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Treatment Method Assessment of the Impact on the Corrosivity and Aggressiveness for the Boiler Feed Water †

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Abstract: The aim of the study was the assessment of corrosivity and aggressiveness for boiler feed water. The negative effects of water corrosivity and aggressiveness may include silting up of the steel water supply system and the destruction of boiler equipment touched or washed by such water. They may cause the whole industrial production system to fail or be destroyed. That is why it was important to reach a high water purification level, including the calculation of water aggressiveness and corrosivity indicators. The carried out test showed that the simple system used before the modernization of the industrial water treatment plant is not sufficient to reach clean and stable water. The authors proposed modernization, including additional processes to improve boiler water quality, and designed new devices for water treatment. As a result of the new idea, groundwater taken as raw water was treated in individual and complex processes, such as pre-aeration, filtration, ion exchange (cation and anion exchange resigns), extra aeration, and extra degassing. The conducted research included chemical analyses of raw and treated water. In the conducted studies, the indirect method of water aggressiveness and corrosivity assessment was applied using mathematical calculation of the Langelier Saturation Index (LSI), the Ryznar Stability Index (RI), the Larson–Skold Index (LI), and the Singley Index (SI). The results proved that the new proposed processes for the boiler feed water treatment station allow reaching a high water quality and low level of water aggressiveness and corrosion.

Keywords: groundwater; stabilization; corrosion; aggressiveness; boiler feed water

1. Introduction

Water used for domestic and industrial purposes should not have aggressive or corrosive features [1–3]. Aggressive water is able to create sediments and precipitations. However, corrosive water is capable of damaging many devices and equipment with which it comes into contact [4–8]. The aggressiveness and corrosivity of water are important indicators for water suitability assessment for industrial production, for the distribution of drinking water and economic purposes [2,4]. The corrosive effect of water on metals involves complex electrochemical and biochemical processes. None of the water components are inert to the metal and can accelerate or delay its corrosion. The corrosion rate is determined by the ratio of protective and corrosive components contained in water [9]. On the other hand, the destructive effect of water aggressiveness is described as an aggressive impact on concrete and a corrosive impact on metals, mainly iron and steel. Removal of aggressiveness and corrosivity of water as its stabilization is carried out by physical methods such as aeration or chemical methods [10,11].

This can also be achieved by water filtration through the masses increasing the water pH. If a suitable bed and filter parameters are selected, then other equipment can be used to remove aggressive carbon dioxide from the water, which is responsible for its corrosive properties [12–14]. According to Shock and Lytle [15], marble grit or roasted dolomite is the best choice for this purpose. The removal of aggressive carbon dioxide should also be projected after water softening and demineralisation of boiler feed water with cations exchange resigns studied by Awual [11,14]. Filter materials used for this purpose bind free and aggressive carbon dioxide. Filtrated water acquires new properties: it becomes free from aggressive carbon dioxide and has a higher pH, alkalinity, and sometimes hardness [3,16,17].

The corrosive and aggressive features of water can be determined by direct methods [18]. These include the evaluation of the effects of corrosive exposure to different materials. Another group of methods of determination is indirect methods. Such methods involve the measurement of selected physical and chemical parameters of the water and the interpretation of reached data by the calculation of corrosivity and aggressiveness indicators, which allow to determine the water tendency to have a corrosive impact on materials. Corrosivity indicators in the literature are divided into two groups [9]. The first group of indicators is used to assess water corrosivity, and includes the Larson–Skold Index (LI) and Singley Index (SI). The second group helps in water aggressiveness evaluation and is based on the Langelier Saturation Index (LSI) and Ryznar Stability Index (RI) [19,20].

Most of the natural groundwater has a high level of aggressiveness and corrosivity [3,20]. The negative effects are described by Awual and his team [8,17] as intensified corrosion, silting up of the steel water supply system, and the destruction of equipment touched or washed by such water. Furthermore, incorrectly purified water is able to damage many devices that stay in contact with it; that is, pipes, water pipe fitting, storage tanks, filters, boilers, and others. The result of a higher level of aggressiveness and corrosivity is elevated concentration of carbon dioxide and change of water color [11,13]. These were the problems of the studied industrial plant that needed clean and stable water to feed the high temperature boiler. That is why authors took the decision to reach a higher water purification level and designed modernization of the industrial water treatment station including additional processes to improve boiler water quality. The modernization idea needed confirmation in water pollution analyses and technological parameters. The aim of the study was also the assessment of the corrosivity and aggressiveness for boiler feed water using indirect calculations of water aggressiveness and corrosivity indicators: Langelier Saturation Index (LSI) and Ryznar Stability Index (RI), Larson–Skold Index (IL), and Singley Index (SI). Additionally, water colour change was observed.

2. Material and Methods

2.1. Analytical Methods

For the conducted studies, the indirect method of water aggressiveness and corrosivity assessment was applied. The Larson–Skold Index (LI) was calculated. According to this index, corrosive properties depend on the concentration of chlorides and sulphates (VI), and the alkalinity of water. It takes on the following form [12]:

$$IL = \frac{2\left[SO_4^{2-}\right] + \left[Cl^-\right]}{\left[HCO_3^-\right] + \left[CO_3^{2-}\right]}. \tag{1}$$

As carbonates do not generally occur in natural water, the formula can be converted to the following form [12]:

$$IL = \frac{2\left[SO_4^{2-}\right] + \left[Cl^-\right]}{\left[HCO_3^-\right]}, \tag{2}$$

$[SO_4^{2-}]$—sulphates concentration (VI) [mg/dm^3],
$[Cl^-]$—chlorides concentration [mg/dm^3],

$[HCO_3^-]$—bicarbonates concentration [mg/dm^3],
$[CO_3^{2-}]$—carbonates concentration [mg/dm^3].

