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CALCIUM CARBONATE EQUILIBRIA IN WATER SUPPLY SYSTEMS

Water corrosion causes substantial damage to ductile, cast iron and steel water distribution systems. The corrosiveness of water depends on many physical, chemical, and even microbiological parameters. Stability indexes in respect of calcium carbonate like the Langelier Saturation Index (LSI) are also considered. First, the roles of inorganic complexes of calcium and manganese are discussed with respect to the accuracy of the calcium carbonate equilibrium calculations. As long as the drinking water parameters were below the EC Directive permissible values, neglecting these complexes had a small effect on the results of LSI computations. A model for computing LSI in water mixtures closed to the atmosphere was presented and partially verified on a small laboratory scale.

Waters produced by all water treatment plants serving Kraków were evaluated in respect of the LSI, buffer capacity, and other parameters characterizing corrosive properties of water – in respect to iron. In general, the waters differed significantly in buffer capacity but all were evaluated as not presenting serious problems in internal corrosion of iron and cast iron, or more recently ductile iron pipes. This conclusion was verified based on a survey of main pipelines transporting water from the largest intake to the town, on the computations of the pipe roughness coefficient and on the mass balance of iron along the main transit pipes.

NOTATION

- Alk_T – total alkalinity of water (M),
- $CO_{2\text{aggr}}$ – aggressive carbon dioxide (M),
- C_T – total inorganic carbon defined by equation (17) (M),
- d – inside diameter of a pipe (m),
- f_m, f_d – mono- and divalent ions activity coefficients assumed to be independent of individual properties of ions,
- I – ionic strength of water (M),
- K_w – ionic product of water (M^2),
- K_1, K_2 – first and second order carbonic acid dissociation constants (M),

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- K_3-K_8 – constants of calcium and magnesium complexes defined in table 1,
 LSI – Langelier Saturation Index (pH) defined by equation (19),
 LSI_E – Langelier Saturation Index (pH) after adjusting concentration of calcium and total alkalinity, to account for the complexes of Ca,
 $p\{\dots\} = -\log\{\dots\}$,
 $pH_s = \text{pH}$ of water saturation with calcium carbonate $\{-\log(M)\}$,
 S – hydraulic gradient (m/m),
 α_1, α_2 – ratios (15), (16) in which the total inorganic carbon C_T (17) exists as bicarbonate $[\text{HCO}_3^-]$ and carbonate $[\text{CO}_3^{2-}]$ species,
 ρ – density of water (kg/m^3),
 τ – shear stress (N/m^2),
 $[\text{HCO}_3^-] = [\text{CO}_2]_{\text{aq}} + [\text{H}_2\text{CO}_3]_{\text{aq}}$ (M).

1. INTRODUCTION

The Langelier Saturation Index (LSI) is one of several parameters used for the predicting the corrosive properties of water. Most large water-distribution systems are supplied with water from several sources, delivered from a few separate intakes. Moreover, due to the fluctuations in water demand and the effect of rainfall variations on raw surface water quality, the composition of the water in a single area of the town will also vary. The method of computing the Langelier Saturation Index for these mixtures is presented in this paper. Some preliminary work on this model was published recently [3]. The impact of inorganic complexes on the value of LSI was tested for a water-supply system for the city of Kraków. Our method of computing LSI of water mixture may easily be used together with a numerical model for water pipe-distribution system, which delivers information on the mixing ratio at any point and at any time in the pipe network. The public domain program Epanet is a good example of such a tool. While the method of LSI calculation had been verified experimentally on a laboratory scale, it was still necessary to investigate the phenomena accompanying water flow through corroding pipes, by the time the method would be directly applicable. Some survey into the existing water supply system has been conducted to compare the primary evaluation of theoretically predicted low water aggressiveness towards inside surface of water pipes after 30 years of operation.

2. GOVERNING EQUATIONS

The Langelier Saturation Index may be calculated approximately from the set of equations shown below, including the first (1) and the second (2) dissociation constants of carbonic acid, the formula for the water equilibrium constant (3), the formula describing the total alkalinity of water (4) (if the carbonate equilibrium is the driving

process), the definition of pH (5), and finally the formula for the solubility product K_S of calcium carbonate (6) [1], [8]:

$$K'_1 = \frac{K_1}{f_m^2} = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*]}, \quad (1)$$

$$K'_2 = \frac{K_2}{f_d} = \frac{[\text{H}_3\text{O}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}, \quad (2)$$

$$K'_w = \frac{K_w}{f_m^2} = [\text{H}_3\text{O}^+][\text{OH}^-], \quad (3)$$

$$\text{Alk}_T = 0.5[\text{HCO}_3^-] + [\text{CO}_3^{2-}] + 0.5[\text{OH}^-] - 0.5[\text{H}_3\text{O}^+], \quad (4)$$

$$\text{pH} = -\log\{f_m[\text{H}_3\text{O}^+]\}, \quad (5)$$

$$K'_S = \frac{K_S}{f_d^2} = [\text{Ca}^{2+}]_{\text{eq}}[\text{CO}_3^{2-}]_{\text{eq}}. \quad (6)$$

It was assumed in all the computations that the values of the activity coefficients for neutral species were equal to 1.0. The equilibrium constants K_1 , K_2 , K_w , K_S are the functions of a temperature T [1] (in kelvins):

$$pK_1 = \frac{17052}{T} + 215.21 \times \lg T - 0.12675 \times T - 545.56, \quad (7)$$

$$pK_2 = \frac{2902.39}{T} + 0.02379 \times T - 6.498, \quad (8)$$

$$pK_w = \frac{4787.3}{T} + 7.1321 \times \lg T + 0.010365 \times T - 22.801, \quad (9)$$

$$pK_S = 0.01183 \times (T - 273.16) + 8.03 \quad (10)$$

described by equations (7), (8), (9), (10) which are valid for temperatures up to at least 333 K (60 °C). p denotes the negative logarithm to the base 10. Equation (10) assumes strong calcite domination over other mineral forms of CaCO_3 and the absence of water soil constituents having an impact on solubility, like humic substances or clay. Aragonite may be another possible form, while vaterite, monohydrate, and hexahydrate are unstable or very unstable, and amorphous CaCO_3 is created only at high oversaturation of water with CaCO_3 , resulting in its rapid precipitation [10]. The solubility products of different calcium carbonate solid forms differ significantly one from the other [8].

In general, there are two different values of the pH_s of calcium carbonate equilibrium for waters of the same total alkalinity Alk_T , calcium concentration, temperature T and ionic strength of water I . However, in the pH range from 6.5 to 9.5 there is only one value of pH_s calculated from the system of equations (1)–(10) [1].

