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A REVIEW ON SATURATION INDEXES OF KARSTIC WATERS (S. I.).

ABSTRACT

This article has been developed to trace the essential elements necessary for the calculation of the karst water saturation index (SI).

Waters over-saturated with respect to calcium carbonate CaCO_3 tend to precipitate CaCO_3 . Waters undersaturated with respect to CaCO_3 tend to dissolve with respect to calcium carbonate CaCO_3 . Saturated waters, i. e, waters in equilibrium with CaCO_3 , have neither precipitating nor dissolving tendency. They represent the dividing line between "probable precipitation" and "not probable precipitation".

In this article the author highlights the calculation system proposed by the AWWA (Joint Task Group on Calcium Carbonate Saturation) by applying it to the water of the Boka karst resurgence (M. Canin - Slovenia).

The importance of pH, pCO_2 , ionic strength, ions activity and alkalinity in the calculation is highlighted.

Also, water characteristic not directly involved in the calculation of index SI such as Mg^{2+} , SO_4^{2-} , ion pairs, kinetic factors, etc., can greatly influence the tendency of water to corrode.

Karstology, speleogenesis and karst morphology are conditioned by a series of phenomena that have not yet been fully understood.

RIASSUNTO

Nell'articolo sono riportati gli elementi di calcolo utilizzati per la determinazione dell'Indice di Saturazione (S.I.) delle acque carsiche.

Nella teoria consolidate si presuppone che acque sovrassature tendano a precipitare il carbonato di calcio mentre le acque sottosature dovrebbero essere responsabili della dissoluzione. Le acque in equilibrio costituiscono la linea divisoria tra una probabile precipitazione ed una altrettanto probabile dissoluzione.

L'autore mette in evidenza il sistema di calcolo suggerito dall'AWWA (Joint Task Group on Calcium Carbonate Saturation) e lo propone per determinare le caratteristiche dell'acqua carsica della risorgiva della Boka (M. Canin – Slovenia).

Viene evidenziata l'importanza delle quantificazioni di pH, pCO_2 , forza ionica, attività ionica e alcalinità.

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Si spiega come alcune caratteristiche dell'acqua come Mg^{2+} , SO_4^{2-} , ioni complessi e cinetica del sistema possono influenzare notevolmente le proprietà corrosive.

E' evidenziato come carsismo, speleogenesi e morfologia carsica possono essere condizionati da una serie di eventi chimico-fisici non ancora ben studiati.

Introduction

Advancements have been made in the understanding of karst processes by studies of the chemical carbonate equilibria of karst waters.

These studies, numerous, have been carried out by technicians during the past forty years.

They require the chemical analysis of the karst water for the main dissolved components (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , NO_3^- , SO_4^{2-} and HCO_3^-) and the determination of pH, alkalinity, temperature, electrolytic conductance.

From the chemical data, the ionic strength (I or μ) and the activity (a) of ionic species in solution can be calculated.

The researchers showed a difficulty in estimating the degree of saturation of karst water (saturation index – S. I.).

The S. I. is a function of many chemical-physical parameters including temperature, pCO_2 , pH, ionic strength, Ca^{2+} , ions activity, alkalinity, soil, etc.

The engine of limestone dissolution is carbon dioxide CO_2 , and its partial pressure pCO_2 which varies greatly on the surface and in depth with the seasons, vegetation, soil characteristics and rainfall.

Surface aquifers, karst springs and percolation water in soil and in depth are under-saturated, the water contained in the soil and groundwater, on the other hand, has a highly degree of saturation.

The excessive interest aroused by researchers is given by the fact that the saturation index suggests only and exclusively the tendency of a karstic water to dissolve or precipitate calcium carbonate– $CaCO_3$. But the rate at which a given karst water reaches equilibrium cannot be derived from the S. I. value.

The author highlights the elements that condition the calculation of the S. I. and presents a simplified calculation system to detect the various problems.

Studies and Research

The Langelier saturation Index was originally developed by LANGEIER (1936) to determine the tendency of a water to deposit or dissolve calcium carbonate. Further important progress has been made in the karst field, including studies on the limestone dissolution and carbonate equilibria in karst water (THRAIKILL J., 1968; PLUMMER ET AL.; 1982; ROSSUM ET AL., 1983). Specific experiments were conducted by PRISGAN ET AL. (1985 a, b) on the calcium carbonate saturation index of water systems.

An advanced computing system was published in 1990 by the JOINT TASK GROUP ON CALCIUM CARBONATE SATURATION (1990).

Advanced studies have been conducted in Italy by BERBENNI (1963) and PORLEZZA (1963). Italian scientists have developed new calculations on the activity of the hydrogen ions in carbonate waters and on the relationships between pCO₂, solubility and pH.

A classic text of Italian scientific literature is: BIANUCCI G. ET AL., 1985.

An accurate calculation system of the CCPP (calcium carbonate precipitation potential), which also takes into account the TDS, has been proposed by Holm et al. (1998).

More recently specific studies have been conducted by the Milano Polytechnic in: *Chimica, chimica-fisica e chimica analitica delle acque naturali* - GEMITI; BERBENNI ET AL., 1999. Some studies on the saturation index of the caves in the classical Karst near Trieste have been published by GEMITI AND MERLAK (1999, 2000).

