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PREVENTING PIPELINE SCALE IN THERMOMINERAL WATER SYSTEMS

Abstract: Systems exposed to thermomineral water are prone to the formation of solid calcium carbonate, which induces significant challenges, including reduced efficiency, increased energy consumption, and high removal costs. The thermomineral spring water of Katlanovo spa shows high carbonate hardness and calcium content, leading to scale formation. As a solution to this problem, our study proposes water treatment with CO_2 gas. Calcium carbonate precipitation is prevented by increasing the partial pressure of CO_2 in the system, due to the decreased pH of water and increased calcium solubility.
Key Words: Thermomineral water, sodid deposits, calcium carbonate, CO_2 treatment

PREVENCIJA STVARANJA KARBONATNIH DEPOZITA U CEVOVODIMA TERMOMINERALNIH VODNIH SISTEMA

Rezime: Sistemi izloženi termomineralnoj vodi podložni su formiranju čvrstog kalcijum karbonata, što izaziva poteškoće, uključujući smanjenu efikasnost, povećanu potrošnju energije i visoke troškove njihovog uklanjanja. Termomineralna voda banje Katlanovo pokazuje visoku tvrdoću i sadržaj kalcijuma, što dovodi do formiranja karbonatnih depozita. Kao rešenje ovog problema, naše istraživanje predlaže korišćenje CO_2 gasa za tretman vode. Porastom parcijalnog pritiska CO_2 gasa u sistemu, sprečava se precipitacija kalcijum karbonata, zahvaljujući smanjenju pH vrednosti vode i povećanoj rastvorljivosti kalcijuma.
Ključne reči: termomineralne vode, cvrsti depositi, kalcijum karbonat, CO_2 tretman

1. Introduction

The scaling process in natural and industrial waters is commonly associated with the formation of undesired solid precipitates, composed mainly of calcium carbonate ($CaCO_3$). These deposits usually form on solid surfaces that come into contact with carbonate-rich media. This occurrence introduces significant problems in both households and industrial settings, and is related to efficiency and the life span of equipment [1].

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Precipitation of calcium carbonate occurs when the solution reaches the oversaturation with calcium (Ca^{2+}) and carbonate (CO_3^{2-}) ions [2]. Factors, including temperature, media acidity/alkalinity, partial pressure of carbon dioxide (CO_2) dissolved in the solution, and a variety of ions in the solution, affect the concentration of saturation of the ions mentioned above, and thus, the carbonate precipitation, too [3]. The formation of carbonate crystals in the system is facilitated at higher temperatures, due to the lower solubility of calcium carbonate in water. Similar to the effect of a temperature, higher alkalinity also promotes easier sediment formation. Reduction of the partial pressure of CO_2 in the system shifts the chemical equilibrium toward the formation of carbonate sediments [3].

Precipitates of $CaCO_3$ exist in several polymorphic crystalline forms. The most thermodynamically stable and the most abundant structure of calcium carbonate is the crystalline form of calcite. The metastable equivalents belong to the minerals aragonite and vaterite [2, 3].

In addition to pure calcium carbonate deposits, water containing different compounds can form scales composed of a mixture of varying carbonate compounds. Such deposits exhibit different morphology and hardness of films, but they also show variant solubility and ease of removal [4].

Solid calcium carbonate precipitated in industrial systems, such as heat exchangers, pipes, boilers, or cooling equipment, leads to several challenges, including reduced process efficiency, increased energy consumption, equipment failure, and other operational challenges [5]. Therefore, strategies that many industries implement to prevent or manage scaling include „water softening“, pH adjustment, or the use of scale inhibitors [4, 5].

As a continuation of our previous study [6] dealing with the affinity of water in Katlanovo Spa to create deposits of calcium carbonate, this work focuses on the potential of water treatment with CO_2 gas as a promising technique to address this issue.

2. Materials and methods

This study, as the previous one [6], covers the thermo-mineral water from Katlanovo Spa. Table 1 [6] presents the chemical composition of water, determined by the Institute for Public Health of the Republic of North Macedonia.

Tabela 1. Hemijski sastav termomineralne vode izvorske i sabirni bazen; Institut za javno zdravlje Republike Severne Makedonije [6]
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 [6]

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

Location	Spring	Collecting pool
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	/

Yet, in accordance with the rulebook for the quality of natural mineral waters, Official Gazette of R. Macedonia number 183/2018, this Table does not include the concentration of ions present in the minimal amounts.

