EXPERIMENTAL SCALING POTENTIAL OF HEATED WATER

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The previously proposed mechanism of bicarbonate ions decomposition by the H-mechanism (with the formation of H^+ *and* CO_3^{2-}*) or OH-mechanism (with the formation of* OH^- *and* CO_2*) is confirmed experimentally without and with heating water up to 190°C. The change decomposition mechanism depends on hardness, alkalinity and pH. The H-mechanism is observed at higher pH values (pH decreases) and the OH-mechanism is observed at lower values (pH increases) in particular solutions.*

The developed technique is based on the measurement of changing the pH (ΔpH_t*) of the solution (at a fixed temperature of 15 to 25°C) after heating it to a given temperature (ranging from 40 to 190°C) and maintaining this temperature for at least 30 minutes. A decrease in the pH of the water after heating (*$\Delta pH_t > 0$*) indicates the formation of carbonate ions and the need for additional water treatment to reduce the hardness, alkalinity or pH. The greater the* ΔpH_t*, the greater the concentration of carbonate ions formed in water. If* ΔpH_t *is zero then this temperature can be used as a water quality index. This temperature is 86.4°C for tap water in Kyiv (pH 7.4). Measurement of* ΔpH *in water meeting standards for water in German heating supply systems (pH 9.06, Hardness 45* $\mu mol/dm^3$ *- 5 times less than in Ukraine) shows that such water is not scale-safe (*$\Delta pH_{150} = 0.15$*).*

The proposed technique will be able to replace the Langelier index (up to 90°C) and the carbonate index (up to 190°C) under the condition of systematic processing of experimental data obtained for the water of different compositions on its basis. This method can be used in addition to the expensive experimental method of dynamic tube blocking.

Keywords: *bicarbonate ions decomposition, carbonate index, changing the pH, heated water, scale prevention, the LSI alternative*

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1. Introduction

Prediction of the possibility of scaling depending on the composition of water is an urgent task. Its solving methods have a long history since the mid-20th century. Langelier Index (LSI) and its derivatives (Ryznar, etc.) are used to assess the properties of water up to 80°C (Skoczko, 2019), and the carbonate index (the product of hardness on alkalinity) is used for heating supply systems in Ukraine (since the time of the USSR) for the temperature range from 70 to 190°C. In fact, the carbonate index (CI) is a simplified LSI used earlier at pH range 6.5-8.5 and now at pH 8.3-9.5 and does not consider a particular pH value. There are also computational models that are not related to the Langelier Index (Berce, 2021). All these approaches do not have an experimental methodology to verify the calculated values (LSI) and were developed based on data processing from real systems (CI). Now the widely used experimental technique is based on the method of dynamic blocking tubes, which actually simulates the work of heating equipment, but considerably accelerates (up to several hours) the scaling in the capillaries of installation by a drastic pressure drop after them (Wang, 2018). The relative quality of water samples depending on their composition is estimated by the time of reaching this drop. However, the cost of such installations does not allow their wide application, especially at the universities and the laboratories of water treatment plants.

It should be noted that for systems in which water is heated without contact with air, the equation of HCO_3^- decomposition is usually as follows:

$$2\ HCO_3^- \rightarrow CO_3^{2-} + CO_2 + H_2O$$

However, such equation cannot explain the change in pH after heating. Moreover, based on this equation, the formation of CO_3^{2-} ions (and consequently $CaCO_3$) is inevitable, which is not true.

Previously, an alternative approach to describe the mechanism of bicarbonate ions (BCI) dissociation under equilibrium conditions has been presented by two reactions (Kontsevoi, 2006):

$$HCO_3^- = OH^- + CO_2$$

$$HCO_3^- = H^+ + CO_3^{2-}$$

The practical application of these mechanisms requires experimental verification under nonequilibrium conditions. The same mechanisms are considered to predict the possibility and intensity of scale forming. The main goal of this research is to develop a technique that could be available at almost any chemical laboratory, allowing not only to estimate the possibility of scaling but also to predict its intensity.