For the investigations into the calcium carbonate equilibrium presented here a more complex model [9] was adapted. In this model, both the total alkalinity and the concentration of calcium were modified in the computations based on the concentrations known from the chemical analyses of water by subtracting the ions involved in inorganic complexes (the so-called ion pairs effect):

$$[\text{Ca}^{2+}] = [\text{Ca}]_T - [\text{CaOH}]^+ - [\text{CaHCO}_3]^+ - [\text{CaCO}_3]^0 - [\text{CaSO}_4]^0, \quad (11)$$

$$\begin{aligned} \text{Alk}_T = & [\text{CO}_3^{2-}]_T - [\text{CaCO}_3]^0 - [\text{MgCO}_3]^0 + 0.5 [\text{HCO}_3^-]_T - 0.5 [\text{CaHCO}_3]^+ \\ & - 0.5 [\text{MgHCO}_3]^+ - 0.5 [\text{H}_3\text{O}^+] + 0.5 [\text{OH}^-]. \end{aligned} \quad (12)$$

Taking into account the formulae for the complex stability constants collected in table 1 [1], [9], the following formulae for $[\text{Ca}^{2+}]$ and Alk_T may be derived:

$$[\text{Ca}^{2+}] = \frac{[\text{Ca}]_T}{\left(1 + \frac{K'_w K'_3}{[\text{H}_3\text{O}^+]} + K'_4 \alpha_1 C_T + K'_5 \alpha_2 C_T + K'_6 [\text{SO}_4^{2-}]\right)}, \quad (13)$$

$$\begin{aligned} \text{Alk}_T = & c_T \{ \alpha_2 (1 - K'_5 [\text{Ca}^{2+}] - K'_8 [\text{Mg}^{2+}]) + 0.5 \alpha_1 (1 - K'_4 [\text{Ca}^{2+}] - K'_7 [\text{Mg}^{2+}]) \} \\ & + \frac{K'_w}{\{2[\text{H}_3\text{O}^+]\} - 0.5[\text{H}_3\text{O}^+]}, \end{aligned} \quad (14)$$

where α_1 and α_2 are the proportions in which the total inorganic carbon C_T exists as HCO_3^- and CO_3^{2-} . α_1 and α_2 are given by the following equations [1], [8], [14]:

$$\alpha_1 = \frac{1}{\frac{[\text{H}_3\text{O}^+]}{K'_1} + 1 + \frac{K'_2}{[\text{H}_3\text{O}^+]}}}, \quad (15)$$

$$\alpha_2 = \frac{1}{\frac{[\text{H}_3\text{O}^+]^2}{K'_1 K'_2} + \frac{[\text{H}_3\text{O}^+]}{K'_2} + 1}}, \quad (16)$$

$$C_T = [\text{H}_2\text{CO}_3] + [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]. \quad (17)$$

Assuming that the system of equations (1)–(6) refers to the thermodynamical equilibrium, hence $[\text{Ca}^{2+}] = [\text{Ca}^{2+}]_{\text{eq}}$ and $[\text{CO}_3^{2-}] = [\text{CO}_3^{2-}]_{\text{eq}}$, the following equation results [9] for the pH_s of the water solution saturated with calcium carbonate:

$$\begin{aligned} \text{pH}_s = & pK'_2 + p[\text{Ca}^{2+}] - pK'_s + p\{2[\text{Alk}_T] - [\text{OH}^-] \\ & + [\text{H}_3\text{O}^+]\} - p\left(\frac{2 \times K'_2}{[\text{H}_3\text{O}^+] + 1}\right) - pf_{m,s}, \end{aligned} \quad (18)$$

where:

p denotes $\{-\log\}$,

$$K'_2 = K_2/f_d,$$

$$K'_s = K_s/f_d^2.$$

The potential necessary for precipitating calcium carbonate or for dissolving it in a protective pipe coating is described by the Langelier Saturation Index (LSI) defined as follows [7]:

$$\text{LSI} = \text{pH} - \text{pH}_s, \quad (19)$$

where pH is known from laboratory measurements and pH_s computed from equation (18), or from a similar mathematical model.

Table 1

Constants of calcium and magnesium complexes as functions of temperature [1]

$K'_3 = f_d K_3 = \frac{[\text{CaOH}^+]}{[\text{Ca}^{2+}][\text{OH}^-]}$	$K_3 = 10^{1.299+260.388\left(\frac{1}{T} - \frac{1}{298.15}\right)}$	(20)
$K'_4 = f_d K_4 = \frac{[\text{CaHCO}_3^+]}{[\text{Ca}^{2+}][\text{HCO}_3^-]}$	$K_4 = 10^{-2.95+0.0133T}$	(21)
$K'_5 = f_d^2 K_5 = \frac{[\text{CaCO}_3]^0}{[\text{Ca}^{2+}][\text{CO}_3^{2-}]}$	$K_5 = 10^{-27.393+\frac{4114}{T}+0.05617T}$	(22)
$K'_6 = f_d^2 K_6 = \frac{[\text{CaSO}_4]^0}{[\text{Ca}^{2+}][\text{SO}_4^{2-}]}$	$K_6 = 10^{\frac{691.7}{T}}$	(23)
$K'_7 = f_d K_7 = \frac{[\text{MgHCO}_3^+]}{[\text{Mg}^{2+}][\text{HCO}_3^-]}$	$K_7 = 10^{2.319-0.011056T+2.29812 \times 10^{-5} T^2}$	(24)
$K'_8 = f_d^2 K_8 = \frac{[\text{MgCO}_3]^0}{[\text{Mg}^{2+}][\text{CO}_3^{2-}]}$	$K_8 = 10^{0.991+0.006677T}$	(25)

Negative values of LSI indicate the tendency for CaCO_3 to dissolve, and positive values – its tendency to precipitate. However, cathodic and anodic corrosive reactions have an impact on the pH of water that occupied pores of a protective layer created by the products of corrosion and precipitation from the stream of water [14]. In consequence, the LSI describes the potential of flowing water to form or dissolve CaCO_3 but not necessarily the potential of the water trapped in the pores of protec-

tive scales [13]. The LSI of a water mixture can be calculated from (19) and (18) if only pH, Alk_T , calcium concentration, temperature and ionic strength are known.

The concentration of $[\text{Ca}^{2+}]$ and the total alkalinity Alk_T in equation (18) should be modified according to formulae (13), (14) to improve the accuracy of the pH_s computations by taking into account the impact of calcium inorganic complexes on pH_s . The amount of calcium ions bounded in inorganic complexes depends on the chemical composition of water [9], [1], [14]. Some tests carried out for several drinking water intakes in the south of Poland have shown that the ion-pair effect is unlikely to have a significant enough impact on pH_s to exceed the uncertainty of the results of calculations caused by the inaccuracy of laboratory measurements, which are shown in figure 1.