Ionic Strength (I or μ) of a karst water.

The ionic strength of a karst water is a function of the concentration of all ions present in a solution. The simplified form of calculation is as follows:

$$I = \frac{1}{2} \sum_i z_i^2 c_i$$

Here, c_i and z_i are the molar concentration and charge of ion i. The sum is taken over all ions in the solution. Due to the square of z_i, multivalent ions (Ca²⁺, Mg²⁺) contribute particularly strongly to the ionic strength.

The calculation is valid only for dilute solutions, and a good approximation is achieved by using the concentrations of the most important species found by the analysis (Ca²⁺, HCO₃⁻, Mg²⁺, etc.).

The analysis of the Boka karst resurgence (M. Canin) serves as an example of this type of calculation:

Conc.	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻
mg/l	30	3,1	0,3	0,3	0,5	1,9	1,6	99
mmoli/l	0,75	0,1275	0,013	0,008	0,014	0,031	0,016 5	1,623
meq./l	1,5	0,255	0,013	0,008	0,014	0,031	0,033	1,623

Tab.1- Karst water (spring Boka, M. Canin, Slovenia). Analysis: F. Gemit (Chemical laboratory ACEGAS, Trieste, February 2, 1999). Water temperature 20°C.

Calculation of the ionic strength of the water from the Boka resurgence, M. Canin – Bovec -Slovenia:

$$I = \frac{1}{2} \sum_i z_i^2 c_i$$

$$0,5 \cdot [(0,75 \cdot 4) + (0,1275 \cdot 4) + (0,013 \cdot 1) + (0,008 \cdot 1) + (0,014 \cdot 1) + (0,031 \cdot 1) + (0,0165 \cdot 4) + (1,623 \cdot 1)] = 0,5 \cdot (3 + 0,51 + 0,013 + 0,008 + 0,014 + 0,031 + 0,066) = 0,5 \cdot 3,642 = 1,821$$

$$I = 1,821 \cdot 10^{-3} = 0,00181$$

The ionic strength of Boka karst water (February 2, 1999) is 0.00181.

For comparison: the average indicative values of the ionic strength of typical waters are as follows:

unpolluted rain water in equilibrium with CO ₂ (pH 5,65)	0,000001
polluted rainwater	0,0004-0,001
karst water (M. Canin, Slovenia)	0,002-0,003
karst water in classical Karst (Trieste, Italy)	0,005-0,02
mineral water	0,05-0,5
thermal water and brine	0,1-1,0
sea water	3,2-3,5

Ionic strength is related to both total dissolved solids and electrolytic conductance. Since the sum of ions is greater than all ions in solution, a complete analysis of the karstic water is implied.

In karst water, when the solute undergoes ionic dissociation in solution, the system becomes decidedly **non-ideal** and the dissociation process must be taken into account.

The activities for cations and anions (a_+ and a_-) can be defined separately. In karst water, the activity coefficient of a given ion (e.g. H⁺, Ca²⁺) cannot be measured because it is experimentally impossible to measure the electrochemical potential of an ion in solution. Therefore, it is necessary to introduce the notions of ionic activity " a " and of activity coefficient " f ".

This coefficient is defined as the ratio of the ionic activity to the molar concentration:

$$f_i = a_i / m_i$$

For dilute solutions and karst waters, the activity coefficients of individual ions can be obtained with sufficient accuracy from the following equation, which is based on the Debye-Hückel theory of interionic interaction, as expressed by the equation

$$\log f_i = A z_i^2 \sqrt{I} / 1 + a_i B \sqrt{I}$$

where A and B are constants depending on the specific pressure and temperature of the solvent (water), z_i is the valency of the ion in the specified solution, I is the ionic strength, and a_i is a term depending on the effective diameter of the ion in the solution. Also the

concept of ionic concentration is replaced by that of ionic activity ($a_{\text{Ca}^{2+}}$, a_{H^+} , $a_{\text{HCO}_3^-}$, etc.). The concept is well expressed in Fig. 1 where the activity coefficients f of the ionic species are indicated as a function of the ionic strength of the aqueous solution.

It is clear that the activity of the single ions depends on the ionic strength of the aqueous solution: increasing the ionic strength reduces the activity of the ionic species.

Monovalent ions have an activity coefficient of approximately 0.95 (indicative value). Divalent ions have an activity coefficient estimated at about 0.83.

Therefore, for the calculation of the saturation index of this water (Boka) it must be assumed that only 83% of calcium and only 95% of H^+ and OH^- contribute to the carbonate equilibria.

It has been pointed out that the concept of individual activity coefficients cannot be precisely defined, and such coefficients may not even be determined experimentally without some supplementary definition of non-thermodynamic nature (KIELLAND, 1937). But this concept (the inaccuracy of the data) can be overcome whenever absolute precision is not required.