Experimental confirmation of the presented BCI decomposition reactions already exists under conditions of water heating in contact with air (for example, in an ordinary kettle). It is known that the pH of such water increases the longer it is heated and then boiled. Carbonate ions are formed in the water and a scale is formed on the surface of the kettle. Obviously, both decomposition reactions of BCI occur simultaneously, but the reaction with the formation of CO_2 and OH^- occurs in greater yield, and this leads to an increase of pH.

2. Materials and Methods

Standard solutions and techniques for determination of water hardness (WH) with EDTA and Alkalinity (Alk), NaOH (0.1 mol/dm^3) and HCl (0.1 mol/dm^3) solutions for pH correction, $CaCl_2$ and $NaHCO_3$ solutions for modeling of natural water (raw and purified), tap water (Kyiv) in a laboratory of Faculty of Chemical Technology, pH meter (Jenway, UK, accuracy 0.01 pH units), photocolorimeter, sealed reactors (stainless steel) for water samples, circulation heater for heating up to 80^{o}C, autoclave for heating above 80^{o}C (up to 190^{o}C).

The technique for the determination of the decomposition mechanism of HCO_3^- ions is based on the fixation of the pH change after water heating. Water samples of certain chemical compositions are heated at a fixed temperature (20°C) for 15 minutes. Then the initial pH_1 value of water is determined.

This auxiliary heating eliminates the impact of temperature on water pH. The temperature compensation of the pH meters was found to be not sufficient. A difference of 1^{o}C leads to a difference in pH values up to

0.1 with a measurement accuracy of 0.01 pH unit. The actual temperature of this stage is determined by the temperature in the laboratory and can be any but fixed from 15 to 25°C. Obviously, the temperature of this heating must be several degrees higher than in the laboratory.

Then the water is poured into 3 stainless steel reactors. It prevents a change of pH value due to corrosion. The sealed reactor has a volume of 150 cm^3.

The reactors are placed in a circulation heater (up to 90°C) or autoclave (up to 190°C) and are heated for 30 minutes (actual heating time at a specified temperature in the heat-exchange equipment) at a certain temperature (40÷190)°C.

The reactors are removed from the autoclave the next day (slow cooling mode). The reactors from circulation heaters can be cooled with slow or quick cooling mode (using tap water) on the same day. The reactors remain closed during the cooling process. The reactors are again placed in a circulation heater at 20°C for 15 minutes and then pH_2 values are measured.

The experimental potential of scale forming is calculated as:

$$\Delta pH_t = pH_1 – pH_2,$$

where index t is the set temperature of the main heating, °C.

This sequence of ΔpH_t calculation allows getting values whose sign corresponds to the sign of the Langelier Index: negative values (OH-mechanism) – no calcium carbonate is formed, and positive values (H-mechanism) – on the contrary.

It should be noted that pH_0 is the pH value of the initial solution and pH_1 is the pH value after its adjustment with acid or alkali solutions and auxiliary heating at 20°C. pH_2 is always the pH after the main heating. Since the heating was performed in 3 reactors in parallel, the corresponding pH values after this heating are marked as $pH_{2.1}$ (1st reactor), $pH_{2.2}$ (2nd reactor), and $pH_{2.3}$ (3rd reactor), pH_{2avg} (average value).

3. Results and Discussion

At the first stage, ΔpH_t values were determined for sodium bicarbonate solutions (see Table 1).

Obviously, the H-mechanism ($\Delta pH_t>0$) is realized only at the maximum concentration, which corresponds to the alkalinity of tap water. There is more potential for both strengthening the observed mechanism and weakening it with slow cooling. Fast cooling allows for more accurately capturing the condition of the water at its maximum temperature.

