QUALITATIVE DETERMINATION OF THE SOLID CALCIUM CARBONATE DEPOSITION TENDENCY FROM NATURAL WATERS

KVALITATIVNO ODREĐIVANJE SKLONOSTI TALOŽENJA ČVRSTOG KALCIJUM KARBONATA IZ PRIRODNIH VODA

ALEKSANDRA PORJAZOSKA KUJUNDZISKI[1]
DRAGICA CHAMOVSKA [2]

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Abstract: Natural waters, during their transportation in the pipelines (metal, plastic, etc.), heat exchangers, their accumulation in reservoirs, and their different applications as technical water, show an affinity to create solid precipitations on the contact surfaces. It is more than clear that these processes are undesirable. In this work, the so-called saturation index for thermo-mineral water of Katlanovo Spa has been determined indicating qualitatively the theoretical affinity of water for the precipitation of calcium carbonate deposits on the contact surface areas. The saturation index for spring water takes values of 1.114 for 50°C and 0.904 for 40°C, and for the water in the collecting pool, 1.35 and 1.15 for 50°C and 40°C, respectively.

Key Words: natural waters, solid depositions, calcium carbonate, saturation index

Rezime: Prirodne vode, tokom transporta u cevovodima (metalni, plastični i dr.), izmenjivačima toplote, njihovom akumulacijom u rezervoarima i različitim primenama kao tehničke vode, pokazuju sklonost stvaranju čvrstih padavina na dodirnim površinama. Više je nego jasno da su ovi procesi nepoželjni. U ovom radu određen je takozvani indeks zasićenosti termomineralne vode Katlanovske banje koji kvalitativno ukazuje na teorijski afinitet vode za taloženje naslaga kalcijum karbonata na kontaktnim površinama. Indeks zasićenosti izvorske vode ima vrednosti od 1,114 za 50°C i 0,904 za 40°C, a za vodu u sabirnom bazenu 1,35 za 50°C, odnosno 1,15 za 40°C.

Ključne reči: prirodne vode, čvrsti talozi, kalcijum karbonat, indeks zasićenja

[1] Aleksandra Porjazoska Kujundziski, International Balkan University, Faculty of Engineering, Makedonsko-Kosovska Brigada bb, Skopje, R. North Macedonia, ORCID: 0000-0001-8177-3328

[2] Dragica Chamovska, University Ss. Cyril and Methodius, Faculty of Technology and Metallurgy, Ruger Boskovic 16, Skopje, Research Center for Environment and Materials,

Macedonian Academy of Sciences and Arts, Bul. Krste Misirkov 2 Skopje, R. North Macedonia

1. Introduction

Natural waters, such as groundwater, surface water, and spring water, often contain dissolved salts, mainly containing calcium carbonate, such as during their transportation throughout metal or plastic pipelines, in the heat exchangers, the storage in the reservoirs, and their usage in different technological processes, show the tendency of the formation of carbonate precipitations, scales on the contact surfaces. Water containing between 150 and 300 mg $CaCO_3$/L is known as „hard" water [1]. As carbonates precipitate on the surfaces inside the hot water pipes, the pipe diameter decreases, disturbing the water flow rate and carrying installation capacity. Also, this phenomenon disturbs the heat transfer through the metal pipes in the heat exchanger elements [2]. In extreme cases, this spontaneous formation of solid deposits can lead to immeasurable damage and interruptions in technological processes due to the clogging of cooling pipes, pipes in steam boilers, chemical reactors, etc. It should be emphasized that these processes also occur in the situations when deionized water is used. Due to the insufficient degree of softness and the content of dissolved salts, mainly calcium carbonate, they can cause significant damage and malfunctions in power plants.

There are various "classical" methods to decrease the water's „hardness" and/or restrict carbonate precipitation, including cation exchange, precipitation, chemical softening, or the use of membranes and inhibitors. In addition, some unconventional techniques, such as magnetic and electromagnetic protocols, have also been implemented [3].

Determining the deposition tendency of solid calcium carbonate is crucial in assessing the potential for scale formation, which can lead to operational challenges and equipment damage. This process depends on various factors, such as pH, temperature, and the presence of other dissolved species [4]. Researchers have explored the mechanisms and dynamics of calcium carbonate precipitation in detail, providing valuable insights into the qualitative assessment of this phenomenon [5].

