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<th>Title</th>
<th>On Shirahama Thermal Springs, Wakayama Prefecture, Japan: Contamination With Sea Water and Deposits Inside the Conduit Pipe.</th>
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</thead>
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<tr>
<td>Author(s)</td>
<td>KIKKAWA, Kyozo</td>
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<tr>
<td>Citation</td>
<td>地球物理 (1954), 9(2): 85-94</td>
</tr>
<tr>
<td>Issue Date</td>
<td>1954-04-30</td>
</tr>
<tr>
<td>URL</td>
<td><a href="http://hdl.handle.net/2433/178361">http://hdl.handle.net/2433/178361</a></td>
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<tr>
<td>Type</td>
<td>Departmental Bulletin Paper</td>
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<td>Textversion</td>
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Kyoto University
On Shirahama Thermal Springs, 
Wakayama Prefecture, Japan

Contamination With Sea Water and Deposits Inside the Conduit Pipe.

Kyozo Kikkawa*

Introduction.

With the rapid developments of the thermal spring areas in Japan, reckless sinkings or overpumpings have so often broken the balance of demand and supply of thermal water, that its pressure has been lowered remarkably. It can be seen that at some hot springs near the coast, as in Beppu, their salinities have tolerably increased owing to the encroachments of the sea water.

Shirahama Spa, composed of about fifteen springs, is situated on the coast of Wakayama Prefecture, and they contain considerable HCO'3. So, Cl' content contrasted with HCO'3 can be used as the indexes of contamination with sea water or the lowering of hot water pressure heads.

The other significant fact in Shirahama Springs is the great amounts of deposits which grow rapidly inside the conduit pipes. Especially at Hashiriyu and Ueyama-yu, the amounts of white deposits, chiefly composed of CaCO3, are so large that they must be removed from a few hundred meters of pipes every tenth day. So, the measurements and the theoretical analysis of their states are necessary to trace the mechanisms of deposition from spring water.

Changes of Cl' and HCO'3 Contents.

Cl' and HCO'3 contents of every springs are measured in August and November, 1951. These results and those obtained from 1901 to 1930 are shown graphically in Fig. 2, from which two groups can be found, the one is named A, the other is B that consists of seven springs flowing near the seashore.

From the interesting facts that the old data are all in A group, and that B group has nearly linear distribution, extrapolation of which cuts the Cl-axis at about 19g/l nearly equal to the Cl' content of the sea water, it appears

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that all of the spring waters included in B group are formed by the mixture of 
the sea water and the hot water system, now named A, which has not changed

Fig. 1. Distribution of springs in Shirahama Spa. Numbers
besides the dots indicate the spring number.

Fig. 2. Comparison of Cl and HCO₃ ions contents from the
three kinds of data.
greatly its composition these 30−50 years. Accordingly, increases of Cl and decreases of HCO$_3^-$ have been induced proportionally to the mixing ratios. Fig. 2. also shows that these salt encroachments still developed from August to November in 1951. But it seems making no progress to the following year and a little decreases of Cl proportional to the increases of HCO$_3^-$ in B group are observed in October 1952. So, in Shirahama Springs, the process of the salt encroachment can be traced by the comparison of only two compositions, Cl and HCO$_3$.

It is noted that the lowering of temperature cannot be observed despite of the contamination.

**The Actual State of the Deposits Inside the Pipes.**

On the various sections of conducting pipes at Hashiri-yu and Ueyamayu, R and r, as in Fig.3 are measured two times.

White deposits inside pipes are distributed concentrically within the smaller errors than 0.2cm and decrease along pipes from the entrance.

The deposits in welling pipes, which are observed in the same way, are also concentric but have harder crystallization, and smaller quantity than in the conducting pipes, and decrease almost linearly with the depths from

Plate 1 and Fig. 3 Section of clogged conducting pipe of Hashiri-yu.
the well mouth.

