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Technical Faculty in Bor

EcoTEK

31<sup>st</sup> International conference

# Ecological Truth & Environmental Research

Editor

Prof. Dr Snežana Šerbula

## PROCEEDINGS

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## PROCEEDINGS

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**MINISTRY OF SCIENCE,  
TECHNOLOGICAL DEVELOPMENT AND INNOVATION**

## **PREFACE**

*The 31<sup>st</sup> international conference Ecological Truth & Environmental Research – EcoTER'24 focuses on showing the latest research findings and innovations in the field of ecology, environmental protection and sustainable development. The conference will be held in Sokobanja (Serbia) in hotel Sunce in the period of 18–21 June 2024.*

*The aim of the conference is to connect the experts in various fields in order to transform attitudes and behaviors in everyday practices, as well as in the industry and economy sector which is essential for achieving the desired changes that our society must undergo.*

*The 31<sup>st</sup> international conference Ecological Truth & Environmental Research – EcoTER'24 is organized by the University of Belgrade, Technical Faculty in Bor, and co-organized by the University of Banja Luka, Faculty of Technology; the University of Montenegro, Faculty of Metallurgy and Technology – Podgorica; the University of Zagreb, Faculty of Metallurgy – Sisak; the University of Pristina, Faculty of Technical Sciences – Kosovska Mitrovica and the Society of Young Researchers – Bor.*

*These Proceedings encompass 119 papers from the authors coming from the universities, research institutes and industries in 15 countries: Brazil, Norway, USA, Spain, Austria, Libya, Italy, Israel, Slovenia, Croatia, Romania, Bulgaria, Montenegro, Bosnia and Herzegovina, North Macedonia, and Serbia. It is a great honor and pleasure to cordially wish a warm welcome to all the participants of the conference.*

*As a part of this year's conference, the 6<sup>th</sup> Student Section – EcoTERS'24 will be held. We appreciate the contribution of the students and their mentors who have also participated in the conference and hope that students will continue to explore and to be curious, since education is a never-ending process, and knowledge is continuously growing.*

*The organization of the EcoTER'24 conference has been financially supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia.*

*The support of the Donors and their willingness and ability to cooperate has been of great importance for the success of the EcoTER'24 conference. The organizing committee would like to extend their appreciation and gratitude to the Platinum donors of the conference – Serbia ZiJin Copper doo Bor and HBIS SERBIA, to the Gold donor of the conference – Elixir Group, as well as to the Silver donor of the conference – Serbian Chamber of Engineers.*

*We would like to express our sincere appreciation to all the authors who have contributed to the Proceedings. We would also like to express our gratitude to the members of the scientific, organizing and honorary committees, reviewers, speakers, chairpersons and all the conference participants for their support of the EcoTER'24. Sincere thanks go to all the people who have contributed to the successful organization of the EcoTER'24.*