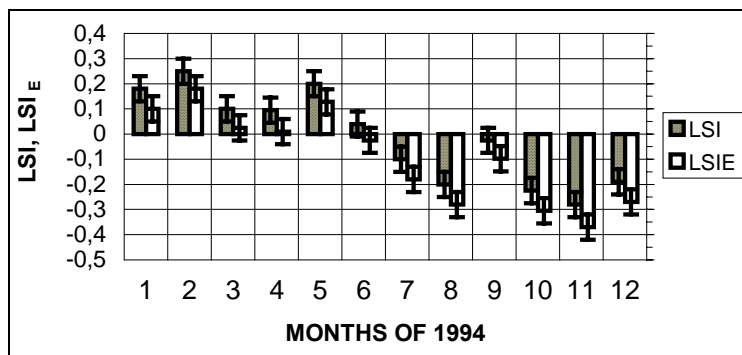


Fig. 1. Comparison of Langelier Saturation Index values computed “before” (LSI) and “after” (LSI_E) adjusting the concentration of calcium and the total alkalinity in equation (18) to the ion-pair effect resulted in the mass balance equations (13), (14) after [3]

Each result of calculations is accompanied by a margin of uncertainty predicted under the assumption that the all measured experimentally values of the total alkalinity Alk_T , pH $[\text{Ca}^{2+}]_T$, temperature, TDS were predicted with an error specified by the standard or by the accuracy of methods [12] and instruments in such a way that once all of them contribute to overestimation and once to underestimation of the computed values of pH_s , LSI, LSI_E.

The waterworks company, reporting the data used for computations, has been using the methods specified in table 2.

In all calculations, the differences between the values of pH_s computed with and without accounting for the ion-pair effect were lower than 0.2. According to other numerical tests [2] this observation was correct as long as the concentration of sulphates did not exceed $300 \text{ mg SO}_4^{2-}/\text{dm}^3$, which is above the value specified in the regulations established by the Polish Ministry of Health for drinking water ($200 \text{ mg SO}_4^{2-}/\text{dm}^3$) and by US EPA secondary standards ($250 \text{ mg SO}_4^{2-}/\text{dm}^3$).

Table 2

Laboratory methods with maximum errors of measurements

Error	Absolute error	Methods of determination
ΔpH	0.05	pH-meter
ΔT (K)	0.1	electronic thermometer
ΔTDS (mg/dm ³)	0.1	gravimetric
$\Delta[\text{Ca}^{2+}]$ (mg Ca/dm ³)	0.1	EDTA titration
ΔAlk_T (mg CaCO ₃ /dm ³)	0.1	titration
$\Delta[\text{Mg}^{2+}]$ (mg Mg/dm ³)	0.1	titration
$\Delta[\text{SO}_4^{2-}]$ (mg SO ₄ ²⁻ /dm ³)	0.1	titration

3. MATHEMATICAL MODEL

Water supply systems may be considered to be closed to the atmosphere. Due to high pressures, the solubility of gases, including CO₂, is much higher in water mains than in raw water sources, so there is no risk of creating air bubbles except in unusual circumstances. This allows the mass balance equations (20), (21), (22), (23) and (24) to be used [3]:

$$T_{\text{mix}} = \frac{\sum_{i=1}^n V_i T_i}{\sum_{i=1}^n V_i}, \quad (20)$$

$$\text{TDS}_{\text{mix}} = \frac{\sum_{i=1}^n V_i \text{TDS}_i}{\sum_{i=1}^n V_i}, \quad (21)$$

$$[\text{Ca}^{2+}]_{\text{mix}} = \frac{\sum_{i=1}^n V_i [\text{Ca}^{2+}]_i}{\sum_{i=1}^n V_i}, \quad (22)$$

$$C_{T\text{mix}} = \frac{\sum_{i=1}^n V_i C_{Ti}}{\sum_{i=1}^n V_i}, \quad (23)$$

$$\text{Alk}_{T_{\text{mix}}} = \frac{\sum_{i=1}^n V_i [\text{Alk}]_i}{\sum_{i=1}^n V_i} \quad (24)$$

to calculate the temperature T_{mix} , total dissolved solids TDS_{mix} , calcium concentration $[\text{Ca}^{2+}]_{\text{mix}}$, total concentration of inorganic carbon $C_{T_{\text{mix}}}$, and total alkalinity $\text{Alk}_{T_{\text{mix}}}$ of a mixture. Then the $\text{pH}_{\text{mix}} = -\log\{[\text{H}_3\text{O}^+]_{f_m}\}$ of the mixture is computed [6] from equation (14) for known alkalinity Alk_T , total inorganic carbon concentration C_T , amount of bicarbonate and carbonate ions. This allows the prediction of the Langelier Saturation Index of the water mixture which completes the computations.

4. EMPIRICAL VERIFICATION

To investigate the accuracy of the model described some laboratory experiments were carried out for artificial and natural waters [2], [3]. In most experiments, waters of significantly different alkalinity and pH were mixed in several proportions. First the samples were stored at room temperature, with contact to the atmosphere, and then injected by nozzles into plastic bags with no air content, equipped with a pH electrode. The water was gently mixed by a magnetic stirrer located inside the bag. The setup is presented in figure 2. Measurements of pH lasted half an hour and then the total alkalinity was measured. An average value was calculated from five experiments carried out under identical conditions.

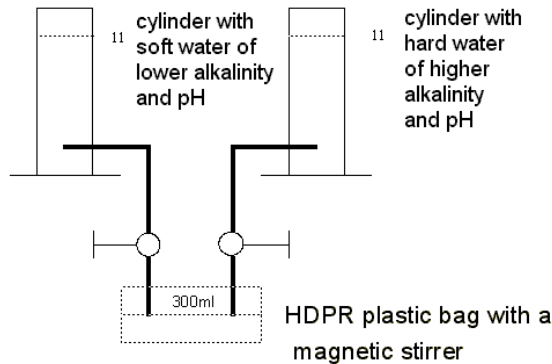


Fig. 2. Laboratory setup [2]

The results of measurements made for the mixtures of waters from a rocky part of the Tatra Mountains and surface waters flowing through soil of high calcium content are presented in figures 3 and 4. Waters of different origin were selected to test their

