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Innovative process solutions in the field of water decarbonisation as an element of integrated management in environmental protection – A case study

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Abstract
Most waters in Poland are classified as medium or very hard. In case of industrial waters, their chemical composition and physical parameters play an essential role. The water ought to be soft and should not contain dissolved salts and gases. This water, which has not undergone a softening process, may cause damage to heating devices and boiler scale within a few years. Therefore, water softening is mainly used for heating and energy purposes. However, an important issue is technological processes in which water is used both as a product additive or as an agent in exchange of heat and mass [Reference Document…2001; Nawrocki, Biłozor 2000; Kiedryńska, Papciak, Granops 2006; Biłozor 2012].
The aim of the work was to determine the effect of changes in the proportion of decarbonised water in the process water stream on its parameters (oxidability, general hardness) and parameters of cooling water in water cycles. The possibility of limiting the consumption of raw water to the processes carried out on the premises of the plant and the possibilities of improving energy efficiency in the area of water and wastewater management with a variable stream of decarbonised water in the technological water was checked. It was found that the increase in the share of decarbonised water in the technological and cooling water stream is important in the implementation of process solutions in this area and has a positive effect on reducing costs related to the operational functioning of the water and wastewater management area.

1. INTRODUCTION

Water softening is a process of removing the so-called overall hardness whereas water decarbonisation is a process of its softening by removing the so-called carbonate hardness. The compounds responsible for water hardness are primarily calcium and magnesium ions, as well as iron, aluminium, manganese, zinc and hydrogen ones. The content of calcium and magnesium ions in the water is definitely higher than the other elements mentioned above, therefore, the hardness of water is mainly considered due to the presence of Ca and Mg. The reduction of carbonate hardness can be obtained by decarbonization: thermal, chemical (with either lime or acid) and by the ion exchange process [Buczkowski 2002; Podstawy…2008; Kowal, Świderska-Bróż 2008].
In everyday communication, the alternating use of the terms softening and decarbonization may be observed, which is a mistake. In general, the methods of reducing water hardness depending on the type of processes used can be divided into thermal, precipitation, ion exchange and membrane ones. The separate division of hard water reduction methods, which is available in the literature, embraces distillation, thermal methods, chemical methods and cation exchangers [(Nawrocki J., Biłozor S. 2000; Kowal, Świderska-Bróż 2008; Weber 2013; Bodzek, Konieczny 2011].
Traditional systems of water hardness reduction are based on precipitation methods, which involve removing calcium and magnesium ions from water by precipitating them in insoluble compounds. The following precipitation methods are used in water treatment processes: decarbonisation, decarbonisation with the use of lime, decarbonisation of water with the use of acid, softening with sodium hydroxide, softening with lime and soda, soda only, and softening with phosphates and also ion exchange [Nawrocki J., Biłozor S. 2000; Buczkowski 2002; Podstawy…2008; Kowal, Świderska-Bróż 2008; Weber 2013; Bodzek, Konieczny 2011].

The chemical methods involve the dissolution of calcium and magnesium bicarbonates dissolved in water, for sparingly soluble neutral calcium carbonate, magnesium hydroxide and carbon dioxide. This decay occurs at an elevated temperature. The most popular method for removing carbonate hardness is lime decarbonisation. It involves the reaction of calcium and magnesium bicarbonates with calcium hydroxide, resulting in the precipitation of neutral calcium carbonates from water and magnesium hydroxides. Lime decarbonization [Nawrocki J., Biłozor S. 2000; Buczkowski 2002; Podstawy…2008; Kowal, Świderska-Bróż 2008; Weber 2013; Bodzek, Konieczny 2011]:

$$Ca(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 + 2\ H_2O$$
$$Mg(HCO_3)_2 + Ca(OH)_2 \rightarrow 2\ CaCO_3 + Mg(OH)_2 + 2\ H_2O$$

Magnesium bicarbonate, which initially together with $Ca(OH)_2$ creates basic carbonate, reacts with hydroxide excess to form less soluble magnesium hydroxide. Should the water contain other magnesium compounds, for example, $MgCl_2$ or $MgSO_4$, which create the magnesium hardness, then it is converted to non-carbonate calcium hardness, and the equivalent amount of $Mg\ (OH)_2$ is precipitated:

$$MgSO_4 + Ca(OH)_2 \rightarrow Mg(OH)_2 + CaSO_4$$

Other components of water that react with lime are carbon dioxide and iron (II) hydroxide:

$$4\ Fe(HCO_3)_2 + 8\ Ca(OH)_2 + O_2 \rightarrow 4\ Fe(OH)_3 + 8CaCO_3 + 6\ H_2O$$
$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

(decarbonizer - lime water [clear solution Ca $(OH)_2$]
or lime milk [suspension of Ca $(OH)_2$ in water])

In technological systems, lime is fed in the form of a saturated lime water solution. Decarbonisation of water with acid, however, involves the removal of calcium and magnesium bicarbonates by dosing hydrochloric or sulfuric acid into the water. The calcium and magnesium chlorides and sulphates produced, as more soluble, no longer pose such a great risk of deposition in the form of stony deposits. However, the use of the method is limited because the overall water hardness does not decrease. There is only a shift in hardness from carbonate to non-carbonate [Nawrocki J., Biłozor S. 2000; Buczkowski 2002; Podstawy…2008; Kowal, Świderska-Bróż 2008; Weber 2013; Bodzek, Konieczny 2011].

In cases where the water has a low carbonate hardness at a high non-carbonate hardness, softening can be done with carbonate and sodium hydroxide solution.

