 3.9 MPa in pressure and also for the closed systems of heat supply. This prevents the emergence of scaliness and metal corrosion.

Development and promoting of the new lower-cost highly effective reagent compositions, analogues to Hydro-X, is an urgent and economically useful task.

Meanwhile, a great quantity of various factors, which have an influence on the efficiency of action of antiscale agents, as well as a low level of knowledge of the mechanism

do not permit to give an unambiguous theoretical estimate of the efficiency of new reagent composition.

The purpose of the present work is to develop a new inhibitor for crystallization of salts and study its efficiency in experiment.

EXPERIMENTAL

The experimental research of the efficiency of action of the worked out reagent composition that prevents a scale formation in the intensive vaporization zones was conducted at the laboratory stand, which models the work of heat exchange systems with evaporative and condensation loops and with natural circulation.

When carrying out the laboratory tests, a model solution was used, which contained Ca^{2+}, Na^{+}, Cl^{-}, and SO_4^{2-} ions. This system has been chosen based on the following reasons:

– Residual concentration of Ca^{2+} ions in the solution in the case of using $CaSO_4$ may be as high as 16.2 mg-eq/l, which makes it possible to provide a mass of depositions that is necessary to perform the gravimetric analysis;

– Crystallization rate depends on supersaturation of the solution;

– The slightly soluble material, namely, calcium sulphate being formed upon mixing of $CaCl_2$ and $NaSO_4$ solutions, is prone to form supersaturated solutions.

Thus the system makes it possible to maintain a preset Ca^{2+} ion concentration, which determines the required water hardness for a long time.

The experiment involved the registration of the following parameters: time of a steam–and–water mixture passing through, a temperature, pressure, medium pH, total hardness of a solution, and an increment of mass of the witness samples that were arranged in the various places of the laboratory setup.

Each experiment was followed by qualitative and quantitative analyses of the hardness salts that had deposited on the check test pieces, conditions of heat-transmitting surfaces of the experimental site were also checked.

Check test pieces were celled meshes from stainless steel.

RESULTS AND DISCUSSION

Resulting from the performed analysis of the chemical ways and reagents of water reclamation that are now used in industrial boiler and thermal networks, a new highly effective reagent composition Hydro-Phos has been developed, which prevents formation of scaliness on the internal heat-transmitting surfaces and on the network water channels. When working out the reagent, the attention was given not only to technical features of composition, but also to its technological, economic, and to ecological indices.

Hydro-Phos constitutes a multicomponent, balanced physicochemical system, wherein the components each are of considerable importance, as is their content.

Thus, sodium hydroxide reduces water hardness (at the expense of precipitation of hardness salts), neutralizes the dissolved carbon dioxide, adjusts the water pH, and preserves a magnetite layer. In addition, the presence of NaOH in the feed water is essential not only for a more effective treatment of carbonate hardness salts due to the reactions

$$Ca(HCO_3)_2 + 2NaOH \rightarrow CaCO_3\downarrow + H_2O + Na_2CO_3$$

$$Mg(HCO_3)_2 + 2NaOH \rightarrow MgCO_3\downarrow + H_2O + Na_2CO_3$$

but mainly for precipitation of sulphate and chloride salts to slimes:

$$MgCl_2 + 2NaOH \rightarrow Mg(OH)_2\downarrow + 2NaCl$$

$$MgSO_4 + 2NaOH \rightarrow Mg(OH)_2\downarrow + Na_2SO_4$$

When calculating the dosage of caustic soda, one must keep in mind that for a more complete precipitation of magnesium salts it is essential that it be introduced into a feed water in some excess, thus raising the alkalinity of water pH 8.5–10.0.

Sodium tripolyphosphate retards the formation of scalinesses, inhibits the crystal growth of the hardness salts being formed, and protects the surface from corrosion.