It suggests the difference in mechanism of deposition between in conducting and in welling pipes.

**Theoretical Treatment.**

It is already known that CaCO₃ which is produced by the reaction, Ca(HCO₃)₂ → CaCO₃ + H₂O + CO₂, with the escape of CO₂, is not deposited at once but is apt to be supersaturated in the water. In the deposition from flowing water as in Shirahama, two processes may be found. The first is the above-mentioned process which accelerates the supersaturation and may be assumed proportional to the length of flow as the first approximation. The second is the deposition of those supersaturated CaCO₃ inside pipes. The latter appears to be introduced only by the contact of supersaturated water with the solid surface, because the process of deposition by gravity can be neglected as the deposits are so concentric at any section of pipes that no difference is seen between upper and lower sides of conducting pipe. Then, it can be assumed that the rate of deposition is proportional to the product of the contact area and the degree of supersaturation.

For the theoretical treatment, symbols are defined as follows.

\[ \alpha \] ; degree of supersaturation of thermal water.
\[ q \] ; flow rate of thermal water in the pipe.
\[ r₀ \] ; \( r \) at \( x=0 \)
\[ α₀ \] ; \( α \) at \( x=0 \)
\[ K, k, N \] ; constants.

\( x \)-axis is taken as plus along the conducting pipes and as minus along the welling pipes from the orifice.

The second process can be explained as

\[ \frac{\partial}{\partial t} \left( \pi r^2 \right) = k \cdot 2\pi r \cdot \alpha \cdot \frac{\partial r}{\partial t} \]

\[ \therefore \frac{\partial r}{\partial t} = - \frac{k}{\rho} \alpha \] \hspace{1cm} (1)

From the continuity of \( q \alpha \) which is the amount of supersaturated CaCO₃ flowing across the section per unit time, we can gain the next equation combining the first and the second processes.

\[ \frac{\partial q \alpha}{\partial x} = - k \cdot 2\pi r \alpha + kq \]

As \( q \) is independent on \( x \) and can be assumed proportional to the sectional area of entrance,
\[
\frac{\partial \alpha}{\partial z} = - \frac{k2\pi \gamma \alpha}{\eta} + K \\
= - \frac{2k\gamma \alpha}{N' \gamma_0^2} + K 
\]  
\(2\)

At \(x = 0\), equation (1) is:

\[
\frac{d\gamma_0}{dt} = - \frac{k}{\rho} \alpha_0 \\
\therefore \gamma_0 = R - \frac{k}{\rho} \alpha_0 t 
\]  
\(3\)

Equation (2) is approximated as follows, regarding that \(r\) and \(\gamma_0\) are the same order.

\[
\frac{\partial \alpha}{\partial z} = - \frac{2k\alpha}{N\gamma_0} + K \\
= \frac{2k}{N(R - \frac{k}{\rho} \alpha_0 t)} \left\{ \frac{KN(R - \frac{k}{\rho} \alpha_0 t)}{2k} - \alpha \right\} \\
\therefore \alpha = \frac{KN(R - \frac{k}{\rho} \alpha_0 t)}{2k} - \left\{ \frac{KN(R - \frac{k}{\rho} \alpha_0 t)}{2k} - \alpha \right\} \cdot e^{-\frac{2kX}{N(R - \frac{k}{\rho} \alpha_0 t)}} 
\]

Substituting this in (1) and integrating it under the condition that makes \(r\) to be equal to \(R\) at \(t = 0\).

\[
\int_0^T d\gamma = -\frac{KN}{2\rho} \int_0^T \left( R - \frac{k}{\rho} \alpha_0 t \right) dt + \frac{KN}{2\rho} \int_0^T \left\{ R - \frac{k}{\rho} \alpha_0 t - \frac{2k}{KN\alpha_0} \right\} \cdot e^{-\frac{2kX}{N(R - \frac{k}{\rho} \alpha_0 t)}} dt 
\]