Table 1. *The determination of ΔpH_t for $NaHCO_3$ solutions at different concentrations and cooling modes (f – fast; s - slow)*

№	**C, mol/dm^3**	**t, °C**	**pH_1**	**pH_{2avg}**	**ΔpH_t**
1f	0.25	40	5.36	5.73	-0.37
1s	0.25	40	5.38	5.953	-0.57
2f	0.25	60	6.43	6.835	-0.41
2s	0.25	60	6.43	6.81	-0.38
3f	1.0	40	7.22	7.59	-0.37
3s	1.0	40	7.32	7.488	-0.17
4f	1.0	60	6.76	6.85	-0.09
4s	1.0	60	6.775	6.808	-0.03
5f	4.0	40	7.56	7.622	-0.06
5s	4.0	40	7.51	7.66	-0.15
6f	4.0	60	7.90	7.855	0.05

ΔpH_t for samples of water prone to scale formation (pH about 9.0) and not prone to scale (pH about 8.0) were further determined (see Table 2).

Table 2. *ΔpH$_t$ of tap water (WH=5 mmol/dm^3, Alk=4 mmol/dm^3)*

t, ^{0}C	pH$_0$	pH$_1$	pH$_{2avg}$	ΔpH$_t$
40	7.66	8.03	8.02	0.01
60	7.65	8.00	7.96	0.04
80	7.67	8.21	8.090	0.12
40	7.61	9.08	9.02	0.06
60	7.62	9.00	8.82	0.18
80	7.65	9.11	8.62	0.49

It is known that tap water in Kyiv at a pH about 8.0 does not form carbonate scale on the heat-exchange equipment. Such water is used without additional treatment in the cooling systems at power plants in Kyiv at a temperature of about 40^{o}C, as well as in heat exchangers of Kyiv heating supply systems at 60^{o}C. ΔpH$_t$ values are positive but close to 0, which confirms their known properties (although not completely).

ΔpH$_t$ values increase with increasing temperature and water pH. At higher pH, the ΔpH$_t$ increase is larger, which adequately reflects well-known facts about scale formation (pH about 9.0).

The standard deviation for pH after heating (σ) was determined for 3 parallel tests in each test series. The obtained values indicate good repeatability of the results at the level of the pH-meter accuracy (see Table 3).

The decomposition of BCI occurs via the H-mechanism (see Table 4) in water samples that correspond to standard accepted in Ukraine (CI=WH*Alk, (mmol/dm^3)^2) and Germany (at 150^{o}C) for circulating water in heating supply systems.

The level of ΔpH$_t$ values indicates a high intensity of this process (see Table 4). This result is expected because the standards developed for pH range 6.5-8.5 are used for another pH range (8.3-9.5) with a much higher concentration of carbonate ions (especially for pH above 9.0).

Table 3. *The repeatability of parallel pH measurements after heating*

t, ^{0}C	pH$_{2.1}$	pH$_{2.2}$	pH$_{2.3}$	pH$_{2avg}$	σ
40	8.03	8.02	8.01	8.02	0.01
60	7.94	7.97	7.97	7.96	0.017
80	8.07	8.11	8.09	8.090	0.02
40	9.01	9.03	9.02	9.02	0.01
60	8.81	8.84	8.81	8.82	0.017
80	8.60	8.64	8.62	8.62	0.02

It should be noted that in systems with a pH close to 8.3, the carbonate scale is only about 5% of the total mass of deposits on the boilers' surface (95% are iron oxides).

Table 4. *Evaluation of current standards for the circulating water (Alk=3.0 mmol/dm^3)*

t, °C	CI	pH$_1$	pH$_{2avg}$	ΔpH$_t$
110	0.36	8.98	8.83	0.15
150	0.135	9.06	8.90	0.16

We propose using a value of water temperature (t$_Δ$), at which ΔpH$_t$ is equal to zero, as a quality index.

The index t$_Δ$, in general, corresponds to LSI, which is also equal to zero at a certain temperature. However, the proposed t$_Δ$ index can also be determined at temperatures above 90^{o}C (the upper limit of the Langelier index).

The data for determining t$_Δ$ of tap water in Kyiv are presented in Table 5 and are well approximated by the following linear equation:

$$\Delta pH_{tApr} = 0{,}0077 \cdot t - 0.6654.$$

ΔpHt is 0 at 86.4^{o}C according to the equation above.

