THE EFFECTS OF COLLOIDAL SiO\textsubscript{2} AND INHIBITOR ON THE SOLID DEPOSIT FORMATION IN GEOTHERMAL WATER OF LOW HARDNESS

Low solubility of SiO\textsubscript{2} and its occurrence in geothermal waters in the form of ionic, colloidal and suspended state are the main cause of the solid deposit occurrence. Certain chemical types of silica, under the influence of Fe\textsuperscript{2+}, Al\textsuperscript{3+}, F\textsuperscript{-}, OH\textsuperscript{-} and other micro-constituents, and due to significantly decreased solubility of SiO\textsubscript{2}, stimulate nucleation, particle growth and solid deposit formation. The aim of this work is to inhibit the process of nucleation and solid deposit formation by adding an originally designed inhibitor in the form of an emulsion, when the total concentration of the present and added colloidal SiO\textsubscript{2} is beyond the solubility limit (120 mg/dm\textsuperscript{3}). By turbidimetric, SEM, EDS and XRD analysis, the processes of solid deposit formation were investigated in Vranjska Banja (Serbia) spa geothermal water source (water hardness of 4°dH), and theoretical and practical conclusions were made.

The problem of solid deposit formation, known as incrustation, in geothermal underground and hard drinking waters, due to high values of dry residue and water hardness, is present in heating systems of spas and rehabilitation centers [1–3]. Due to the dominant presence of calcium and magnesium in many hyperthermal geothermal waters, the impact of colloidal silicon(IV) oxide and its other forms on solid deposit formation processes was neglected.

However, microelements such as iron, aluminum, zinc, boron and fluorine and colloidal SiO\textsubscript{2} have a significant impact on the solid deposit formation processes [4,5]. During the interaction of minerals that contain SiO\textsubscript{2} with acid geothermal waters at temperatures above 40 °C, formation of the monomeric orthosilicic acid Si(OH)\textsubscript{4} takes place first. Solid particles of SiO\textsubscript{2} and colloidal SiO\textsubscript{2} are formed by the mixture polymerization, [6], as well as crystalline and amorphous forms of SiO\textsubscript{2} with different solubility in water, the former being less dissolved (70 mg/dm\textsuperscript{3}) than the latter (100 to 120 mg/dm\textsuperscript{3}) [5]. The solubility of SiO\textsubscript{2} is influenced by many factors: pH, temperature, pressure, specific surface, porosity, the ratio of crystalline and amorphous states, the presence of foreign ions, the coefficient of mass transfer due to potential barriers at the contact of water – solid, geometric factors, morphology of crystals, crystal anisotropy, etc. [5].

Until now, not enough attention has been paid to the impact of low SiO\textsubscript{2} solubility on solid deposit formations, although it has been observed [5,6] that this phenomenon in boiler systems occurs due to the presence of dissolved colloidal and suspended solid particles of SiO\textsubscript{2} and their interaction with Fe\textsuperscript{2+} and Al\textsuperscript{3+}. The composition of colloidal particles is defined by the presence of polysilicic (xSiO\textsubscript{2}·yH\textsubscript{2}O) or metasilicic (SiO\textsubscript{2}·2H\textsubscript{2}O) acid. The ratio of different silicic acid forms (free acid, hydroxilicate, HSiO\textsubscript{3}–, and silicate, SiO\textsubscript{3}\textsuperscript{2–}) depends on the pH values [7]: free silicic acid is present at pH < 8, while in the pH range between 8 and 11 free silicic acid and HSiO\textsubscript{3}– are in equilibrium. This is attributed to the Si(OH)\textsubscript{4} monomer that is rather inert at lower pH values and to the catalytic effects of OH\textsuperscript{-} at higher pH values. The first ionization of Si(OH)\textsubscript{4} occurs at pH 9, when (OH)\textsubscript{3}SiO\textsuperscript{2–} is formed, and at higher pH values ionization goes to (OH)\textsubscript{2}SiO\textsubscript{3}–. When the Si(OH)\textsubscript{4} monomer is in equilibrium with colloidal SiO\textsubscript{2} particles at pH 7–8, then they have a negative electric charge. The existing conditions are suitable for the interaction of colloidal particles and positive ions (Fe\textsuperscript{3+} and Al\textsuperscript{3+}) presented in geothermal waters [5,8]. An almost negligible concentration of Fe\textsuperscript{3+} of only 5 μg/dm\textsuperscript{3} is enough for the incrustation to occur [5].