*Prof. Snežana Šerbula,*

*President of the scientific and organizing committee*

<b>Darko Anđelković, M. Branković</b>	PERFORMANCES OF QuEChERS BASED GC-MS AND LC-MS/MS METHODS FOR PESTICIDES ANALYSIS IN APPLES	49
<b>Darko Anđelković, M. Branković</b>	COMPARISON OF PESTICIDES STABILITY STORED IN TWO SOLVENTS OF DIFFERENT VISCOSITY	55
<b>Milena Tadić, I. Nikolić, D. Đurović, N. Cupara, J. Vuković</b>	TRISALOMETHANES CONTENT IN HOTEL'S SWIMMING POOLS WATER IN A SOUTH OF MONTENEGRO	61
<b>Jelena Vranković, K. Jovičić, V. Đikanović</b>	FIRST LINE DEFENCE ANTIOXIDANT ENZYMES IN <i>Blicca bjoerkna</i> (LINNAEUS, 1758) FROM THE BELGRADE SECTION OF THE DANUBE RIVER	66
<b>Miomir Mikić, R. Marković, V. Marjanović, R. Rajković, M. Jovanović</b>	RECUltIVATION OF RTH FLOTATION TAILINGS IN BOR, SERBIA	71
<b>Miomir Mikić, V. Marjanović, R. Marković, M. Jovanović, R. Rajković</b>	MINING AND THE ENVIRONMENT, ENVIRONMENTAL IMPACT MONITORING PROGRAM FOR FLOTATION TAILING RTH-BOR, SERBIA	77
<b>Vesna Obradović, M. Perović, T. Vučković</b>	EVALUATING CORROSION AND BIOFOULING POTENTIAL BASED ON GROUNDWATER MICROBIOLOGICAL COMPOSITION	83
<b>Vesna Obradović, M. Perović, J. Lekić</b>	EVALUATION OF CORROSION POTENTIAL USING PHYSICOCHEMICAL WATER QUALITY ASSESSMENT	89
<b>Jelena Čanak Atlagić, A. Marić, K. Jovičić, J. Stanković, V. Đikanović, T. Mitić, M. Raković</b>	QUESTIONING THE RESILIENCE OF THE DANUBE FISH FAUNA UNDER THE PRESSURE OF BELGRADE WASTEWATERS	95
<b>Vladan Marinković, M. Maksimović, M. Jovanović, S. Trujić</b>	MONITORING OF THE STATE OF THE ENVIRONMENT IN THE BOR DISTRICT, GIVEN THROUGH THE EXAMPLE OF THE DISTRIBUTION OF Pb IN THE SOIL LOCATED IN THE IMMEDIATE VICINITY OF THE BOR RIVER	101
<b>Mirjana Ocokoljić, Dj. Petrov, N. Galečić, D. Skočajić, D. Vujičić, J. Čukanović, I. Simović</b>	EFFECTIVENESS OF <i>Photinia × Fraseri</i> 'RED ROBIN' IN THE URBAN LANDSCAPE: TOWARDS OF CLIMATE CHANGE	106
<b>Mirjana Ocokoljić, Dj. Petrov, N. Galečić, D. Skočajić, D. Vujičić, J. Čukanović, I. Simović</b>	<i>Chaenomeles japonica</i> (Thunb.) Lindl. ex Spach IN THE DESIGN OF URBAN PARKS: LEARNING FROM NATURE	113



## EVALUATION OF CORROSION POTENTIAL USING PHYSICOCHEMICAL WATER QUALITY ASSESSMENT

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### Abstract

*To select an appropriate location for well installation, and to decide on its construction, materials, operational regime, and the necessity for additional infrastructure such as drains, a comprehensive assessment of water quality at the site of interest is imperative. Moreover, forecasting the water quality under the anticipated operational conditions of the well holds even greater significance. Water quality assessment including calcium saturation provides insights into the mineral content of groundwater, which is essential for assessing water quality and optimizing treatment processes. By understanding calcium saturation levels, appropriate corrosion control measures can be implemented to mitigate these risks. Excessive calcium saturation and scale formation can impact aquatic ecosystems by altering water chemistry and habitat conditions. Overall, understanding calcium saturation in groundwater is very important for maintaining water quality, preventing infrastructure corrosion, minimizing environmental impacts, and optimizing water treatment processes. Subsequently, this discussion delves into an analysis of the findings derived from water quality testing conducted at eight observation piezometers. With the aim of assessing the corrosivity of water and its potential to form calcium carbonate scale the Langelier Saturation Index and Ryznar Stability Index were calculated.*

**Keywords:** Langelier Saturation Index, Ryznar Stability Index.

### INTRODUCTION

As a part of the groundwork for various studies conducted by the Jaroslav Černi Water Institute and projects of the Ministry of Science, Technological Development and Innovation, physico-chemical analyses of groundwater quality in the Wn well zone, between 2007 and 2012, were conducted. In-situ measurements of redox potential, oxygen content, pH values, electrolytic conductivity, and temperature were also conducted. Laboratory analyses included heavy metal content, organic matter, and other relevant micro and macro components of groundwater significant for assessing drinking water quality. Additionally, key physico-chemical parameters and indicators necessary for assessing the transformation processes of organic matter, iron, manganese, sulfur, and nitrogen components, as well as the potential for mechanical and chemical corrosion, were analysed in hydro-technical facilities and their key elements. The last sampling campaign was conducted in July 2023, when eight piezometers (from Wn1 through Wn8) in the vicinity of Ranney well Wn were analysed. Considering that Ryznar and Langelier classifications for determination of the corrosion and incrustation potential, are crucial for groundwater development and exploitation, these indices have been calculated. Numerous studies have been conducted with the aim of determining the potential



for well corrosion by calculating these indices, illustrating the importance of their application [1–7].