2. Theoretical consideration of the hard deposit formation from natural waters

Calcium carbonate is a polymorphic material composed of different constitutional minerals created depending on the medium and the presence of other elements. The most common minerals are calcite, aragonite, and vaterite [3].

Calcium carbonate has small water solubility, with the solubility product taking values of $S_p = 4.57 \cdot 10^{-9}$ ($pS_p = 8.34$) for calcite and $6.03 \cdot 10^{-9}$ ($pS_p = 8.22$) for ara-

gonite at 25°C; $CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}$. This means the concentration of Ca^{2+} ions in the water would be 2.8 mg/L (or around 7 mg $CaCO_3$/L).

The contact of natural waters with the atmospheric air containing 0.03% CO_2 ($P_{CO_2} = 3 \cdot 10^{-4}$atm) and its solubility in water of around 50 mg/L at 25 °C leads to the formation of carbonic acid with a small concentration of around 70 mg / L.

$$H_2CO_3 = CO_2 + H_2O \qquad (pK_{CO_2} = 1.47)$$

Carbonic acid is a weak acid and it dissociates in two steps:

$$H_2CO_3 \Leftrightarrow H^+ + HCO_3^- \ , K_1 = 4.467 \cdot 10^{-7} \ (pK_1 = 6.35) \ (25\,℃)$$

$$HCO_3^- \Leftrightarrow H^+ + CO_3^{2-} \ , K_2 = 4.68 \cdot 10^{-11} \ (pK_2 = 10.33) \ (25\,℃)$$

Thus, the system $CaCO_3$ / H_2O - atmospheric air contains the following ions: Ca^{2+}, CO_3^{2-}, HCO_3^-, OH^- and H^+.

The dissociation constants of H_2CO_3, K_1, K_2, and the solubility product of $CaCO_3$, *S*p depend on temperature.

The decrease in the concentration of CO_2 promotes the precipitation of the calcium carbonate in the system while increasing the amount of CO_2 assists in its' dissolution following the equation:

$$CO_2 + H_2O + CaCO_3 \Leftrightarrow Ca^{2+} + 2HCO_3^-$$

CO_2 is more soluble in cold water, which shifts the reaction toward the production of more carbonic acid and thus, the solution of calcite in the water.

Dissolution of carbonates was noticed in acidic solutions (pH<7) [3].

The total water alkalinity, basically determined by the potentiometric titration with 0.1M HCl, is one of the most important factors in the estimation of the tendency of hard deposit precipitation, basically composed of calcium and magnesium carbonates and/or their sulfates, silicates, and mixtures. With the application of potentiometric (pH) titration (0.1M HCl) and the fact that the quantity of added acid is proportional to the carbonate and bicarbonate quantities in the water, plus the concentration of OH^- ions or minus the amount of the H^+ ions, depending on the water acidity, the following equation can be written:

$$(alk) + (H^+) = 2(CO_3^{2-}) + (HCO_3^-) + (OH^-) \qquad (1)$$

In addition to this equation, the dissociation constant of bicarbonates (K_2) and the calcium carbonate product of solubility (S_p) participate in the calculation of the pH value that represents the value of pH in the water in the conditions of equilibrium between $CaCO_3$ precipitate and the saturated solution.

$$pH_s = \left(pK_2 - pS_p\right) + p(Ca^{2+}) + p(alk) + log\left[1 + \frac{2K_2}{(H^+)_s}\right] \quad (2)$$

As the most common pH values for natural waters range between 6 and 8.5, the last term in the previous equation takes very small values and it can be neglected:

$$pH_s = \left(pK_2 - pS_p\right) + p(Ca^{2+}) + p(alk) \quad (3)$$

It should be mentioned that the K_2 and S_p values (i.e., pK_2 and pS_p) depend on temperature and the total ionic strength of the solution and their values can be found in the table or nomogram. The term $p(Ca^{2+})$ represents the negative logarithm of the Ca^{2+} ions mole concentration and p(alk) shows the negative logarithm of the alkalis' total concentration in water, determined by the potentiometric titration and given as calcium carbonate.

Based on the calculated pH value of the water (pH_s) and the measured pH value at a given temperature (pH_m), one can calculate the saturation index (SI) as a parameter that qualitatively determines the tendency of water for calcium carbonate scale formation [6].

$$SI = pH_m - pH_s \quad (4)$$

Thus, for $SI > 0$, the water will form hard calcium carbonate precipitates.

Determination of the saturation index facilitates the planning of the approaches to preventing possible damage to industrial equipment and plants.