Table 5. *Determination of the conditionally acceptable water temperature*

t, °C	pH_1	pH_{2avg}	ΔpH_t	ΔpH_{tApr}
150	7.48	6.99	0.49	0.49
110	7.48	7.29	0.19	0.18
80	7.48	7.53	-0.05	-0.05

Such an indicator can be valuable when determined for a large number of water with a wide variety of chemical compositions (Hardness, Alkalinity and pH). In this case, it will really be able to fully replace and expand the Langelier index as a calculated index.

4. Conclusions

The mechanism of bicarbonate ions decomposition based on two reactions has been experimentally confirmed. The pH increase of the heated water indicates the formation of CO_2 and OH^-, while the pH decrease indicates a reaction with the formation of H^+ and CO_3^{2-}.

A method for the determination of bicarbonate ions decomposition mechanism in water heated to a certain temperature (up to 190°C) is developed. Scaling potential is determined as the difference in pH of the water before and after heating (ΔpH). A negative sign of ΔpH value indicates the scale-safe of water (OH-decomposition mechanism), and a positive value indicates the formation of carbonate ions (H-mechanism). Obviously, the greater the changing value the greater the concentration of formed carbonate ions, taking into account the alkalinity and pH of the water.

The developed methodology has been applied to solutions of different compositions and temperatures: from scale-safety (pH about 8 – absent of carbonate ions) to not scale-safety (pH about 9 - carbonate ions are present). The results indicate a direct dependence of the ΔpH sign and value on the composition and temperature of the heated water. The existing standard for water quality in heating supply systems has been tested at a temperature of 110 and 150°C. It is found that such water is not scale-safety (ΔpH=0.15). At the same time, water hardness (45 μmol/dm^3) at a temperature of 150°C corresponds to standard accepted in Germany for such water (pH 9.06) and 5 times lower than in Ukraine.

An index (“conditionally acceptable water temperature”) for assessment of the scale-safety of water with a given composition is proposed. Due to the linear dependence of the index on temperature, it is easy to determine it by two temperatures (minimum and maximum). The function of ΔpH versus temperature allows determining this index when ΔpH is equal to zero. Its value for tap water in Kyiv is 86.4°C.

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ЕКСПЕРИМЕНТАЛЬНИЙ ПОТЕНЦІАЛ НАКИПОУТВОРЕННЯ НАГРІТОЇ ВОДИ

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Запропонований раніше механізм розпаду бікарбонат-іонів за Н-механізмом (з утворенням H^+ і CO_3^{2-}) або ОН-механізмом (з утворенням OH^- і CO_2) підтверджено експериментально з нагріванням води до 190°С. Зміна механізму розкладання залежить від твердості, лужності та рН. Н-механізм спостерігається за більш високих значеннях рН (рН зменшується), а ОН-механізм за нижчих значеннях (рН зростає).

Розроблена методика заснована на вимірюванні зміни рН (ΔpH_t) розчину (за фіксованої температури від 15 до 25°С) після його нагрівання до заданої температури (від 40 до 190°С) і підтримці цієї температури не менше 30 хвилин. Зниження рН води після нагрівання ($\Delta pH_t>0$) свідчить про утворення карбонатних іонів і про необхідність додаткової обробки води, що знижує твердість, лужність або рН. Чим більше ΔpH_t, тим більша концентрація карбонатних іонів, що утворюються у воді. Якщо ΔpH_t дорівнює нулю, то цю температуру можна використовувати як показник якості води. Для водопровідної води в Києві ця температура становить 86,4°С (рН 7,4). Вимірювання ΔрН у воді, що відповідає нормам для води в німецьких системах теплопостачання (рН 9,06; твердість 45 мкмоль/дм^3 – у 5 разів менша, ніж в Україні), показує, що така вода не є накипобезпечною ($\Delta pH_{150}=0,15$).

Запропонована методика зможе замінити індекс Ланжельє (до 90°С) і карбонатний індекс (до 190°С) за умови систематичної обробки експериментальних даних, отриманих для води різного складу на її основі. Цей метод можна використовувати як доповнення до дорогого експериментального методу динамічного блокування трубок.

Ключові слова: *розкладання гідрокарбонатних іонів, карбонатний індекс, зміна рН, нагріта вода, запобігання накипу, альтернатива індексу Ланжельє*