As it was observed, a significant number of factors influence the corrosion rate (on which the increase in water colour depends). Iram [12] and Nawrocki and others [5] state that a modified Larson–Skold Index can be used, also taking into account sodium concentration, water temperature, and retention time in the water supply system. The new formula took the form of the Singley Index (SI): [5,12]:

$$SI = \frac{\left([Cl^-] + \left[SO_4^{2-}\right] + [Na^+]\right)^{\frac{1}{2}}}{zasad} \frac{T}{25} HRT. \quad (3)$$

The effect of water corrosion could be the colour increment (ΔB). This parameter depends on water temperature, retention time, dissolved oxygen concentration, sodium, sulphates (VI), chlorides, and water alkalinity. The dependence of water colour increase ΔB on the above mentioned factors is expressed by the following equation [21]:

$$\Delta B = \frac{[Cl^-]^{0.485}[Na^+]^{0.561}\left[SO_4^{2-}\right]^{0.118}[O_2]^{0.967}[T]^{0.813}[HRT]^{0.836}}{10^{1.321}[alk]^{0.912}}, \quad (4)$$

$[SO_4^{2-}]$—sulphates concentration (VI) [mg/dm^3],
$[Cl^-]$—chlorides concentration [mg/dm^3],
$[Na^+]$—sodium concentration [mg/dm^3],
$[O_2]$—initial dissolved oxygen content [mg/dm^3],
T—temperature [^{0}C], alk—alkalinity [mg $CaCO_3$/ dm^3],
HRT—hydraulic retention time [days].

The description of water aggressiveness and corrosion requires the determination of the level of stability. Water stability was established by the Langelier Saturation Index [15]:

$$\mathrm{LSI} = \mathrm{pH} - \mathrm{pH_s}, \quad (5)$$

pH—real reaction of water,
pH_s—pH value of the water in the saturated state.

Saturation Index [15]:

$$\mathrm{pH_s} = \mathrm{f(T_{Ca}, Alk_{og}, L, K_2)}, \quad (6)$$

L—the solubility product of calcium carbonate $CaCO_3$,
K_2—the second carbonic acid dissociation constant.

In reality, simplified methods of pH determination are used, taking into account its dependence on the total content of dissolved salts in water, temperature, calcium hardness, and general alkalinity [3,6,14]. The tendency of water to form protective layers can also be determined by the Ryznar Stability Index (RI), determined by the following formula [9,12,22]:

$$\mathrm{RI} = 2\mathrm{pH_s} - \mathrm{pH}. \quad (7)$$

2.2. Technological Methods

The research was conducted using water treatment experimental devices located in the technological side-line of the chosen industrial plant produced boiler feed water. The analyzed water treatment plant before the experiment was designed to realize such processes as primary aeration (under atmospheric pressure), filtration, and cation exchange. The basic technological system of water treatment (before modernization) consisted of quartz sand filters, cation exchange columns, and a primary aeration tank.

Technological parameters of water treatment plant before modernization:

- Water flow chart—20 m^3/h,
- Water flow rate—1–1.5 m/s,
- Primary aeration: open tank volume—3 m^3, retention time—10 min, non-pressure aerators with air flow 0.5–1 Nm^2/h,
- Quartz sand filtration: two filters DN800, H = 1.8 m, V load = 17 m^3/m^2 h,
- Cation exchange: five columns with weak cation exchange resign, DN300, H = 1.5 m, Q = 4 m^3/h.

The technological research included analyses of raw and purified water. Raw water was taken from a deep well, which was the company's source of water supply. Water samples were taken after individual treatment processes, that is, after water aeration from a non-pressure aeration chamber, and after water filtration in sand filters and ion exchange columns. Water samples were taken once a week over the period of three months (total 14 research series).

An assessment of water corrosivity and aggressiveness required a full analysis of the pollution parameters: pH, dissolved oxygen, temperature, conductivity, chlorides, sulphates (VI), total hardness, calcium hardness, free carbon dioxide, carbon dioxide, bicarbonate carbon dioxide, aggressive carbon dioxide, total salinity, total alkalinity, HRT (time of water retention in the system), and sodium. Aggressiveness indicators—Saturation Index (LSI), the Ryznar Stability Index (RI), and corrosion indicators: the Larsoni–Skold Index (LI) and Singley Index (SI)—were calculated for raw water and for the water after every individual purification process.

The technology of industrial water purification applied before modernization did not allow removing the corrosivity and aggressiveness of water. The obtained results and calculation of the indexes clearly indicated that the raw, as well as treated, water collected after quartz sand filters and cation exchange columns is aggressive (Tables 1 and 2). The analyses showed that the water, owing to its aggressive CO_2 content, will not be suitable for the technological production of boiler water. It cannot be used for industrial applications because its aggressive CO_2 concentration (exceeding 2.2 mg/dm^3) affects the corrosivity of water.

On the basis of the obtained results, modernization of water treatment station was projected. Owing to the production profile, it was impossible to use chemical corrosion inhibitors. Therefore, the following processes, which should supplement the system of industrial water purification, were proposed:

- Pre-aeration of raw water taken from the well. For experiments, a new aeration system was designed, including an in-line mixer combined with compressor with air flow of about 2–3 Nm^2/h. Samples of aerated water were taken after flow compensation and the escape of air bubbles from the analysed water after venting valves.
- Use of weak base anion exchange resin, which eliminates from the water disturbing ions of strong acids: SO_4^{2-} and Cl^-. Such mass additionally increases the water pH and influences the aggressiveness indexes.
- Additional (extra) aeration of treated water. The process was planned after water deionization. In-line aerators combined with a compressor with air flow of 4–5 Nm^2/h were used.
- Extra deaerator (degassing system) as the last process of water purification. For experiments, a thermal pressure deaerator was used. Degassing occurred at temperatures above 150 °C and operating pressures around 6 to 8 bar.

Technological parameters of water treatment plant after modernization:

- Water flow chart—20 m^3/h,
- Water flow rate—1–1.5 m/s,
- Pre-aeration: in-line static mixer DN80 combined with compressor with air flow of about 2–3 Nm^2/h,

- Quartz sand filtration: two filters DN800, H = 1.8 m, V load = 17 m^3/m^2 h,
- Cation exchange: five columns with new weak cation exchange resign, DN300, H = 1.5 m, Q = 4 m^3/h,
- Anion exchange: five columns with weak base anion exchange resin, DN300, H = 1.8 m, Q = 4 m^3/h,
- Extra aeration: two in-line static mixers DN80 combined with compressor with air flow of about 5–6 Nm^2/h,
- Thermal pressure deaerator: DN1000, H = 2 m, V = 2 m^3.

3. Results and Discussion

Water quality at the studied water treatment plant changed during the time of its exploitation. Changes depending on the water chemical composition are shown in Table 1, as well as other parameters associated with water flow, that is, hydraulic retention time (HRT). According to Awual [2,11], water may also react with a material with which it is in contact. If a water attack on the exposed metals can be characterized by its corrosion and influence against other surfaces, we can talk about its aggressiveness. Corrosion and aggressiveness of water are common problems, especially for the industrial production of boiler water [10,13].