As a result of the process, calcium carbonate and magnesium hydroxide precipitate to the limits of their solubility and the appearance of sodium salts in water. The range of application of the method is currently not very wide, because it has been supplanted by more modern and effective ion exchangers. Water softening with calcium and soda, on the other hand, involves simultaneous dosing into the water of a sodium carbonate solution and in a lime water reservoir. It is a combination of cheap decarbonisation of water with lime and precipitation of non-carbonate hardness with sodium carbonate. Softening with sodium phosphate is another method. This method allows obtaining relatively low residual hardness. Neutral trisodium phosphate and acid sodium phosphates are used for the reaction. They effectively remove both carbonate and non-carbonate hardness equally. Further methods of softening the water are ion exchange methods by passing water containing calcium and magnesium ions through the ion exchanger layer – ion-exchange resin. Ion exchangers are substances of natural origin or artificially produced, insoluble in water, having the ability to exchange ions from the solution for ions associated with the mass of the exchanger. Such substances having the character of acids or salts of acids, exchange cations and are called cation exchangers. Alkaline substances or their salts exchange anions with the solution and are called anion exchangers. During ion exchange, the ions and molecules present in the water having a certain charge are bound by the ion exchanger, which simultaneously releases harmless ions into the solution [Nawrocki J., Biłozor S. 2000; Buczkowski 2002; Podstawy…2008; Kowal, Świderska-Bróż 2008; Weber 2013; Bodzek, Konieczny 2011].

Solutions for the use of decarbonised water to fill losses in cooling systems are used in installations of small and medium capacity, but primarily in the so-called clean systems that do not require continuous disinfection (minimal risk of contact of cooling water with process media). In facilities with large system capacity, this issue depends on many factors, including possibilities of filtration systems, sludge management from decarbonisation processes, season of the year and economic. The aim of the experiment was to investigate the possibilities of improving the parameters of make-up water and reducing the consumption of raw water as well as the impact of innovative solutions in the field of water and wastewater management on integrated management in this component of the environment.

The process of decarbonisation with lime takes place at different speeds, depending on the conditions. Cold sets slowly (3–6 hours), and near 100°C, the time is shortened to 10 minutes. PKN ORLEN S.A. units need a minimum of 10–12ºC. This process is influenced by: water hardness, content of organic compounds in it, method of mixing water with the reagent and the presence of contact mass. The optimum temperature for calcium carbonate crystallization is 20–30ºC. Lime is consumed to remove carbonate hardness, replace magnesium hardness with calcium hardness and bind free carbon dioxide, hence, the chemical composition of raw water should be determined in advance.

Table 1. Production capacity of a water production unit [own study]

No.	Product	Production [m³/h]	Production [m³/day]	Production [m³/year]
1.	Decarbonised water	2,500	60,000	21,900,000
2.	Process water	2,500	60,000	21,900,000
3.	Utility and fire-fighting water	1,200	28,800	10,512,000

2. DESCRIPTION OF THE RESEARCH FACILITY

Water and sewage management at the Production Plant of Polski Koncern Naftowy ORLEN S.A. consists of two units, which include the Water Production Department (WPD) and the Central Sewage Treatment Plant (CSTP) (Fig. 1).
CSTP has existed since 1965, a water and sewage management system was created in parallel with the development of the Production Plant. When characterizing water and wastewater management, it can be divided into three main elements:

Water production:
– water intake (from the Vistula river) water intake 23,000,000 m^3/year, 5x1 MW pumps, three collectors ~ 3.5 km each;
– production plant and decarbonized water network;
– production unit and make-up water network for water blocks;
– unit of production and utility water and fire protection network.

Water blocks:
– 8 water blocks;
– about 170 refrigeration cells and fans;
– about 100 pcs. of high power pump aggregates (including 48 x 800 KW, and the remaining 250 KW);
– circulation water production approx. 850,000,000 m^3/year.

Sewage treatment plant:
– area: 20 ha;
– capacity: 58,800 m^3/day;
– two industrial sewage systems and two rainfall and drainage systems;
– independent physicomechanical treatment of all wastewater streams;
– a common biological treatment plant for all wastewater;
– recycling of part of treated wastewater for the production of utility and fire-fighting water.

Water Production Department with the use of physicochemical processes prepares raw water pumped from the Vistula River and recycled sewage so as to obtain the right types of industrial waters, that is, raw water for the needs of the CCGT (Combined Cycle Gas Turbine) CHP plant, process water supplementing losses in cooling circuits, decarbonised water intended mainly for energy purposes, utility and fire water presented in Table 1. Fire-fighting water for the research facility can also be produced from retention water. Utility water is used for economic purposes, among others for tank washing, cooling of pumps, compressors, tanks, washing of halls. Fire-fighting water supplies the fire network on site and, in addition to fire actions, is used for spraying tanks, pressure testing of pipelines and tanks during repairs and modernization of units and so on.
Water treatment for cooling and energy purposes includes physical, physicochemical and chemical processes (Fig. 1.), which include:
– **Water clarification and filtering**. The clarification process involves the initial purification of raw water from suspended bodies and suspensions by settling or settling supported by a coagulation process. Water filtration is the correct removal of water from suspensions that have not been removed in the pre-treatment process.
– **Water chlorination**. The process aims to neutralize microorganisms found in natural waters and oxidize iron and manganese compounds. The currently used water disinfectant is an aqueous ClO_2 solution. The biocidal/bacteriological/chlorine action is the oxidative effect of this element on enzymes involved in the metabolism of microorganisms. The aqueous ClO_2 solution generates the Nalco MSA18DS generator as a result of the reaction of sodium chlorate with hydrogen peroxide and sulfuric acid. The advantages of this method are high reaction speed and no harmful by-products, for example, chlorine.
– **Water coagulation**. Coagulants added to the purified water are dissociated and then hydrolysed. The reaction produces $Fe(OH)_3$ and sulfuric acid. Coagulation facilitators are polyelectrolytes, high molecular weight polymers with ionogenic groups capable of dissociating, binding colloidal particles with each other through chemical bonds or agglomerations of colloidal particles.
– **Water decarbonisation**. The process of decarbonising water involves removing carbonate hardness, that is, converting Ca^{+2} and Mg^{+2} ions into sparingly soluble, precipitating compounds that are separated in the filtration process.