## MATERIALS AND METHODS

### Langelier index

To assess the stability of groundwater under natural conditions, based on the results of chemical analysis, the pHs value is calculated, which corresponds to the equilibrium state in the solution of carbonate compounds. The pHs value represents the index of hydrogen ions corresponding to the equilibrium saturation of groundwater with carbonic acid compounds. The pH value represents the actual concentration of hydrogen ions in groundwater (measured on-site). The pH value measured in the laboratory will always be higher than the actual pH value measured on-site. The calculation procedure involves water temperature, pH, total dissolved solids, calcium concentration, and total alkalinity. Based on the analysis and interpretation of available literature data, the following Eq. (1) is proposed for the practical calculation of the pHs value:

$$\text{pH}_S = 9,92 - \frac{t \left[ ^0\text{C} \right]}{40} - \log \left[ \text{Ca}^{++} \text{ (mg/l)} \right] - \log \left[ \text{HCO}_3^- \text{ (mg/ekv/l)} \right] + 0,2 \log \left[ \text{S.O. (mg/l)} \right] \quad (1)$$

t – groundwater temperature (°C)

s.o. – total dissolved solid (mg/l)

The Langelier index (Li) of saturation represents a parameter indicating conditions for the deposition of a calcium carbonate layer that can prevent corrosive processes, Eq. (2):

$$\text{Li} = \text{pH} - \text{pH}_S \quad (2)$$

If the value of the index is positive (>0.3): water is saturated and tends to deposit calcium carbonate. If this value is negative (<-0.3): water is undersaturated and tends to dissolve calcium carbonate, i.e., water has a corrosive effect. In practice, water is in equilibrium if the index values range from -0.3 to 0.3.

### Ryznar Stability Index

Ryznar index (RSI) indicates the stability of carbonate systems in water and can be calculated using Eq. 3:

$$\text{RSI} = 2\text{pH}_S - \text{pH} \quad (3)$$

RSI has only positive values, and the higher the values, the more corrosive the water is based on the obtained values, the tendency of groundwater according to this index is described as follows: when RSI is greater than 9.0, it indicates very strong corrosion; For RSI values between 7.5 and 9.0, the groundwater is characterized by severe corrosion; when RSI



falls between 7.0 and 7.5, significant corrosion is observed. RSI values ranging from 6.0 to 7.0 suggest little carbonate formation or corrosion. If RSI lies between 5.0 and 6.0, it indicates easy carbonate formation. When RSI falls between 4.0 and 5.0, severe carbonate formation is expected.