3. Materials and methods

The saturation index, and thus the potential for precipitation of carbonate precipitates, was determined for thermo-mineral water of Katlanovo Spa, taken from two locations, a spring, and a collecting pool. The chemical composition of water from both places, shown in Table 1, was determined by the Institute for Public Health of the Republic of North Macedonia.

The concentrations of some cations and anions, such as iron, manganese, copper, zinc, lead, cadmium, cobalt, nickel, chromium, arsenic, mercury, strontium, and also, ammonia, nitrates, and nitrites, are not given in Table 1. These cations and anions are present in minimal concentrations in the natural water of Katlanovo Spring following the rulebook for the quality of natural mineral waters, Official Gazette of R. Macedonia number 183/2018.

Conductometry was used to measure the electrolytic conductivity of the spring water and the water from the collecting pool.

Table 1. Chemical composition of thermo-mineral water from spring and collecting pool; analyses done by the Institute for Public Health of the Republic of North Macedonia

Tablela 1. Hemijski sastav termomineralne vode izvorske i sabirni bazen; Institut za javno zdravlje Republike Severne Makedonije

Location	Spring	Collecting pool
pH	7.27	7.88
Dry residue (mg L^{-1})	1980	1650
El. Conductivity (293 K, μScm^{-1})	2307	1663
Suspended particles (mg L^{-1})	38	37
Chlorides, Cl^- (mg L^{-1})	165	162
Sulphates, SO_4^- (mg L^{-1})	56	55
Fluoride, F^- (mg L^{-1})	2.6	2.5
Calcium, Ca^{2+} (mg L^{-1})	359	172
Magnesium, Mg^{2+} (mg L^{-1})	99	114
Silicon dioxide, SiO_2 (mg L^{-1})	750	732
Total water hardness, °dH	74.60	51.8
Carbonate hardness of water, °dH	73.10	49.7
Potassium, K^+ (mg L^{-1})	158	165
Sodium, Na^+ (mg L^{-1})	99.9	91.3
M-alkalinity (ml L^{-1}; 0.1M HCl)	261	177
Bicarbonates, HCO_3^- (mg L^{-1})	1588	1080
Free CO_2 (mg L^{-1})	144	/

4. Results and discussion

Based on the data presented in Table 1, the following could be emphasized:

- Thermo-mineral water from Katlanovo Spa is rich in fluorides and belongs to the group of highly mineralized bicarbonate waters.
- This water contains big concentrations of calcium, magnesium, sodium, potassium, and bicarbonates with high hardness, mainly of carbonate origin.
- A reduction in the concentrations of potassium and bicarbonates in the relation spring-collecting pool resulted in the decrease of dry residue, electrical conductivity, and alkalinity of water. Based on this statement, it could be pointed out that the solid deposits formed on the walls of pipes, pools, etc., are mainly composed of calcium carbonates.

Figure 1 shows the temperature dependence of the water's electrical (ionic) conductivity. Considering the lowered concentration of some ions, mainly calcium and bicarbonates, the electrical conductivity of the water from the collecting pool is significantly lower compared to that of the spring water.

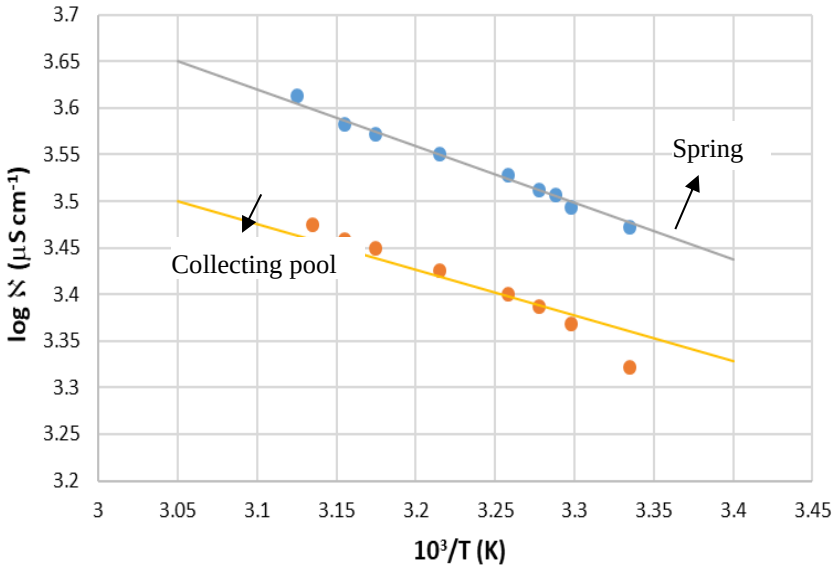

Figure 1. Log ϰ - 1/T dependences of thermo-mineral water from Katlanovo Spa, taken from the spring and collecting pool