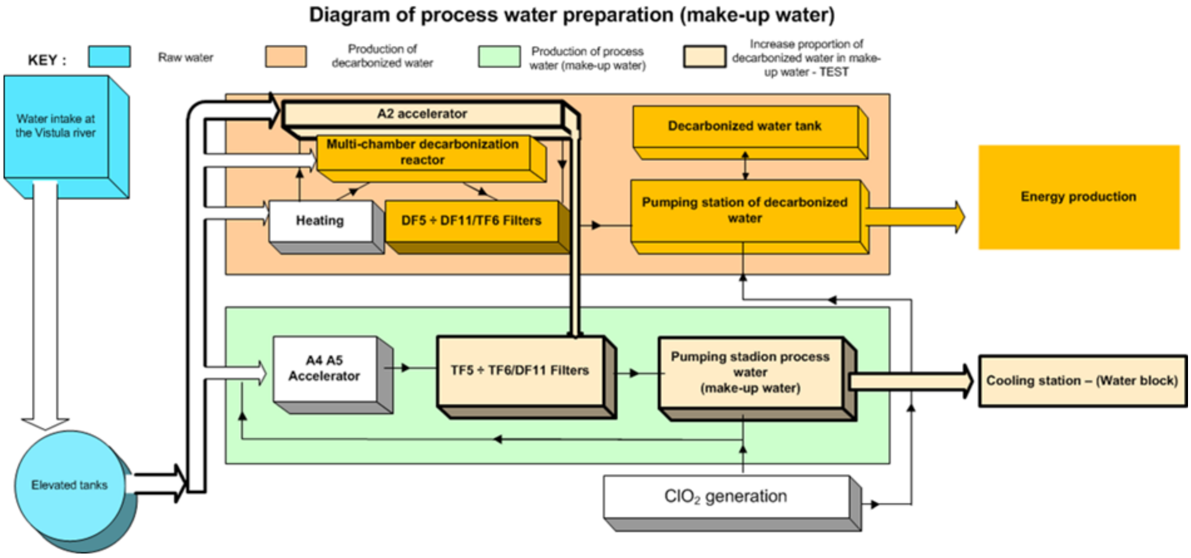

Figure 1. Diagram of the process water preparation unit for the needs of the test [own study]

3. DESCRIPTION OF THE RESEARCH TEST CARRIED OUT

The main objective of the test was to investigate the possibility of improving the parameters of make-up water and reducing the raw water uptake from the Vistula River, which translates into the optimization of operating costs of the water and sewage management area.

The purpose of water decarbonisation at PKN ORLEN S.A. Production Plant is, among others, improving the quality of cooling water. Water supplementing the cooling circuits (process water) has been obtained from pre-purified raw (Vistula) water so far, which, after the coagulation and filtration process has been directed to supplement the cooling circuits. Currently, make-up water is a mixture of coagulated and filtered raw water and decarbonised water, and depending on the needs and quality of the Vistula water, it is a ratio of 1:1, 1:3 and 1:5.

In the era of improving efficiency at the Production Plant in Płock, an attempt was made to use economic assets in the form of out-of-use accelerators, which replaced the multi-chamber decarbonisation reactor. Today, the Production Plant is moving towards improving the operation of the unit, product quality, reducing energy consumption and emissivity, and a greater share of water directed to the Production Plant (for heat exchange processes) is pre-purified and technologically prepared water and decarbonised as well.

The scope of the research:

– launch of the A2 accelerator for the production of decarbonised water,
– change in the share of decarbonised water in the process water stream (from 50% to 30%) 1000–500 m^3/h,
– observation of process and cooling water parameters (oxidability, general hardness, quantity of bacteria) and preparation costs,
– analysis of the work of production units in terms of heat exchange (before and during the test),
– analysis of the work of the existing raw water coagulation unit and its impact on process water parameters.

4. DISCUSSION OF THE RESULTS

While conducting the test, that is, in July and August 2019, the significant influence on the oxygen consumption parameter of make-up water was observed after adding the decarbonised water to the water supplementing the cooling circuits (Fig. 2). The lowest values of this indicator were noticed with a 50% share of decarbonised water in the make-up water estimated at 800-1000 m^3/h. When the share of decarbonised water in the make-up water decreased from 50% to 30%, an increase in oxygen consumption parameter was observed on average by 1.5 mgO_2/dm^3.

An improvement of the general hardness of the make-up water was noticed (Fig. 4). The lowest value of this parameter was observed for the share of 50% (800–1000 m^3/h) of decarbonised water. This led to a significant reduction of the bleeds (desalination) as a result of the improvement of cooling water parameters and the possibility of maintaining a higher concentration of cooling water without the need to operate the cooling tower on the so-called 'overflow', that is, with continuous water bleed (Fig. 3).

Adding the decarbonised water to the make-up water influenced the uptake of make-up water. In the specified period of analyses, the consumption of make-up water was lower by about 3,672 m^3/day, that is, 113,832 m^3/month, compared to the same period in 2018 (Fig. 5 and 6). It contributed to reduced number of actuations of the