Treatment method assessment of the impact on the corrosivity and aggressiveness for the boiler feed water was the aim of laboratory and technical experiments conducted for treated groundwater directed to the chosen industrial plant. The plant prepared technological water in an old and ineffective water treatment station. Stains, rust, and poor damage have appeared inside the water supply system and in the water storage tank. This resulted in a greater amount of sediments and increased water color. The chemical reactions produce ferrous, then ferric hydroxides, forming nodules and tuberculation, which can, in the long term, reduce the pipe cross section and significantly increase the head loss. There was a need to stop such processes, especially for boiler feed water, because of the destruction of boiler equipment touched or washed by such water. Awual [17] writes that water not sufficiently treated could have been driving the whole industrial production system to fail or be destroyed. That is why it was important to reach a high water purification level, including the calculation of water aggressiveness and corrosivity indicators.

For the assessment of water corrosivity and aggressiveness, analyses were carried out of the water pollution parameters: pH, dissolved oxygen, temperature, conductivity, chlorides, sulphates (VI), total hardness, calcium hardness, free carbon dioxide, carbon dioxide, bicarbonate carbon dioxide, aggressive carbon dioxide, total salinity, total alkalinity, HRT (time of water retention in the system), and sodium. The results are presented in Table 1.

The estimation of oxygen concentration in water was the first step in the conducted research. Pre-aeration before modernization of the water treatment plant was realized by inefficient open pipes for many years. Old pipes transported air into an open aeration chamber about 1 m under the water surface and did not allow the increase of water alkalinity and removal of carbon dioxide. It was proved by Naykki and others [17] that aeration makes it possible to remove dissolved gases in raw water, especially aggressive CO_2. In industrial systems, the most optimal solution for pre-aeration is the use of venturi aerators (at constant water intake) or a linear compressor pumping air regulated by a manometer (at variable water intake during the day). The authors decided to the change primary aeration system. This was the first process at the analysed industrial water treatment plant. For experiments, an aeration system including a static in-line mixer combined with an air compressor was designed. After modernization, the oxygen concentration changed from 0.5 mg/dm^3 in raw water to 3.5 mg/dm^3 after aeration and 2.6 mg/dm^3 after filtration. The oxygen fed into the water during primary aeration oxidizes Fe(II) to Fe(III) and other reduced substances, for example, the sulphate ion (IV) to the sulphate ion (VI). Apart from refreshing the water, removing the smell, and initiating the iron precipitation reaction, the influence of this process on water aggressiveness and corrosivity indexes was not noticed. Therefore, deacidification of water by introducing air is important for the treatment of groundwater.

Table 1. Parameters of water pollution after successive treatment steps. HRT, hydraulic retention time.

Water Parameter	Raw Water	Pre-Aeration	Sand Filter	Cation Exchange	Anion Exchange	Extra Aeration	Extra Deaerator
pH	7.15	7.62	7.47	6.58	8.65	8.45	8.35
Dissolved O_2 [mg/dm^3]	0.5	3.5	2.6	0.5	0.5	3.2	0.0
Temp. [^{0}C]	11.7	13.6	15.1	15.4	15.2	15.1	97.9
Conductivity [mS/dm^3]	0.75	0.73	0.56	0.13	0.07	0.07	0.07
Cl^-[mg/dm^3]	80	80	80	80	12	12	12
$SO^{2-}{}_4$ [mg/dm^3]	176	176	112	112	18	18	18
Total Hardness [mg$CaCO_3$/dm^3]	450	450	380	0.0	0.0	0.0	0.0
Ca [mg/dm^3]	132	132	115	0.0	0.0	0.0	0.0
CO_2 (free) [mg/dm^3]	91	65	56	47	6	0.0	0.0
CO_2 (bicarb.) [mg/dm^3]	0.0	0.0	0.0	0.0	0.0	0.0	0.0
CO_2 (carb.) [mg/dm^3]	231	185	176	155	25	25	25
CO_2 (aggress.) [mg/dm^3]	2.5	1.9	1.9	2.0	0.2	0.0	0.0
Tot.Diss.Solids [g/dm^3]	32	32	13	2.5	0.4	0.4	0.4
Tot. alk. [mval/dm^3]	3.4	4.5	4.1	3.5	5.5	5.5	5.5
HRT [day]	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Na^+ [mg/dm^3]	170	98	98	98	98	98	98
ΔB [mg Pt/dm^3]	3.1	4.9	2.1	0.3	0.3	0.0	0.0

Source: Own elaboration.

Concerning scientific literature, the role of dissolved oxygen is not exactly known, because different authors [4,5,9,16,17] give contradictory reports. Some of them [23,24] explain that dissolved oxygen is the main electron acceptor and has a significant impact on the rate of corrosion, which grows with oxygen concentration. Moreover, Sozański et al. [25] found that an increase in dissolved oxygen concentration reduces the iron release to water and also reduces water turbidity. On the other hand, a lack of oxygen in water can be conductive for anaerobic processes [26]. They are seriously unfavourable for natural water and for water quality, because they make water organoleptic features worse [1,2]. Next, purification processes in the tested water treatment station including cation and anion exchange also required oxygen control. During anion and cation exchange, there is the possibility to create gases as a side effect of water purification [14,20]. Furthermore, CO_2 is generated as a result of ion exchange. The analysed raw water contained 91 mg CO_2/dm^3. After pre-aeration and sand filtration, its concentration dropped to 56 mg CO_2/dm^3. Free carbon dioxide was present even in deionized water at the level of 6 mg CO_2/dm^3, when its maximal concentration should be under 2.2 mg CO_2/dm^3. Secondary aeration may remove all gasses from the water. This was the reason to design extra aeration for experiments. Static in-line aerators combined with an air compressor were used.

After water aeration, it is necessary to check whether only carbon dioxide, which is bound in the form of bicarbonates or hydrocarbonates, remains in the water. If aggressive CO_2 is also present, it must be chemically removed [26]. The conducted study indicated that bicarbonates were never present in the water at any treatment stage. The carried out tests showed the presence of hydrocarbonates in the water. It is total alkalinity, which is the parameter calculated based on HCO_3 in the water. First, processes of water treatment at the station did not remove it from the boiler feed water. The greatest amount was in the raw water—over 200 mg/dm^3. With primary aeration, filtration, and cation exchange, we can see a slow reduction from 185 to 155 mg/dm^3. Anions exchange remove it efficiently from the water to 25 mg/dm^3. Next, processes did not change its concertation.

