The carbonate aggressiveness of water in the karst areas of the basin of the Chochołowski and Kościeliski streams (Western Tatra Mts.)

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ABSTRACT


Changes of the carbonate aggressiveness of water in the karst areas of the basin of the Chochołowski and Kościeliski streams (Western Tatra Mts.) are presented. The saturation index $SI_c$ is lowest for rainwater, higher for groundwater and highest for surface water. Most of the surface water flowing out of the West Tatra Mountains has the ability to dissolve carbonate rocks.

INTRODUCTION

The water which dissolves rocks plays a significant role in the process of chemical denudation. The ability to dissolve a specified amount of calcium or magnesium carbonates is defined as the carbonate aggressiveness of water.

Up to now, the problem of carbonate aggressiveness of water in the area of the Tatra has been mentioned only sporadically. OLEKSYNOWA (1970) tried to define a balance of the $\text{CO}_2\text{-H}_2\text{O}$-$\text{CaCO}_3$ system for the water of calcareous basins. For the samples taken only at the outflow of streams from the Tatra Mountains OLEKSYNOWA found that the water was almost saturated with calcite. In qualifying chemical denudation for the calcareous-dolomitic area of the West Tatra, KOTARBA (1972), who carried out his research in the Malá Łąka Valley, made some remarks regarding the aggressiveness of both rainwater on rock surface and the water of the Malolącki stream. In the first case the water was aggressive only to a small extent, while in the second case its
The carbonate aggressiveness was also considered by Pulina (1975, 1992), and Krawczyk & Opolska (1992), who specified the aggressiveness of the Kościeliski stream in the karst areas. This paper has been written on the basis of the results obtained during the stationary field research (Malecka 1984, 1996; Barczyk 1994).

CALCULATIONS

The amount of dissolved carbonate mass is specified by the saturation limit of the solution, which is dependent upon the content of aggressive CO$_2$, the concentration of hydrogen ions (pH) and the solution temperature (Pulina 1992). The carbonate aggressiveness is measured by means of either direct or indirect — graphic methods (Markowicz & Pulina 1979), or by using the Saturation Index (SI$_c$), which quantitatively defines the deviation of a particular type of water from the equilibrium state with calcite. In this work which concerns rain-, surface and karst-fissure water, the Saturation Index estimation method is used.

A general formula for the Saturation Index was given by White (1988): 

$$SI_c = \log \left( \frac{a_{Ca} \times a_{CO_2}}{K_c} \right)$$  \[1\]

where $K_c$ — the equilibrium constant [Ca$^{2+}$][CO$_2$]$^-$

The activities $a_i$ given in the numerator can be calculated by the multiplication of the concentrations and activity coefficient of a particular ion:

$$a_i = \gamma_i \times C_i$$  \[2\]

where: $\gamma_i$ — activity coefficient of a particular ion in a solution

$C_i$ — content of a particular ion in the solution

The activity coefficients are calculated by means of the Debye-Hückel (White 1988) equation:

$$-\log\gamma_i = \left( \frac{A \times Z_i^2 \times \sqrt{I}}{1 + \frac{a}{\gamma_i} \times B \times \sqrt{I}} \right)$$  \[3\]

where: $A$, $B$ — temperature-dependent constants (White 1988)

$$z_i$$ — charge of the ion

$\sigma_i$ — the diameter of the ion

$I$ — the ionic strength of the solution

For volume fractions (mval/dm$^3$), according to the composition of water, the ionic strength is formulated as:

$$I = 10^{-3}[Ca^{2+} + Mg^{2+} + SO_{4}^{2-} + CO_{3}^{2-} + 0.5(HCO_3^- + CO_3^{2-} + NO_3^- + Na^+ + K^+)$$  \[4\]

After conversions, SI$_c$ is given as (Krawczyk & Opolska 1992):

$$SI_c = \log \gamma_{Ca} + \log(0.5 \times 10^{-3} \times C_{Ca}) + \log \gamma_{HCO_3}$$

$$+ \log(10^{-8}C_{HCO_3}) - pH + pK_c - pK_n$$  \[5\]

where:

$C_{Ca}$, $C_{HCO_3}$ — content of calcium and hydrogen carbonates determined (mval/dm$^3$)

$pH$ — water reaction measured in field conditions

$pK_c$, $pK_n$ — equilibrium constants for carbonates

$\gamma_{Ca}$, $\gamma_{HCO_3}$ — activity coefficients.