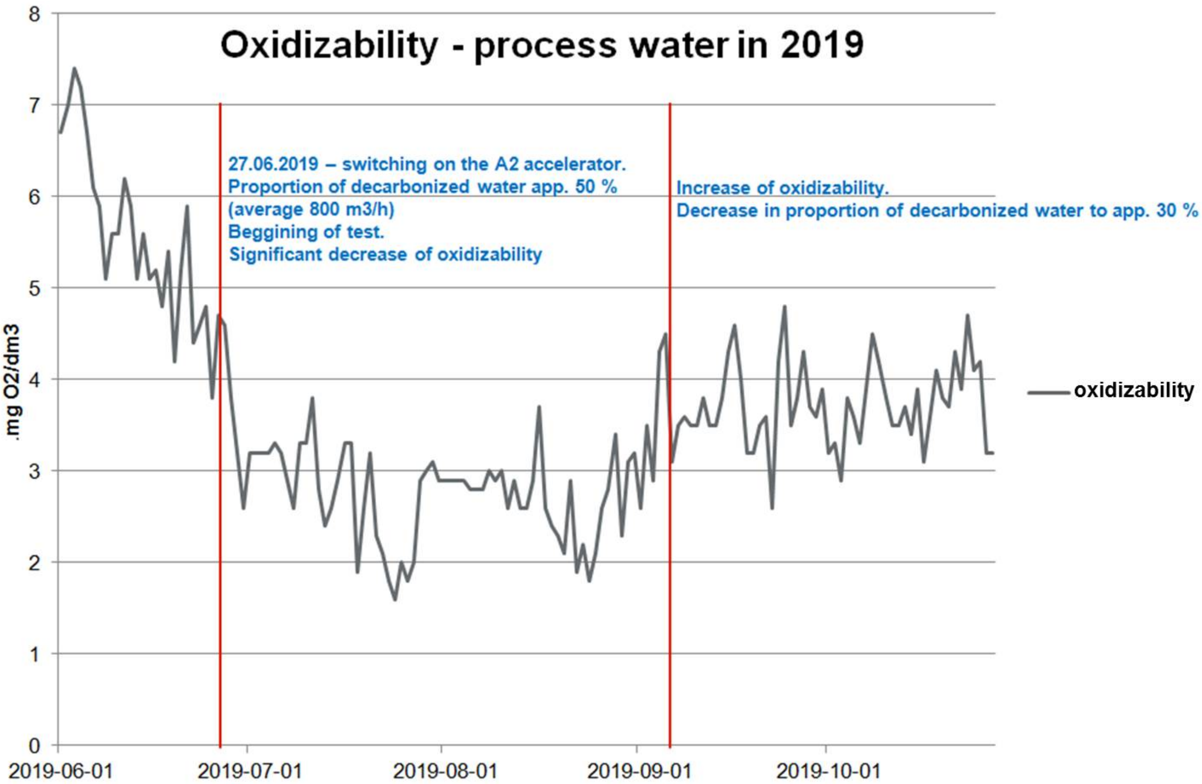

Figure 2. Impact of a larger share of decarbonised water on oxidation in make-up water [own study]

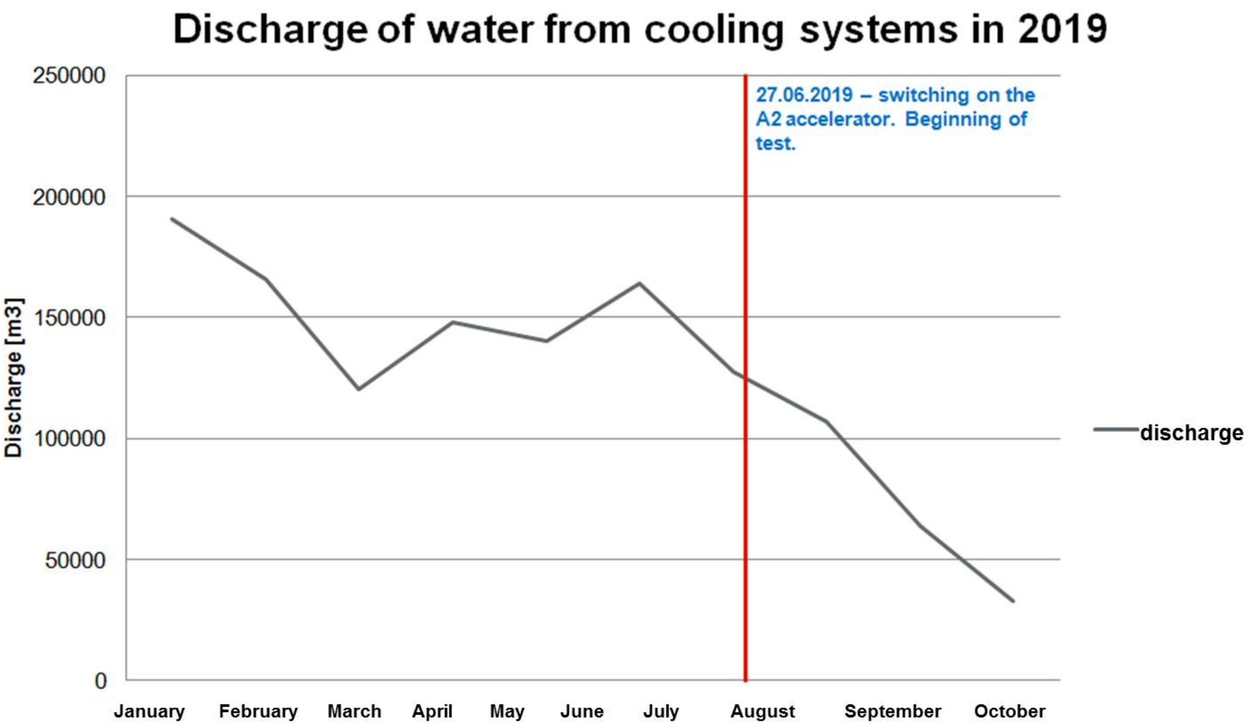

Figure 3. Clear reduction of the bleeding (desalination) as a result of improved cooling water parameters [own study]