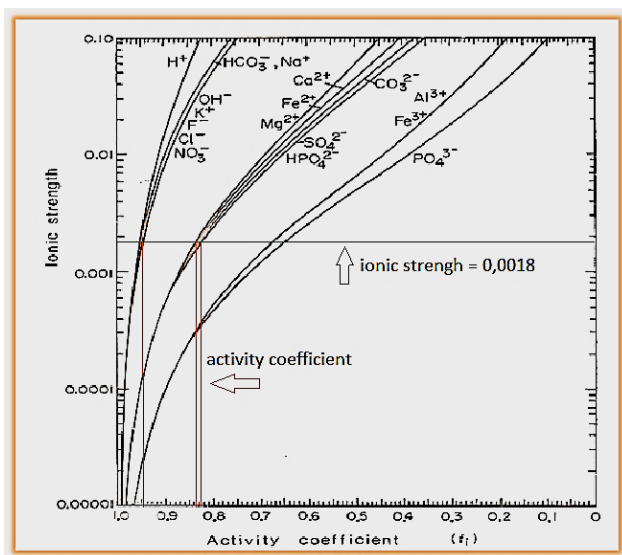


Fig. 1 – Relation between the activity coefficients of dissolved ions and the ionic strength. The horizontal line corresponds to the ionic strength 0.0018. The lines indicate the corresponding activity coefficients of the ions. Karst water (Boka spring M. Canin, Slovenia). Analysis: F. Gemiti (Chemical laboratory ACEGAS, Trieste, February 2, 1999). The values were obtained from the original study by LEWIS AND RANDALL (1923) AND KIELLAND (1937), subsequently taken up by HEM (1970) and MATTHES (1982).

Saturation Index – S. I. and Carbonate Equilibria

The saturation index can theoretically be expressed as the logarithm of the ratio of the hydrogen activity at CaCO_3 saturation ($a_{\text{H}^+}^{\text{sat.}}$) to the actual hydrogen activity (a_{H^+}) – at the time of the pH measurement.

$$\text{SI} = \log_{10} [(a_{\text{H}^+}^{\text{sat.}}) / (a_{\text{H}^+})]$$

the simplified equation is:

$$\text{SI} = \text{pH}_{\text{measured}} - \text{pH}_{\text{sat.}}$$

where $a_{H^+}^{sat.}$ is the saturation pH and a_H^+ is the instrumentally measured pH of the solution.

The symbol a_i refers to the activity of ionic species i and the activity is a measure of the actual concentration of a species i in a mixture, meaning that the chemical potential of the species depends on the activity of a real solution in the same way that it would depend on concentration in an ideal dilute solution.

The activity and the concentration are significantly different and, as such, it is not valid to approximate with concentrations where activities are required.

Several solutions have been elaborated to formulate a correct equation that determines the $pH_{sat.}$.

The JOINT TASK GROUP ON CALCIUM CARBONATE SATURATION (1990) suggests the analytical solution with the following formula:

$$pH_{sat.} = pK_2 - pK_s - \log Ca^{2+} - \log Alk - 5pf_m$$

where: pK_2 = second dissociation constant for carbonic acid; pK_s = solubility product constant for $CaCO_3$; Ca^{2+} = calcium ion concentration gr-mol/l; Alk= total alkalinity; f_m = activity coefficient for monovalent species.

In the pH range 6,5 – 9,5 (and therefore for all karst waters) $Alk (alkalinity) = HCO_3^-$.

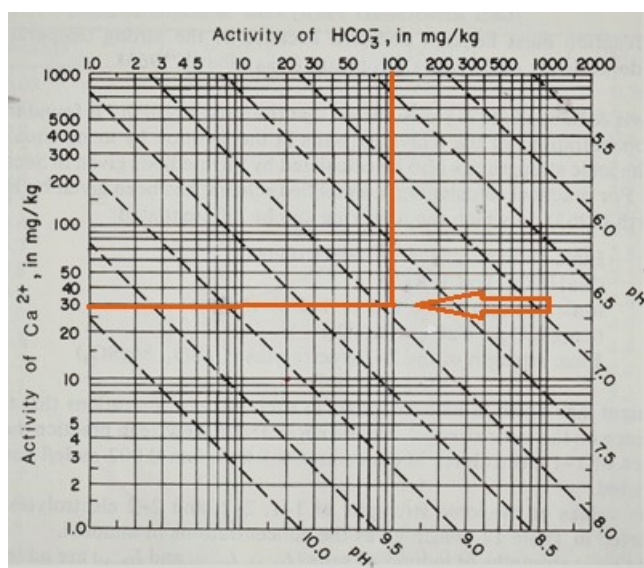


Fig. 2 – The figure shows the relationship between equilibrium pH and the Ca^{2+} and HCO_3^- and HCO_3^- activities for range 1-2000 mg/l in contact with calcite with standard temperature and pressure (according to HEM, 1961b). The two orange lines indicate the concentrations of Ca and HCO_3^- ; the blue arrow indicates the theoretical saturation point. Karst water of Boka, M. Canin, Slovenia.

Theoretically, the equation could solve the pH calculation and therefore that of SI, but it doesn't work like that.

In the formula, the concentrations of the pairs of ions, always present in karst water, have been left out.

Furthermore, the other ions present in the karst water, especially Mg^{2+} and SO_4^{2-} , are not taken into account.

Ion pairs and complexes.

The ions, instead of being widely separated in solutions of karstic water, tend to interfere with one another. So new types originate alongside the free ions.