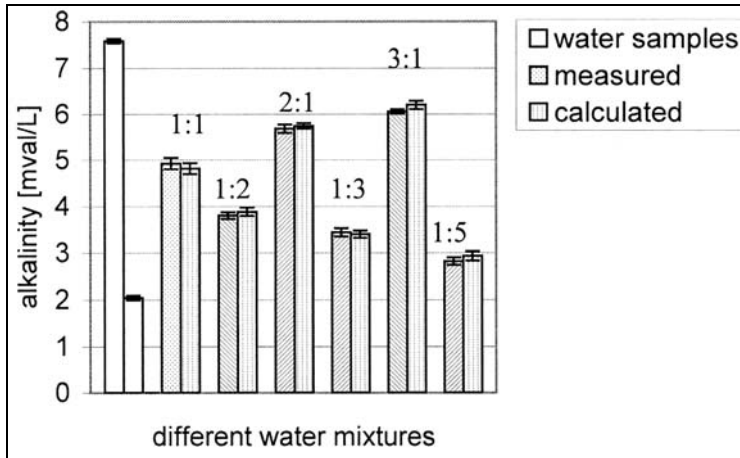


Fig. 3. An example of a comparison of measured with calculated total alkalinity of natural water mixtures

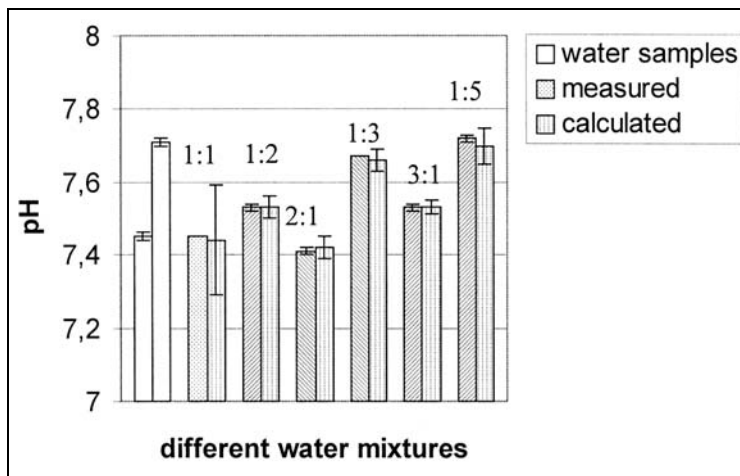


Fig. 4. An example of a comparison of measured with calculated pH of natural water mixtures

formulae under extreme conditions. Standard deviations are given both for measured and computed pH and the total alkalinity of water mixture. Measurements of the parameters used in the formulae to calculate both pH and total alkalinity were not exactly repeatable, hence being responsible for a standard deviation of the total alkalinity and pH values computed. For each of measured and calculated values the standard deviation was calculated. The values of standard deviations are presented in figures 3 and 4 on the top of each bar presenting the results of measurements and calculations of total alkalinity and pH of natural water mixtures. An acceptable accuracy of the

model was demonstrated by experiments [2]. Blank columns denote measured values of the total alkalinity Alk_T and pH of water samples. Then some results of measured and computed values of Alk_T and pH in water mixtures were presented for the mixture ratios 1:1, 1:2, 2:1, 1:3, 3:1, 1:5 starting from the left-hand side of figures 3 and 4.

5. APPLICATION

The set of equations (20), (21), (22), (23), (24) was used for computing pH_{mix} , $\text{Alk}_{T\text{mix}}$, $[\text{Ca}]_{\text{mix}}$, ionic strength $I_{\text{mix}} = I_{\text{mix}}(\text{TDS})_{\text{mix}}$, temperature T_{mix} , and finally LSI_{mix} of water mixtures in the water supply systems of Kraków, south of Poland. Activity coefficients were calculated using the widely accepted equations (25)–(30) based on the value of the ionic strength I of water, predicted from the values of TDS [11]:

$$\log(f_i) = -AZ_i^2 I^{0.5} \quad \text{for } I < 0.005 \text{ M}, \quad (25)$$

$$\log(f_i) = -AZ_i^2 \{I^{0.5}/(I+1)^{0.5}\} \quad \text{for } I < 0.1 \text{ M}, \quad (26)$$

$$\log(f_i) = -AZ_i^2 \{I^{0.5}/(I+1)^{0.5} - 0.3I\} \quad \text{for } I < 0.5 \text{ M}, \quad (27)$$

$$\log(f_i) = -AZ_i^2 \{I^{0.5}/(1+B \cdot b \cdot I^{0.5}) + C_i I\} \quad \text{for } I < 1.0 \text{ M}, \quad (28)$$

$$I = 0.5 \sum C_i Z_i^2, \quad (29)$$

$$I = 2.5 \cdot 10^{-5} (\text{TDS} - 20), \quad (30)$$

where:

$$A = 1.82 \cdot 10^6 (78.3 T)^{-1.5},$$

b – ion diameter [A^0] ($b = 4$ for HCO_3^- , $b = 6$ for Ca^{2+} , $b = 9$ for H_3O^+ , $b = 3$ for OH^- [1]),

$$B = 50.3 \cdot (78.3 \cdot T)^{0.5},$$

C_i – concentration of ion i ,

T – temperature (K),

TDS – total dissolved solids (mg/dm^3),

Z_i – charge of ion i .

As water is always delivered at the pressure significantly exceeding the atmospheric pressure, there is no risk of forming gas bubbles in pipes and the model presented here is reasonable for systems closed to the atmosphere. The diagram of computations is presented in figure 5, and the examples of LSI computations – in figures 6 and 7. The Raba and the Rudawa are the rivers supplying Kraków with surface water. The values of LSI presented in figure 6 are calculated as algebraic average values in a given month of 1994. The data for all calculations were collected from the company operating

within the whole water supply system for the city. Because of the lack of water stabilisation after coagulation the Langelier Saturation Index of most waters in 1994/95 was slightly negative, but its value rather rarely dropped below allowed -0.5 for steel and cast iron pipes. The results of the computations presented here were used to argue for water stabilisation in respect of calcium carbonate, which is a common practice now, at least in the largest treatment plant (to be exactly strict two parallel plants) supplied with water from the Raba River.

