Technical paper

The Influence of Physico – chemical Parameters on Water Scale Precipitation on Washing Machines´ Heaters

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Dedicated to the memory of professor Vojko Ozim

Abstract

The paper presents the results of analysis of physico – chemical parameters´ influence on the intensity of water scale precipitation on washing machines´ heaters. Washing machines of the same producer were, to this end, modified to an endless cycle of washing with the same amount of cotton fabric at the same conditions. On the basis of various experiments it was determined that water hardness, the amount of exceeded carbon dioxide, water turbulence around the heater, the amount of cotton fibres in water exceeded from fabrics, and heater specific heat strength have the key role in water scale building up in washing machines´ heaters.

Keywords: Water scale, calcium carbonate, washing machine, electrical heater

1. Introduction

Water, the most important and most widespread substance, comprises approximately 70% of entire Earth surface and does not exist in nature in pure chemical form. Rainwater is the cleanest and contains dissolved gases and impurities from the atmosphere such as O_2, N_2, CO_2, NH_3, SO_2, SO_3 and dusty particles.[1]

Ground and underground waters are in contact with rocky base from which inorganic salts dissolve, which are most often $CaCO_3$, $MgCO_3$, sulphates, nitrates and chlorides of calcium and also magnesium.[2]

The concept of water hardness occurs due to different inorganic salts secretions, which are composed of earth – alkaline metal ions. Ca^{2+} and Mg^{2+} concentration in water are usually much larger than that of other ions of the second group of periodic system; therefore, above mentioned elements most often present water hardness.[3]

Water from rivers and other sources is rich in mineral substances that precipitate in the form of water scale in water supply systems and cause large technological and economic problems, such as reduction or whole pipes blockage, larger energy consumption, frequent maintenance works and often replacement of expensive parts of devices.

Energy consumption increases due to the scale's thermal conductivity being extraordinary small. For instance, at 1 mm water scale layer, energy consumption is larger for 15%, and at 7 mm for 40%.

According to one of the world's most important thinking on how to use energy most efficiently it is reasonable to search for the solution of how to reduce the building up of water scale.[4, 5, 6]

A lot of chemical methods for scale prevention are known (cation exchange, acid addition, demineralisation methods); however, these methods are useless for the systems where water should not be chemically treated.[7]

In such cases, different physical methods for scale prevention are used. Examples of those are magnetic water treatment,[8,9] electrical methods,[10] and ultrasonic methods;[11] then again, these are still not investigated completely.

2. Water Composition and Scale Precipitation

Scale deposits are mainly composed of calcium carbonate. In natural waters, calcium is present in ionic form Ca^{2+}. Ca^{2+} is transferred to water as a result of chemical decomposition of calcareous minerals. Ca^{2+} and CO_3^{2-} ions are always present in natural water. CO_2 from the air is dissolving in water, where a weak carbonic acid is formed.[12]

$$CO_2 + H_2O \leftrightarrow H_2CO_3 \quad (1)$$

Formed acid then dissociates in two steps:

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \quad (2)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \quad (3)$$

Carbonate ions react with Ca^{2+} ions and a very slightly soluble calcium carbonate precipitates, according to the equation:

$$Ca(HCO_3)_{2(aq)} \Leftrightarrow CaCO_{3(s)} + CO_{2(g)} + H_2O \quad (4)$$

If we increase the concentration of CO_2 in balance (4), the balance will be moved to the left, which means that $CaCO_3$ will dissolve and pH value will increase. Vice versa, by feeding the alkalis to the system, the concentration of H^+ reduces, which means that balance (2) and (3) will move to the right, more CO_3^{2-} ions will evolve and because of this more solid $CaCO_3$ will precipitate.

$CaCO_3$ starts to precipitate when the concentration of Ca^{2+} ions is larger from the equilibrium. At certain point in time, at specific T and pH, the solution is oversaturated. In carbonate balance Ca^{2+}, CO_3^{2-}, H^+, OH^- in HCO_3^- ions are present.

