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# PREDICTION OF STABILITY OF THE CIRCULATING WATER

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**Abstract:** In the work, on the basis of the data of the analysis of theoretical works and the laboratory studies carried out, the prediction of the values of corrosion rates in the circulating systems of coke plants was carried out using the Langelier and Ryznar stability indixes. The laws governing changes in the thermal stability of water as a function of temperature and water quality indicators (pH, alkalinity, total salinity, calcium ion content) have been established. Analysis of the obtained data showed that there is a clear dependence of the scale-corrosion properties of water on temperature and its chemical composition. A stable and effective supplying water composition for the circulating water supply system of the Kharkiv Coke Plant has been established.

**Keywords:** circulating water supply, coke plant, aggressive Index, Langelier Saturation Index, Puckorius Scaling Index, Ryznar Stability Index, Water Corrosion Index, Water Scaling Index



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## INTRODUCTION

Circulating water in the cooling systems are among the largest consumers of industrial water. Reducing the amount of natural water consumed to feed recycling systems is carried out through the reuse of various categories of treated industrial wastewater.

In this case, in order to avoid such negative processes as scale formation, corrosion and biological formations, it is necessary to carry out a detailed assessment and forecasting of the operating modes of coke-plant cooling systems. Otherwise, there is a deterioration in the work of not only the water-cooling systems, but also the entire production cycle, such as idle time for cleaning, equipment replacement, deterioration of heat transfer parameters between the cooling agent and the product, etc. (Marangou *et al.*, 2001; Ternovtsev, 1986; Balaban *et al.*, 2004; Kenny *et al.*, 2015).

Now almost all of the existing water-circulating systems of industrial plants of Ukraine dump sewage into reservoirs in the form of a purge system to maintain the salt composition of circulating water at a certain level, not only leads to environmental degradation of the environment, but also causes additional damage to plants themselves associated with these actions.

The need to adjust the quality and technological properties (thermal stability, biogenicity and corrosivity) of the water used to cool the equipment depends on the quality and properties of natural water, the conditions of its use and the heating temperature. (McNeill, 2002; Ternovtsev, 1986; Mokhtari *et al.*, 2010; Suvorin *et al.*, 2010; Marangou *et al.*, 2001).

To maintain the thermal stability of the circulating water of coke plants, inhibitor protection of heat exchange equipment is used at the same time, the reagents can be divided into the following main groups: (a) inhibitors of corrosion, scale formation and their composition; (b) biocides (bactericides); (c) reagents used in alkalizing water, its softening or acidification (pH adjustment)ç and (d) coagulants and/or flocculants to remove suspended substances.

## MATERIALS AND METHODS

Prediction of water stability, based on its chemical composition, is carried out according to standard methods of determination (Hoseinzadeh 2013; Kenny *et al.*, 2015; Suvorin *et al.*, 2010; Marangou *et al.*, 2001):

- Langelier saturation index stability Langelier saturation index (*LSI*);
- Ryznar Stability Index (*RSI*);
- Aggressive index (*AI*);
- Pucorius scaling index (*PSI*) for determining the tendency of water to scale;
- Larson-Skold index, which allows to characterize the corrosive ability of water in relation to low carbon steel;
- Oddo-Thompson index for rapid assessment of the propensity of water to dissolve or form calcium carbonate.

One of the most common and accurate methods for assessing the thermal stability (corrosion-scaling properties) of water is the Langelier method (Bower *et al.*, 1965; Ternovtcev, 1986; Hoseinzadeh E. *et al.*, 2013). The Aggressiveness index (*IA*) is defined as follows (Hoseinzadeh *et al.*, 2013):

$$IA = pH + log\ (AH) \qquad (1)$$

where: *AI* = Aggressiveness index, *A* = total alkalinity, mg/L as calcium carbonate, and *H* = calcium hardness, mg/L as calcium carbonate.

*IA* > 12 Water is non-aggressive; *IA* = 10-11.9 Water is moderately aggressive; *IA* < 10 Water is very aggressive.