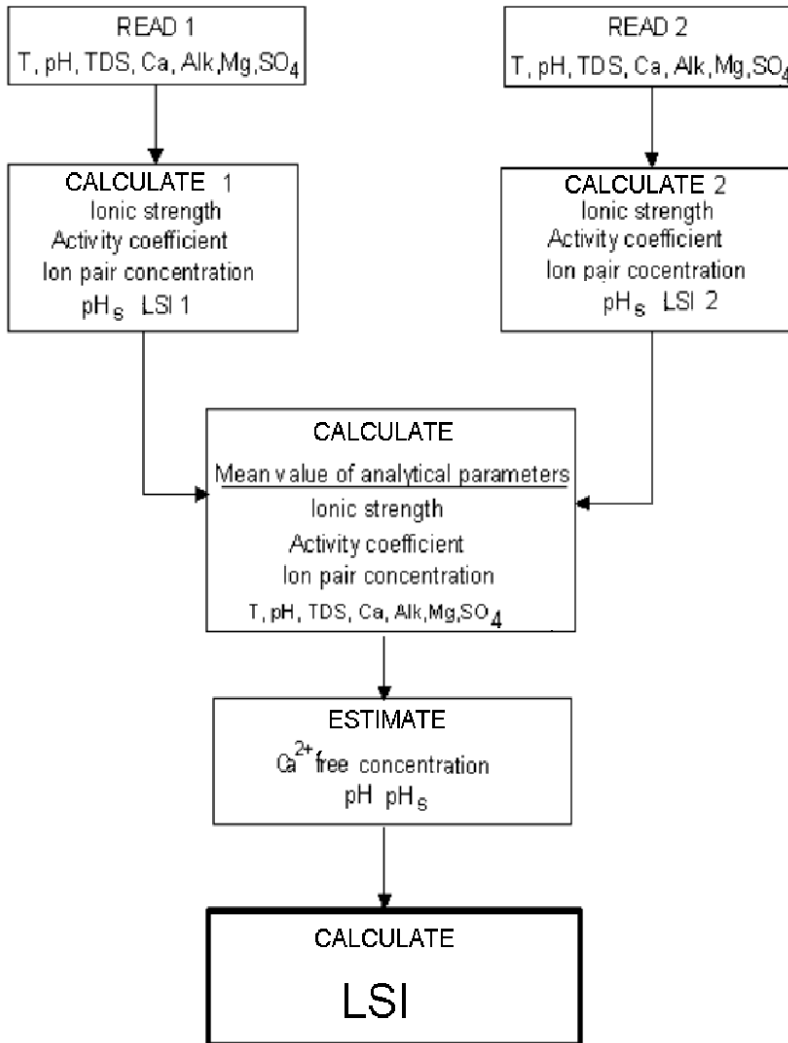


Fig. 5. Block diagram of the numerical model for computing LSI and some other parameters of water mixture in water supply systems

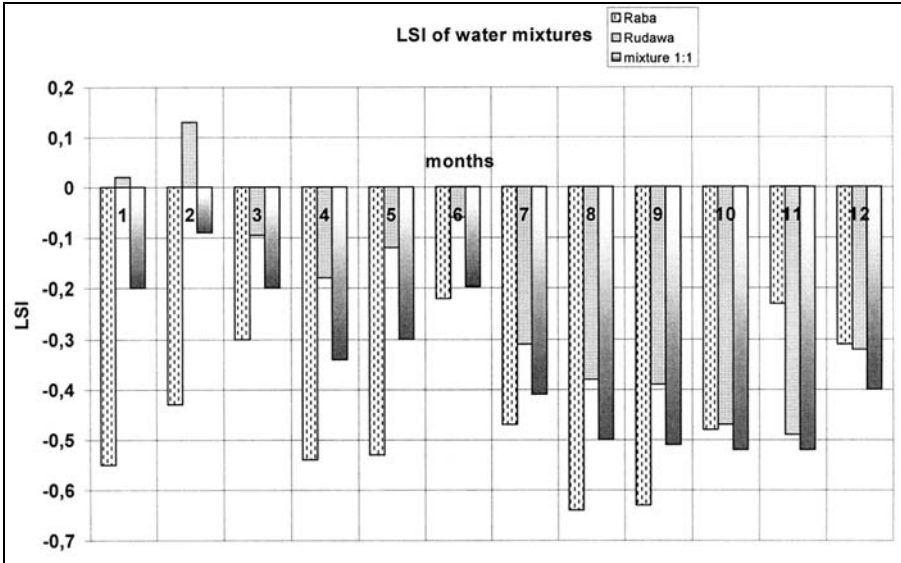


Fig. 6. Calculated Langelier Saturation Index (LSI) of water mixtures delivered in 1994 from the Raba and the Rudawa treatment plants to the distribution system [2]. Assumed ratio of mixing for this figure was 1:1

An example of the impact of the mixture ratio on the value of LSI is shown in figure 8 for waters of average quality produced by the Raba and the Rudawa treatment plants in January of 1994. The values of LSI of the original waters are presented in figure 7.

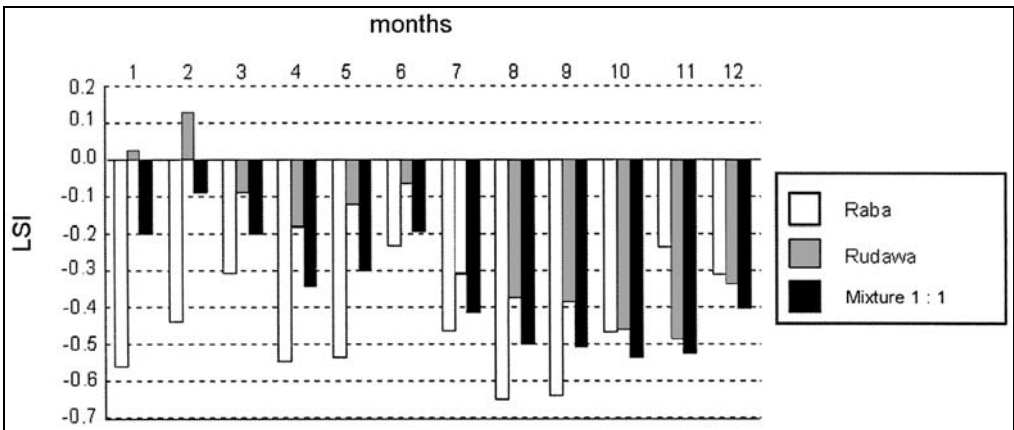


Fig. 7. Calculated Langelier Saturation Index (LSI) of water mixtures delivered in 1994 from the Raba and the Rudawa treatment plants to the distribution system. Assumed ratio of mixing for this figure was 1:1

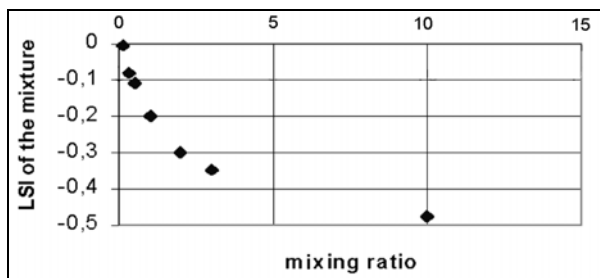


Fig. 8. Impact of mixing ratio of the Raba to the Rudawa waters on LSI of the water mixture in the system closed to the atmosphere