Nevertheless, industrial boiler feed water cannot include a higher concentration of oxygen or carbon dioxide, which may lead to boiler damage. This was the reason to design the last water treatment process—extra deaeration. For experiments, a thermal pressure deaerator was used. Deaeration removes all the gases dissolved in the water up to trace amounts. The solubility of gases in water is determined by its temperature. As the temperature increases, the partial pressure of the gases dissolved in the water decreases. At the boiling point of the water, these pressures drop to zero. At this and higher temperatures, the theoretical solubility of a gas in water also drops to zero. The conducted research confirmed this theory. Oxygen and free carbon dioxide concentrations dropped to 0.0 mg/dm^3 after degassing.

The other water parameters mentioned in the Table 1 were used to calculate the aggressiveness and corrosion indicators: the Saturation Index (LSI), the Ryznar Stability Index (RI), the Larsoni-Skold Index (LI), the Singley Index (SI) and the color increase. The results of calculations are presented in the Tables 2 and 3 as well as in the Figures 1–5.

Table 2. Aggressiveness and corrosion indicators of raw water and treated industrial water.

	LSI	**RI**	**LI**	**SI**
Raw water	−0.34	8.24	0.22	1.04
Pre-aerated water	−0.12	7.23	0.25	0.93
Filtrated water	−0.23	7.57	0.36	0.85
Deionized water (cation and anion exchange)	−0.83	9.03	0.28	0.81
Secondary aeration	0	7.05	0.23	0.75
Extra deaeration	0	5.89	0.21	0.67

Source: Own elaboration.

Table 3. Values of water aggressiveness and corrosivity indicators. LSI, Langelier Saturation Index; RI, Ryznar Stability Index; LI, Larson–Skold Index (LI); SI, Singley Index.

Values of Water Aggressiveness and Corrosivity Indexes				
Index	LSI	RI	LI	SI
Corrosive/aggressive water	$J_L < 0$	$J_R > 7$	$I_L >> 1.2$	$I_L >> 1.2$
Stable water	$J_L = 0$	$J_R = 6–7$	$1.0 < I_L < 1.2$	$1.0 < I_L < 1.2$
Not corrosive/not aggressive water	$J_L > 0$	$J_R < 5$	$I_L < 0.8$	$I_L < 0.8$

Source: Own elaboration on Frayne [21] and American Water Works Association [22].

Corrosion may be defined as the destruction of a metal, usually by chemical or electrochemical reaction. The water aggressiveness is defined as its propensity to attack calcium-containing materials. At the water treatment station, it is water hardness. The treated water at the studied station had negative corrosive and aggressive features. The calculations of indicators resulting from the conducted research interchangeably proved that raw water and treated water have revealed aggressive features.

Lee and others [26] list the water parameters that determine its corrosive properties. These include pH, alkalinity, chlorides, sulphates (VI) and other inorganic ions, water temperature, dissolved oxygen concentration, and natural organic matter. Such parameters include in its formula the Singley Index (SI) presented in Table 2 and Figure 1. The reached results showed that water going through the first treatment processes is corrosive. This property was noticed after primary aeration and sand filtration. The SI for pre-aeration oscillated was about 0.93, which was close to the corrosion level. The sand filtration process and ion (cation and anion) exchange helped the SI decrease to the level of 0.81. However, the water, despite advanced purification processes, was not safe for a high-temperature boiler. Limits of water corrosivity and aggressiveness are presented in Table 3, and show that stable water becomes by SI between 1 and 1.2, and neither corrosive nor aggressive water is for SI < 0.8. The new designed process, extra aeration, reduced water corrosion. The SI achieves a value of about 0.75 and comes to a stable state. The last process, degassing, improved the effect. It made water neither corrosive nor aggressive and allowed obtaining SI = 0.67.

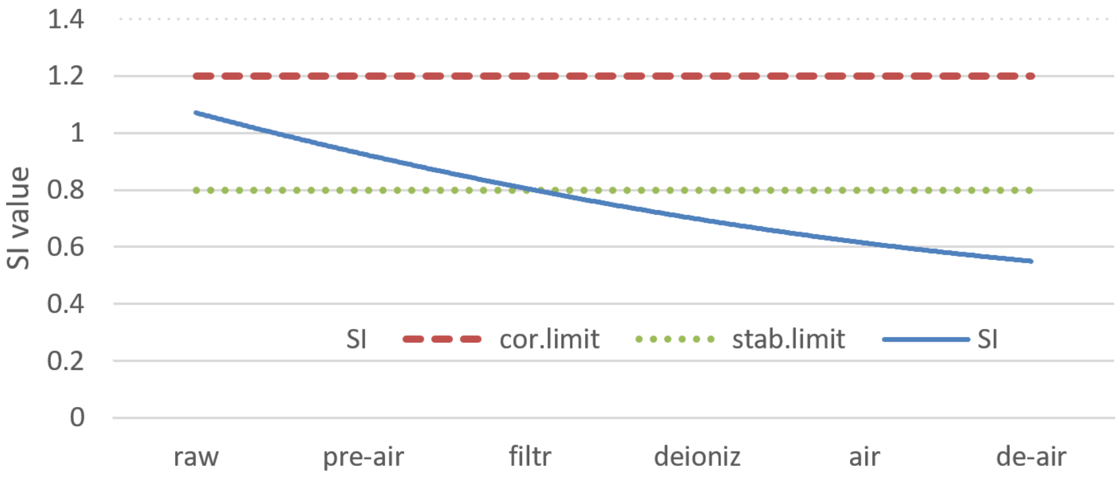

Figure 1. Changes of Singley Index (SI). Source: Own elaboration.

The Larson–Skold Index (LI) indicates that higher salinity, higher temperature, and a longer retention time significantly increase corrosion. The LI is presented in Table 2 and Figure 2. Sarin [26] describes the operating parameters affecting corrosion and writes that the intensity of corrosion is also influenced by other factors related to the water station exploitation and the real state of the water supply system. The following are mentioned in particular: the flow rate of water, the retention time of the water in the system, the condition of the installation, its age, and pipes' diameter. Only bicarbonate ions have inhibiting properties. That is why corrosion may be prevented by water alkalinity increase [6,7]. In this study, the Larson–Skold Index calculations proved that water treatment processes after modernization did not have any influence on water corrosion. Purified water in every individual purification process was neither corrosive nor aggressive. Analysis of the corrosivity indexes, that is, LI and SI, indicated some divergences. Calculations of the Larson–Skold Index showed that the every process of water treatment at the studied station did not influence the change of water corrosivity. Water was not corrosive. However, the Singley Index, which additionally takes into account the alkalinity parameter and water retention time in its formula, showed the opposite situation.