Puckorius Scaling Index (*PSI*) (Hoseinzadeh *et al.*, 2013; Bower *et al.*, 1965; Ashassi-Sorkhabi *et al.*, 2008):

$$PSI = 2(pHs)-pHeq \qquad (2)$$

where: де $pHeq=1.465\times log10\ [Alkalinity] + 4.54$; *PSI* <6 Scaling is unlikely to occur; *PSI* >7 likely to dissolve scale.

The Langelier saturation index (W.F.Langelier) (Kenny *et al.*, 2015; Hoseinzadeh *et al.*, 2013; ; Bower *et al.*, 1965) allows to judge the assessment of thermal stability of water [24, 36, 120], that is, the behavior of water in relation to the saturation of water with calcium carbonate, showing the dominant tendency of water to scale formation (*LSI*> 0) or corrosion (*LSI* <0):

$$LSI = pH_0 - pH_S \qquad (3)$$

where $pH_0$ – measured pH of the source water; $pH_S$ – pH equilibrium water saturation with calcium carbonate.

For the calculation of $pH_S$ I.E. Apeltsin, a nomogram was compiled, according to which factors such as alkalinity (**Fig. 1**), total salt content, concentration of calcium ions, as well as the pH of the source water directly influence $pH_S$ (Suvorin *et al.*, 2010; Bower CA *et al.*, 1965) and is determined by the formula:

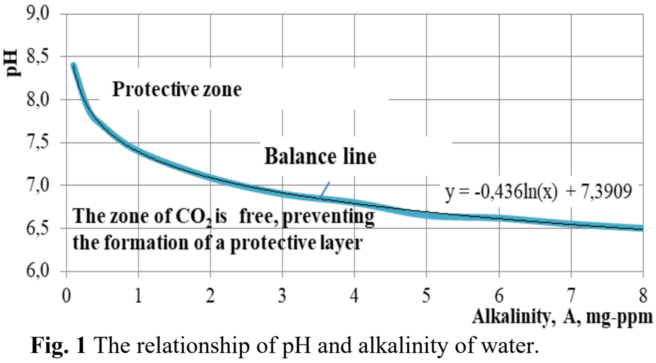


**Fig. 1** The relationship of pH and alkalinity of water.

$$pH_s = f_1(t) - f_2(Ca^{2+}) - f_3(A) + f_4(P) \quad (4)$$

where: де $f_1(t) = pK_2 - pS_{CaCO3}$ – water temperature function; $f_2(Ca^{2+})=lg(Ca^{2+})$ – function of calcium cations in water; $f_3(A) = lgA$ – water alkalinity function; $f_4(P) = 2{,}5\sqrt{\mu}$ – water salinity function.

Ryznar stability index (*RSI*) is used to determine the corrosivity of water in relation to steel (cast iron), which takes into account the scale layer on the metal surface, which can prevent corrosion, and is based on the calculation factors of the Langelier index (Kenny *et al.*, 2015; Hoseinzadeh *et al.*, 2013; Mokhtari *et al.*, 2010):

$$RSI = 2 \cdot pHs - pH_0 \quad (5)$$

A layer of scale on the surface of the metal can prevent corrosion and when the Ryzner *RSI* is 6, the solution will be stable. This method can only serve as a qualitative indicator of the "inclination" of natural water before a given process, since not all properties of water are determined by sediment or corrosion of metals and concrete, but only those that depend on the presence of carbon dioxide when using water. This water in systems direct-flow or reuse (without intermediate cooling). For water-circulating systems, this method is difficult to implement, especially when using wastewater, because according to modern views, the total alkalinity of water is due to a wider range of components.

The values of the Langelier and Ryzner stability indices relative to its thermal stability are given in **Table 1**. The aim of the research is to determine the stability of water in coke plants of different chemical composition and to predict its corrosion-scaling properties depending on temperature, pH, calcium concentration and total salinity of water.

## RESULTS AND DISCUSSION

Requirements for the quality of water used in industry are set depending on the requirements of the process and production scheme. Cooling water of water-circulating systems of ferrous metallurgy plants should be safe for service personnel, should not cause deterioration of corrosion, biological fouling and carbonate and other salt deposits, as well as worsen technical and economic indicators of the production process [29, 35-37]. Indicative indicators of the quality of such water are as follows: total hardness – 5 ppm/dm$^3$, coal hardness – 3 ppm/dm$^3$; total salt content – 300 mg/dm$^3$; pH = 7.2-8.5; chloride content – 400 mg/dm$^3$, sulfates – 500 mg/dm$^3$ (Ternovtsev, 1986; Nesterenko *et al.*, 2013).