It is found that

\[
\gamma - R = \frac{KN}{4\alpha_0 k}(\gamma_0^2 - R^2) + \frac{KN}{4\alpha_0 k}(R^2 e^{-\frac{2kX}{N\gamma_0^2}} - \gamma_0^2 e^{-\frac{2kX}{N\gamma_0^2}}) \\
+ \left( \frac{Kx}{2\alpha_0} + 1 \right) \left\{ \gamma_0 e^{-\frac{2kX}{N\gamma_0^2}} - R \cdot e^{-\frac{2kX}{N\gamma_0^2}} \right\} + \frac{2kX}{N} \int_{\gamma_0}^{\frac{2kX}{N\gamma_0^2}} e^{-\frac{u}{N\gamma_0^2}} \cdot du \\
\]

\[u = \frac{2kX}{N(R - \frac{k}{\rho} \alpha_0 t)} \]

(a) In the conducting pipe, \(x \geq 0\)

\[
R - \gamma = \frac{KN}{4\alpha_0 k}(R^2 - \gamma_0^2) - \frac{KN}{4\alpha_0 k}(R^2 e^{-\frac{2kX}{N\gamma_0^2}} - \gamma_0^2 e^{-\frac{2kX}{N\gamma_0^2}}) 
\]
\[ + \left( \frac{Kx}{2\alpha_0} + 1 \right) \left[ Re e^{-\frac{2kx}{NR}} - \tau_0 e^{-\frac{2kx}{N\tau_0}} + \frac{2kx}{N} \left\{ Ei\left(-\frac{2kx}{NR}\right) - Ei\left(-\frac{2kx}{N\tau_0}\right) \right\} \right] \] (4)

(b) In the welling pipe, \( x \leq 0 \)

\[ R - \tau = \frac{KN}{4\alpha_0 k} \left( R^2 - \tau_0^2 \right) - \frac{KN}{4\alpha_0 k} \left( R^2 e^{-\frac{2kx}{N\tau_0}} - \tau_0 e^{-\frac{2kx}{NR}} \right) \]

\[ + \left( \frac{Kx}{2\alpha_0} + 1 \right) \left[ Re e^{-\frac{2kx}{NR}} - \tau_0 e^{-\frac{2kx}{N\tau_0}} + \frac{2kx}{N} \left\{ Ei\left(-\frac{2kx}{NR}\right) - Ei\left(-\frac{2kx}{N\tau_0}\right) \right\} \right] \] (5)

Though the distributions of \( r \) can be shown by (4) or (5), the more simplified forms of the expression are desirable for the calculation.

When thermal water flows horizontally in the closed pipes, \( CO_2 \) is so slightly made free in the course of the flow that the increase of supersaturation through the first process may be negligibly small compared to its decrease through the second process. From this assumption, let \( K \rightarrow 0 \) in equation (4),

\[ R - \tau = Re e^{-\frac{2kx}{NR}} - \tau_0 e^{-\frac{2kx}{N\tau_0}} + \frac{2kx}{N} \left\{ Ei\left(-\frac{2kx}{NR}\right) - Ei\left(-\frac{2kx}{N\tau_0}\right) \right\} \] (6)

Putting the observed values of \( R \) and \( \tau_0 \) into (6), values of \( r \) corresponding to various \( x \) can be obtained and they agree with the observed values inside the conducting pipes as shown in Table 2 and Fig.4.

For the decreases of \( r \) with time, the validity of the above-mentioned theory can be ascertained as follows. Substituting \( R=4.9 \), \( \tau_0=2.8 \), \( x=9380 \) from Table 2 in (5), we can obtain \( \tau=4.62 \) nearly equal to the observed \( \tau=4.5 \).

Fig.4. Distributions of deposits along conducting pipes. Dots are observed values and curves are obtained theoretically by writer.