The stability of waters supplying Kraków was investigated with respect to calcium carbonate. The Langelier Saturation Index (19) was calculated using equation (18) for the pH_s of equilibrium, as it was proved by calculations that the ion-pair effect was negligible for all the waters investigated here. The results of some calculations are presented in figures 9–12. They refer to historical data as now all waters are stabilized by lime or sodium carbonate during treatment processes. To avoid computing some thousands of values, average values of water quality parameters were calculated separately for each month. Then they were used to calculate the Langelier Saturation Indexes. It is not possible to prove theoretically that this approach results in negligible errors, so for one of the months, monitoring of the LSI value was carried each day. The average values of this index for the whole month did not differ more than 0.1 from the values calculated for average month water quality parameters. In figures 9–12, only points have a physical meaning and lines are used exclusively to help localize them easier.

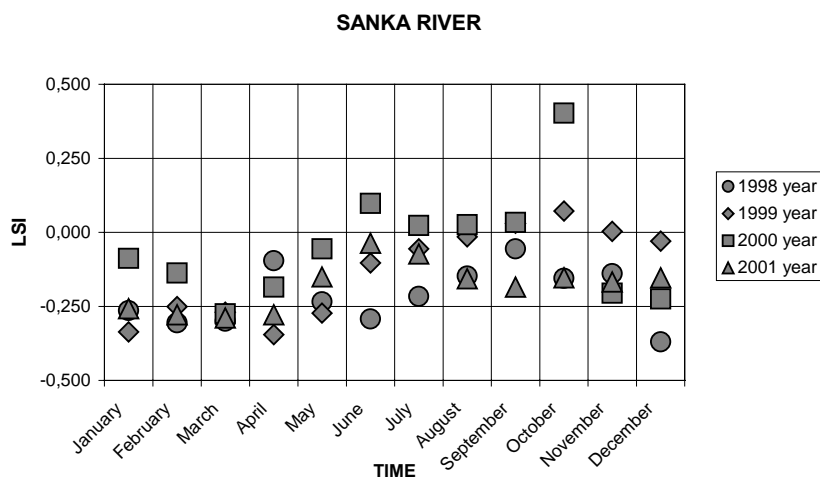


Fig. 9. Results of LSI computations for drinking water delivered from the Sanka River

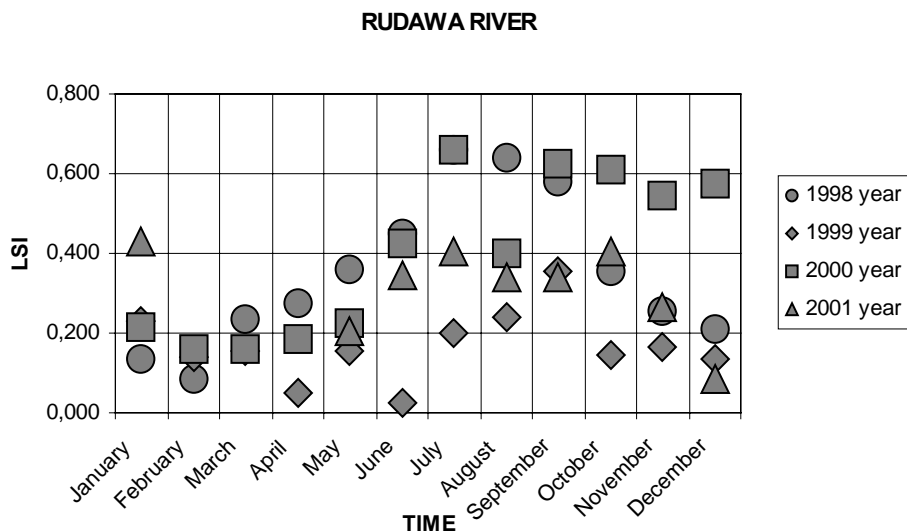


Fig. 10. Results of LSI computations for drinking water delivered from the Rudawa River

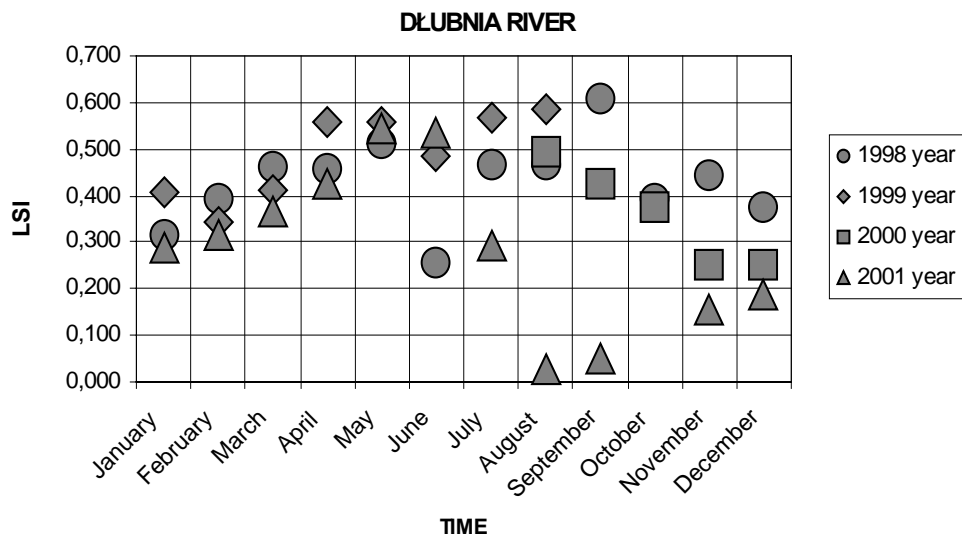


Fig. 11. Results of LSI computations for drinking water delivered from the Dłubnia River