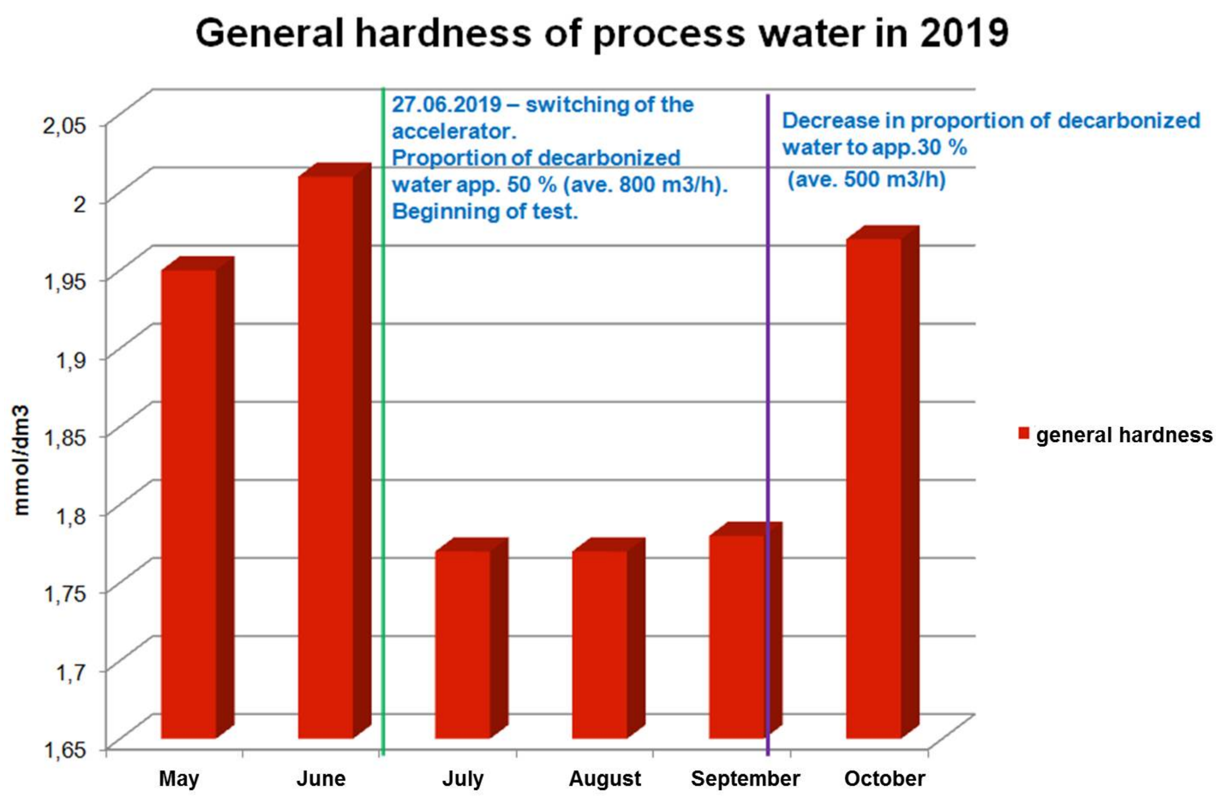

Figure 4. Impact of a larger share of decarbonised water on total hardness in make-up water [own study]

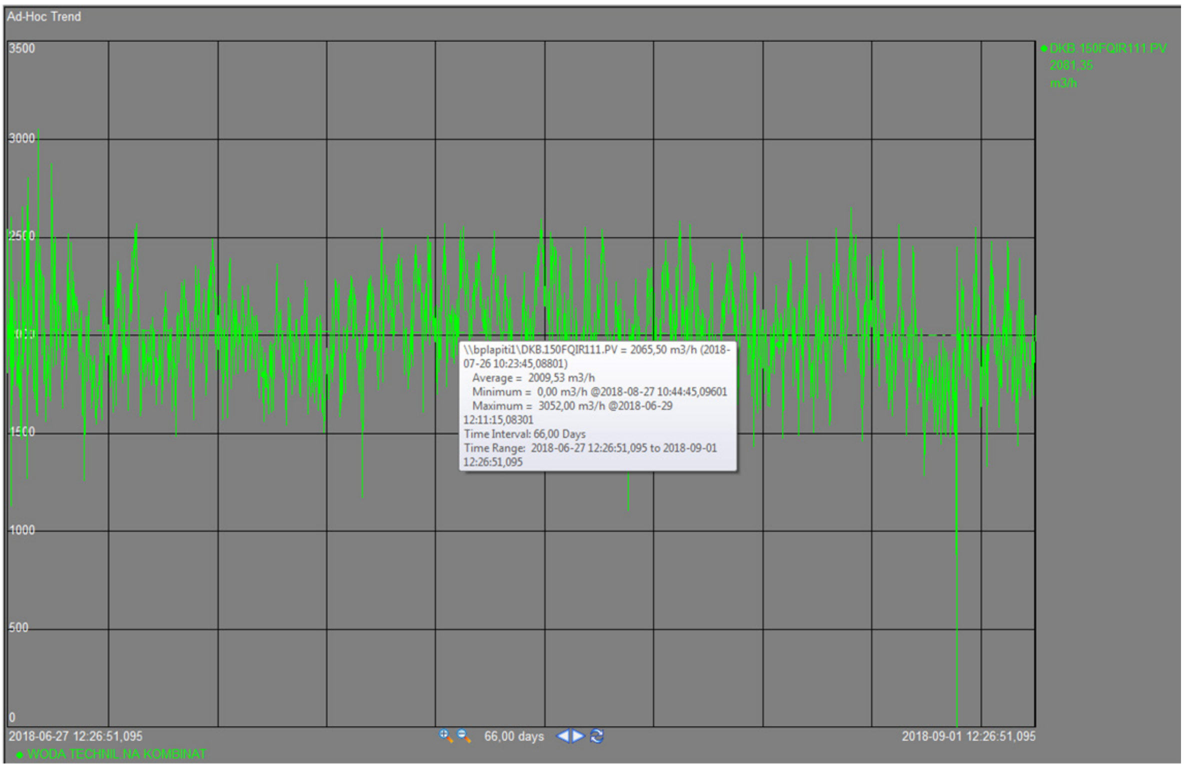

Figure 5. Make-up water intake in a selected period (27.06.2018–01.09.2018) of 2018 [own study]