Conditional upon the electro neutrality of the solution and upon the charge of all present cations being equal to all present anions, the following relationship can be written:

$$2 \cdot c_{Ca^{2+}} + c_{H^+} = 2 \cdot c_{CO_3^{2-}} + c_{HCO_3^-} + c_{OH^-} \quad (5)$$

Considering equations (2), (3) and (5), the relationship for Ca^{2+} concentration in dependence of pH can be written:

$$c_{Ca^{2+}} = \frac{K_w - c^2_{H^+} + \sqrt{(c^2_{H^+} - K_W)^2 + 8K_s \cdot c^2_{H^+} \cdot (2 + \frac{c_{H^+}}{K_2})}}{4c_{H^+}} \quad (6)$$

The relationship is graphically presented in figure 1, from where it is seen that $CaCO_3$ solubility changed with changed temperature. When pH < 9, the solubility of $CaCO_3$ decreases with increased pH value, and a hard $CaCO_3$ is formed. At certain value of pH, the solubility starts increasing, because CO_3^{2-} ions are being formed.

If we make a vice versa analysis, we determine that in range pH < 9 solubility decreases (2) with increased temperature. Majority of natural waters are in this range. When pH > 9, the $CaCO_3$ solubility increases with increased temperature.

Diagram (figure1) is valid for ideal solutions, presuming the infinitive dilution and a solution without addition.

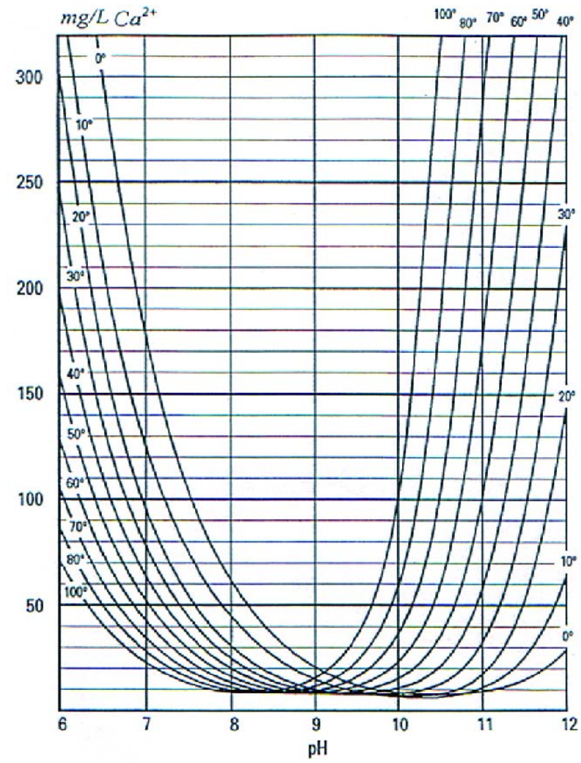


Figure 1. $CaCO_3$ solubility in ideal solution as a function of pH at certain temperature[12]

The shape of the diagram for real solutions is a bit different, because of ions interactions, what is considered with ionic strength.

2. 1. Crystal Structures of Calcium Carbonate

The most frequent component of water scale is calcium carbonate, which precipitates in three different forms:

- calcite (rhombohedra structure),
- aragonite (orthorhombic structure),
- vaterit.

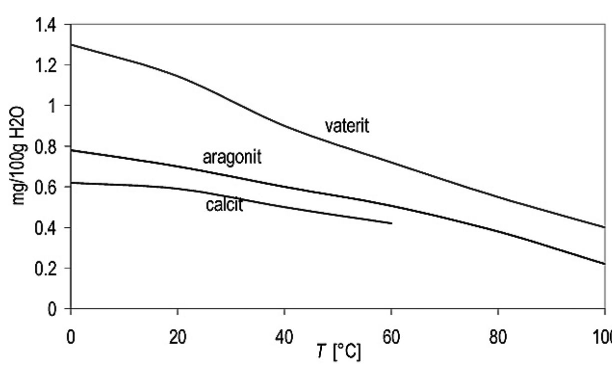


Figure 2. Solubility of different crystal forms of calcium carbonate

Their stability is falling according to the listed order.[13] Very often aragonite precipitates first, more rarely vaterit, which then crystallises into most stable calcite.[14] Figure 2 presents the solubility of individual calcium carbonate forms in dependence of temperature.