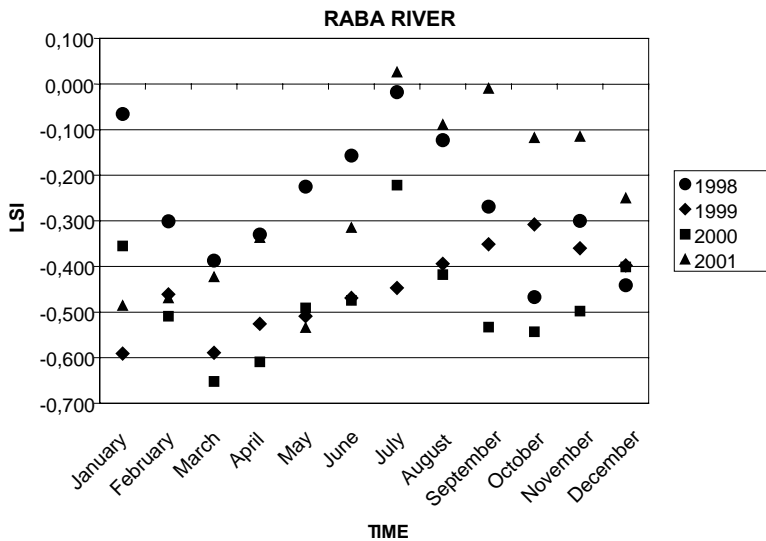


Fig. 12. Results of LSI computations for drinking water delivered from the Dobczyce reservoir (the Raba River)

Low values of the Langelier Saturation Index sometimes corresponded to predicted analytically concentrations of aggressive carbon dioxide ($\text{CO}_{2\text{aggr}}$), but not always, and poor linear and exponential correlations were predicted between LSI and $\text{CO}_{2\text{aggr}}$. Concentrations of $\text{CO}_{2\text{aggr}}$ for the Raba River are presented in figure 13. Measured concentrations of $\text{CO}_{2\text{aggr}}$ were the highest for water supplied from this river.

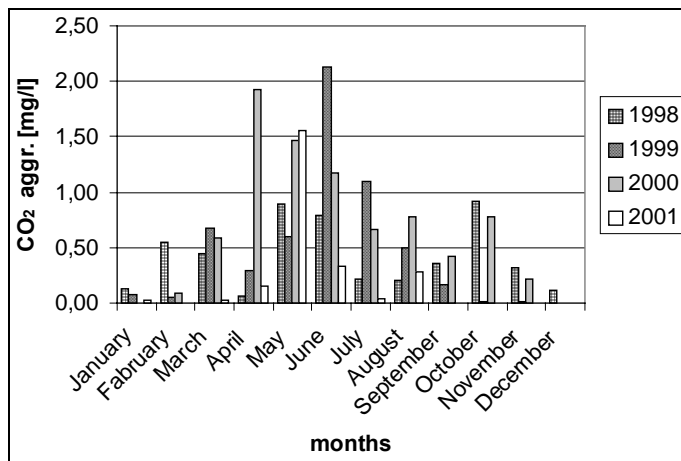


Fig. 13. Monthly average concentrations of $\text{CO}_{2\text{aggr}}$ measured by the waterworks laboratory (MPWiK) for finished water from the Dobczyce reservoir (the Raba River)

It is expected that negative values of LSI correspond to some concentrations of $\text{CO}_2_{\text{aggr}}$, but then there is no theoretical reason for a simple correlation between $\text{CO}_2_{\text{aggr}}$ and LSI. However, the main reason for a lack of a well documented correlation for water withdrawn from the same river may be a low precision of $\text{CO}_2_{\text{aggr}}$ measurements and comparisons of average values from whole months. The methods applied in the measurements of Alk_T , pH and the concentrations of calcium, used for the calculations of LSI, are much farther precise. Some simplifications assumed for describing the value of pH_s by equation (18) also may contribute to the lack of a strong correlation between CO_2 and LSI.

6. BUFFER CAPACITY

Buffer capacity of water is one of significant parameters determining its aggressiveness. Electrochemical corrosion tends to change pH values of water flowing along cathodic and anodic areas [1]. As long as the pipe wall is not covered with a passive film consisting of corrosion products, precipitates and bacteria, the changes in pH are not visible. However, it is not the case that the differences between pH values of water trapped in pores of this film speed up corrosion processes. At the beginning when a pipe is new, the changes in pH of flowing water are not important because water flowing along anodic and cathodic areas is mixed so the final corrosion impact on water pH is negligible. However, when a film grows on an inside surface of pipe walls some water is trapped in the pores of this film. Corrosion processes change the pH of this water in an opposite direction along anodic and cathodic areas. The differences in pH of waters trapped in the pores of corrosion products speed up corrosion. These differences depend on buffer capacity of water, representing its ability to resist changes in pH when acids or bases are added. The value of buffer capacity is not specified directly in WHO, US EPA and the EC Directive No. 98/83/EC, but it is limited indirectly by setting limits on total alkalinity Alk_T and pH. At a given temperature these two parameters can be used to calculate (32) the value of buffer capacity defined by the following equation:

$$\beta = \left| \frac{dC}{d\text{pH}} \right| \quad (31)$$

in which C is the concentration of strong monoprotic acid or strong base of one hydroxyl group. The method of calculating a natural water buffer capacity has been known for very long period but it is not frequently used in water treatment practice. Using the water supply system of Kraków as an example, it is shown here how strongly it depends on the geology of a river basin.

The system of equations used for buffer capacity calculations has been published elsewhere [1], [4], [5], [8], [9], [14]. In most of these waters, the buffer capacity β is shifted by carbonate equilibrium and calculated from the following equation:

$$\beta = 2.3 \left\{ \frac{\alpha_1 ([0.5 \text{Alk}_T] - [\text{OH}^-] + [\text{H}_3\text{O}^+]) ([\text{H}_3\text{O}^+] K_1' K_2' / ([\text{H}_3\text{O}^+] + 4 K_2'))}{(K_1' (1 + 2 K_2' / [\text{H}_3\text{O}^+]) + [\text{H}_3\text{O}^+] + [\text{OH}^-])} \right\}. \quad (32)$$

The results of buffer capacity computations for raw surface waters used for water supply of Kraków are shown in figure 14.