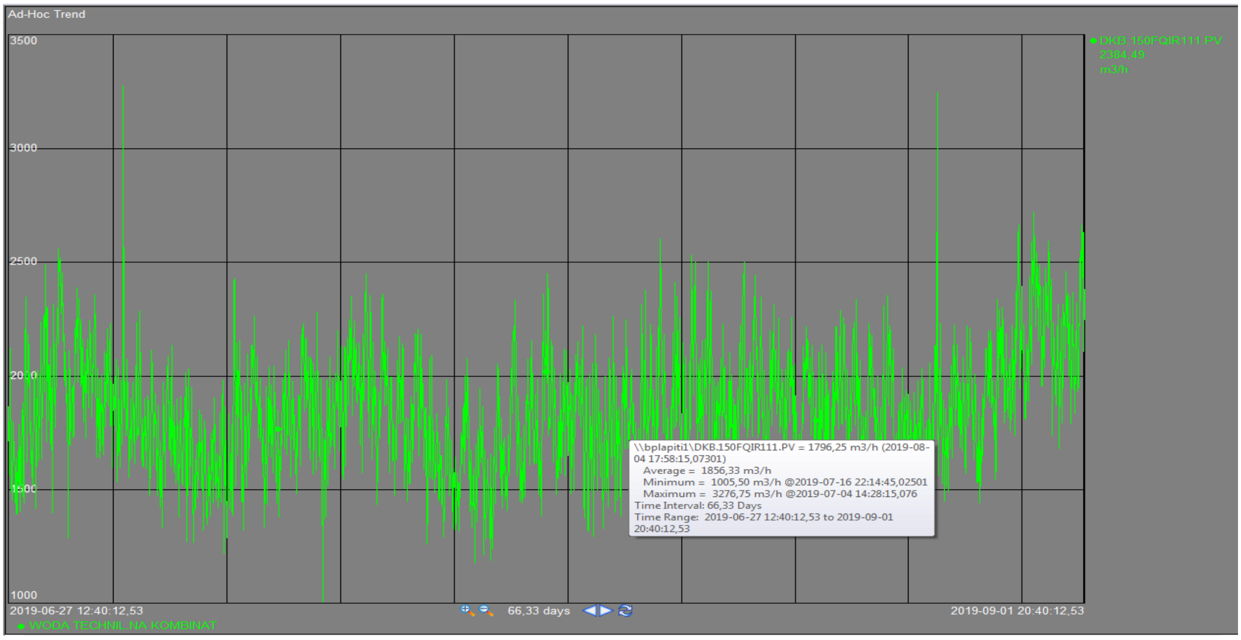

Figure 6. Make-up water intake in the selected period (27.06.2019–01.09.2019) of 2019 during the test [own study]

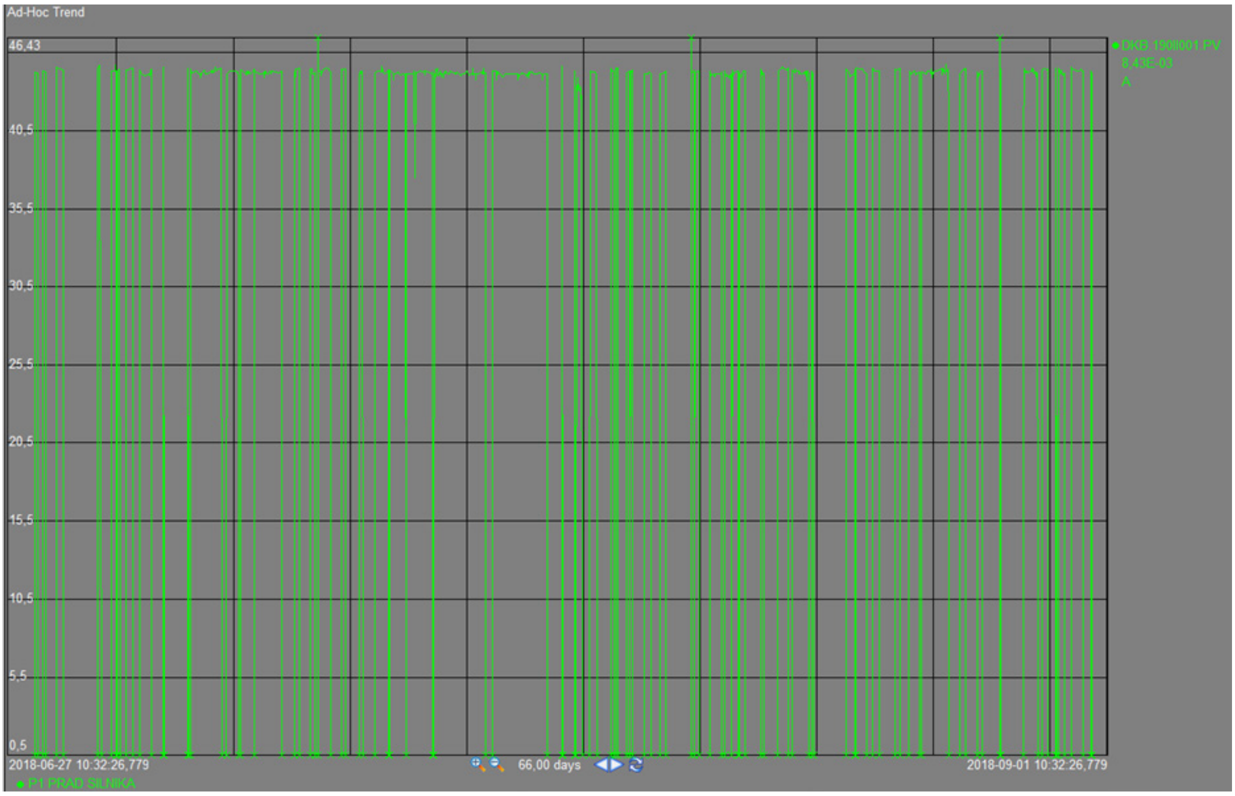

Figure 7. Illustration of the number of starts of the 190P1 (booster) pump - water intake on the Vistula River 27.06.2018–01.09.2018. 500 kW pump power.[own study]