Figure 2. Changes of Larson–Skold Index (LI). Source: Own elaboration.

Apart from water corrosivity, its aggressiveness was also assessed. Water, depending on its composition and other flow-related parameters, may change during its exploitation and react with the material in contact. For the assessment of water aggressiveness, parameters such as the saturation index, the Langelier Saturation Index (LSI), and Ryznar Stability Index (RI) are used. However, these indexes do not characterize the corrosive properties of water and cannot be used to assess the water corrosivity [21]. These indexes determine the state of carbonate–calcium balance of the water. They point to the chemical stability of water and its ability to form and/or dissolve protective layers, that is, precipitation/dissolution of $CaCO_3$ sediments. The state of calcium–carbonate balance is determined by the water temperature, total salt content, calcium ions bicarbonate concentration, and water pH [13,14]. Also, bicarbonates with total water hardness (calcium and magnesium) are corrosion inhibiting ions. The Larson–Skold Index shows that an increase in water alkalinity can compensate for the aggressive action of chloride and sulphate ions (VI). Higher alkalinity is associated with water storage and usually higher pH. Sarin and his team [27] showed a positive influence of alkalinity increase on the decrease of iron compounds release to water from the installation. This was confirmed by the authors of this paper, considering the reached results of water parameters after anion exchange. Chloride and sulphate ions (VI) have the greatest influence on corrosion. Their high concentration in the transported water affected its aggressiveness [3,4,28].

The Langelier Saturation Index (LSI) calculation results are presented in Table 2 and Figure 3.

According to LSI values in the Table 3, water is stable and does not have aggressive properties if LSI >0. The reached results proved that most of the water treatment processes used at the studied boiler feed water station are inefficient in water aggressiveness removal. The LSI changed from −0.34 for raw water to −0.12 for pre-aerated water. It was close to the stability level when LSI = 0. However, the next processes allow LSI to go down up to −0.23 for quartz sand filtration and −0.83 after cation and anion exchange. Additional aeration neutralized this negative result. The LSI increased from the lowest level up to 0, which made water stable. Extra deaeration sustained this value and kept water from being aggressive.

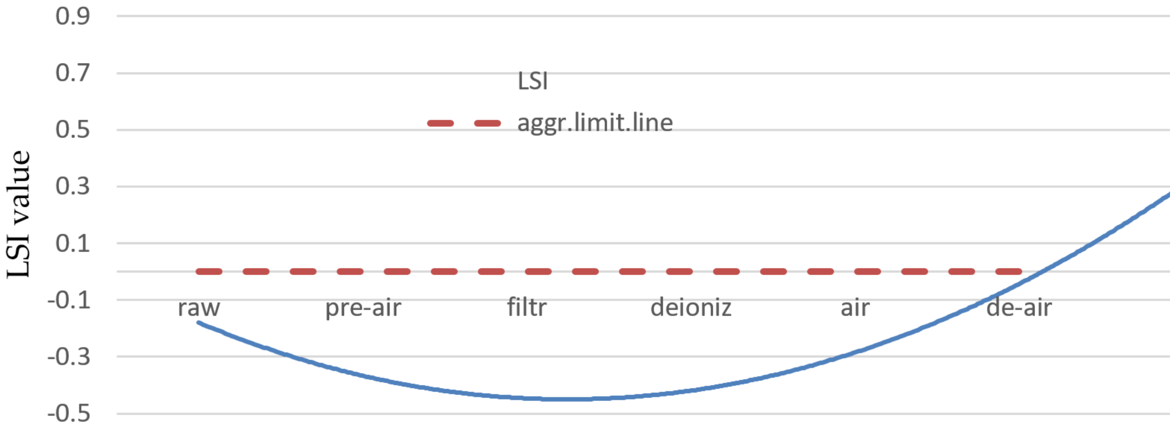

Figure 3. Changes of Langelier Saturation Index (LSI). Source: Own elaboration.

The calculation formula of LSI is the simplest one among other indicators, and considers only water pH [15,29]. For most natural waters, the water pH should not affect the aggressiveness rate. In the pH range of 4.5–9.0, the corrosion rate is almost constant. However, the pH value may determine the type of corrosion. According to Schock and Lytle [15], homogeneous corrosion occurs at pH <6.5, whereas pitting corrosion is observed in the pH range between 6.5 and 8.0. The pH range of the water flowing through the studied treatment station ranged from 7 to 7.5 for the first treatment processes, that is, pre-aeration and sand filtration. Cation exchange reduced its value to 6.58, but anion exchange increased it to over 8.0. Additional aeration and degassing kept the pH value at this level. Slightly alkalic water stopped corrosion, which faced in values of the Langelier Saturation Index [9].

Ryznar Stability Index (RI) calculation formula is based on the same parameters as those of LSI, that is, the pH of water. The RI values in Table 3 confirm that water is stable when RI hesitates between 6 and 7, and it is not aggressive when RI < 5. The reached results of RI are presented in Table 2 and Figure 4. The calculation showed that experimental water in the whole purification system was aggressive. Higher values were noticed for raw water when RI was 8.24. Pre-aeration and sand filtration allowed it to decrease slightly to 7.23 and 7.56. The next processes of ion exchange increased its value to the top point of RI = 9.03. Additional aeration closed it to the level of stability and RI was about 7. The last process, deaeration, allowed RI to decrease and reach the not-corrosive-standard of about 5.0.