### The research of prediction of water stability in accordance with the requirements of use in the water-circulating systems

The research of the prediction of the stability of the circulating water was carried out in accordance with the requirements of its use in the water-circulating system. According to the maximum allowable concentrations ($Ca^{2+}$ concentration – 140 mg/dm$^3$, alkalinity *A* - 4 ppm/dm$^3$, total salt content *P*=2 g/dm$^3$, temperature *t*=55 ºC) and for the circulating water of the coke plants, the stability index will change if at least one the parameter deviates from the recommended values.

Therefore, studies of the stability of circulating water were carried out when one of the parameters changed to the state of the reversible system (subject to other constant values) and regression equations were constructed. The obtained values of the correlation coefficients indicate that there is a strong direct relationship between the measured values and the value of the Langelier index ($LSI > 0.9$) (**Fig. 2**).

The alkalinity was changed with the following constant parameters: calcium concentration ($Ca^{2+} = 140$ mg/dm$^3$), ($P = 2$ g/dm$^3$), temperature ($t = 55$ ºC).

It was found that with decreasing alkalinity of the studied water from 0.1 to 1 ppm/dm$^3$, there is a tendency to corrosion and with large values of alkalinity, there is a slight tendency to scale formation without causing strong scale. If there is a layer of scale in the system, then, according to the Ryzner stability index, stable values will be observed only at alkalinity values of 4–8, and values of 0.1–3 will cause equipment corrosion.

**Table 1.** Summary table of Langelier and Ryzner indexes (Hoseinzadeh *et al.*, 2013)

| Langelier index | Ryzner index | Characteristic of the solution |
|---|---|---|
| 3 | 3 | Extremely high scale formation |
| 2 | 4 | Very high scale formation |
| 1 | 5 | Serious scale formation |
| 0,5 | 5,5 | Tendency to scale formation |
| 0,2 | 5,8 | Easy scale formation |
| 0 | 6 | Stable solution |
| -0,2 | 6,5 | Very light degree of corrosion |
| -0,5 | 7 | Mild corrosion |
| -1 | 8 | Corrosion tendency |
| -2 | 9 | Very high corrosion |
| -3 | 10 | Extremely high corrosion |

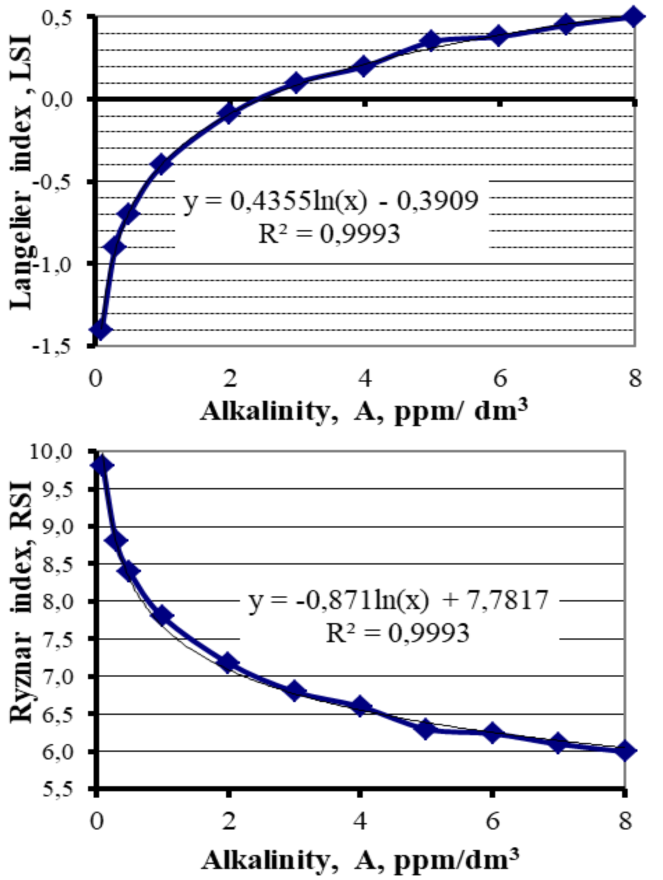


**Fig. 2** Graphic characteristics of Ryznar stability index and Langelier saturation index on alkalinity of circulating water: $Ca^{2+}$ concentration = 140 mg/dm$^3$, total salt content $P$ = 2 g/dm$^3$, temperature, $t$ = 55°C.

