



Zero-waste initiatives – waste geothermal water as a source of medicinal raw material and drinking water

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ABSTRACT

An assessment of whether it is possible to use chilled geothermal water which has been classified as waste is presented in this paper. Two different sources of waste geothermal water (GT-1 and GT-2), previously used for heating purposes, were purified by membrane processes (nanofiltration/reverse osmosis [RO]). Nanofiltration caused the removal of divalent ions from the geothermal water and protected the RO membrane against scaling effects from the deposition of secondary minerals on its surface. In both cases analysed, high-quality permeate was obtained as a result of the geothermal water treatment processes. The physical and chemical properties of the concentrates obtained during water desalination were also evaluated in terms of the usefulness of the product. The results of the research showed no potentially toxic components that would prevent their commercial use for external balneological purposes. Waste geothermal water recycled in this way may be reused, which is very important especially in areas with problems of a lack or deficit of high-quality water. Additionally, benefits may arise from the utilisation of high-quality geothermal water concentrate for bathing in balneological facilities.

Keywords: Zero waste; Waste geothermal water; Medicinal raw material; Drinking water; Desalination

1. Introduction

In 2015, the United Nations adopted Sustainable Development Goals (SDG) which are a challenge to the World over the next 15 years. The SDG target 6.3 requires an improvement in water quality by 2030 by reducing pollution, eliminating dumping and minimising the release of hazardous chemicals and materials, reducing the proportion of untreated wastewater and increasing recycling [1]. The problem of waste and its role in water management is so important that in 2017 World Water Day, an annual holiday established by the UN General Assembly, will be celebrated as 'Wastewater: The untapped resource'. Issues related to

wastewater will be widely discussed in a special report [2]. According to the UN, nearly 70% of humanity will be living in urban areas by 2050 [3], so this will be the cause of the most important task for the future – preparing the appropriate infrastructure and tools to effectively and sustainably reduce solid waste – and wastewater. Some actions of this type are known as 'zero-waste initiatives'.

Apart from water and sewage management issues, the second major environmental goal is widespread, efficient and rational use of renewable energy resources. The use of sun, wind, water or geothermal energy is seen as an alternative to conventional energy sources, but also a solution that contributes to the achievement of environmental goals,

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cuts greenhouse gas emissions and reduces the generation of waste [4–6].

The use of geothermal energy, which offers significant resources that are widely available on a global scale, plays an important role in this regard. In Europe, there are many regions where geothermal energy is utilised. The Paris and Aquitaine Basins (France), the Larderello region (Italy), where it is mainly steam resources that are utilised, the Central European Basin (Denmark), the North German Basin (Germany), the Polish Basin (also called the Polish Lowland), the Pannonian Basin (Hungary, Slovakia, Serbia, Slovenia, Romania and Austria), the Inner Carpathians using the Mesozoic floor series of the tertiary basins surrounding the Tatra mountains (Poland and Slovakia) and several other areas (Slovakia), the Subalpine Molasse Basin (Germany), the Upper Rhine Graben (France, Germany and Switzerland), and other Alpine and older regions of Southern Europe (Italy, Bulgaria, Macedonia, Greece and Turkey). The main lithological types found in the rocks forming geothermal water reservoirs are sedimentary structures (limestones and dolomites, sandstones) as well as volcanic rocks and fractured sections of crystalline and metamorphic rocks [7]. In physical and chemical terms, the geothermal water present in the structures examined exhibit different properties. There are freshwater, in which total dissolved solids (TDS) are below 1.0 g/L, brackish water (TDS from 1 to 10 g/L), saline water (TDS from 10 to 30 g/L) and brine (TDS more than 30 g/L). Brine and saline geothermal water are mostly used for heating purposes, but low mineral content and fresh geothermal water are mainly made available for both heating and leisure purposes [8]. Development and commercialisation of geothermal water as energy and water sources provide great potential to generate clean energy and water for different purposes.