These complex ions can be treated as thermodynamic entities. Complexes are combinations of cations with molecules and anions containing free pairs of electrons.

The ion pairs and complexes in karst water (in the presence of magnesium) are as follows: CaHCO_3^+ , CaSO_4° , CaCO_3° , CaOH^+ , MgHCO_3^+ , MgSO_4° , MgCO_3° , MgOH^+ . Thus, total Ca (measured) is the sum of free Ca and ion pairs and complexes.

In an attempt to give some solution to the problem of theoretical calculation of saturation pH, PISIGAN ET AL. (1985) developed and proposed a new set of equations including the other ions present in karst water. The most convincing equation takes into account the presence of magnesium and sulphates:

$$\text{pH sat.} = 11.207 - 0.916 \log \text{Ca}_{\text{tot.}} + 0.039 \log \text{Mg}_{\text{tot.}} - 0.991 \text{Alk}_{\text{tot.}} + 0.032 \text{SO}_{4\text{ tot.}}$$

This equation takes into account the fact that Mg and SO₄ increase the ionic strength and decrease the activity of Ca^{2+} and CO_3^{2-} ; but it is only an empirical equation that does not necessarily hold for all waters.

Sample calculation

<u>Conc.</u>	<u>Ca²⁺</u>	<u>Mg²⁺</u>	<u>Na⁺</u>	<u>K⁺</u>	<u>Cl⁻</u>	<u>NO₃⁻</u>	<u>SO₄²⁻</u>	<u>HCO₃⁻</u>
<u>mg/l</u>	<u>30</u>	<u>3.1</u>	<u>0.3</u>	<u>0.3</u>	<u>0.5</u>	<u>1.9</u>	<u>1.6</u>	<u>99</u>
<u>mmoli/l</u>	<u>0.75</u>	<u>0.1275</u>	<u>0.013</u>	<u>0.008</u>	<u>0.014</u>	<u>0.031</u>	<u>0.0165</u>	<u>1.623</u>

Calculation of the saturation pH of karst water: Boka resurgence (20°C). Formula proposed by the JOINT TASK GROUP ON CALCIUM CARBONATE SATURATION:

$$\text{pH}_{\text{sat.}} = \text{pK}_2 - \text{pK}_s + \text{pCa}^{2+} + \text{pHCO}_3 - 5\text{p}f_m$$

Alkalinity as HCO_3

Calculated in mmoli/l.

$$\text{pK}_2 = 10.38; \text{pK}_s = 8.45; \log \text{Ca}^{2+} = 3.13; \log \text{Alk} = 2.8; 5\text{p}f_m = 0.085$$

A = 0.506 for t = 20°C

The calculation of $\text{p}f_m$, valid to I < 0.5, is as follows:

$$\begin{aligned} \text{p}f_m &= 0.506 \cdot [(\sqrt{I} / 1 + \sqrt{I}) - 0.3 I] = 0.506 \cdot [(\sqrt{0.00181} / 1 + \sqrt{0.00181}) - 0.3 \cdot 0.00181] = \\ &= 0.506 \cdot [(0.042 / 1.042) - 0.0054] = 0.506 \cdot [0.040 - 0.0054] = 0.506 \cdot 0.034 = 0.017 \\ 5\text{p}f_m &= 5 \cdot 0.017 = 0.085 \end{aligned}$$

pH saturation of Boka = 7.74 SI = 7.80 - 7.74 = 0.06 (karst water in theoretical equilibrium).

In fig. 3 the Excell sheet containing the chemical-physical characteristics of Boka water. The data are obtained from Fabio Gemiti's analyses, and the parameter were calculated with a personal program developed by the author.

The program was originally created for the calculation of conductivity but it can also calculate the sat pH and the saturation index following the values indicated by the

	A	B	C	D	E	F	G	H	N	
1	parametri	valori	ioni	mg/l	meq/l	c.eq.inf.	c.eq.	cond.spec.	millimoli/l	
2	t°C	20	Ca	30,00	1,500	53,04	48,14	72,2	0,750	
3	T assoluta	293,16	Mg	3,10	0,255	47,13	40,07	10,2	0,128	
4	C diel.	80,366	Na	0,30	0,013	44,93	43,16	0,6	0,013	
5	visc.	0,01004	K	0,30	0,008	66,37	63,98	0,5	0,008	
6	pH sol.	7,80								
7	forza ion. l	0,00263	H	0,0000	0,000	323,85	318,88	0,0	0,000	
8	radice quadrata	0,05131								
9	rqi (1+rqi)	0,04881								
10	Q rilassazione	0,4580	Cl	0,50	0,014	68,76	66,75	0,9	0,008	
11			NO3	1,90	0,031	64,74	62,77	1,9	0,031	
12			SO4	1,60	0,033	70,64	60,96	2,0	0,017	
13			HCO3	99,0	1,623	39,91	38,19	62,0	1,623	
14			OH	0,0107	0,001	182,65	179,46	0,1	0,001	
15			SiO2	0,4	0,007	monomero in soluzione				
16			eq.cation		1,8		Kt calc.	150,5		
17			eq.anion.		1,7		Kt mis.	150,0		
18			unbalanc. %		4,3		diff % K	0,3		
19			HCO3 teor.	103,527	1,697		K equiv.	86,55		
20			pH sat	7,90						
21		S.I.	-0,1							
22			valori fisico - chimici del campione rilevati o ricavati							
23			concentrazione in milligrammi/litro							
24			concentrazione in milliequivalenti/litro							
25			conducibilità ionica equivalente a diluizione infinita alla temperatura t°C							
26			conducibilità ionica equivalente per il campione in esame							
27			conducibilità specifica attribuita ai singoli ioni per il campione in esame							
28			conducibilità specifica calcolata, misurata e differenza %							
29			concentrazione in milliMoli							
30	Enrico Merlak CGEB Trieste 2015		pH di saturazione							
31			indice di equilibrio							
32			conducibilità equivalenti lente: vale solo per singoli sali in soluzione							
33	Risorgiva carsica Boka Canin sloveno analisi Fabio Gemiti 2 febbraio 1999									