Dissolution and precipitation of silicon(IV) oxide in water involves hydration and dehydration reaction catalyzed by OH\textsuperscript{-}, as shown by Eq. (1):

\[
\text{(SiO}_2\text{)}_x + 2\text{H}_2\text{O} \xrightleftharpoons{\text{Hydration}} \text{(SiO}_2\text{)}_{x-1} + \text{Si(OH)}_4 \quad (1)
\]

It can be noted that the crystalline form of SiO\textsubscript{2} (quartz) is significantly less soluble in water (6 mg/dm\textsuperscript{3}). Oversaturated solutions of Si(OH)\textsubscript{4} monomer are formed when SiO\textsubscript{2} or silicates dissolve in water at high temperatures and under pressure, similar to the interaction of geothermal waters with minerals at greater depths. In laboratory conditions, oversaturated solution of Si(OH)\textsubscript{4} can be obtained by acidifying the sodium silicate water solution:

\[
\text{Na}_4\text{SiO}_4 + \text{H}_2\text{O} + 2\text{HCl} \rightarrow \text{Si(OH)}_4 + 2\text{NaCl} \quad (2)
\]

The oversaturated solution of silicic acid in water is thermodynamically unstable due to the dehydration that leads to condensation and polymerization. As it can be seen from Eq. (1), the monomer molecule and preci-
The behavior of SiO$_2$ dissolved in water is very interesting, probably in the form of silanol groups Si–OH [10]. At high temperatures and neutral or alkaline pH values, somewhat oversaturated monomer solutions, especially if the concentration significantly lower than 10 ppm, due to the synergistic effect of the present ions. Some impurities, for example, aluminum in very small quantities, decrease the rate of SiO$_2$ dissolution, as well as its solubility by chemisorption of ions on SiO$_2$ surface. Although their surface concentration is negligible, aluminosilicate anions reduce the dissolution rate and affect the equilibrium solubility of SiO$_2$.

In this paper, the process of solid deposits formation in geothermal water was studied at temperatures of 40 and 65 °C. The former temperature is significantly below the temperature of spontaneous solid deposit formation and the latter is the lowest temperature at which the spontaneous solid deposit formation occurs. An inhibitor in the form of an emulsion was used to control the process of solid deposit crystallization. The main aim was to elucidate the effects of colloidal SiO$_2$ and some microelements on the process of solid deposits formation.

**EXPERIMENTAL MATERIALS AND METHODS**

Materials

The studied geothermal water was taken from Vranjska Banja spa, Serbia. The colloidal SiO$_2$ [7] was prepared from water glass (density 1.355–1.380 g/cm$^3$) purchased from Galenika Magmasil, Belgrade. Water glass (100 cm$^3$) was poured into a filtering funnel covered with a 3–5 µm filter, so water glass did not pass through the filter. An aqueous HCl solution was added to water glass to initiate the hydration process and the Si(OH)$_4$ monomer formation. After neutralization with NaOH, Si(OH)$_4$ monomer was dehydrated and the colloidal SiO$_2$ was obtained, containing 5.272 g of SiO$_2$ per dm$^3$.