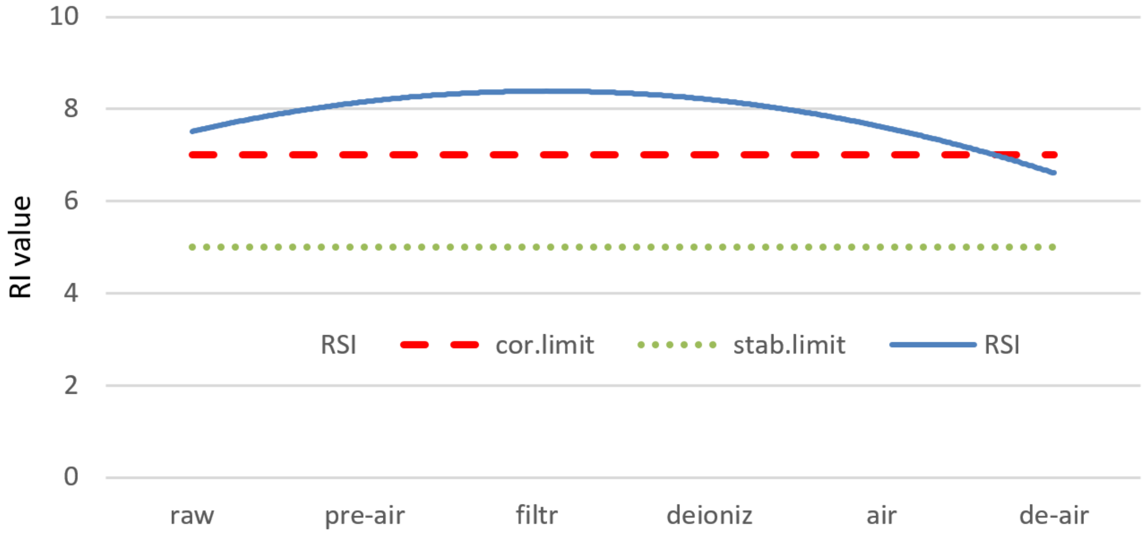

Figure 4. Changes of Ryznar Stability Index (RI). Source: Own elaboration.

As written above, the newly designed processes at the studied water treatment station, additional aeration and degassing, do not fully remove its aggressive properties, as confirmed by Soldatov and others [30]. However, on the basis of the conducted studies, a clear positive effect of pre-aeration and extra aeration was observed. The values of the Langelier Saturation Index and the Ryznar Stability Index were closer to stability than with the advanced purification process—ion exchange. The figures show that the ion exchange with cation exchange columns affected the water aggressiveness by its significant increase. The usage aeration clearly neutralizes this negative character.

Ofman [31] and Awual [11] write that water conductivity below 1000 µS/cm indicates weaker corrosion properties. It is indirectly related to the Langelier Saturation Index and Ryznar Stability Index. Apart from sulphates (VI) and chlorides, these water properties are also influenced by calcium and magnesium ions and bicarbonates forming the alkalinity of water [25]. The decrease in the concentration of these ions in water was observed after weak base exchange columns when a decrease in aggressiveness and corrosivity indices was calculated. On the other hand, the decrease in hardness and calcium ion concentration after cation exchange columns resulted in an additional increase in the LSI and RI values.

An important indicator of water corrosivity and aggressiveness is the change of water colour ΔB. It is calculated with a developed formula that includes many cations and anions. This parameter depends on water temperature, dissolved oxygen, sodium, sulphates (VI), chlorides, water alkalinity, and water retention time in the system. The ΔB analyses are presented in Table 1 and Figure 5. The higher water colour was noticed for primary aeration and reached the value close to 5.0 mg Pt/dm^3. An increase in comparison with raw water when ΔB = 3.1 may be caused by reduced substances oxidation. Sand filtration started its decrease from 2.1 to 0.0 after extra aeration and degassing.

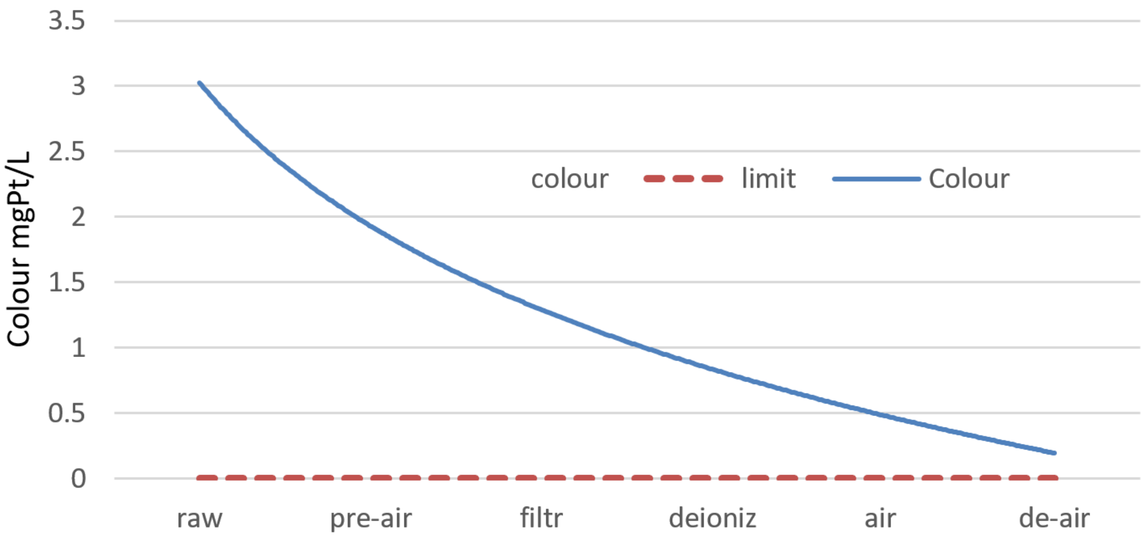

Figure 5. Changes of water colour. Source: Own elaboration.

Included in the ΔB formula, water temperature has a significant influence on the speed of chemical reaction and the intensity of corrosion. Ranjbar [29] noted that with higher temperature, the rate of diffusion of oxygen to the metal surface is higher, while its solubility decreases. Temperature influences many processes and parameters important for the corrosion rate, as well as the composition and properties of formed sediments. The following should be mentioned in particular: salt and oxygen solubility, viscosity, diffusion, reaction enthalpy, oxidation rate, and biological activity. The corrosion rate and water colour change depend on seasonal changes in water temperature [6,32]. It also has a direct effect on the Langelier Saturation Index, the Ryznar Stability Index, and the Larson–Skold Index. It can be compared to the conducted study at the boiler feed water station. The obtained results proved that a sudden increase in the Larson–Skold Index was noticed when the temperature in the extra deaerator was increased. The aggressiveness indexes, LSI and RI, where an increase in temperature caused a decrease in their value, show an opposite relationship.