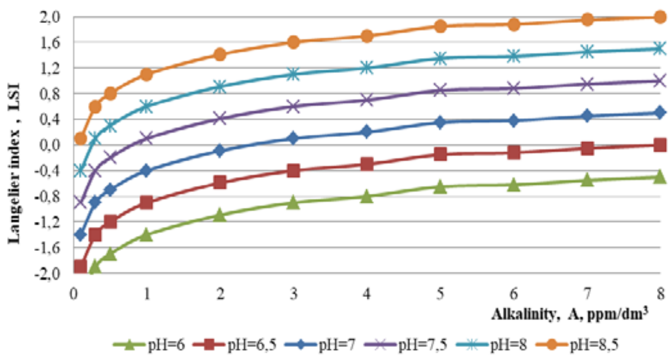


**Fig. 3** Dependence of the Langelier Index on pH and alkalinity of circulating water.

Prediction of changes in water stability as a function of changes in water salinity and the dependence of the Langelier index (**Fig. 3**) on this parameter in the operating conditions of the coke plant is shown in **Figs 4–5**. The analysis of the obtained dependences showed that when the salts are concentrated in the circulating system of the plant, there will be a change in the stability of the circulating water and a tendency towards corrosion (**Fig. 4**). The influence of pH is in the range of 6-8.5 units. The value of the Langelier Index as a function of the salinity of circulating water is shown in **Fig. 5**. At the same time severe corrosion is predicted at pH values 6 and tendency to scale formation at pH values 7.5–8.5. The prediction of the stability of water depending on the concentration of calcium in the circulating water in the range from 0 to 300 mg / dm$^3$ is summarized in **Figs 6–7**.

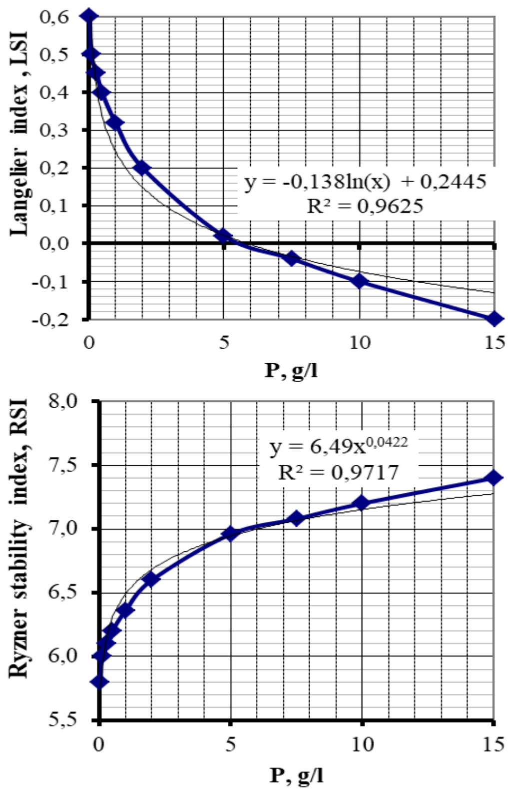


**Fig. 4** Graphs of the dependence of Langelier and Ryzner indexes on the total salt content of circulating water: $Ca^{2}$ + concentration = 140 mg/dm$^3$, alkalinity $A$ = 4 ppm/dm$^3$; temperature, $t$ = 55 °C.