Carbonate group fits more into aragonite than into calcite network, which is why aragonite is denser (2.93 g/cm^3) as calcite (2.71 g/cm^3). In aragonite Ca^{2+} ion is surrounded with nine oxygen ions, but in calcite only with six. Although aragonite structure is denser, the cation places in aragonite are wider, therefore calcium ions are more distant from oxygen, the bond is weaker and the structure is thermodynamically less favourable. Other than that, aragonite forms needle crystal and the structure is bitter.

Additions often impede calcite growth and indirectly allow development of a less stable phase. Bivalent ions, which can precipitate in calcite structure, impede the calcite growth, for instance the presence of Mg^{2+} ions essentially reduces calcite precipitation. Natural vaterit rarely occurs as sediment due to demanding conditions of secretion and high instability.

Vaterit can be found at technological parboiling. It has the same crystal structure as aragonite, only the places of Ca^{2+} and CO_3^{2-} are exchanged. It has the lowest density (2.6 g/cm^3) and round crystals. The presence of magnesium ions is interfering with its crystallization into calcite.

3. Experiments

With the view of investigating the phenomena of scale formation, the causes of intensity of scale precipitation on washing machine heaters at different operating conditions were examined.

Chemical analysis of tap water used for experiments is presented in table 1.

Crucial parameters for the conducted experiments were water hardness and the amount of exceeded carbon dioxide.

The calculation of exceeded CO_2 value has shown that the concentration of dissolved carbon dioxide is smaller than equilibrium value, which means that water was already oversaturated at room temperature and that is why precipitation of scale on washing machines´ heaters was expected.

Experimental analyses were done on more washing machines of the same producer at the same time. Testing was conducted without the addition of washing powder, at endless (for testing arranged) cycle of washing. Thus, completely equal conditions were achieved and the results received were comparable.

Calcium water hardness was measured on the input and output of water throughout the experiment. On the basis of the difference between those two measured hardness, it was indirectly predicted how much water scale was precipitated on the washing machine heater.

Table 1: Results of chemical analysis for tap water

Parameter	Value
pH	7.54 (T = 21.8 °C)
Conductivity	526 μs/cm (T = 20.2 °C)
Total hardness	14.7°n
Carbonate hardness (KT)	12.5°n
Noncarbonate hardness (NKT)	2.2°n
Calcium hardness (CaT)	10.7°n
Magnesium hardness (MgT)	4°n
m-value	4.45
Chloride	19 mg/l
Nitrating nitrogen	4.31 mg/l
Nitrate	19.1 mg/l
Sulphate	32 mg/l
Whole phosphor	< 0.04 mg/l
Phosphate	< 0.12mg/l
Ca	81.6 mg/l
Mg	18.3 mg/l
Na	12.9 mg/l
K	1.8 mg/l
S	9.9 mg/l
Si	4.7 mg/l
Al	<0.1 mg/l
Fe	<0.1 mg/l
Zn	<0.1 mg/l

Two sensors were inserted into each washing machine for on – line temperature measuring. The first sensor was touching the heater surface and the second was measuring water temperature.

The research comprised five experiments with different number of washing cycles in several washing machines. Each machine was filled with 540 g of cotton towels.