Fig. 3 - Calculation program elaborated by the author for the definition of the chemical-physical parameters (ionic strength, dielectric, viscosity, relaxation, conductivity, saturation pH and saturation index).

AWWA. In this case the saturation pH detected by the program is 7,90 with saturation index -0,1 (equilibrium). The insignificant difference between measured and calculated conductivity (0.3%) demonstrates the accuracy and reliability of the analysis.

Field measurements

The author has carried out numerous instrumental investigations on the ground to obtain reliable data on the pH and SI of karst waters.

Karst basin of Bresovica (Matarsko podolje-Slovenia)

Fig. 4 shows the diagram of the hydrological basin of the Lozice stream in the Bresovica area (Matarsko podolje, Slovenia).

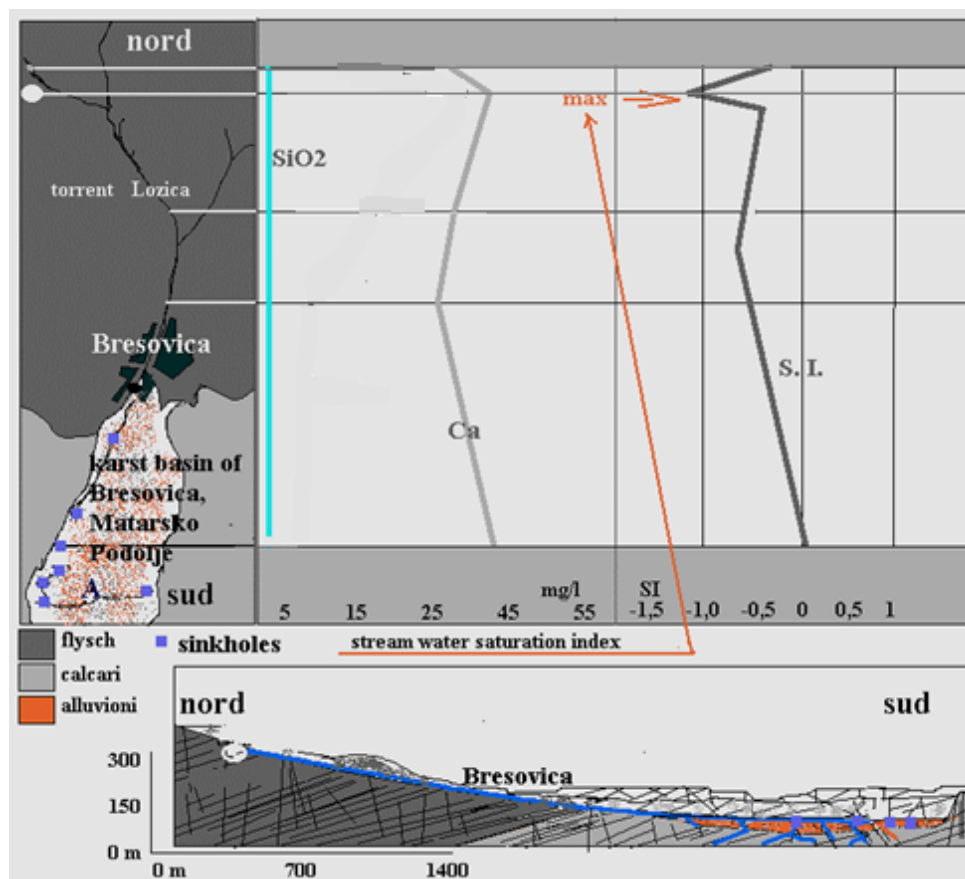


Fig. 4 – Karst basin of Bresovica. Evolution of the S. I. saturation index along the Lozice stream (Matarsko podolje – Slovenia). By MERLAK E., 2007. From the water source to the final basin, the saturation index goes from 0 to -1.1. Calculation based on indications from the JOINT TASK GROUP (AWWA). The maximum aggressiveness of the water corresponds to the highest concentration of CO₂ detected in the stream.

Direct pH and CO₂ measurements and water sampling were carried out following the course of the stream. It was thus possible to calculate the SI variations of the stream water.