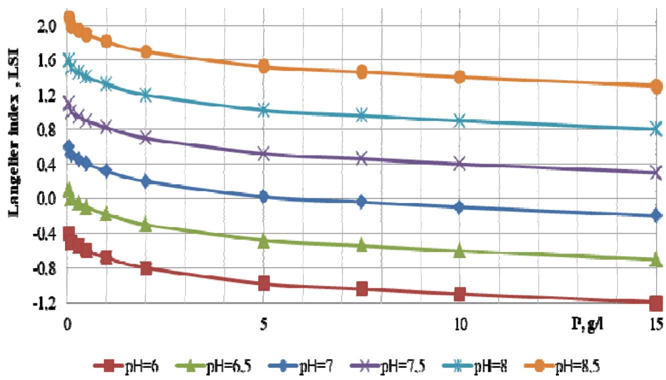


**Fig. 5** Dependence of the Langelier index on the total salt content and the pH of the circulating water.

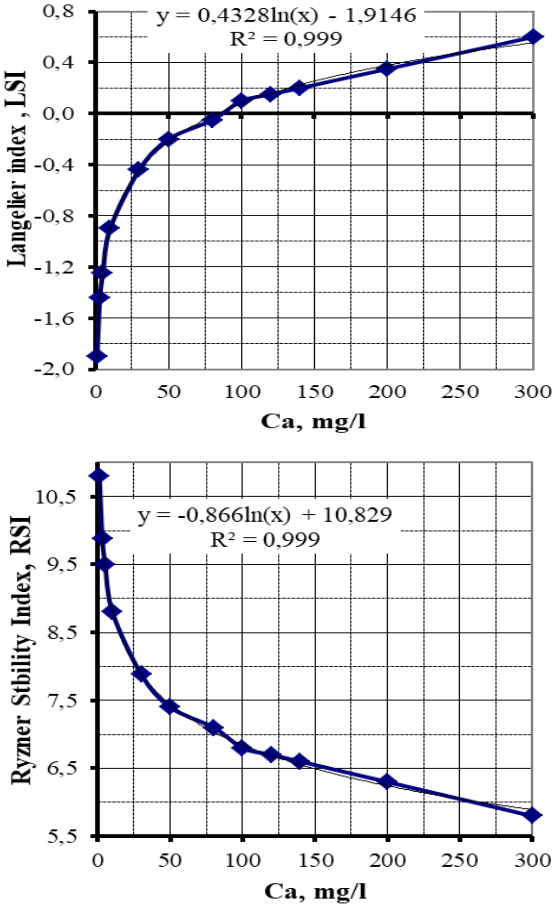


**Fig. 6** Graphs of dependence of Langelier and Ryzner indexes on the concentration of calcium of circulating water provided: salt content $P = 2$ g/dm$^3$, alkalinity $A = 4$ ppm/dm$^3$; temperature, $t = 55$ ºC.

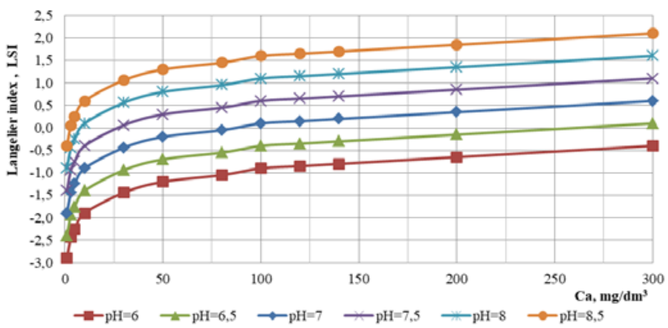


**Fig. 7** Dependence of the Langelier indexes on calcium concentration and circulating water pH.

Calculations of the Langelier and Ryzner stability index were carried out for a temperature range of 10 ÷ 80 °C with a step of 10 °C. Graphs and equations describing the dependence of the Langelier and Ryzner index on water temperature of different pH values are presented in **Figs 8–9**.

The analysis of the dependencies showed that when at least one of the water quality parameters in the water-circulating systems changes, its mode of operation and water stability change, and, accordingly, the reliability of the enterprise operation. Therefore, it is recommended to add necessary quality water to the system and dose corrosion inhibitors to the water-circulating system to maintain its stability.