4. Experimental Results

4. 1. First Experiment

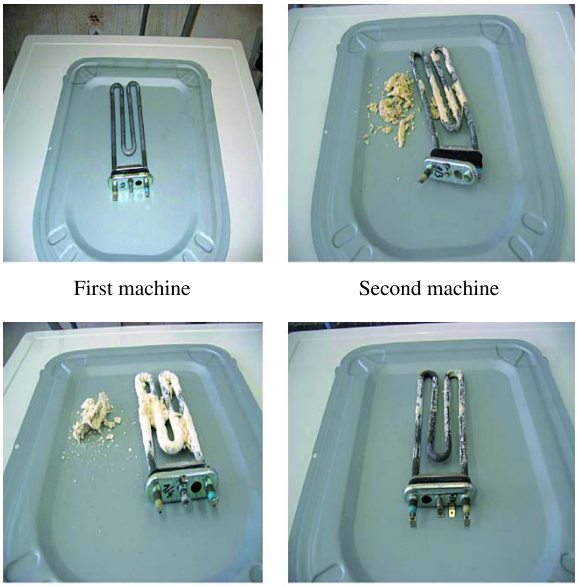
In the first experiment, four washing machines which were working simultaneously, continually for 300 cycles of washing were tested.

The first washing machine had a plastic bath and a heater with the power of 2000 W built – in; it worked at 60 °C. The second and the third washing machines had plastic baths and heaters with the power of 2000 W built – in, but they were working at 95 °C. The fourth washing machine had a metallic bath and a heater with the power of 2000 W built in, and it was working at 95 °C.

Results of the experiment are presented in figure 3.

Results show that after 300 cycles of washing at 60 °C, water scale did not precipitate on heaters. But if washing machines work at 95 °C for the same amount of time, a thick, porous deposit precipitates on heaters, which is actually a mixture of scale and fibres of fabrics that were in the washing machine.

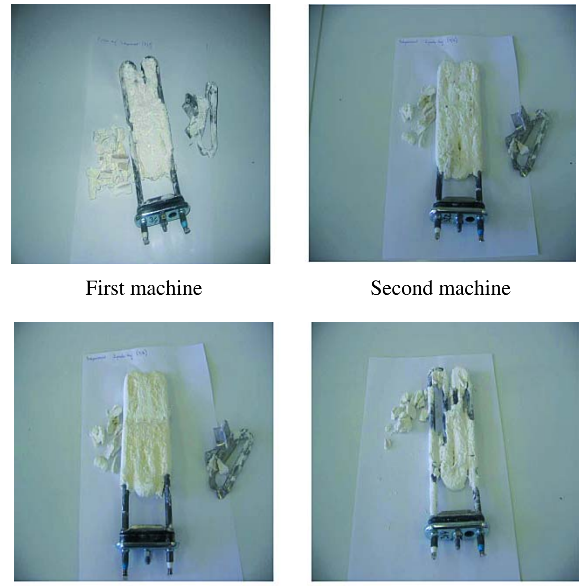
On the basis of experiment it can be concluded, that the key factor besides oversaturated water is the amount



First machine Second machine

Third machine Fourth machine

Figure 3. Precipitated scale on heaters of washing machines after the first experiment



First machine Second machine

Third machine Fourth machine

Figure 4. Precipitated scale on heaters of washing machines after the third experiment

of fibres of fabrics, which contributes to the building up water scale on heaters.

4. 2. Second Experiment

At the second experiment washing cycles were carried out at grounded and ungrounded drums in plastic baths.

The testing included 300 washing cycles with equal amount of fabrics as in the first experiment. Two washing machines had heaters with the power of 2000 W built in, and were operating at 95 °C. The other two machines were operating at the same conditions, only that they additionally had grounded drums.

Results showed that grounding the drums does not have the influence on scale precipitation at washing machine heaters.

4. 3. Third Experiment

In the third experiment washing cycles were done in a plastic bath with changed bottom. Testing included 300 washing cycles at 95 °C with the same fabrics as in the first experiment, in four washing machines with heaters of 2000 W power.

The first and the second machine had an existent bath built – in and other two the bath with changed bottom.

On heaters with changed shape of the bottom less scale welled up as on heaters with existent shape (figure 4).

The difference between lower and upper side of heater is visible. On the upper side of the heater, where the flow is more turbulent, the deposit is thinner as on the lower side, where additionally long fibres agglutinated, because water turbulence was not strong enough to flow away the fibres.

Throughout the experiment the temperature was measured on the heater surface and in the water.

At the beginning, the temperature of the heater surface increases slowly, but later, when a deposit of water scale is on the heater, the temperature of heater surface increases quickly (figure 5 and 6).