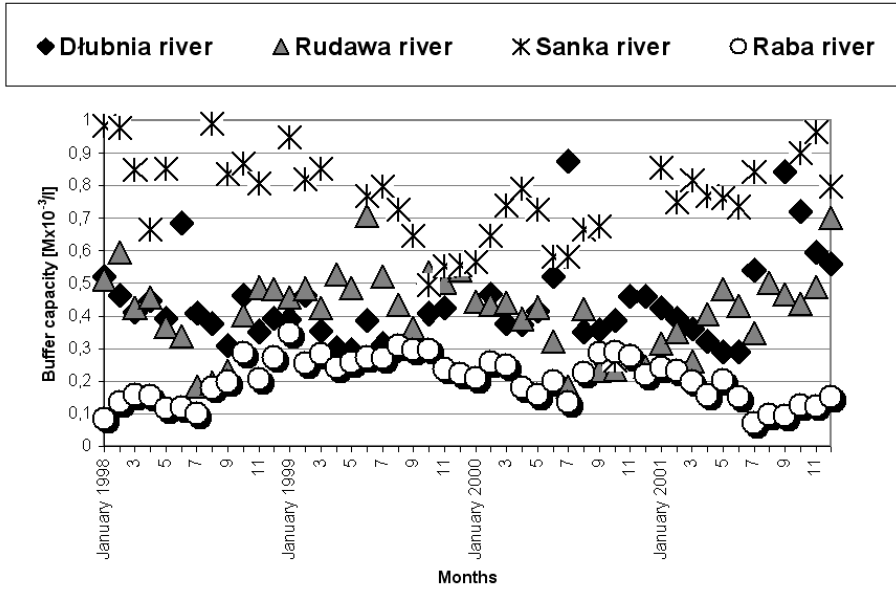


Fig. 14. Buffer capacities of waters of different origin used for water supply of Kraków [4]

The company supplying Kraków with drinking water delivered the data for calculations. The changes in buffer capacities are significant. Larger values are predicted for the Sanka, the Dłubnia, and the Rudawa Rivers which flow through clay soil rich in calcium. The smallest are reported for water from the Raba River of partially granite basin.

7. PIPE INTERIORS

Evaluation of water corrosive properties based on its physicochemical parameters and stability indexes is used on a primary level of investigations. Then laboratory measurements should be conducted, but usually they do not last longer than a few weeks or months. With time a protective scaling is formed on pipe walls and a biofilm grows, which in contrast may speed up corrosion processes. This is why even laboratory results are not necessarily representative for predicting corrosivity of water over

a long period. According to our primary evaluations all the waters investigated were believed to be non-corrosive (though some corrosion always exists) or slightly corrosive to steel and cast iron pipes of cold water distribution systems. To verify these expectations the survey of main transit pipes delivering water from the largest water treatment plants to Kraków was made in 2004. Both direct inspections of some accessible fragments of the pipelines and hydraulics computations of pipes roughness were chosen as diagnosis tools. Moreover, iron(III) concentration along the transportation pipes was measured by the company managing the system, and a small increase of iron(III) concentration was documented along about 20 kilometres of the pipeline. Assuming that this small increase is typical of the 30 years of operation it could be expected that less than 0.5% of iron(III) has been removed from the pipes during this period.

There are many water reservoirs on the way from the treatment plant to the city, so water levels could be measured precisely with an accuracy of ± 1 mm in several points, but the precision of measurements in other places along the pipeline was much worse than ± 0.5 m of water height. A widely applied Epanet software developed by the U.S. Environmental Protection Agency was used for predicting the sand roughness coefficient k of exactly 30-year-old iron and cast iron pipeline of the 1000-mm diameter. The predicted values of k were in a range of 1.5–3.0 mm with the accuracy not better than from ± 0.5 mm to ± 1.0 mm, depending on local circumstances of pressure (or water level) measurements along the pipeline. Fully turbulent character of flow was ensured during collecting measurements. The sediment of corrosive products was not found at the pipe bottom in any of the inspected places. Some corrosion products, mostly siderite, were observed on the pipe walls.

8. SHEAR STRESSES

It is interesting that loose sediment of corrosion products have never been found accumulated on the large pipeline bottom. This can be explained by the values of the shear stresses along pipe walls. An average value of this shear stress τ can be calculated as follows:

$$\tau = \frac{\rho g d S}{4}. \quad (33)$$

Formula (33) shows that large-diameter pipes usually work under much higher shear stresses along the inside wall than small-diameter pipes in spite of the fact that the hydraulic gradient S is likely smaller in pipes of larger diameters d . Siderite growing can resist large shear stresses, but if iron is oxidized to three valence form it might settle only forming mechanically weak structures, likely to be transported with water under high stresses. This explains why sudden small changes of flow rates create more problems with red water in small than in large pipes.

9. CONCLUSIONS

A mathematical model describing the equilibrium of water mixtures, with respect to calcium carbonate, was developed, experimentally verified on laboratory scale and used for investigating some water supply systems in the south of Poland. All equations incorporated into the model are well known and a few similar models can be found in the literature, but this time a part of the model has been verified on laboratory scale and it accounts for inorganic complexes formed by calcium and magnesium. This so-called ion-pair effect [9] was found to produce lower changes of the Langelier Saturation Index for water investigated here, hence a possible error of calculations might result from inaccuracy of the data used in the computations. According to numerical experiments the ion-pair effect was more visible for waters of high concentration of salts, higher than specified in drinking water standards. The model may be useful for predicting the tendency for calcium carbonate to dissolve or precipitate in water mixtures of water supply systems.

The calculations proved that:

- Inorganic complexes can be neglected in calculations of LSI for all waters supplying Kraków as they change its value by less than 0.1.
- The pH of water saturation with calcium carbonate computed by the methods taking into account ion-pair effect for all waters supplying Kraków is almost identical as that predicted from the C-L diagrams and from the Polish Standards. The old simple methods seem to give quite accurate results as long as calcium carbonate crystallizes in the form of calcite.
- In the period from 1995 to 2002, the largest treatment plant produced the water of negative LSI for some parts of a year. However, the LSI values above -0.5 were usually recognized as acceptable for iron, cast iron and ductile iron pipes. Days during which this parameter was negative were different each year, depending greatly on coagulation. Different coagulants were used and their doses depended on storm-water runoff. Not always the water of slightly positive values of LSI is produced, which results also in higher buffer capacities.
- No well documented correlations between negative values of the Langelier Saturation Index and measured concentration of aggressive carbon dioxide were computed.
- Buffer capacity is an important water quality parameter for evaluation of its corrosive properties. It can easily be calculated based on the total alkalinity, pH and water temperature which are monitored in all water-treatment plants. Calculations prove that the values of the buffer capacity of waters supplying Kraków differ significantly, depending on the geology of river basins.
- Shear stresses along the walls of large-diameter pipes likely contribute to the removal of loosely deposited corrosion products while siderite is more likely to survive in these circumstances.

The model presented here may be applied to calculate the LSI of water mixtures in the systems closed to the atmosphere, if the mixing proportions are known and water

temperature is not affected by surrounding soil temperature. Such information is available from some software used for computing water supply systems, such as a public domain numerical program Epanet 2.0, accessible through internet from the U.S. E.P.A.

In the mid-nineties, numerical tests indicated rationality of water stabilisation in the periods of water coagulation in Kraków and in some other communities in the south of Poland. Now the largest water treatment plant for the city of Kraków uses soda ash or calcium hydroxide for those purposes, which significantly improved the situation.

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