From the interesting fact that these thermal water does not spring out by the water pressure but due to the action of CO₂ made free from the thermal water, it is expected that the lifting of thermal water in the vertical pipes is accompanied by the active emission of CO₂ from the water with the lowering of water pressure. Accordingly, the first process is so vigorous in the welling pipes that the second can be negligible. Then assuming $k \to 0$ in (5), we can get

$$R - r = (R - r_0) \left(1 + \frac{Kx}{2\alpha_0}\right)$$  \hspace{1cm} (7)

The linear relation between $r$ and $x$ in the equation (7) agrees with the observed distribution of $r$ in Fig.5. Then, it is found that since the equations (6) and (7) are approximated closely to the observed states in the pipes, the above-mentioned various assumptions satisfy essentially the actual states for the deposition.
Summary

Cl' and HCO₃' contents and temperature have been measured three times in Shirahama Thermal Springs. Comparing these results to the old data, considerable contamination with sea water can be found in several springs on the west and east coasts. In spite of the salt encroachment, the lowering of temperature cannot be found.

The amounts of deposits inside the conduit pipes are measured. Theoretical equations of the deposition can be obtained and show quite agreements with the observed states. The deposition is produced by the contact of CaCO₃ supersaturated water and the wall inside the pipes. The supersaturated CaCO₃ produced in the conducting pipes has negligibly small rate compared to that deprived by deposition. In the welling pipes, the former is so large that the latter can be neglected. It is owing to the large rate of CO₂ made free from thermal water with its rising in the well.

Acknowledgments.

Greatful thanks are extended to Dr. Kinzō Seno for his helpful suggestions; to Hiroshi Kawabata and to Kōzō Yuhara for their excellent cooperations in the measurements.

This study is supported by a grant from the Science Research Fund, Department of Education.
Table 1. The observed values of Cl', HCO₃ contents and temperature in Shirahama Springs.

<table>
<thead>
<tr>
<th>Spring Number</th>
<th>Aug. 1951</th>
<th></th>
<th>Nov. 1951</th>
<th></th>
<th>Oct. 1952</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cl, g/l</td>
<td>HCO₃, g/l</td>
<td>Temp. °C</td>
<td>Cl, g/l</td>
<td>HCO₃, g/l</td>
<td>Temp. °C</td>
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<tr>
<td>1</td>
<td>7.14</td>
<td>1.76</td>
<td>76.</td>
<td>9.48</td>
<td>1.603</td>
<td>76.</td>
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<tr>
<td>2</td>
<td>6.40</td>
<td>2.29</td>
<td>58.</td>
<td>7.12</td>
<td>2.160</td>
<td>59.1</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>4.74</td>
<td>2.362</td>
<td>73.5</td>
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<tr>
<td>4</td>
<td>7.50</td>
<td>2.01</td>
<td>78.</td>
<td>8.63</td>
<td>1.61</td>
<td>75.2</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td></td>
<td></td>
<td>1.31</td>
<td>2.85</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td></td>
<td></td>
<td></td>
<td>1.10</td>
<td>2.184</td>
<td>63.6</td>
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<tr>
<td>7</td>
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<td>0.85</td>
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<td>51.6</td>
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<td>8</td>
<td></td>
<td></td>
<td></td>
<td>2.20</td>
<td>2.56</td>
<td>58.5</td>
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<td>3.05</td>
<td>2.80</td>
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<td>1.61</td>
<td>2.79</td>
<td>62.5</td>
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<tr>
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<td></td>
<td></td>
<td></td>
<td>1.09</td>
<td>2.64</td>
<td>61.6</td>
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<tr>
<td>13</td>
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<td></td>
<td></td>
<td>1.06</td>
<td>2.24</td>
<td>53.</td>
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<tr>
<td>14</td>
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<td></td>
<td>0.64</td>
<td>1.78</td>
<td>62.5</td>
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<tr>
<td>15</td>
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<td></td>
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<td>1.315</td>
<td>2.50</td>
<td>77.4</td>
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<tr>
<td>16</td>
<td></td>
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Table 2. (a) The observed and computed values of the amounts of deposits inside the conducting pipes.