The values of the equilibrium constants for reaction of carbonates, and of the constants A and B specified for particular temperatures, that are necessary for the calculation of the carbonate aggressiveness, are given in Table 1.

| $t^{[\mathbf{OC}]_{\mathbf{}}} | \begin{array}{c|c|c|c|c} \mathbf{pK}_c & \mathbf{pK}_n & \mathbf{A} & \mathbf{B} \\ \\
0 & 10.63 & 8.38 & 0.4883 & 0.3241 \times 10^8 \\
5 & 10.55 & 8.39 & 0.4921 & 0.3249 \times 10^8 \\
10 & 10.49 & 8.41 & 0.4960 & 0.3258 \times 10^8 \\
15 & 10.43 & 8.43 & 0.5000 & 0.3262 \times 10^8 \\
20 & 10.38 & 8.45 & 0.5042 & 0.3273 \times 10^8 \\
25 & 10.33 & 8.48 & 0.5085 & 0.3281 \times 10^8 \\
\end{array} |

$pK_c$ — negative logarithm of the equilibrium constant

$$[H^+] [CO_3^{2-}] / [HCO_3^-]$$

$pK_n$ — negative logarithm of the equilibrium constant

$$[Ca^{2+}] [CO_2^-]$$

Table 1. The equilibrium constants for reactions of carbonates used in the calculation of water aggressiveness (Appelo & Postma 1993) and the constants A and B for the Debye-Hückel equation (White 1988)
It has generally been assumed that $SI_c = 0$ for the equilibrium of water with calcite. $SI_c < 0$ indicates the likelihood of water aggressiveness in relation to calcite, $SI_c > 0$ indicates the high likelihood that a mineral precipitates from a solution (Malecki 1995). Jenne & Ball (1980) expanded the range of equilibrium towards a particular mineral to the value of Saturation Index $SI_c$ in the range ±5% log $K$.

The values of the Saturation Index $SI_c$ of the rainfall, surface water and groundwater of the karst areas of the Chocholowski and Kościeliski streams have been calculated using the above formula. Calculations of the $SI_c$ index for the rainwater from the station in Polana Chocholowska were carried out as shown in the example below:

1. Calculations of the ionic strength of the solution $I$ (equation [4]):
   \[
   I = 10^{-3 \times (0.52 + 0.28 + 0.12 + 0.5 \times (0.58 + 0.16 + 0.04 + 0.01))} \\
   I = 0.0013 \\
   \sqrt{I} = 0.036
   \]

2. Calculations of the activity coefficient for calcium ions $\gamma_{Ca}$ (for a particular solution) (equation [3]):
   \[
   -\log\gamma_{Ca} = 4 \times 0.4921 \times 0.036/[1 + (4 \times 10^{-8}) (0.3249 \times 10^8) \times 0.036] \\
   \gamma_{Ca} = 0.858
   \]

3. Calculations of the activity coefficient for hydrogen carbonate ions $\gamma_{HCO_3}$ (for a particular solution) (equation [3]):
   \[
   -\log\gamma_{HCO_3} = 0.4921 \times 0.036/[1 + (4 \times 10^{-8}) (0.3249 \times 10^8) \times 0.036] \\
   \gamma_{HCO_3} = 0.96
   \]

4. Calculations of the saturation index $SI_c$ (eq. [5]):
   \[
   SI_c = -0.066 + \log(0.5 \times 10^{-3} \times 0.52) - 0.017 + \log(10^{-3} \times 0.58) + 4.5 + 8.39 - 10.55 \\
   SI_c = -4.56
   \]

The calculations were based on the analysis of particular water samples. In the case of rainwater, estimated mean values of temperature and pH had to be assumed. A temperature of 5°C and pH value of 4.5 were used in the calculations (Wellburn 1988, Mason 1991, Malecka 1991, Miechowka 1993). If such assumptions are made, the values of $SI_c$ at particular measuring points do not significantly differ: all are in the range from -4.56 to -4.95, and the mean value for the whole area equals -4.69 (Table 2).

Similarly, the distribution of the $SI_c$ values for rainwater over a period of one year does not show any significant differences (Table 3).

In almost all cases (except for the water from Hala Ornak), the summer rainfall has the highest values of $SI_c$.