3. Results and discussion

The thermo-mineral water, used for the treatment of patients in Katlanovo spa, is located about one kilometre from the spa, at a depth of around eighty meters. At the same time, spring capacity ranges between 4 and 4.6 L s^{-1}. The thermal water from the spring to the spa is transported by gravity through a pipeline with a length of about 840 m to a receiving pool in front of the spa and later to the spa facilities (pools, bathtubs, etc.).

Since its inception, Katlanovo spa has encountered a recurring issue with the accumulation of solid deposits on the surfaces of pipelines, pools, etc., which in previous years has been addressed via mechanical removal. The problem with the solid deposits is mainly attributed to the chemical composition of the water (high carbonate hardness, i.e. high calcium content, high alkalinity, etc.), Table 1 [6].

The total amount of calcium carbonate deposits on the walls of the transport pipeline and the spa facilities is more than 82 tons/year. Thus, in addition to the high operational costs of the frequent removal of solid deposits, the costs related to the frequent interruptions in the spa's operation also incur substantial expenses.

In accordance with the equation of qualitative determination of the tendency of water to accumulate carbonate deposits [6], the saturation index (SI) must be lower, and/or equal to 0, for the prevention of precipitation. This means that to prevent carbonate precipitation, it is necessary to either significantly reduce the calcium concentration in the water and its total alkalinity, or to reduce the pH value of the water. Such a conclusion is based on the understanding that smaller values of SI indicate a lower risk of precipitation and underscores the need for a particular chemical treatment.

The standard chemical procedures (using complexing salts, ion exchangers, etc.) are inapplicable in this case, due to the introduction of undesirable, often toxic chemical substances, the change in the water composition used in patients' treatment, as well as the lack of economic reasonableness.

Therefore, the authors firmly believe that one of the acceptable procedures to decrease carbonates (mainly calcium carbonate) from these waters is their treatment with CO_2. This

method would significantly reduce the pH value and, at the same time, drastically increase the solubility of calcium in the water. In this way, the high concentrations of calcium (about 360 mg L^{-1}) in the spring water would remain in the water until they are discharged from the pools.

The basic reactions responsible for the prevention of carbonate deposits from forming in the $CaCO_3 – H_2O – CO_2$ system are as follows [3]:

$$CaCO_3 \Leftrightarrow Ca^{2+} + CO_3^{2-}$$

$$CO_3^{2-} + H_2O \Leftrightarrow HCO_3^- + OH^-$$

$$HCO_3^- + H_2O \Leftrightarrow H_2CO_3 + OH^-$$

$$H_2CO_3 \Leftrightarrow CO_{2(g)} + H_2O$$

Accordingly, the system under consideration will contain the following ions (molecules): Ca^{2+}, CO_3^{2-}, HCO_3^-, H_2CO_3, CO_3, H^+, OH^-.

The calculated ion concentrations in the $CaCO_3 – H_2O – CO_2$ system are given in Table 2. A temperature of 50 °C was chosen because it is close to the temperature of the spring water, which is 54 °C, and the temperature of the water in the transport pipeline ranges between 54 and 49 °C.

Табела 2. Израчунате концентрације јона у систему $CaCO_3 – H_2O – CO_2$ на 50 °C
Table 2. Calculated concentrations of ions in the $CaCO_3 – H_2O – CO_2$ system at 50 °C