Emulsion of inhibitor of a concentration 0.2 mg/cm$^3$ was prepared as follows. A solid mixture (200 mg) containing sodium polyphosphate (Na$_{x+y}$P$_x$O$_{3x+y}$), stearic acid (C$_{17}$H$_{35}$COOH), carboxymethyl cellulose sodium salt (NaCMC) and glycerol was dissolved in distilled water in a measuring flask (1 dm$^3$). Production technology of emulsion was deposited with the Intellectual Property Office, under the name Antiinkrustal puroni 2000 (A-641/06/01, 25.01.2007).

### Methods

The effect of colloidal SiO$_2$ on turbidity of the geothermal water was studied at two temperatures (40 and 65 °C) and different amounts of colloidal SiO$_2$ (10, 20, 30, 40, 50 and 60 mg/dm$^3$). The geothermal water (200 cm$^3$) was heated to 40 °C and, while stirring, an amount of the colloidal SiO$_2$ was added to achieve the predetermined concentration. The turbidity of the samples was measured using a turbidimeter. Then, the heating was raised to 65 °C, the mixture was cooled down and the turbidity measurement was repeated. Finally, the samples were filtered under vacuum. The concentration of residual SiO$_2$ in the filtrate was determined chemically, while the precipitates were saved for the SEM, EDS and XRD analysis.

The concentration of added colloidal SiO$_2$ in geothermal water was calculated by Eq. (3):

$$c(\text{coll SiO}_2) = \frac{c_0^{\text{coll}}V_0^{\text{coll}}}{V_t}$$

where $c_0^{\text{coll}} = 5.272$ g/dm$^3$ is the concentration of stock colloidal SiO$_2$, $V_0^{\text{coll}}$ is the volume of added stock colloid, and $V_t$ is the total volume of added stock colloid and geothermal water.

In the presence of the inhibitor as an emulsion (6 mg/dm$^3$), the turbidity of the geothermal water was measured at the SiO$_2$ amount added of 60 mg/dm$^3$ at different temperatures of 40, 65, 80 and 100 °C as described previously.

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) analysis was performed on a JEOL JSM-5300 equipped with EDS LINK QX 200. The X-ray diffraction analysis was taken on Siemens D-500 diffractometer using the standard powder diffraction procedure and Cu-K$_\alpha$ radiation. The turbidity of water was measured using a WTW TURB 355 IR turbidimeter, which was calibrated with 1000 NTU, 10 NTU and 0.01 NTU standards. The chemical composition of the samples was determined using an ICP-OES spectrometer iCAP 6000, Thermo Electron Corporation, Great Britain.
RESULTS

The chemical compositions of water taken from the Vranjska Banja in the period from 4 May 1998 until 3 November 2003 are given in Table 1. Bold values refer to elements that are important to the process of solid deposit formation.

The water belongs to sodium-hydrocarbonate, sulphate, fluoride and sulphide hyperthermal spa waters with hardness 4 °dH, pH 7.1–7.95 and temperature 81–94.2 °C; containing fluorine, silicon and increased levels of HBO₂ and iron. The SiO₂ content was 76 mg/dm³ as mean value. According to its chemical composition, which has been almost constant in years, the formation of solid scale residue in the water was not to be expected.

Figures 1 and 2 show the change of water turbidity with increasing the colloidal SiO₂ amount added to the geothermal water. Starting from the value of 0.48 NTU for natural geothermal water, the turbidity values in the ranges from 1.15 to 3.88 NTU and 2.3 to 6.27 NTU at 40 and 65 °C, respectively were determined. The water turbidity increased with increasing the colloidal SiO₂ amount added, especially when the total SiO₂ concentration approached the solubility of 120 mg/dm³ or surpassed it. However, somewhat lower turbidity was found for 60 than for 50 mg/dm³ of colloidal SiO₂ added (Figure 2).

In the presence of the inhibitor in the form of emulsion (6 mg/dm³), the turbidity of the geothermal water was measured at the SiO₂ amount of 60 mg/dm³ at different temperatures of 40, 65, 80 and 100 °C. Figure 3 shows that the turbidity increases with increasing the temperature (54.5 NTU at 40 °C and 115 NTU at 100 °C).