The 21st century has brought a new approach to ‘travelling for health’ and to treatment itself. Classic health resorts using balneological therapy have to satisfy the expectations of more and more demanding customers [9]. The therapeutic value of geothermal water is determined by their temperature, variety of dissolved ions, gases and trace elements. In many countries, there are specific regulations and rules in laws used for the classification of groundwater. In Poland, if groundwater is not contaminated and with natural variations in physical and chemical parameters and contains at least one specific pharmacodynamic component, and/or has a temperature above 20°C, it is then considered as a therapeutic water [10]. Moreover,

whole mineral water in which TDS is more than 1 g/L can be medicinal water, or medicinal raw material, regardless of whether it contains specific components (Table 1).

Medicinal and geothermal water are widely used for medical treatment in spas, in baths and in swimming pools, in a drinking treatment (crenotherapy) and also for inhalations, irrigations and rinsing [11–14]. The effects of different types of thermomineral and geothermal water used for treatment purposes in spas have been presented by Cruz and Franca [15], Balderer et al. [16] and Karagülle and Karagülle [17]. The results of investigations of the therapeutic effects of using clays and mineral water combinations, known as pelotherapy have also been presented by Tenti et al. [18], Gámiz et al. [19] and Rebelo et al. [20,21].

Sustainable and efficient management of geothermal water should be focused on the comprehensive utilisation of energy resources obtained and water extracted from the reservoir. Space heating is a key sector for the geothermal energy industry in Poland. It is also worth noting that a growing interest in recreation and balneotherapy. The paper presents the results of comprehensive research related to the effective use of waste (cooled) geothermal water, classified as waste, as a source of medicinal raw material and drinking water.

2. Materials and methods

Raw geothermal water from particular wells was selected to test opportunities for the comprehensive utilisation of cooled geothermal water resources and the optimisation of the operation of existing geothermal systems. For these purposes, membrane technologies were supplied to examine the opportunities for obtaining drinking water, and also specific concentrate which could be a source of medicinal raw material.

A schematic diagram of the apparatus used in the test is shown in Fig. 1. Experiments were conducted using a semi-industrial scale pilot installation, equipped with an iron-removal device, ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) systems. The tests were performed at the Geothermal Laboratory of the Mineral and Energy Economy Research Institute, Polish Academy of Sciences (PAS MEERI). The pilot facility was fitted with typical industrial plant components. Its continuous-cycle (i.e., 24 h/d) capacity was expected to be 1 m³/h. The spiral wound DOW FILMTEC polyamide thin-film composite membrane type has been matched to the quality of the raw water and

Table 1
Balneological classification of mineral water in Poland (on the basis of [10])

Total dissolved solids (TDS)	Temperature (°C)	Pharmacodynamic factors – specific components	Chemical type of water
≥1 g/L – mineral water	>20 – geothermal water	2 mg F ⁻	Fluoride
<1 g/L – slightly mineralised	<20 – cold water	1 mg I ⁻	Iodated
		1 mg S(II)	Sulphuric
		70 mg H ₂ SiO ₃	Silica
		10 mg Fe(II)	Ironic
		74 Bq	Radon or radioactive
		250 mg free CO ₂	Carbonate
		1,000 mg free CO ₂	CO ₂ -rich, carbonised