The investigations, carried out in the karst over several months, suggest that the pH and SI of the water are strictly conditioned by CO₂, water flow rate, temperature and biological activity.

b) Grotta di Trebiciano: pH measurements



Fig. 5a - Trebiciano cave (near Trieste). Positioning of the detection points (-100m and -220m).

Investigations were conducted in the Trebiciano cave near Trieste, ascertaining a specific variation of the SI as a function of seasonality (MERLAK ET AL., 2007). The surveys were conducted continuously for 18 months at depths of 100 and 220 meters. PH measurements were performed on site using precision electrodes (fig. 9a, 9b).

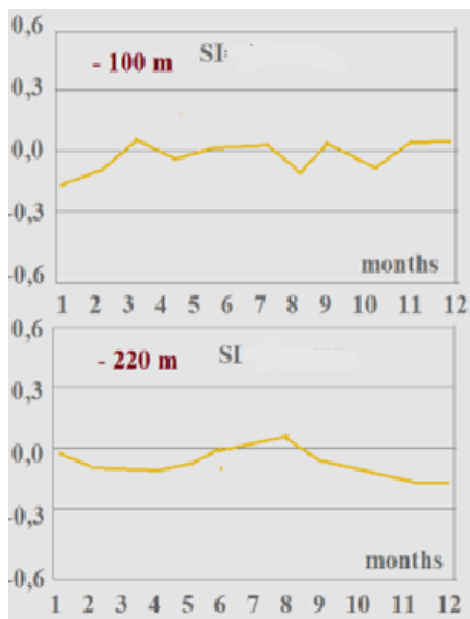


Fig. 5b - Average of the SI values in the survey points at -100m and -220m. Survey period: fortnightly from January to February. MERLAK E., BRUN C., GEMITI F., SEMERARO R., 2007. The pH measurements were performed on site using precision electrodes (fig. 9a; 9b).

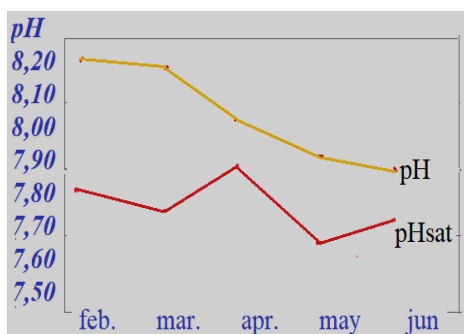


Fig. 6 - Cave II N of Gropada (VG 857 - Classic Karst). Variation of mean pH values and calculated pHsat values. Months from January to June. GEMITI F., MERLAK E., 1999; 2000).

c) Analytical study of percolation water: Cave II N of Gropada - VG 857.

In the months from February to June 1999 samples of percolation water were taken in order to determinate the variations of the saturation pH (GEMITI F., MERLAK E., 1999). The analyses concerned 3 sampling points and were performed under the supervision of Fabio Gemiti - chemical laboratory ACEGAS-Trieste of ACEGAS - Trieste.

Fig. 6 shows the average pH values, obtained from several measurements conducted at the 3 collection points, and the corresponding saturation pH obtained from the AWWA calculations.

The pH and alkalinity values

pH

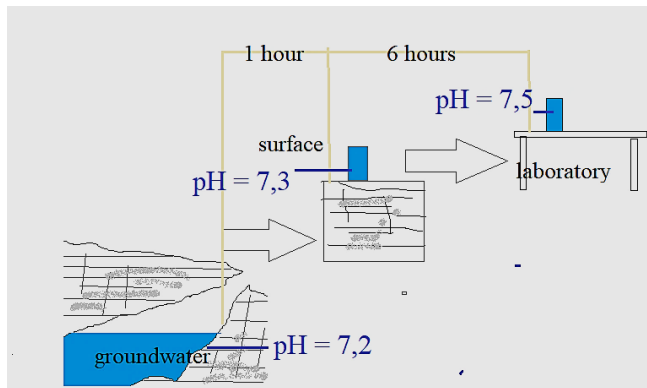


Fig. 7 - Showing illustration of the pH variation from the measurement in the cave to the laboratory. The slightest variations are on the order of 0.3 pH units or greater. Temperature in the cave: 11°C, outdoor: 19°C, in the laboratory: 20°C.



Fig. 8 - To guarantee the reliability of the data, the calibration of the pH meter and the pH measurement must be performed in the cave, using the calibration solutions and a precision thermometer (photo: Merlak).

The pH values used for the study of solubility require the most accurate measurement possible. These are made almost exclusively with a glass electrode in conjunction with calomel electrode as a reference electrode. The ordinary glass electrode allows accurate measurements in the pH range below 11. The pH of karst water depends on the temperature. This should be enabled by incorporating temperature compensation and standardizing before and after reading the instrument.