The XRD patterns of solid deposits formed at different amounts of colloidal SiO₂ added to the geother-

### Table 1. Analysis of geothermal water of Vranjska Banja spa, Serbia

<table>
<thead>
<tr>
<th>Species</th>
<th>Institute for Rehabilitation, The Balneoclimatology Service, Belgrade, Serbia</th>
<th>Institute of Public Health of Serbia “Dr. Milan Jovanović Batut”, Belgrade, Serbia</th>
<th>Date of analysis</th>
<th>Concentration, mg/dm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>323</td>
<td>291,1</td>
<td>392,2</td>
<td>430</td>
</tr>
<tr>
<td>K⁺</td>
<td>27,8</td>
<td>11,8</td>
<td>18,5</td>
<td>18,84</td>
</tr>
<tr>
<td>Li⁺</td>
<td>0,28</td>
<td>0,2</td>
<td>0,3</td>
<td>–</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>0,13</td>
<td>–</td>
<td>–</td>
<td>0,04</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>16,4</td>
<td>20</td>
<td>23</td>
<td>21,87</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>3,4</td>
<td>17</td>
<td>19</td>
<td>19,6</td>
</tr>
<tr>
<td>Sr²⁺</td>
<td>0,67</td>
<td>0,7</td>
<td>0,4</td>
<td>–</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>0,07</td>
<td>0,1</td>
<td>0,02</td>
<td>0,15</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>0,06</td>
<td>0,04</td>
<td>0,02</td>
<td>1,0</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>&lt; 0,05</td>
<td>0,05</td>
<td>0,05</td>
<td>–</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>457</td>
<td>414</td>
<td>610</td>
<td>–</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>50,4</td>
<td>62</td>
<td>78</td>
<td>44</td>
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<tr>
<td>Br⁻</td>
<td>&lt; 0,5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>J⁻</td>
<td>&lt; 0,5</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>F⁻</td>
<td>12,3</td>
<td>11,5</td>
<td>12</td>
<td>10,93</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>&lt; 0,5</td>
<td>–</td>
<td>–</td>
<td>0,44</td>
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<tr>
<td>HPO₄²⁻</td>
<td>&lt; 0,5</td>
<td>0,05</td>
<td>0,05</td>
<td>–</td>
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<tr>
<td>SO₄²⁻</td>
<td>394</td>
<td>368</td>
<td>370</td>
<td>305</td>
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<tr>
<td>Metasilicic acid</td>
<td>59</td>
<td>90</td>
<td>147,2</td>
<td>–</td>
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<tr>
<td>Metaboric acid</td>
<td>5,6</td>
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<td>4,6</td>
<td>–</td>
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<tr>
<td>TDS</td>
<td>1392</td>
<td>1290,7</td>
<td>1675,3</td>
<td>–</td>
</tr>
<tr>
<td>H₂S</td>
<td>1,2</td>
<td>1,5</td>
<td>2,1</td>
<td>–</td>
</tr>
<tr>
<td>CO₂</td>
<td>–</td>
<td>15</td>
<td>15,2</td>
<td>–</td>
</tr>
<tr>
<td>Density, g/cm³</td>
<td>1,0036</td>
<td>1,0015</td>
<td>1,0019</td>
<td>–</td>
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<tr>
<td>pH</td>
<td>7,07</td>
<td>7,1</td>
<td>7,7</td>
<td>7,95</td>
</tr>
<tr>
<td>Dry residue at 180 °C, mg/dm³</td>
<td>834</td>
<td>989,5</td>
<td>1218,5</td>
<td>1230</td>
</tr>
<tr>
<td>Temperature of water, °C</td>
<td>90</td>
<td>81</td>
<td>94,2</td>
<td>–</td>
</tr>
</tbody>
</table>
mal water are compared in Figure 4, where trona (Na₃H(CO₃)₂·2H₂O) peaks are marked as T, and halite (NaCl) peaks as H. Upon inhibitor addition, a suspension was formed. The solid phase contained halite as the only crystalline phase after separation and drying, as identified by the XRD analysis (Figure 5).