Owing to their adsorptive and complexing properties, tripolyphosphates exert a pronounced effect on colloid systems. They are known as deflocculating, peptizating, dispersing, solubilizating, and stabilising agents [5, 6]. The discussions as to the advantage of one or the other of phosphates occurred in the

literature many times. They were caused most often by the fact that the sequestrating capacity of the same compound can vary according to temperature, pH, the nature of cation, presence of extraneous ions, solutes, etc. Advantage of sodium polyphosphate, besides a high performance, lies in the fact that it is a good combination with other admixtures. In addition, technical sodium tripolyphosphate is 3.5 times lower in cost than Graham's salts (hexametaphosphate), is much more quickly dissolvable, and is to a lesser degree prone to sticking. Treatment of water with tripolyphosphates typically pursues several objectives: preventing precipitation of hardness salts, decreasing the corrosion aggressiveness of water, and keeping ions of iron and manganese in the solution. Besides stabilization and inhibition of corrosion, a clearing or decreasing of the scaliness layer on the heat exchange surfaces, and a removal or loosening of an aged scaliness followed by its removal take place.

Sodium alginate accelerates a process of precipitation of hardness salts and prevents scaliness formation.

Starch raises the rate of flakes formation of coagulated suspension.

Polyacrylamide-gel forms spatial mesh-like flocculation structures from the particles of hardness salts, inhibits a process of scaliness formation and growth of hardness salt crystals.

Polyethylene glycol (PEG-400) prevents froth formation and moisture carry-over.

Application of high-molecular flocculants makes possible a sharp accelerating of formation and precipitation of flakes of coagulated suspension. The flocculants, which are used in boiler-water conditioning, constitute the natural or synthetic water-soluble and linear polymers of anionic, cationic, amphoteric, and nonionic types. Alginate-containing flocculants are produced by alkali treatment of seaweeds and partially are applied for water purification [4]. Synthetic flocculants, specifically, sodium polyacrylate, polyacrylamides, and their copolymers, received a more widespread application. This is associated with their much better flocculation properties and less expenses for their production. Flocculation during the processes of boiler-water conditioning is considered as "a cross-linking of microflakes and their integration into larger and heavier aggregates (flocculas)" [2].

Hydro-Phos represents an almost uncoloured odourless liquid of a density of 1.12 g/cm^3. It presents no danger and involves no special handling and storage procedures; it is easily dosed with water, and it does not lose its properties upon a long-term storage.

The performed laboratory investigations have demonstrated that Hydro-Phos provides an effective protection against corrosion and formation of scaliness on the internal walls of heating elements and provides in their bulk formation of the fine suspension that is readily removed during the nominal blowdowns of boiler units. In addition, it is an effective water softener and gradually removes aged corrosion products, which have been accumulated before it is applied.

For example, upon circulation of a steam-and-water mixture through a working site of a laboratory setup (the simulator of a water-heating boiler) with the flow rate being 20 l/h, 0.04 g of hardness salts have precipitated in a witness sample during 96 h with a preset water hardness being equal to 8.95 mg-eq/l. Qualitative Ca^{2+}, Fe^{2+}, Fe^{3+}, OH^-, CO_3^{2-} and SO_4^{2-} ion determination have been made in depositions. Water hardness changed within the limits of 8.95–10.2 mg-eq/l.

It is obvious, that depositions consist of corrosion products of the heater material (steel) exposed to Ca^{2+} and Ca^{2-} ions.

Addition of Danish reagent composition Hydro-X (a dosage of 1–2 ml/l) into a model solution reduced water hardness to 3.9 mg-eq/l; alkalinity of the solution varied within the pH range 9.7–8.9. In the bulk, formation of a fine-dispersed crystalline solid phase was evidenced, which was compacted later on. These particles were freely circulating within the working line and were collecting step-by-step near a mechanical filter. The mass of depositions on the reference witness sample comprised 0.02 g during 96 h.

Hydro-Phos dosing in the system (1–2 ml/l) allowed maintaining the quality of water with the following indices: total hardness of 2.9 mg-eq/l, carbonate hardness of 2.1 mg-eq/l and pH 10.8.