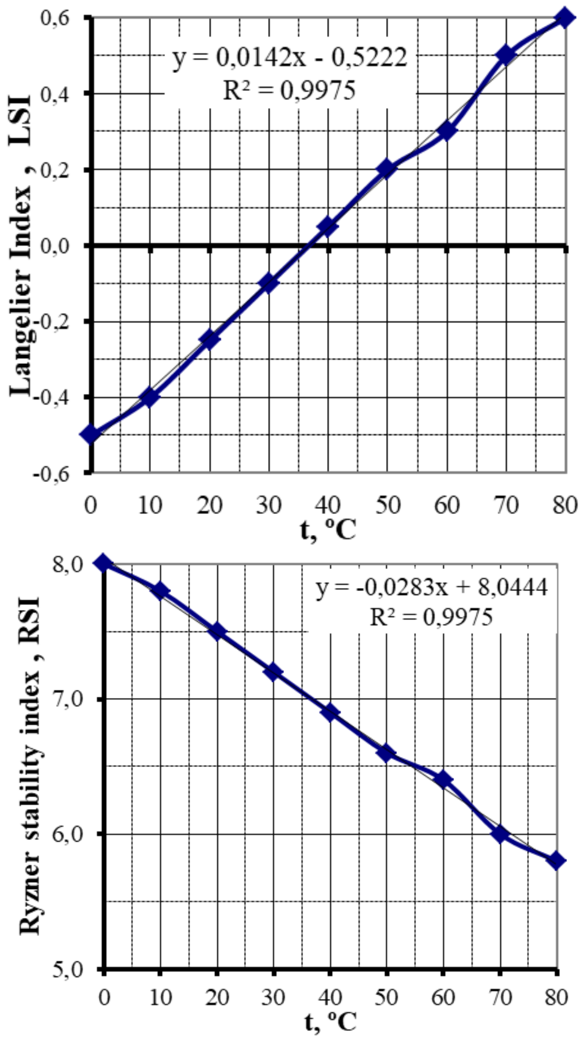


**Fig. 8** Graphs of dependence of Langelier and Rysner indexes on the water temperature provided: salt content $P = 2$ g/dm$^3$, alkalinity $A = 4$ ppm/dm$^3$; concentration of calcium $Ca^{2+} = 140$ mg/dm$^3$.

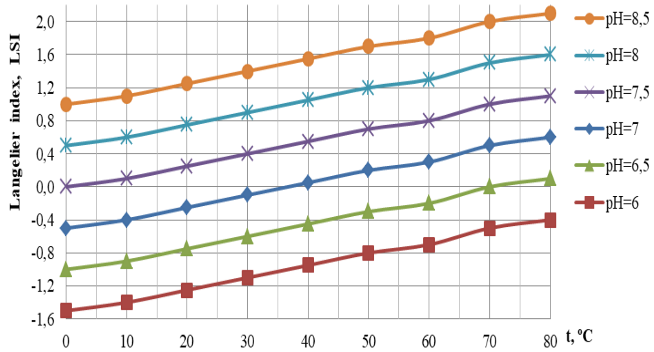


**Fig. 9** Dependence of the Langelier Index on the temperature and pH of circulating water.

## The research of prediction of the water stability at the Kharkiv coke plant

The use of phenolic wastewater requires some preparation for use as a feed for water-circulating systems (Kucherenko and Gladkov, 1980; Balaban-Irmenin Yu.V. *et al.*, 2004), because the balance of salt content of water-circulating systems is important because the process of scale formation and corrosion in heat exchange equipment.

The research to determine the effective and stable composition of supplying water were carried out at the Kharkiv Coke Plant. Replenishment of the water-circulating systems of primary gas cooling was carried out with the artesian water. The quality of supplying water is unsatisfactory, because this water has high hardness and alkalinity.

In the present work, we develop methods of the stability protection of the Kharkiv Coke Plant, when using biologically treated phenolic wastewater in the circulating water for primary gas cooling. Quality indicators of the supplying and circulating water of the Kharkiv Coke Plant, the average annual rate (**Table 2**). In order to study the conditions of water use in closed water supply systems, studies were conducted to determine the effect of the technological parameters of the circulating water systems and the main components of the salt composition of water on its stability. Analysis of the thermal stability of water at the Kharkiv Coke Plant showed a tendency of water to corrosion, which is confirmed by the data in **Table 3**.