Slika 1. Log ϰ - 1/T zavisnosti termomineralne vode Katlanovske banje, uzete sa izvorišta i sabirnog bazena

In both cases, ϰ-T dependences follow the equation:

$$\varkappa = \varkappa_0 \exp(-E_a/RT) \qquad (5)$$

So that:

$$\varkappa = 3.32 \cdot 10^5 \exp(-11.750/RT)\ \mu S \cdot cm^{-1} \quad \text{for the spring water}$$

$$\varkappa = 4.04 \cdot 10^5 \exp(-12.980/RT)\ \mu S \cdot cm^{-1} \quad \text{for the water in a collecting pool}$$

The activation energy, E_a, for ionic conductivity in both cases takes values between 12 and 13 kJ mol^{-1}, characteristic of the process controlled by the ionic diffusion in the solutions.

The total alkalinity of water, determined by the potentiometric titration (0.1M HCl) from the point of inflection, is one of the most significant factors for the

determination of the potential of hard deposit precipitation, containing primarily carbonates of calcium and magnesium and/or their sulfates, silicates, and mixtures. Water with higher total alkalinity contains bigger concentrations of calcium, hydrocarbonates, and carbonates and shows an increased potential for hard deposit precipitation.

Thermo-mineral water from the spring shows the largest total alkalinity with 250 ml 0.1M HCl/L H_2O in the inflection point, while that in the collecting pool was determined as 145 ml 0.1M HCl/L H_2O, which is a consequence of the calcium concentration decrease as a result of its precipitation in the pipelines in the form of carbonates.

Based on the above-explained procedure and equations 2-4, the saturation indexes of the thermos-mineral water from Katlanovo Spa from the spring and the collecting pool, at 50° and 40°C, were determined as follows:

For the spring water:

$$\left(pK_2 - pS_p\right) = 1.78\ (50\ ℃) and\ 1.95\ (40\ ℃)$$

$$p(Ca^{2+}) = -log(Ca^{2+}) = -log\left(\frac{0.36}{40}\right) = 2.046\ (50\ ° and\ 40\ ℃)$$

$$p(alk) = -log(alk) = -log\left(\frac{0.025}{2}\right) = 1.9\ (50\ ° and\ 40\ ℃)$$

$$pH_m = 6.84\ (50\ ℃) and\ 6.80\ (40\ ℃)$$

$$SI = 6.84 - (1.78 + 2.046 + 1.90) = 1.114\ (50\ ℃)$$

$$SI = 6.80 - (1.95 + 2.046 + 1.90) = 0.904\ (40\ ℃)$$

For the water in the collecting pool:

$$\left(pK_2 - pS_p\right) = 1.77\ (50\ ℃) and\ 1.95\ (40\ ℃)$$

$$p(Ca^{2+}) = -log(Ca^{2+}) = -log\left(\frac{0.172}{40}\right) = 2.37\ (50\ ° and\ 40\ ℃)$$

$$p(alk) = -log(alk) = -log\left(\frac{0.0145}{2}\right) = 2.14\ (50\ ° and\ 40\ ℃)$$

$$pH_m = 7.63\ (50\ ℃) and\ 7.61\ (40\ ℃)$$

$$SI = 7.63 - (1.77 + 2.37 + 2.14) = 1.35\ (50\ ℃)$$

$$SI = 7.61 - (1.95 + 2.37 + 2.14) = 1.15\ (40\ ℃)$$

5. Conclusion

Natural waters often exhibit an affinity to form solid precipitates when transported through pipelines, used in heat exchangers, and stored in reservoirs, resulting in a decrease in the effectiveness of the technological processes and significant energy losses. Saturation index determination, a metric that qualitatively assesses the theoretical tendency of water to precipitate calcium carbonate deposits on contact surfaces, serves as valuable information mitigating potential damage in pipelines and industrial plants.

Determined values of the saturation index for spring water in Katlanovo Spa were 1.114 for 50 °C and 0.904 for 40 °C, while for the water in the collecting pool, 1.35 and 1.15 for 50 °C and 40 °C, respectively.

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