The mass of depositions on the reference witness sample 96 h later since the beginning of Hydro-Phos dosing was equal to 0.0157 g that is

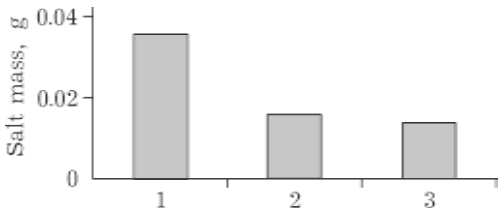

Fig. 1. Precipitation of hardness salts on the witness samples with the time of circulation of steam-and-water mixture for 96 h: *1* – with no admixtures, *2* – using Hydro-X, *3* – using Hydro-Phos.

almost an order of magnitude higher than without corrosion inhibitor. As may be seen from the data acquired (Fig. 1), Hydro-Phos competes well in its efficiency with Hydro-X import analogue, which is widely applied in Europe.

The developed Hydro-Phos reagent composition is highly effective salt formation inhibitor and water softener. In addition, the previously accumulated corrosion products are gradually removed with its application. Reagent composition is multi-purpose and it can be used for purification of water with various impurities including iron salts.

Under the effect of Hydro-Phos, the scaliness separates from walls and transforms to a fine-dispersed suspension (slimes), which circulates in the system presenting no problems in the work of the equipment and which can be easily removed upon regular blowdowns of boilers and filter washing.

The basis for the mechanism of action of the Hydro-Phos reagent composition is the processes, by which the sludge-forming cations are partially fixed into water-soluble complexes and are partially precipitated as slimes of sparingly soluble Ca and Mg salts. Organic components play a large part in its action. Although their quantity is minimal, their active reaction surface is reasonably great owing to deep dispergation. Large molecular weight of organic components provides a physical effect of attracting the water contaminant molecules, which makes it possible to collect and to concentrate the molecules responsible for hardness, specifically, salts of iron, of calcium, and of silicon acid.

CONCLUSIONS

The completed laboratory investigations of water treatment under a heat extraction regime testify that the Hydro-Phos reagent composition is an effective inhibitor of salt formation on the internal surfaces of the heat exchange equipment and of the elements of the network water channels. Upon little addition of Hydro-Phos (less than 0.5–1 l/m^3 of water) into the feed water, formation of a fine-dispersed suspension (slimes) was evidenced, which circulates in the system presenting no problems in the work of equipment and which can be easily removed upon regular blowdowns of boilers and upon washing or clearing the filters.

Hydro-Phos is the ready-to-use solution, which appears as an opalescent colourless liquid with a little deposit, the liquid being prone to easy homogenisation upon stirring. It presents no fire hazard and needs no special handling and storage procedures; it is easily dosed with water. The solution composition is stable and no separation of liquid occurs upon a long-term storage.

The advantages of this product are as follows:

– Simplicity and efficiency of chemical boiler-water conditioning;

– It is available to a consumer as a ready-to-use product;

– It can be added to water in amounts that are an order of magnitude less as compared to traditional methods of water treatment with active chemical compounds;

– Ecological safety, since it contains no toxic components;

– It neutralizes oxygen and passivates metal forming phosphate film.

Application of the new reagent composition Hydro-Phos makes it possible to raise considerably the economic efficiency of water-, heat-supplying systems, increasing smoothness of operations and prolonging useful life of the equipment.

REFERENCES

1 T. Kh. Margulova, Primeneniye kompleksonov v energetike, Energoatomizdat, Moscow, 1986, 280.
2 A. K. Zapolskiy, Koagulyanty i flokulyanty v protsessakh ochistki vody, Khimiya, Leningrad, 1987, p. 230.
3 E. M. Marchenko, A. B. Permyakov, *Energosberezheniye i Vodopodgotovka*, 3 (2003) 87.
4 E. D. Babenko, Ochistka vody koagulyantami, Nauka, Moscow, 1977, p. 205.
5 Ingibitory otlozheniy neorganicheskikh soley (Review Information), Energiya, Moscow, 1978, p. 44.
6 L. G. Vasina, O. V. Guseva, *Teploenergetika*, 7 (1999) 35.