The experimental research were carried out with biochemically purified phenolic wastewater, as well as their mixture of fresh (artesian) water, which were used as supplying water of the water-circulating system at the Kharkiv Coke Plant in the laboratory. During the preparation of circulating water by mixing different ratios of fresh water from purified phenolic water stability was investigated (**Fig. 10**).

The results of experimental data show that the region of stability in the Langelier index is observed with the proportion of phenolic water of 15-20% in the supplying water (**Fig. 10**). Considering the layer of scale formed in the water-circulating system, according to the Ryzner index at 0; 15 and 20% - the state of the system is close to stable. Based on the Langelier index, artesian water after evaporation is scaled, and with increasing from 30% share of phenolic water in the supplying – corrosion. According to the Ryzner index, regardless of the ratio of the supplying water, it is subject to corrosion: at 0; 15; 20% - light corrosion and a tendency to the formation of corrosion are observed, and at 10 and 30% - very high corrosion, and with a higher percentage of phenol wastewater in the supply, a high and unacceptable degree of corrosion is observed. Therefore, for the water of this composition, the Langelier index is a more objective indicator.

## CONCLUSIONS

Based on the data of the analysis of theoretical and laboratory researches, the prognosis of water to corrosion or scale formation in industrial water-cooling systems at coke plants using water stability indices (aggressiveness index, Langelier index, Ryzner and Pakkorius) was made. The obtained data indicate the feasibility of using the Langelier and Ryzner indexes as an index of water stability for the water-circulating

**Table 2.** Results of the analysis of the quality of supplying and circulating water at the Kharkiv Coke Plant

| Indicators | Artesian water | Purified water after biological oxygen consumption | Circulating water |
|---|---|---|---|
| pH, unit | 7,48–7,65 | 6,9–7,2 | 5,5–7,6 |
| Iron, $mg/dm^3$ | **0,52–0,76** | – | 9–45 |
| Sulphates, $mg/dm^3$ | 89,3 | – | – |
| Chlorides, $mg/dm^3$ | 28,0–71,6 | 470-1 100 | 600–1300 |
| Dry residue, $mg/dm^3$ | 183,6–565 | 3670–4884 | 2200–5500 |
| Resins and oils, $mg/dm^3$ | – | 36,2 | – |
| Total hardness, $ppm/dm^3$ | 4,6–4,9 | 3,0 | 17-43 |
| Calcium of hardness, $mg/dm^3$ | 58,1 | – | – |
| Magnesium hardness, $mg/dm^3$ | 20,7 | – | – |
| Alkalinity, ppm $/dm^3$ | 5,0–5,2 | 1,4-2,0 | – |
| Chemical oxygen consumption, $mgO/dm^3$ | – | 480,0 | – |
| Suspended substances, $mg/dm^3$ | 5 | – | 48–700 |
| Ammonia total, $mg/dm^3$ | 0,86 | 48,5 | 145 |
| Phenols, $mg/dm^3$ | – | 2,1–2,6 | 1,2–4,2 |
| Thiocyanates, $mg/dm^3$ | – | 46–98,7 | 4,8–13 |
| Conductivity, TDS, ppm | 383 | 3490 | 4380 |
| Oxidation-reduction potential, ORP, mV | 31–55 | 109–(80-130) | 104–98 |

* Analysis of water composition was carried out according to standard methods

**Table 3** Water stability indicators at the Kharkiv Coke Plant on the basis of annual average values

| Test water | Index results | | | |
|---|---|---|---|---|
| | Langelier Indication Saturation Index, *LSI* | Ryzner Stability Index, *RSI* | Puckorius Scaling Index, *PSI* | Aggressiveness index, *AI* |
| Artesian water | -0,02<br>Stable water | 7,52<br>Lightweight corrosion | 7.5<br>Likely to dissolve scale | 11,08-11,8<br>Water is moderately aggressive |
| Biologically treated phenolic wastewater | -1,38<br>Water is under-saturated with respect $CaCO_3$ and it has tendency to corrosion | 9,66<br>Very high corrosion | 8.8-9.9<br>Water has tendency to corrosion | 7.8 – 9.9<br>Water is very aggressive |
| Circulating water | -0,03 ÷ -0,3<br>Lightweight corrosion | 7,47÷7,97<br>Tendency to corrosion | 7.5-8.8<br>Water has tendency to corrosion | 10.3-11.5<br>Water is moderately aggressive |