Loewenthal with others [4] and Cocorilo et al. [33] state that the ΔB formula clearly indicates that the corrosive properties of water increase with the content of sulphate (VI) and chloride ions, and decrease with the water alkalinity. At the studied water treatment station, the concentration of sulphates in water ranged from 176 mg/dm^3 for raw water and pre-aeration to 18 mg/dm^3 for anion exchange and the next processes. Similarly, chloride concentration decreased from 80 mg/dm^3 for raw water, pre-aeration. Filtration and cation exchange to 12 mg/dm^3 for anion exchange, extra aeration, and degassing. Consequently, an increase in water alkalinity may compensate for the undesirable corrosive effect of chloride and sulphate ions (VI). Total alkalinity for examined water increased from about 3 mval/dm^3 to 5.5 mval/dm^3 in the purified water.

4. Summary and Conclusions

The corrosive and aggressive effects of water come into contact with different surfaces and involve complex electrochemical and biochemical processes [4,8,23,34]. Many indicators of water pollution (including pH, salinity, alkalinity, some cations, and anions) can accelerate or delay the destruction of materials wetted by water [12,17,20]. Therefore, the control of aggressiveness and corrosivity indicators in industrial plants by production of technological water should be the basis for the planning and design of water treatment systems [35]. The quality requirements of water supplying industrial production and the technological line of the industrial plant analysed by the authors and described in this manuscript do not impose special conditions, except for the reduction of water colour, turbidity, iron concentration, and hardness. On the other hand, the quality parameters of boiler feed water require a high purification level, including the lack of aggressiveness and corrosivity. Moreover, most of the machine park in the production hall requires warm or hot water. Negative effects of water corrosivity and aggressiveness could silt up the steel water supply system and destruct boiler equipment that is touched or washed using such water. It may cause the whole industrial production system to fail or be destroyed. The research carried out proved that the application of previous simple water treatment processes in industrial water treatment stations as a result of the corrosivity and aggressiveness of water were not sufficient. The old boiler feed water treatment station was not sufficient to reach clean and stable water. The authors proposed modernization, including additional processes to improve boiler water quality, and designed new devices of water treatment. As a result of the new idea, groundwater taken as raw water was treated in individual and complex processes, such as pre-aeration, filtration, ion exchange (cation and anion exchange resigns), extra aeration, and extra degassing. Secondary aeration and degassing did not take extra space at the station and proved to be an efficient and uncomplicated process.

The conducted research allowed the following conclusions to be drawn:

1. Studied boiler feed water has special requirements and must be free of most impurities, corrosivity and aggressiveness. Such a purification level required highly-efficient treatment, such as pre-aeration, filtration, cation exchange, anion exchange, extra aeration, and extra degassing.
2. The estimation of O_2 and CO_2 concentration in water was important in the conducted research. After modernization, the oxygen concentration changed from 0.5 mg/dm^3 in raw water to the maximal level of 3.5 mg/dm^3 after aeration and 2.6 mg/dm^3 after filtration. CO_2 changed gradually from over 90 mg/dm^3 to 6 mg/dm^3 in deionized water. Oxygen and free carbon dioxide concentrations dropped to 0.0 mg/dm^3 after extra aeration and extra degassing.
3. In the conducted studies, the indirect method of water aggressiveness and corrosivity assessment was applied using mathematical calculation of the Langelier Saturation Index (LSI), the Ryznar Stability Index (RI), the Larson–Skold Index (LI), and the Singley Index (SI).
4. In this study, the Larson–Skold Index calculations proved that water treatment processes after modernization did not have any influence on water corrosion. Purified water in every individual purification process was neither corrosive nor aggressive.
5. The Singley Index also describes water corrosivity, but its formula contains more variables than LI. The results showed that water was corrosive from the first treatment up to ion exchange. Extra aeration reduced water corrosion to SI = 0.75 and degassing improved the effect. It made water neither corrosive nor aggressive by SI = 0.67.
6. The results of the Langelier Saturation Index proved that the most water treatment processes used at the studied boiler feed water station are inefficient in water aggressiveness removal. The LSI change from −0.34 for raw water to −0.83 in deionized water. With additional aeration, LSI increased from the lowest level up to 0, which made water stable. Extra deaeration sustained this value and kept the water from being aggressive.
7. The Ryznar Stability Index (RI) calculation formula is based on the same parameters as LSI. Its calculation showed that experimental water in the whole purification system was aggressive, from RI = 8.24 for raw water to additional aeration with RI of about 7. The last process, deaeration, allowed RI to decrease and reach the not-corrosive-standard of about 5.0.
8. An important indicator of water corrosivity and aggressiveness is the change in water colour ΔB. It is calculated with a developed formula that includes many cations and anions. The higher water colour was noticed for primary aeration: about 5.0 mg Pt/dm^3. Sand filtration helped in its decrease from 2.1 to 0.0 mg Pt/dm^3 after extra aeration and degassing.