**DISCUSSION**

The results obtained unequivocally indicate the well-marked aggressiveness of rain water in the
whole area studied, as well as a lack of seasonal variability. The aggressiveness of ground water originates both from ground water that discharges into the streams and by contacts with bed rocks, in which a channel is incised. In the Tatra Mountains, the streams draining the crystalline core of the Western Tatra Mts. are characterised by the highest aggressiveness and, at the same time, by the lowest susceptibility of rocks to leaching. The values of the carbonate aggressiveness of the Tatra streams at the foot of the mountains are given for comparison in Table 4.

As the Chocholowski and Kościeliski streams (Text-fig. 1) flow along the valleys, crossing the diversified Tatra series in the boundary areas between rocks of the crystalline core of the Western Tatra Mts., Seisian sandstones and shales and carbonate rocks of a High Tatric Succession, rapid change of the susceptibility of formations to leaching takes place, despite the fact that the water has a constant aggressiveness. The changes of the $\text{SI}_c$ values caused by a contact between water and rocks in the longitudinal profile of streams are shown schematically in Text-fig. 2.

In both cases, the $\text{SI}_c$ index increases along the course of the stream, which means a gradual decrease in the aggressiveness of water. This is additionally illustrated by the data comparison in Table 5. The analysis of the $\text{SI}_c$ values indirectly enables some conclusions to be drawn concerning hydrogeology. For instance, the high water aggressiveness of Wyplyw spod Raptawickiej Turni (point D in Text-fig. 2) indicates a fast flux of water in the karst system and direct contact with rainfall water through open fractures. In the investigated basins karst waters are represented mainly by vaucluse springs. The comparison of the $\text{SI}_c$ values for water of Wywierzysko Chocholowskie (point A in Text-fig. 2) and Wywierzysko Lodowe (point F in Text-fig. 2) confirms the influence of the participation of surface water in the supplying of Wywierzysko Chocholowskie (SOLICKI & KOISAR 1973; BARCZYK 1994) and the exclusiveness of substratum discharge in the case of Wywierzysko Lodowe. In addition, the comparison indicates a long water residence in contact with the rock environment. In the case of Wywierzysko Chocholowskie ($\text{SI}_c = -0.77$), the duration of this contact is a little shorter than in the case of Wywierzysko Lodowe ($\text{SI}_c = -0.69$). The carbonate aggressiveness of both vaucluse springs is comparable with the values found for other springs in the Tatra (Table 6).
The analysis of the variability of the $S_i$ index in the studied areas enables us to assume two alternative scenarios for forming the final carbonate aggressiveness of surface water and groundwater. One possibility is the following chain: rainfall – a karst system – vaucouleurs springs; the water circulates long enough to cause a visible decline in the $S_i$ values. The other possibility is: surface water – a karst system – outflows, in which water residence time is much shorter. In addition, it is worth noticing the fact that in some cases both systems might be connected (Wypływ spod Pisanej, Wypływ spod Raptawickiej Turni). A persistence of this connection depends on

<table>
<thead>
<tr>
<th>Vaucouleurs spring</th>
<th>Valley</th>
<th>Saturation index $S_i$</th>
</tr>
</thead>
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<tr>
<td>Chocholowskie</td>
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<tr>
<td>Lodowe</td>
<td>Kościeliska</td>
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</tr>
<tr>
<td>Bystre Górne</td>
<td>Bystra</td>
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<td>Bystre Dolne</td>
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<td>Goryczkowe</td>
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</tr>
<tr>
<td>Olczyskie</td>
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<td>-0.84</td>
</tr>
</tbody>
</table>

Table 6. Saturation index $S_i$ in the water of the selected vaucouleurs springs in the Tatra Mts.

Fig. 2. The scheme of the variability of the saturation index $S_i$ along the course of the Chocholowski and Kościeliski streams; A – Wyw. Chocholowskie, B – Chocholowskie spring, C – Wypływ spod Pisanej, D – Wypływ spod Raptawickiej Turni, E – karst springs (Kościeliska valley), F – Wyw. Lodowe, K1, K2, K3, K4, K5 – sampling localities from the Kościeliski stream, Ch1, Ch2, Ch3, Ch4 – sampling localities from the Chocholowski stream (location see Text-fig. 1 and Table 5)
climatic conditions and, especially on the amount of rainfall, which influences the water table in streams and enables direct connections between a karst system and surface water to open, while the water level is high. It is reasonable to suppose that these scenarios can also be inferred in other karst areas of the Tatra Mountains.

REFERENCES