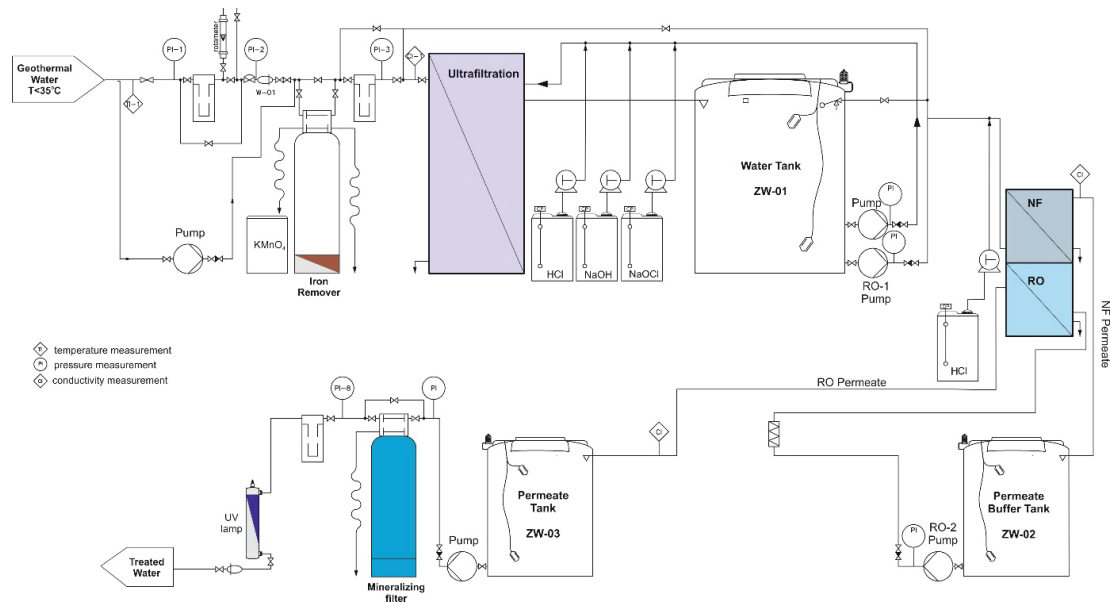


Fig. 1. Process diagram of the geothermal water desalination facility.

its content of microelements. The inorganic and radon concentrations of treated water (permeate) and concentrate have been analysed in accredited laboratories.

3. Results and discussion

Exploitation of geothermal water in double or triple systems (with production and injection wells) is costly due to the necessity to drill two wells and/or risk the corrosion or clogging of the injection wells. This is why entrepreneurs are more likely implementing solutions with waste discharging into streams or drains as long as the wastewater quality meets legal requirements. Geothermal water with a mineralisation below 1,000 mg/L is considered to be drinking water and can be used as a water supply for the local community. This is the way geothermal wastewater is utilised after being used for heating processes in Mszczonow, a town located in central Poland [4]. However, the vast majority of companies operate using very concentrated brine which must be subjected to processes for the removal of excessive concentrations of macroelements and microelements before discharge.

In Table 2, the chemical compositions of water tested in research are shown. Geothermal water from the Polish Lowlands and from two different geothermal systems were tested, that is, the Lower Cretaceous (GT-1) and Lower Jurassic (GT-2). The total dissolved solids (TDS) ranged from 6.16 g/L (GT-1) to 4.86 g/L (GT-2). The water contained high concentrations of iron, silica, sulphates, strontium and carbonate, which in consequence may affect desalination using membranes due to membrane scaling. This is why the pretreatment process was equipped with iron removal, UF and NF facilities (Fig. 1). UF membranes serve as a barrier to dispersed substances, including colloids and microorganisms. The NF membranes were used to soften water and to retain colloids, many low- and medium-molecular weight organic compounds and divalent ions. These processes are recommended by Bodzek and Konieczny [22]. The treatment was as follows:

Table 2

Physical properties and chemical composition of the tested geothermal water

Element	GT-1 ^a	GT-2 ^a
TDS (mg/L)	6,157.3	4,863.3
pH	6.41	7.67
Total hardness (mg CaCO ₃ /L)	392.7	374.0
Carbonate hardness (mg CaCO ₃ /L)	242.7	204.1
Na (mg/L)	2,178.0	1,713.81
K (mg/L)	18.70	22.66
Ca (mg/L)	120.5	99.40
Mg (mg/L)	22.39	30.627
Cl (mg/L)	3,543.0	2,645.0
SO ₄ (mg/L)	84.33	68.48
As (mg/L)	0.015	0.008
F (mg/L)	0.96	0.21
Cr (mg/L)	0.011	0.010
Cd (mg/L)	<0.0003	<0.0003
Ni (mg/L)	0.002	0.002
Pb (mg/L)	0.0008	0.0024
Hg (mg/L)	<0.0001	0.0005
Al (mg/L)	<0.005	<0.005
Mn (mg/L)	0.029	0.122
Fe (mg/L)	0.12	1.38
Sr (mg/L)	4.94	2.34
H ₂ SiO ₃ (mg/L)	32.18	25.84
²²² Rn (Bq/L)	5.4	6.0

^aAverage value.