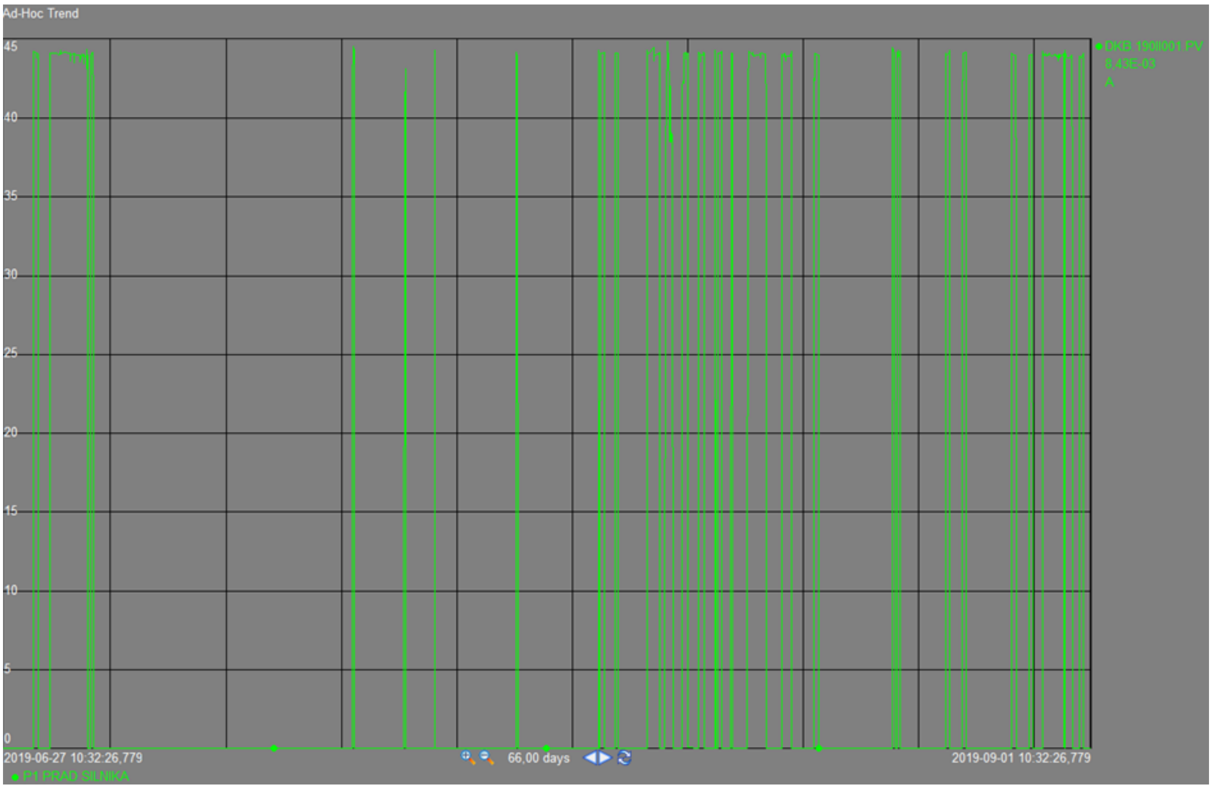

Figure 8. Illustration of the number of starts of the 190P1 (booster) pump - water intake on the Vistula River 27.06.2019–01.09.2019. 500 kW pump power [own study]

(supplementary) pump (Fig. 7 and 8), and thus, also to energy savings.
Fig. 7. Illustration of the number of starts of the 190P1 (booster) pump - water intake on the Vistula River 27.06.2018–01.09.2018. 500 kW pump power.[own study]
Fig. 8. Illustration of the number of starts of the 190P1 (booster) pump - water intake on the Vistula River 27.06.2019–01.09.2019. 500 kW pump power [own study]
The effect of adding the decarbonised water to the make-up water had a positive effect on the amount of total bacteria (microbiological contamination) in the cooling water (Fig. 9 and 10).

5. SUMMARY

Adding decarbonised water to the process, make-up water supplementing the cooling circuits leads primarily to:

1. Improvement of make-up water parameters:
   - decarbonised water, that is, pre-softened by reducing carbonate hardness (removal of calcium and magnesium ions as well as organic matter) is definitely more resistant to deposit loss in the heat exchange process;
   - has a smaller amount of suspension, that is, organic compounds and other substances (iron, magnesium found in raw water, and CO_2, which translates into the carbon footprint of products and organization;
   - it is devoid of acidity, which means more transparent water, which translates into a higher potential for identifying process breakthroughs;
   - biologically protects systems (pipelines, cold storage basins, pumps, heat exchange apparatuses) through less microbiological potential, which translates into less disinfectant consumption (ClO_2 disinfection dose has been reduced by 40%) and reduction of circulation water preparation costs;
   - has greater potential in the scope of concentration of refrigeration systems, which translates into better operation of refrigeration blocks and smaller wastewater discharges through desalination (smaller losses and losses);
   - reduction: water oxidation – less consumption of chlorine dioxide disinfectant.
2. Reduction in the frequency of rinsing the filter beds, which translates into lower water consumption, that is, management in the direction of saving water flow, estimated daily at 3000 m^3.
3. Technical and procedural aspects are:
   - improving the quality of cooling water circulating between the heat exchange apparatus and fan coolers, which translates into an improvement in the availability of heat exchange apparatus and, consequently, the reliable and safe operation of