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References

1. Odum, B.; Odum, H. Concepts and methods of ecological engineering. *Ecol. Eng.* **2003**, *20*, 339–361. [CrossRef]
2. Awual, R.; Hasan, M.; Islam, A.; Rahman, M.M.; Asirib, A.; Khalequed, A.; Sheikhe, C. Introducing an amine functionalized novel conjugate material for toxic nitrite detection and adsorption from wastewater. *J. Clean. Prod.* **2019**, *228*, 778–785. [CrossRef]
3. Awual, R. New type mesoporous conjugate material for selective optical copper(II) ions monitoring & removal from polluted waters. *Chem. Eng. J.* **2017**, *307*, 85–94. [CrossRef]
4. Loewenthal, R.E.; Morrison, I.; Wentzel, M.C. Control of corrosion and aggressiveness in drinking water systems. *Water Sci. Technol.* **2004**, *49*, 9–18. [CrossRef] [PubMed]
5. Nawrocki, J.; Stanisławiak, U.R.; Swietlik, J.; Olejnik, A.; Sroka, M.J. Corrosion in a distribution system: Steady water and its composition. *Water Res.* **2010**, *44*, 1863–1872. [CrossRef]
6. Ahmad, J.; Purbolaksono, J.; Beng, L.C. Thermal fatigue and corrosion fatigue in heat recovery area wall side tubes. *Eng. Fail. Anal.* **2010**, *17*, 224–343. [CrossRef]
7. Awual, R. Ring size dependent crown ether based mesoporous adsorbent for high cesium adsorption from wastewater. *Chem. Eng. J.* **2016**, *303*, 539–546. [CrossRef]
8. Awual, R.; Alharthi, N.H.; Hasan, M.; Karim, M.R.; Islam, A.; Znad, H.; Hossain, M.A.; Halim, E.; Rahman, M.M.; Khaleque, A. Inorganic-organic based novel nano-conjugate material for effective cobalt(II) ions capturing from wastewater. *Chem. Eng. J.* **2017**, *324*, 130–139. [CrossRef]
9. Głuszko, M. *Atmospheric corrosion of steel structures. Protection methods according to EU requirements. Conference Proceedings New Chemical Products for Mine Industry*; Scientific Conference New Chemical Products for Mine Industry: Ustron, Poland, 2007.
10. Skoczko, I.; Szatylowicz, E. The analysis of physico-chemical properties of two unknown filter materials. *J. Ecol. Eng.* **2016**, *17*, 148–154. [CrossRef]
11. Awual, R. Novel nanocomposite materials for efficient and selective mercury ions capturing from wastewater. *Chem. Eng. J.* **2017**, *307*, 356–465. [CrossRef]
12. Imran, S.A.; Dietz, J.D.; Mutoti, G.; Taylor, J.S.; Randall, A.A. Modified Larsons Ratio Incorporating Temperature, Water Age, and Electroneutrality Effects on Red Water Release. *J. Environ. Eng.* **2005**, *131*, 1514–1520. [CrossRef]
13. Skoczko, I.; Piekutin, J.; Ignatowicz, K. Efficiency of manganese removal from water in selected filter beds. *Desalin. Water Treat.* **2016**, *57*, 1611–1619. [CrossRef]
14. Awual, R. A novel facial composite adsorbent for enhanced copper(II) detection and removal from wastewater. *Chem. Eng. J.* **2015**, *266*, 368–375. [CrossRef]
15. Schock, M.R.; Lytle, D.A. Internal Corrosion and Deposition Control. In *Water Quality and Treatment: A Handbook of Community Water Supplies*, 6th ed.; AWWA, Edzwald, J.K., Eds.; McGraw-Hill, Inc.: New York, NY, USA, 2010; Chapter 20; pp. 20.1–20.68.
16. Skoczko, I.; Piekutin, J.; Roszczenko, A. Iron and manganese removal from groundwater by filtration on selected masses. *Rocznik Ochrona Srodowiska* **2015**, *17*, 1587–1608.
17. Awual, R. Novel conjugated hybrid material for efficient lead(II) capturing from contaminated wastewater. *Mater. Sci. Eng. C* **2019**, *101*, 686–695. [CrossRef]
18. Konieczny, K.; Rajca, M.; Bodzek, M.; Kwiecińska, M. Water treatment using hybrid method of coagulation and low pressure membrane filtration. *Environ. Prot. Eng.* **2009**, *35*, 5–23.
19. Siwiec, T.; Michel, M.M.; Reczek, L. Effect of aeration on the change of corrosive aggressiveness of underground water in relation to concrete and steel. *Acta Sci. Pol. Archit.* **2016**, *15*, 95–105.
20. Skoczko, I. Experience with the implementation and design of boiler water treatment station. *Annu. Set Environ. Prot.* **2011**, *13*, 657–671.
21. Frayne, C. *The Metro Handbook of Water Treatment for HVAC Systems*; The Metro Group, Servicing Water Systems with Environmental Care: New York, NY, USA, 2011.
22. American Water Works Association. *AWWA J100-10 (R13) Risk and Resilience Management of Water and Wastewater Systems*; AWWA Catalog No: 40100; AWWA: Denver, CO, USA, 2010.
23. Anielak, A.M.; Arendacz, M. Iron and manganese removal efficiency using zeolites. *Annu. Set Environ. Prot.* **2007**, *9*, 1034–1043.

24. Sobczyk, M. Pure oxygen usage for groundwater treatment. *Environ. Prot.* **2001**, *4*, 466–472.
25. Shannon, K. *Eco-engineering for water: From soft to hard and back. Resilience Ecology and Urban Design*; Springer: Dordrecht, The Netherlands, 2012; Volume 3, pp. 163–182.
26. Sozański, M.M.; Dymaczewski, Z.; Jeż-Walkowiak, J. Development directions and new technologies of water purification. In *Conference Procedeengs of IV Scientific Conference, Development Directions of Water Distributions Systems*; Seidel-Przywecka, M., Ed.; Seidel-Przywecki Publisher: Warszawa, Poland, 2007; pp. 68–124.
27. Lee, S.H.J.; Themelis, N.J.; Castaldi, M.J. High-Temperature Corrosion in Waste-to-Energy Boilers. *J. Therm. Spray Technol.* **2006**, *16*, 104–110. [CrossRef]
28. Sarin, P. Corrosion Control Optimization Using Lead Pipe Loops. In Proceedings of the AWWA Water Quality Technology Conference, Miami Beach, FL, USA, 13–17 June 2004; Volume 130, pp. 364–373.
29. Näykki, T.; Jalukse, L.; Helm, I.; Leito, I. Dissolved Oxygen Concentration Interlaboratory Comparison: What Can We Learn? *Water* **2013**, *5*, 420–442. [CrossRef]
30. Ranjbar, K. Failure analysis of boiler cold and hot reheater tubes. *Eng. Fail. Anal.* **2007**, *14*, 620–625. [CrossRef]
31. Soldatov, V.S.; Polus, Z.; Pawłowska, M.; Mączka, I.; Shunkevich, A.; Kasandrovich, E.; Polikarpova, A. A Strong Acid Nonwoven Filtering Medium for Deep Air Purification. *Fibres Text. East. Eur.* **2004**, *4*, 56–61.
32. Ofman, P.; Skoczko, I. PAH removal effectiveness comparison from hydraulic fracturing model wastewater in SBR reactors with granular and flocked activated sludge. *Desalin. Water Treat.* **2018**, *134*, 41–51. [CrossRef]
33. Čokorilo Ilić, M.; Mladenović, A.; Ćuk, M.; Jemcov, I. The Importance of Detailed Groundwater Monitoring for Underground Structure in Karst (Case Study: HPP Pirot, Southeastern Serbia). *Water* **2019**, *11*, 603. [CrossRef]
34. Awual, R. Innovative composite material for efficient and highly selective Pb(II) ion capturing from wastewater. *J. Mol. Liq.* **2019**, *284*, 502–510. [CrossRef]
35. Skoczko, I.; Szatylowicz, E. Studies on the efficiency of grundwater treatment process with adsorption on activated alumina. *J. Ecol. Eng.* **2017**, *18*, 211–218. [CrossRef]