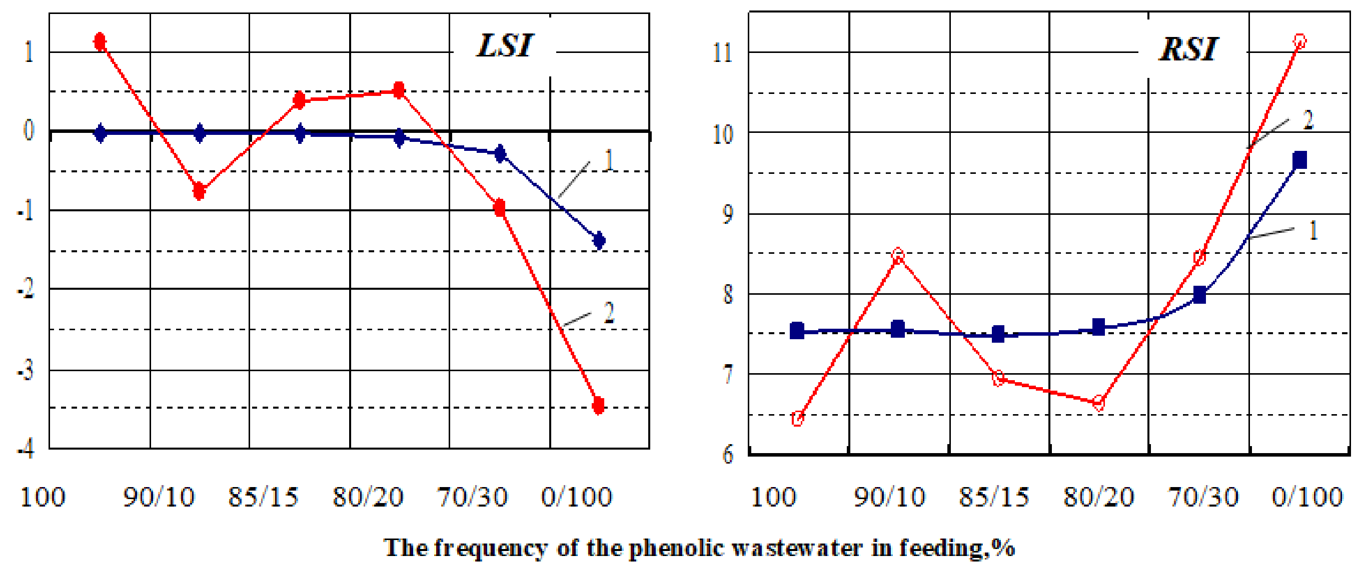


**Fig. 10** Dependence of the Langelier Saturation Index (LSI) and Ryzner stability index (RSI) on the content of the phenolic wastewater in supplying water if wastewater evaporation 2-2,2 without adding an inhibitor: 1 – before evaporation (t = 30 ºC); 2 – after evaporation (t = 55 ºC): (a) Langelier index, and (b) Ryzner index.

system at coke plants. Analyzing the data obtained, it can be argued that there is a clear dependence of the scum-corrosion properties of water on temperature and its chemical composition.

In addition, it is determined that water with an increase in temperature loses its aggressive properties, and water, prone to the formation of deposits, on the contrary, with increasing temperature becomes more aggressive.

The obtained dependences make it possible with a high degree of probability to estimate the tendency of water to form or dissolve carbonate sediments, which allows it to be used to predict the corrosion-scaling properties of water-circulating systems and to evaluate the aggressive properties of water in order to predict the system's performance when its quality composition changes.

The obtained data of changes in the properties of circulating water, depending on the choice of a stable composition of supplying water in circulating systems while protecting the heat exchange equipment from corrosion damage, allow predicted water stability. The results indicate an effective ratio between the artesian and purified water after the biochemical plant, which is (artesian - purified phenolic water) 4: 1, respectively, which makes it possible to slow down the corrosivity and stable operation of the system.

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