## RESULTS AND DISCUSSION

### Groundwater quality

The groundwater quality from the well Wn was analysed in the period 2007–2012. Based on a total of six pH measurements, a range from 7.1 to 8.4 and a mean value of 7.5 were determined, indicating slightly alkaline conditions in the groundwater environment of the tested site. The measured redox potential of the Wn ranged from 125 to 244 mV, with a mean value of 146 mV for the period from 2007 to 2012. Redox potential values  $<135$  mV and oxygen levels  $<0.5$  mg/l indicate that microbial processes likely dominate over chemical oxidations in iron transformation. Experiences from the Belgrade aquifer have shown that wells with redox potentials  $<130$  mV and total iron values  $>1.2$  mg/l are usually associated with flow rates ( $Q_{\text{average}}$ ) of 40 L/sec [2–4]. The electrical conductivity varied over time and was measured within a range of values from a minimum of 491 to a maximum of  $650 \mu\text{Scm}^{-1}$ . The difference between the maximum and minimum measured values was  $159 \mu\text{Scm}^{-1}$ . The mean electrical conductivity value measured between 2007 and 2012 was  $561 \mu\text{Scm}^{-1}$ , placing examined groundwater at the upper limit of the group of low-mineralized freshwater bodies (with oligosalinity), characterized by conductivity ranging from 20 to  $650 \mu\text{Scm}^{-1}$ . The dominant cationic species in terms of concentration were arranged as follows:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^{+} > \text{K}^{+}$ , while the anionic species followed the order  $\text{HCO}_3^{-} > \text{SO}_4^{2-} > \text{Cl}^{-} > \text{PO}_4^{3-} > \text{NO}_3^{-}$ . The dominant anion was bicarbonate (consistent with the measured pH values), with a maximum value of 360.51 mg/l. Among the cationic species, calcium ions predominated (max. 90.59 mg/l) followed by magnesium ions (max. 24 mg/l). According to the dominant ions and the classification by Alekin, the groundwater from well Wn belonged to the type I hydrocarbonate (calcium-magnesium) water, which is in accordance with a general characteristic of Sava alluvium ( $\text{HCO}_3^{-} > (\text{Ca}^{2+} + \text{Mg}^{2+})$ ). Out of 8 measurements of dissolved oxygen concentration in groundwater, the maximum recorded value was 0.1 mg/l, while the minimum was below quantification limit of the applied method. Considering the multi-year period, in the degradation of organic matter (originating from infiltration through the unsaturated zone and/or infiltration of Sava water), oxygen was not dominating electron acceptor, but rather other redox-sensitive species, which is a general characteristic of Sava alluvium. The maximum concentration of total iron was 2.55 mg/l. The ratio of the maximum observed values of divalent iron to total iron ( $\text{Fe}^{2+}/\text{Fe}_{\text{tot}}$ ) was 0.46, indicating anaerobic and occasionally aerobic conditions in the zone of this well. Based on the concentrations of sulfates, which varied in a relatively wide range (28.96–94 mg/l), with a mean value of 51 mg/l, higher than the average values for the Sava River, it can be assumed that iron sulfide oxidation was likely one of the processes in the genesis of divalent and trivalent iron and sulfate in the examined groundwater (Wn well zone). The manganese content was measured in the range of 0.290–0.547 mg/l. After the consumption of organic matter or if its concentration is below the usability threshold for microorganisms ( $<1$  mg/l),

the groundwater microbiome may be dominated by species that can utilize inorganic carbon sources as donors ( $\text{CO}_2$  and  $\text{HCO}_3^-$ ) or reduced sulfur and  $\text{H}^+$ , and as acceptors ferrous ions, manganese, nitrates, sulfates,  $\text{CO}_2$ , which can affect the chemical quality of water. The concentration of ammonium ions varied to a maximum of 0.31 mgN/l. Oxidized forms of nitrogen, nitrates, were detected with a maximum value of 0.4 mgN/l, and nitrites were detected only in one sampling campaign (0.005 mgN/l).