From the temperature measured on heater surface it is possible to determine the association between the temperature and the speed of building up of water scale on the heater.

According to figure 7, it can be seen that a bit less scale had precipitated on the heater in washing machines with changed bottom shape.

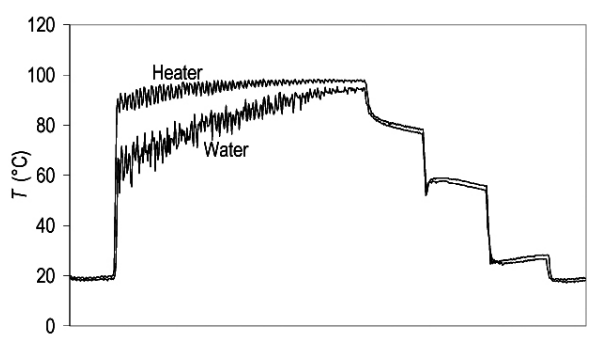


Figure 5. Changing of heater and water temperature after 140 washing cycles in the second washing machine

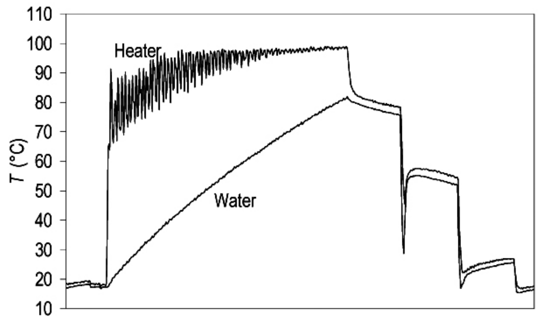


Figure 6. Changing of heater and water temperature after 140 washing cycles in the third washing machine

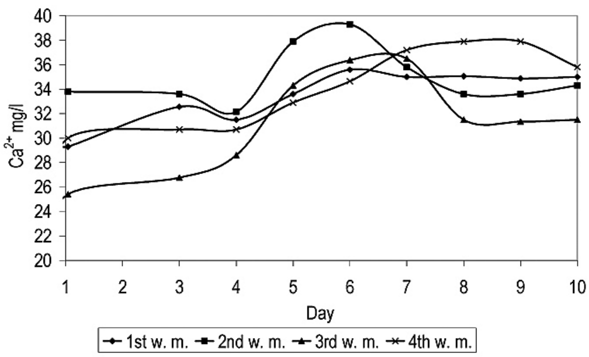


Figure 7. Calcium precipitation through the days in the third experiment

4. 4. Fourth Experiment

The fourth experiment was conducted at 80 washing cycles at 95 °C in four washing machines:

- the first washing machine with existing plastic bath and with heater of 2000 W power
- the second washing machine with existing plastic bath and with longer heater of 2000 W power
- the third washing machine with existing plastic bath and with heater of 2000 W power
- the fourth washing machine with existing plastic bath and with longer heater of 2000 W power

Considering testing results – figure 8, it is shown, that on longer heaters less scale precipitated and it was pilling off from the surface. A little more scale was on the lower side of the heater, where water turbulence is weaker.

The fifth experiment was conducted at the same conditions as experiment 4 so that the repeatability of the results was proven.

First machine

Second machine

Third machine

Fourth machine

Figure 8. Precipitated scale on heaters of washing machines after the fourth experiment

4. 5. Scale Sample Analysis

Samples were analysed with the x-ray diffraction. From the spectra (figure 9 and 10) it was determined that in the majority of cases water scale on heaters is aragonite or a mixture of aragonite and dolomite, while in the sediment on the outflow of washing machine beside aragonite and dolomite was also calcite.