On the 11th day. \( R=5.25 \text{cm.} \) \( 2k/N=8.32 \times 10^{-4} \).

<table>
<thead>
<tr>
<th>( x )</th>
<th>0m.</th>
<th>5.5</th>
<th>12.</th>
<th>42.</th>
<th>94.</th>
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</thead>
<tbody>
<tr>
<td>Obs. ( r )</td>
<td>2.5cm.</td>
<td>2.8</td>
<td>3.0</td>
<td>4.15</td>
<td>4.8</td>
</tr>
<tr>
<td>Comp. ( r )</td>
<td></td>
<td>2.8</td>
<td>3.15</td>
<td>4.15</td>
<td>4.9</td>
</tr>
</tbody>
</table>

Hashiri-yu, Nov. 13, 1951.

On the 10th day. \( R=5.25 \text{cm.} \) \( 2k/N=8.32 \times 10^{-4} \),

<table>
<thead>
<tr>
<th>( x )</th>
<th>0m.</th>
<th>6.</th>
<th>12.</th>
<th>49.</th>
<th>98.</th>
<th>98. (On the 20th day)</th>
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<tr>
<td>Obs. ( r )</td>
<td>2.8cm.</td>
<td>3.2</td>
<td>3.5</td>
<td>4.4</td>
<td>4.9</td>
<td>4.5</td>
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<tr>
<td>Comp. ( r )</td>
<td></td>
<td>3.07</td>
<td>3.37</td>
<td>4.37</td>
<td>4.9</td>
<td>4.62</td>
</tr>
</tbody>
</table>
Ueyama-yu, Nov. 14, 1951.

On the 12th day. R=5. 25cm. 2k/N=0.2×10⁻⁴.

<table>
<thead>
<tr>
<th>x</th>
<th>0m.</th>
<th>5.</th>
<th>11.</th>
<th>17.</th>
<th>22.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs. r</td>
<td>3.0cm</td>
<td>3.5</td>
<td>3.75</td>
<td>4.15</td>
<td>4.5</td>
</tr>
<tr>
<td>Comp. r</td>
<td>3.5</td>
<td>3.94</td>
<td>4.28</td>
<td>4.51</td>
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(b) The observed values of the amounts of deposits inside the welling pipes.


On the 30th day. R=4.0cm.

<table>
<thead>
<tr>
<th>x</th>
<th>0m.</th>
<th>-5.4</th>
<th>-11.4</th>
<th>-17.0</th>
<th>-22.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Obs. r</td>
<td>3.1cm</td>
<td>3.35</td>
<td>3.75</td>
<td>3.95</td>
<td>4.0</td>
</tr>
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</table>

(b) The observed values of the amounts of deposits inside the welling pipes.


On the 30th day. R=4.0cm.

白浜温泉の海水汚染と導管内壁えの沈澱物附着（抄録）

吉川 恭三

白浜温泉の泉温、Cl⁻と HCO₃⁻の含有量が3回にわたって繰返し測定され過去の結果と比較されて、温泉水系自身には余り化学組成の変化が認められないと考えられている。海岸部に於てかなり多量の海水の混入があることが認められた。又、白浜の二三の泉源で、温泉水からの沈澱物が導管内壁に附着する状況を測定した。其等は極めて多量であり、管壁に略々同心円的に附着し、その性質及び分布の状況は引湯管と湯口管で異っている。その附着の速度が温泉水中の過飽和度と接触面積に比例するとして解釈され、実測結果との対応をみた。湯口管内では温泉水が地表に向け上昇するに伴い多量の CO₂ガスが放出されて温泉水中の CaCO₃過飽和度を高めてゆく機構が活発に行われて居り、引湯管と沈澱物の状況を異にする原因となっていると解釈される。