### Groundwater quality of the piezometers

Selected piezometers: Wn1, Wn2, Wn3, Wn4, Wn5, Wn6, Wn7, Wn8 are sampled and analysed in a campaign conducted in July 2023 (Table 1). The maximum dissolved oxygen value was measured in the Wn6 (1.50 mg/l), while the minimum was recorded in Wn7 (0.36 mg/l). The average oxygen content for groundwater in the Wn zone was 0.7 mg/l, significantly higher than the values measured between 2007 and 2012 in the Wn. The *in-situ* pH value was measured within the range of slightly alkaline values, from 7.27 to 7.76. The redox potential values in the Wn zone were unusually high for the Belgrade aquifer, with significant spatial variations. The maximum value of 511.96 mV was measured in the Wn1, while the minimum value of -252.47 mV was observed in Wn3. The average redox potential value (294.10 mV) was significantly higher compared to the average values measured in Belgrade aquifer. Observed range suggests that groundwater in the Wn zone is not in redox equilibrium and that processes in the groundwater of this well include reduction processes (e.g., sulfate reduction) and complementary oxidation processes, involving electron transfer between chemical species. Variable redox potential values also indicate mixing of different hydrochemical zones and a trace of organic pollution in the recent past. The electrolytic conductivity was not uniform across space. The measured range varied from 444.6  $\mu\text{Scm}^{-1}$  in Wn3 to a maximum of 672  $\mu\text{Scm}^{-1}$  in Wn4. The dominant cationic species, follow the order:  $\text{Ca}^{2+} > \text{Mg}^{2+} > \text{Na}^+ > \text{K}^+$ , while the anionic species follow the order:  $\text{HCO}_3^- > \text{SO}_4^{2-} > \text{Cl}^- > \text{PO}_4^{3-} > \text{NO}_3^-$ . According to the ionic species and classification by Alekin, the groundwater in the Wn zone can be categorized as Type I hydrocarbonate calcium-magnesium soft water with low salt and potassium content ( $(\text{HCO}_3^- > (\text{Ca}^{2+} + \text{Mg}^{2+}))$ ), which is a general characteristic of the Sava alluvium. The total organic carbon content (TOC) was measured in the range of values from a minimum of 0.94 mg/l in the Wn2 to a maximum of 1.63 mg/l in the Wn3, where significantly negative redox potential values were observed. The content of readily oxidizable organic matter, estimated through  $\text{KMnO}_4$  consumption, was maximum 5.06 mg/l, which was accompanied by low boron concentrations in all examined water samples in the Wn zone ( $< 100 \mu\text{g/l}$ ). In eight samples, the concentration of ferrous iron was in the range of 0.10 to 0.21 mg/l, with a mean value of 0.14 mg/l, significantly lower than the average value for the Belgrade aquifer and the Sava alluvium. Similarly, the average total iron content was also lower compared to the average measured in the water from the Belgrade aquifer wells (0.33 mg/l). The measured concentrations of manganese exhibited a wide range of values, ranging from a minimum of 0.16 to a maximum of 0.68 mg/l. The minimum measured concentration of sulfates of 14.44 mg/l (Wn1), while the maximum of 25.25 mg/l (Wn4), on average, lower than the average sulfate concentrations in the Sava River (26.60 mg/l). The average concentration of ammonium ions, (eight groundwater samples in the Wn zone), was 0.27 mgN/l, and for nitrites, it was 0.33 mgN/l, with nitrites being more

frequently detected (in three samples) compared to nitrates. Nitrates were only detected in the groundwater sample Wn6, with a maximum oxygen concentration of 1.5 mg/l. The average oxygen concentration for groundwater in the Wn zone was 0.7 mg/l, suggesting that the oxygen concentration in the groundwater in the Wn zone likely limits nitrification processes and favours denitrification. The first intermediate of denitrification is represented by nitrites (possible DNRA transformation of nitrates).

**Table 1** Selected parameters of groundwater quality

Sample	Unit	Wn1	Wn2	Wn3	Wn4	Wn5	Wn6	Wn7	Wn8
Date		2023	2023	2023	2023	2023	2023	2023	2023
pH		7.59	7.58	7.67	7.26	7.76	7.62	7.47	7.7
E. Conductivity	μS/cm	498	489	445	672	472	503	464	458
DO	mg/l	0.48	0.5	0.56	0.51	0.54	1.50	0.36	0.49
Turbidity	NTU	0.8	1	1.2	1.1	1.2	3.3	5.3	3
Alkalinity	mg/l	235	230	195	315	205	220	205	200
Bicarbonates	mg/l	286.7	280.6	237.9	384.3	250.1	268.4	250.1	244
CO <sub>2</sub>	mg/l	12.1	12.1	8.3	33.8	7.1	10.6	13.9	8
Chlorides	mg/l	14.64	13.57	23.21	18.85	23.92	27.13	20.35	22.13
Sulfates	mg/l	14.44	16.24	14.88	25.25	19.06	18.67	20.87	18.7
TP	mg/l	0.021	0.042	0.022	0.368	0.046	0.083	0.06	0.13
TDS	mg/l	248	250	221	412	257	280	259	246
TOC	mg/l	1.36	0.94	1.63	1.39	1.05	1.39	1.19	1.45