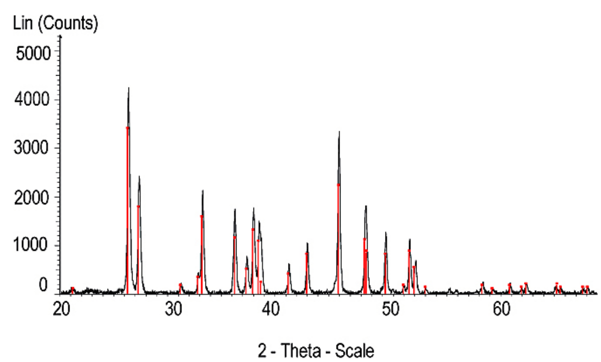


Figure 9. Scale sample from the first experiment

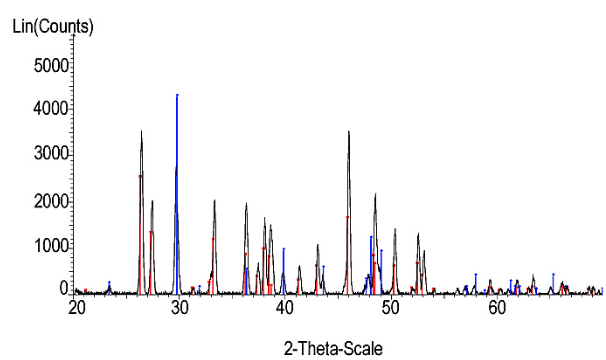
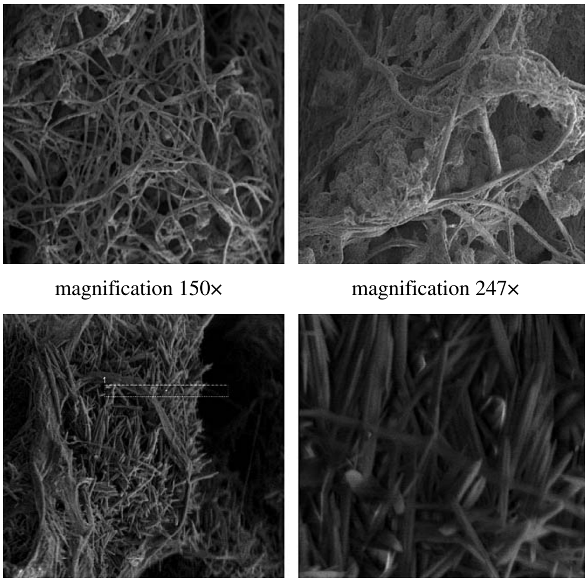


Figure 10. Scale sample from the third experiment

Additionally, a micro structural analysis of the samples of the water scale, which had built up on the heaters, was done. Results of different magnification are presented in figure 11, from where a composite, porous structure of fibres and scale crystal is seen.



magnification 150× magnification 247×

magnification 3111× magnification 14113×

Figure 11. Snapshots of scale samples with laser electronic microscope at different magnifications

5. Conclusion

The analysis of influence of physico – chemical parameters on scale precipitation at washing machine heaters was done at different bath shapes and on heaters with the power of 2000 W and of different dimensions.

Washing programme was reprogrammed to an endless washing cycle at 95 °C, without washing powder addition.

Several experiments were conducted on the basis of which it was concluded that less scale precipitated on longer heaters with smaller specific strength.

The micro structural analysis has showed a composite, porous structure of fibres and scale crystal. Also, with the x-ray diffraction it was determined that in majority of cases scale on heaters is aragonite or a mixture of aragonite and dolomite, while calcite is only in the sediment by the outflow from the machine.

6. References

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Povzetek

V prispevku so podani rezultati analize vpliva fizikalno kemijskih parametrov na intenzivnost izločanja vodnega kamna na grelcih pralnih strojev. Pralni stroji istega proizvajalca so bili v ta namen posebej prirejeni na neskončen cikel pranja z isto količino bombažnih tkanin pri istih pogojih. Na osnovi več različnih eksperimentov je bilo ugotovljeno, da imajo ključno vlogo pri nalaganju kamna na grelce pralnih strojev trdota vode, količina presežnega ogljikovega dioksida, turbulenca vode okoli grelca, količina iz tkanin izločenih bombažnih vlaken v vodi in specifična grelna moč grelca.