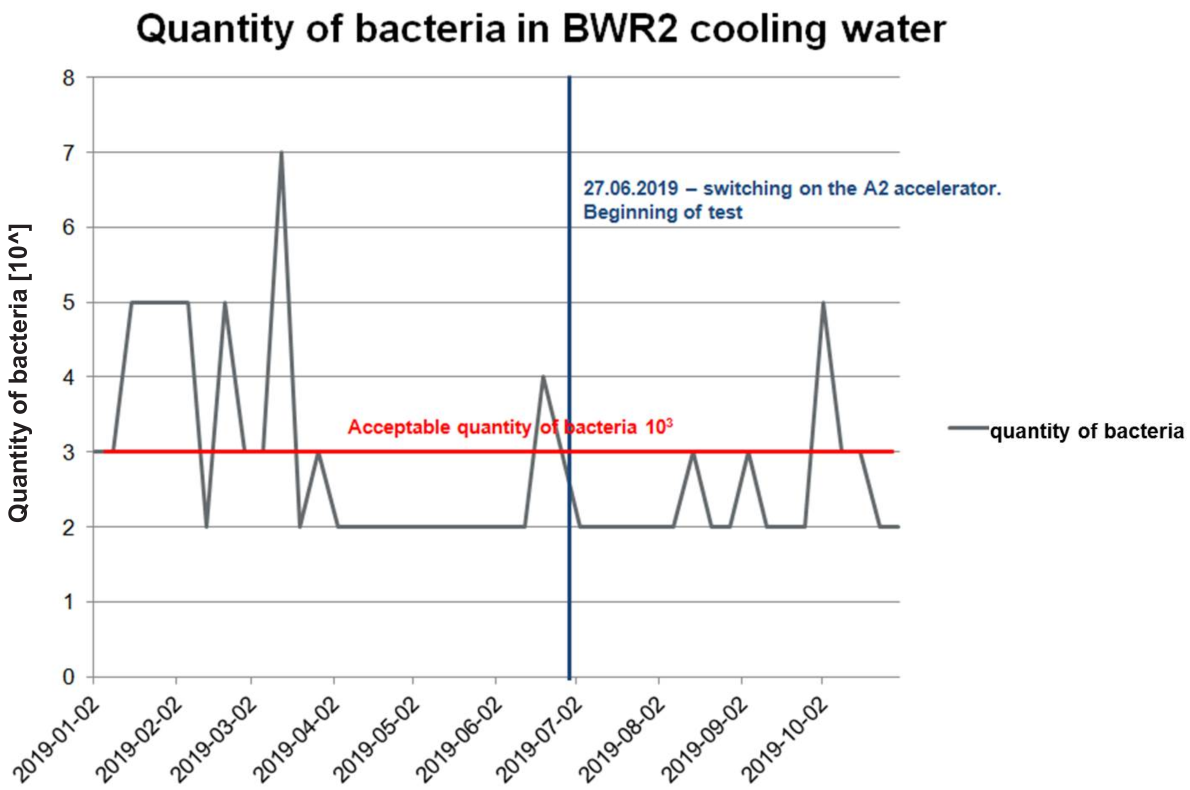

Figure 9. Microbiological contamination of circulating water on the example of a selected refrigeration system [own study]

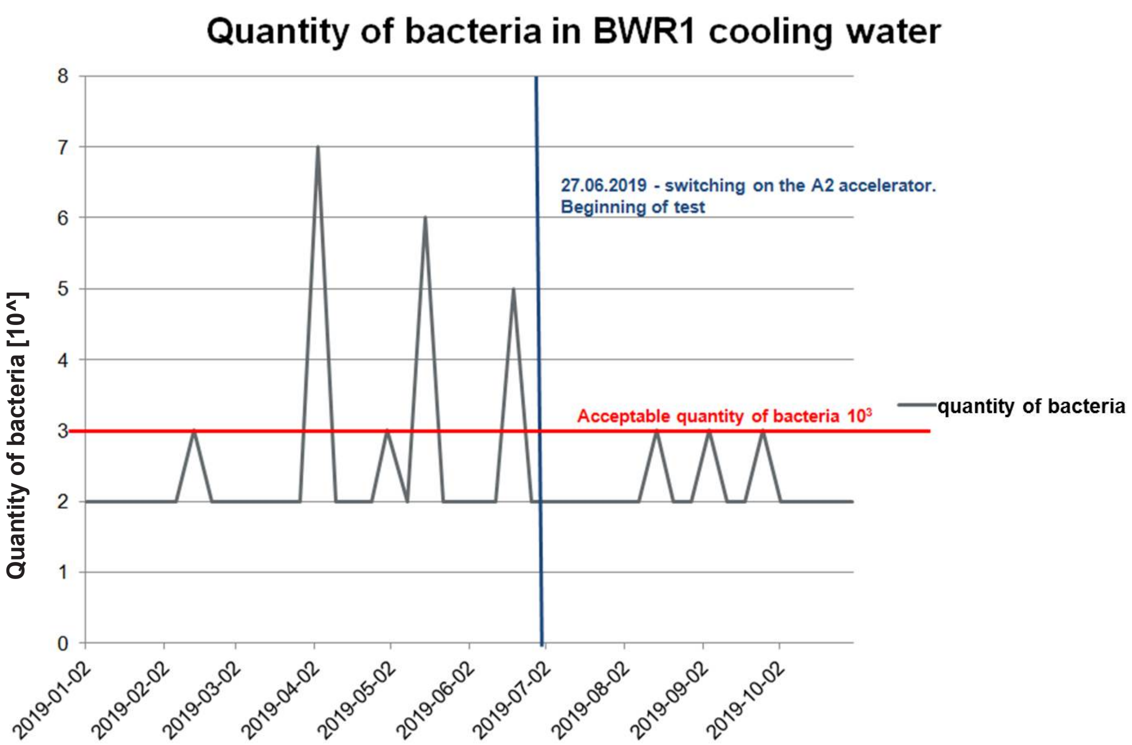

Figure 10. Microbiological contamination of circulating water on the example of a selected refrigeration system. Visible improvement of the situation after adding more decarbonised water [own study]

production units, which, due to better quality of cooling water, will not be subjected to frequent purifications and refurbishment;

- better physicochemical water condition also protects heat exchange apparatus against corrosive processes and the negative impact of microbiology;
- cooling water of better quality is also needed less for the so-called desalination of refrigeration systems. Desalination, that is, discharge of water into the sewage system (water with significant salinity) is reduced. This has a direct impact on the volume of make-up water as well as the amount discharged into the sewage system and charged to the sewage treatment plant.

4. Lower raw water intake from the Vistula river.

6. CONCLUSIONS

The following was observed during the test:

1. Visible improvement in the quality of process (make-up) water reflected in laboratory analysis, which translated into an improvement in the quality of cooling water (circulating in cooling circuits).
2. Reduction of discounts from water blocks due to the possibility (and also the necessity) of greater concentration of water (the effect of increasing the amount of decarbonised water with better physical and chemical parameters) A significant decrease in the amount of water needed to supplement losses.
3. Definitely fewer operational problems (negligible compared to the same period in previous years) on the side of heat exchange apparatuses in production units confirmed by the observations of the technological services of the Refinery, Petrochemical and Energy Plant.
4. A significant and promising decrease in costs associated with the disinfection of refrigeration systems. This was due to factors such as: limitation of discharges from water blocks due to the possibility of greater water concentration, limitation of consumption of ClO2 disinfectant, limitation of raw water intake from the Vistula, lower inflow of sewage (limitation of discharges) to the plant treatment plant.
5. Limitation of raw water intake from the Vistula. Smaller sewage inflow (reduction of discounts) to the sewage treatment plant.

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