The peaks assigned to trona cannot be detected since the particles were covered with amorphous layer of surface active matters that prevented the crystal growth and compact solid deposit formation. SEM micrographs of the solid deposit surface, as well as corresponding EDS spectra show a needle-like structure of SiO₂ and trona crystals (Figures 6–8). Amorphous precipitate that was formed by the inhibitor addition, also observed by the SEM analysis, is shown in Figure 9.
DISSCUSSION

The addition of colloidal SiO₂ to the geothermal water affected the formation of crystallization nuclei as shown by the turbidimetric measurement (Figures 1 and 2). However, due to partial agglomeration of suspended deposit particles into larger ones that easily precipitated, a maximum water turbidity was observed when the amount of added colloidal SiO₂ was 50 mg/dm², corresponding to the total SiO₂ concentration of 126 mg/dm². Therefore, further increase of the colloidal SiO₂ concentration did not cause the increase of water turbidity.

In the presence of colloidal SiO₂, significant changes in turbidity did not occur because it led to the formation of larger agglomerates of the solid phase, so that heterogeneous system of water–solid was formed. Thus,
this observation proved that the solid deposit formation is possible in very soft hyperthermal geothermal waters if the colloidal SiO$_2$ is presented.

In the presence of inhibitor, as shown in Figure 3, the water turbidity significantly increased, indicating the formation of a great number of tiny dispersed solid particles. The growth of dispersed solid particles and their agglomeration were prevented by a thin film of surface active matter enveloping the particles. When the maximum concentration of colloidal SiO$_2$ was added to the geothermal water (60 mg/dm$^3$) together with the inhibitor in the critical concentration of 6 mg/dm$^3$, turbidity increased almost 20 times. Thus, a micro-heterogeneous system was created without agglomeration, even after prolonged storage.

The solid deposit formation influenced by the colloidal SiO$_2$ and the inhibitor is also possible, but this process can be controlled at the critical inhibitor concentration (6 mg/dm$^3$). A rather uniform distribution of small spherical crystals can be seen on SEM images of the solid deposit formed under these conditions (Figure 9). The EDS analysis shows (Figures 6–8) that the solid deposit contained dominantly sodium and silicon, while magnesium, aluminum and zinc were presented in smaller
As concluded from the XRD analyses, the solid deposits contained dominantly trona (T) and halite (H) phases, and may be related to the chemical composition of geothermal water and added colloidal SiO₂. Halite originated from the process of colloidal SiO₂ formation (Eq. (2)).

Solid deposit appearance in hard and geothermal waters is connected to the formation of poorly soluble carbonates and sulphates. However, it is still unclear how mixed calcium and magnesium silicates appeared in the solid deposit, as well as chalcedony and opal crystals. Plausibly, this could be attributed to the synergistic effects of soluble, colloidal and polymeric (suspended) forms of SiO₂ [12] with microelements, supported by the increase in pH and the neutralization of H₂CO₃. During the solid deposit formation and precipitation, valuable colloidal and other impurities were occluded, adsorbed, or in some other way isolated, from geothermal water.

For the processes of nucleation and solid particle growth, colloidal particles of SiO₂ as well as iron and aluminum ions that form weakly soluble hydroxides play an important role [13,14]. These hydroxides act as coagulants, supporting the formation of crystallization nuclei, followed by flocculation and agglomeration, which leads to the spontaneous and relatively fast solid deposit formation. Besides, chemical interactions of F⁻ and HS⁻ presented in geothermal water with colloidal particles should not be ignored.