The glass electrode (fig. 9a, 9b) should be rinsed in distilled water after use to remove absorbed ions. The reading

should not be taken until the measured voltage has stopped fluctuating, indicating that has been reached the equilibrium between electrodes and solution. During experimental works the measurements are influenced by the exchange of gas (CO_2) with the atmosphere and the variations in temperature cause a constant drift in the pH readings. In karst water, differences in pH values of 0.5 or more can occur between cave, field and laboratory. In the case studied here, the measurements in the field or in caves are essential for the exact measurement of natural conditions and for the calculation of the S. I. (Fig. 7, 8) It shows

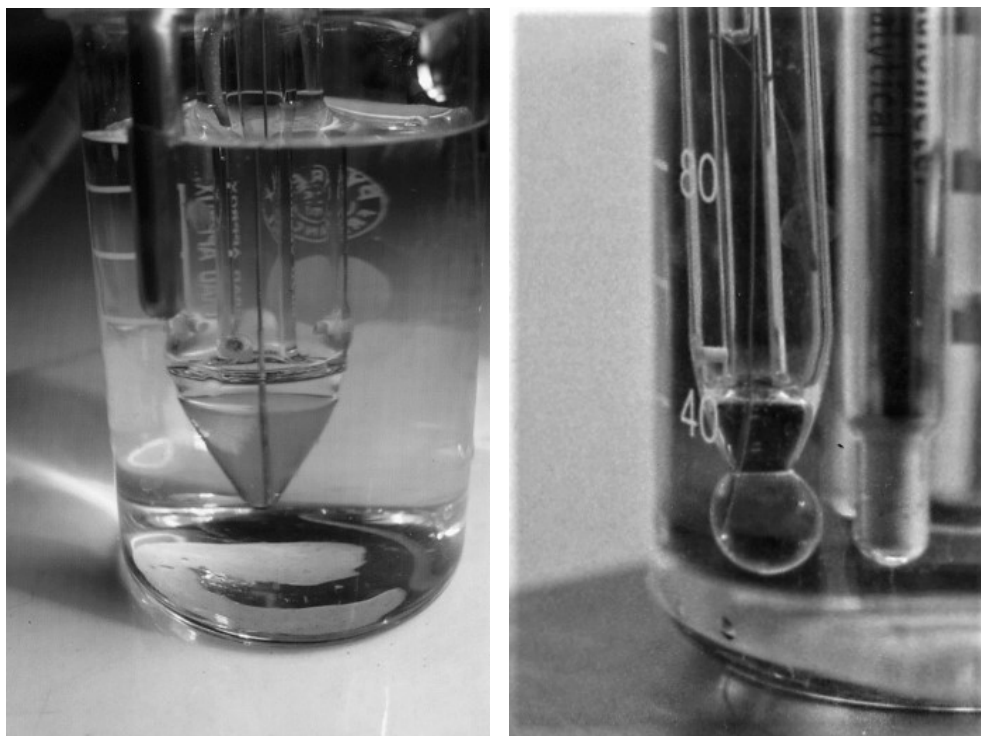


Fig. 9a, 9b - Precision glass electrodes, used by the author for pH measurements. The measurements require the use of a precision thermometric probe. To obtain the fastest electrode response, the glass electrode should be stored in a slightly acidic solution. In the protective cap for the glass electrode, put one or two drops of pH 4 buffer and put the cap on the electrode, carefully (photos: Merlak).

an example of modification of the pH of a water sample extracted from the Trebiciano cave, near Trieste. During a series of samplings carried out over 18 months, the author found that between the measurements in the cave and those in the laboratory, the pH varied between 0.3 and 0.6 units.

Alkalinity

Using specific attention, it is also possible to measure alkalinity (total carbonic species such as HCO_3^-) in caves or on the surface (outdoor) avoiding the gaseous exchanges that occur with the change in temperature and with transport to the laboratory (BURNES, 1964).

Alkalinity is commonly measured by titration, using either a burette or the drop count technique. A sample is titrated with an acid solution, which neutralizes the alkaline species present. The endpoint is determined by titrating to a pH value of 4.5, using a pH electrode as an indicator. The volume of titrant required to reach the endpoint is then used to calculate total alkalinity. The method has limitations: using a burette or dropper is tedious and time-consuming; measuring in caves is not recommended because you operate in uncomfortable situations and the environmental difficulties make it complicated to reach the endpoint.

Therefore, the author suggests to carry out the alkalinity measurement outdoors, near the cave, setting up a small portable laboratory.

Discussion

Many chemical-physical qualities of karst water must be measured and analyzed to calculate the CaCO_3 S.I saturation index: it is assumed that the SI is indicative of the karst water's ability to corrode or crystallize. This is because the concept of unsaturated or supersaturated water is associated with the corrodibility of limestone.