	PCO_2 / atm						
C / mol · L^{-1}	$3 \cdot 10^{-4}$	$3 \cdot 10^{-3}$	$8 \cdot 10^{-2}$	0.167	0.3	0.6	1.2
$[HCO_3^-]$	$8.6 \cdot 10^{-4}$	$1.83 \cdot 10^{-4}$	$5.54 \cdot 10^{-3}$	$7.08 \cdot 10^{-3}$	$8.60 \cdot 10^{-3}$	$1.09 \cdot 10^{-2}$	$1.37 \cdot 10^{-2}$
$[CO_3^{2-}]$	$2.69 \cdot 10^{-5}$	$1.25 \cdot 10^{-5}$	$4.17 \cdot 10^{-6}$	$3.27 \cdot 10^{-6}$	$2.69 \cdot 10^{-6}$	$2.14 \cdot 10^{-6}$	$1.69 \cdot 10^{-6}$
$[Ca^{2+}]$	$4.30 \cdot 10^{-4}$	$9.29 \cdot 10^{-4}$	$2.77 \cdot 10^{-3}$	$3.54 \cdot 10^{-3}$	$4.30 \cdot 10^{-3}$	$5.42 \cdot 10^{-3}$	$6.84 \cdot 10^{-3}$
$[OH^-]$	$1.13 \cdot 10^{-5}$	$2.43 \cdot 10^{-4}$	$2.73 \cdot 10^{-7}$	$1.66 \cdot 10^{-7}$	$1.13 \cdot 10^{-7}$	$7.14 \cdot 10^{-8}$	$4.51 \cdot 10^{-8}$
pH	8.315	7.65	6.70	6.48	6.315	6.114	5.914

It is evident that the increase in the partial pressure of CO_2 (from that in atmospheric air, $3 \cdot 10^{-4}$ atm) significantly affects the concentration of ions in the water (the calcium carbonate-bicarbonate balance) as well as its pH value.

At the higher values of PCO_2, the concentration of bicarbonates increases significantly, and the concentration of carbonates decreases, resulting in a drastic growth in the concentration of calcium in the water (from about 17 mg/L in atmospheric conditions, at $PCO_2 = 3 \cdot 10^{-4}$ atm to about 275 mg L^{-1} for $PCO_2 = 1.2$ atm, at 50°C). On the other hand, the pH value of the water decreases to about 6, which also suggests a reduced tendency for the formation of calcium carbonate deposits.

According to previously calculated values of the saturation index from 0.9 to 1.35 in the temperature range from 40 to 50 °C, it was shown [6] that the examined thermomineral water displays a pronounced tendency for precipitation, mainly calcium carbonate solid deposits on the inner walls of the pipelines and collection pools. This result was also confirmed under

water usage conditions, when a drastic drop in the concentration of dissolved calcium in the water occurs (from 360 mg L^{-1} in the spring water to 172 mg L^{-1} in the receiving pool), as well as an increase in the pH value of the water from 6.4 to 7.43.

It follows that the CO_2 content in the spring thermomineral water (145 mg L^{-1} and P_{CO_2} = 0.17 atm) does not provide conditions for preventing the process of calcium carbonate precipitation from waters containing 360 mg (Ca^{2+}) L^{-1}, such as that of our concern.

This result implies that due to insufficient confinement of the system (transport pipeline with a length of 840 m), there is practically complete desorption of the CO_2 present in the water, i.e. the establishment of equilibrium with CO_2 in the atmospheric air, which leads to the conclusion that the pH value for a given water (chemical composition) mainly depends on the amount of adsorbed CO_2 (P_{CO_2}).

For example, spring water at 27°C with pH = 6.4 and C_{CO_2} = 145 mg L^{-1} after 24 hours of contact with atmospheric air reaches a pH value of around 7.6. On the other hand, spring water with a pH of 6.4, after intensive treatment with CO_2, reaches a pH of 5.9, and in contact with atmospheric air for a period of 24 hours, it achieves a pH of 6.2.

A contact of the spring water with CO_2 having a partial pressure of at least 0.5 atm is needed to ensure a minimal concentration of CO_2 of 370 mg L^{-1} in the thermal mineral spring water at 50 °C. This approach would provide a concentration of CO_2 in the water greater than 400 mg L^{-1}. To implement the above procedure, one should install a carbonation column with intense control of the parameters such as temperature, pH, flow of the incoming and outgoing spring water, as well as the flow of CO_2 gas for carbonation of the spring water.

4. Conclusions

Katlanovo spa has faced a persistent problem with the scaling of solid deposits in pipelines, pools, and other surfaces, which in the past was managed primarily through mechanical cleaning methods. Regular removal of solid deposits requires frequent interruptions in the spa's operation and incurs additional expenses.

As a solution to this problem, our research proposes a chemical method of using CO_2 gas for water treatment. The CO_2 significantly reduces crystallisation of carbonate deposits on contact surfaces, keeping them as fine suspended particles from the source until they are discharged from pools.

5. Literature

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