According to earlier calculations, water from all wells in the Belgrade water source had Lsi values ranging from -0.98 to 0.88 [2,3,5]. At some point, Li values were >0, and at another, they were <0, indicating that the groundwater from the source was somewhere around the carbonate equilibrium. At one point, it tended to form calcium carbonate, and at another, it tended to dissolve it [2]. In practice, it has been shown that values in the range of  $\pm 0.3$  to  $\pm 0.5$  cannot reliably indicate water properties, as small changes in temperature, pH, or calcium and bicarbonate content in the water can change the sign of Li. The Ryznar Stability Index in the groundwater from piezometers Wn1 to Wn8 ranged between  $7.5 < \text{RSI} < 9.0$ , suggesting that the groundwater in the Wn zone was aggressive with the potential for severe corrosion (Table 2).

**Table 2** Values of calculated Langelier saturation index and Ryznar stability index in groundwater in zone Wn

	Wn1	Wn2	Wn3	Wn4	Wn5	Wn6	Wn7	Wn8
Langelier saturation index	-0.02	-0.07	-0.17	-0.05	-0.03	0.13	-0.03	-0.09
Ryznar stability index	7.62	7.72	8.00	7.37	7.82	7.78	7.81	7.88

## CONCLUSION

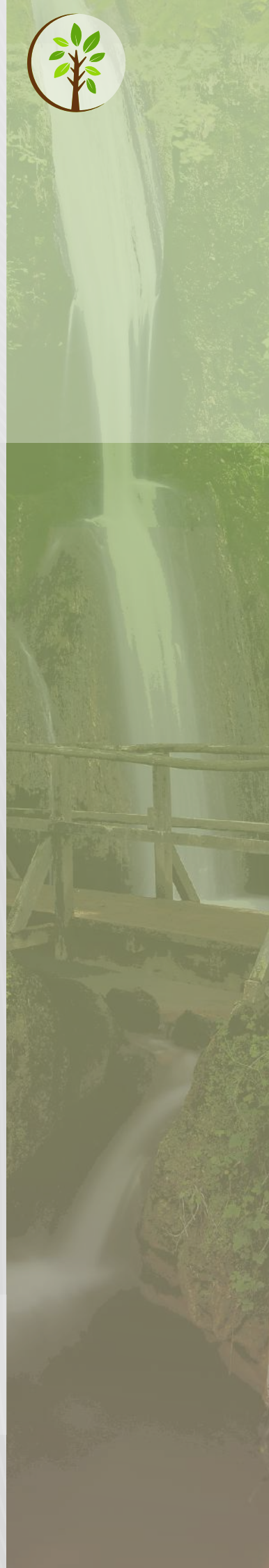
Based on the values of LI obtained from the calculated parameters for the examined piezometers (LI ranging from -0.02 to 0.13), groundwater in zone Wn is generally undersaturated and tends to dissolve calcium carbonate, except in the case of sample Wn6 where the water showed a tendency for carbonate deposition. Based on the values of the

calculated parameters LI, carbonate deposition in groundwater in zone Wn is unlikely to dominate. The Ryznar Stability Index calculated for the groundwater sampled from piezometers indicated the aggressive nature of the groundwater in the Wn zone and its potential for severe corrosion. The Langelier Index serves as an approximation rather than a direct measure of water corrosiveness. Nevertheless, it presents a valuable tool for assessing this tendency. The LI value is subject to variation, influenced by factors such as temperature and ionic strength. Understanding the LI's significance is crucial for implementing appropriate control strategies. In oversaturated conditions, excessive calcium carbonate precipitates, forming scales that can obstruct pipes and impair water flow. Conversely, in undersaturated conditions, the relationship between calcium carbonate and alkalinity may heighten water corrosiveness. Therefore, water operators must take proactive measures to ensure water equilibrium, minimizing both corrosive and scale-forming tendencies. It's important to recognize that these indices, such as LSI, and RSI do not directly forecast the corrosion of steel and other metals. Corrosion of metals typically depends on factors like pH, concentration of anions (such as sulfates and chlorides), and oxidants, which must also be considered.

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