Sampling date	n°	1 5.02	2 13.02	3 23.02	4 8.03	Average 5.2-8.3	5 23.03	6 28.03	7 18.04	8 23.04	9 1.05	10 16.05	11 30.05	Average 23.3-30.5	12 12.06	13 23.06	Average 5.2-30.5
Dripping	ml/h	40	48	30	25	36	15	72	190	350	130	6	7.5	110	1	0	83
Calcium	mg/l	67	78	76	66	72	66	74	79	80	80	78	84	77	68		75
Magnesium	mg/l	3.6	3.6	2.2	3.6	3.3	2.9	2.9	2.9	2.9	3.2	2.9	2.9	3.0	2.7		3.1
Sodium	mg/l	0.7	1.6	1.2	1.3	1.2					0.5	0.0			0.6		0.9
Potassium	mg/l	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2		0.2
Bicarbonates	mg/l	204	239	233	206	221	201	227	243	245	244	238	257	237	220		231
Chlorides	mg/l	1.0	1.6	1.3	1.3	1.3					0.8				1.0		1.2
Nitrates	mg/l	0.6	0.5	0.3	0.4	0.5					0.4				0.7		0.4
Sulphates	mg/l	7.4	5.8	4.5	5.9	5.9					6.0				6.3		5.9
Cat. + Anions	mg/l	285	330	319	285	305					335				299		318
Cond. 25° C	µS/cm	336	382	362	340	355	323	364	394	392	390	382	412	380	366		371
Cond. 20° C	µS/cm	297	338	320	301	314	286	322	349	347	345	338	365	336	324		328
TDS	mg/l	288	328	310	292	305	277	312	338	336	335	328	354	326	314		318
Total hardness	°F	18.2	21.0	20.0	18.1	19.3	17.6	19.7	21.0	21.2	21.4	20.6	22.2	20.5	18.1		20.1
Calcium hard.	°F	16.7	19.5	19.1	16.6	18.0	16.4	18.5	19.8	20.0	20.1	19.4	21.0	19.3	17.0		18.8
Alkalinity	°F	16.7	19.6	19.1	16.9	18.1	16.5	18.6	19.9	20.1	20.0	19.5	21.1	19.4	18.0		18.9
Silica	mg/l	1.1	1.1	1.1	1.0	1.1											
U.V. Absorption		0.14	0.15	0.10	0.125	0.13						0.12			0.13		0.11
Outdoor Air Temp.	°C	5.0	-2.0	2.5	7.0	3.1	6	7	5	10	12	13	16	10	18	18	7.4
Indoor Air Temp..	°C	6.5	6.0	6.1	6.0	6.2	7.5	7.5	7.5	7.3	8.5	7.9	8.0	7.7	9.5	8.8	7.4
Soil Temp.	°C	2.0	1.0	2.0	3.2	2.1	4.0	4.0	6.0	6.5	9.0	11.0	14.0	7.8	15.0	12.0	5.7
Water temp.	°C	6.5	6.0	6.0	6.5	6.3	7.5	7.2	7.5	7.3	8.0	7.9	8.5	7.7	8.6	9.0	7.2
pH		8.21	8.07	8.16	8.19		8.06	8.03	7.97	7.86	7.90	7.86	7.92		7.80		
pHs		7.85	7.74	7.76	7.85		7.82	7.72	7.67	7.67	7.67	7.67	7.61		7.72		
SI Langelier		0.36	0.33	0.40	0.34	0.36	0.24	0.31	0.30	0.19	0.23	0.19	0.31	0.25	0.08		0.29
CCPP (CaCO ₃)	mg/l	7.4	9.6	10.5	7.2	8.7					8.2						
Tot. hard. - Alk.	°F	1.5	1.4	0.9	1.2	1.3					1.4				0.1		1.3
Calc. hard.-Alk.	°F	0.0	-0.1	0.0	-0.3	-0.1					0.1				-1.0		-0.1
K ₂₀ /Alk.		17.8	17.2	16.8	17.8	17.4					17.3				18.0		17.4
Cat+An/K ₂₀		0.96	0.98	1.00	0.95	0.97					0.97				0.92		0.97

Fig. 1 Appendix. - Summary of analytical and chemical- physical data relating to a sampling point. Cave II N of Gropada - VG 857 (Gemiti, Merlak – 1999, 2000). A particular software was used: LISA-CRR (AGAC-CISE, 1994). This program is similar to the AWWA calculation system but allows displaying all the chemical-physical parameters of the water.

But there are limitations in the computational reliability of SI.

Oversaturation of karst water does not guarantee the precipitation of CaCO_3 . The water may be oversaturated but not sufficiently to initiate crystallization and calcite deposition; conversely, unsaturated water may not be aggressive towards limestone.

The SI value should be interpreted in combination with the environmental conditions, karst water flow rate, temperature and continuous gaseous exchange with CO_2 .

The measured alkalinity and total calcium exert greater influence on the pH of CaCO_3 saturation. Significant levels of magnesium and sulfate can affect the carbonate balance with ion pair formation, reducing the activity of free Ca^{+2} and CO_3^{-2} ions.

The dissolution of calcite under conditions of high pH (8.0-9.0) is shown to be strongly inhibited by the presence of magnesium (Mg^{2+}) cations (COMPTON ET AL., 1994).

The same goes for TDS (total dissolved solid).

Appendix

Determination of the pH_{sat} and Langelier index - Cave II N of Gropada (VG 857 - Classic Karst). Spreadsheet.

The study of the percolation water of the Cave involved 3 sampling points and 39 complete analyses carried out in the laboratory of F. Gemiti (Lab. ACEGAS - Trieste).

For calculating the pH_{sat} and SI the LISA-CRR program was used. This program also allows the calculation of the CCPP (fig. appendix).

The results made it possible to ascertain that the dripping waters are mainly super-saturated and, therefore, calcifying.

The differences are minimal and may be partly due to incomplete chemical characterization, partly to physical and chemical variations (temperature, soil effects, vegetation, rainfall).

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