The processes of nucleation and solid particle growth can be prevented by the addition of inhibitor, which contain surface active matters. The active components from the inhibitor emulsion are adsorbed on each suspended particle, tightly binding to calcium and magnesium, cover them completely, thus preventing nucleation and solid particle growth processes. Also, the chemical affinity of the emulsion components to Mg²⁺ and Ca²⁺, causes their complexation, apparently decreasing the total water hardness.

CONCLUSION

This study confirms that solid deposits can be formed even in soft geothermal waters that contain small amounts of calcium, magnesium and bicarbonates, if colloidal SiO₂ and microelements such as iron, aluminum, boron and fluorine are presented. Minor changes in turbidity result from the appearance of visible depo-
sits, i.e., macro-heterogeneous system solid–water with relatively low values of turbidity of 1.15 to 3.88 NTU at temperature of 40 °C, which increase to values of 2.3 to 6.27 NTU at temperature of 65 °C.

In the presence of an inhibitor affecting the nucleation process and solid deposit formation, it is possible to prevent the solid deposit formation in geothermal waters. The increase in turbidity of almost 20 times in the presence of inhibitor (6 mg/dm³) and after the addition of a maximum concentration of SiO₂ (60 mg/dm³) is evidence that a relatively stable micro-heterogeneous system of solid–water was created. The effect of inhibitor has been confirmed by the SEM analysis, which detected small spherical grains wrapped in a thin film of inhibitor. The addition of inhibitor prevents precipitation of trona (T) phase as confirmed by the XRD analysis. SEM analysis emphasized dendritic structure of SiO₂ while EDS detected Na, Si, Mg and Al elements. In this way water retains its composition, while the solid particles that are formed make a micro-heterogeneous disperse system. In the waters of high hardness, the formation of solid deposit (scale) under the influence of colloidal SiO₂ and inhibitor occurs besides the incrustation.

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REFERENCES


IZVOD
UTICAJ KOLOIDNOG SiO₂ I MODIFIKATORA NA FORMIRANJE ĆVRSTIH DEPOZITA U GEOTHERMALNIM VODAMA NISKE TVRDOĆE

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(Naučni rad)

Stvaranje čvrstih depozita (kamenca) često se dovodi u vezu sa obrazovanjem slabo rastvornih karbonata i sulfata kalcijuma i magnezijuma, narušavanjem karbonatne ravnoteže (inkrustacija) pri zagrevanju vode, kao i sa povećanjem čvrstog ostataka u jako mineralizovanim geotermalnim i podzemnim vodama. U ovom rada je ispitivano obrazovanje čvrstih depozita u jako mineralizovanim alkalnim geotermalnim vodama male tvrdoće, pod uticajem prisutnog i dodatog SiO₂ kao i drugih mikroelemenata. Pokazano je da se primenom originalnog modifikatora procesa kristalizacije i stvaranja čvrstih depozita, inhibira nukleacioni proces i sprečava agregacija suspendovanih čestica u veće agregate čvrstih depozita. Modifikator je spravljen od emulziona rastvornih organskih površinski aktivnih materija i aktivnih neorganskih materija. Za karakterizaciju čvrstog depozita korišćene su SEM, EDS i rendgenska strukturalna analiza kao i turbidimetrija koloidnih i suspendovanih čestica. Rezultati su pokazali da u prisustvu koloidnog SiO₂ dolazi do stvaranja čvrstog depozita u geothermalnim vodama male tvrdoće, uz obrazovanje makroheterogenog sistema čvrsto-tečno. Međutim, u prisustvu modifikatora i koloidnog SiO₂ sprečeno je stvaranje čvrstog depozita, uz obrazovanje veoma disperznog mikroheterogenog sistema čvrsto-tečno.

Ključne reči: Koloidni SiO₂ ● Inkrustacija ● Čvrsti depoziti ● Nukleacija ● Hidratacija
Key words Colloidal SiO₂ ● Incrustation ● Solid deposits ● Nucleation ● Hydration