- GT-1: the NF process was carried out at a transmembrane pressure of 1.0 MPa, NF permeate recovery at 70% and 30% of concentrate, and in RO processes the transmembrane pressure was 1.5 MPa, 67% of RO permeate and 33% of concentrate was obtained. The temperature of the geothermal water tested was about 20°C.
- GT-2: the NF process was carried out at a transmembrane pressure of 1.0 MPa, NF permeate recovery of 75% and 25% of concentrate, and the RO process was carried out at a transmembrane pressure of 1.5 MPa, 72% of RO permeate and 28% of concentrate was obtained. The temperature of geothermal water tested was about 17°C.

Cooled and prefiltered geothermal water were directed to the iron-removal filter. Water at a pressure of ca. 0.3–0.5 MPa was filtered through a catalyst bed layer, on the surface of which oxidised iron hydroxides were retained, precipitating as flocs that settled easily. In order to remove the pollutants accumulated during operation, the filter was regularly rinsed in two stages: backwashing (counter-current rinsing) and concurrent rinsing. The rinse process was initiated and conducted fully automatically in line with the schedule programme. After filtering major contaminants and removing iron, the water was fed into the UF module, which was an extension of water treatment prior to NF and RO. UF membranes were used to remove microsuspensions that limited the possibility of feeding the water tested to the RO stage. It was envisaged that after the UF module, the silt density index would be below 3. The pressure of the water feeding the UF module was 0.3 MPa.

Following the UF process, the water was directed to an intermediate tank with a capacity of 2 m³. All processes related to the operation of the UF module were fully automated.

After the intermediate tank, separate pumps were installed for the water feeding the NF and RO stages. To avoid problems with scaling during water treatment, the pH of feed water was brought down to 5 ± 0.5 before NF. The permeate from the NF stage was fed to the RO station. Desalinated water was produced at a rate of 1 m³/h in a continuous cycle, that is, 12 h a day. At the same time, about 0.5–0.6 m³/h of NF concentrate and 0.4–0.45 m³/h of RO concentrate were received. After subjecting desalinated water to subsequent processing (mineralisation by filtering it through a dolomite bed and UV sterilisation), the technological cycle was complete.

In both the cases analysed, high-quality permeate was obtained as a result of the geothermal water treatment process whose physical and chemical properties are presented in Table 3. As a result of the NF process applied, the water was free of carbonate hardness. NF caused the removal of divalent ions from geothermal water and at the same time protected the RO membrane against the deposition of secondary minerals such as aragonite, calcite, gypsum and silica on its surface. Low concentrations of calcium and magnesium in the permeate had to be increased to at least 60 mg/L. For this purpose, a remineraliser was used, which was filled with a dolomite (CaMg(CO₃)₂) bed. As a result, after additional UV sterilisation, high-quality water was obtained from the geothermal water that met the requirements for drinking water. It was therefore demonstrated that geothermal water is a renewable energy and also a possible source of freshwater.

An ability to dispose of chilled geothermal water, considered as waste, can be an extremely important factor affecting the amount of energy extracted from water [24]. In the case of reservoirs located outside active seismic and volcanic zones, geothermal water is present at considerable depths, more than 1,500–2,000 m below ground level. This raises the TDS level in geothermal water. The tests presented in this paper were conducted on water extracted from Lower Cretaceous and Lower Jurassic formations in the Polish Lowlands. The aquifers present in these geological structures exhibit great reservoir parameters and cause a high capacity of geothermal wells with a production level from 25 to more than 200 m³/h [23,24]. The Lower Cretaceous reservoir with a surface of ca. 115,521 km² [23] consists of discontinuous complexes, and interspersed sandy, sandy-marly and sandy-mudstone layers with thicknesses ranging from a few to 300 m. In this area, the water temperature ranges from 20°C to 40°C [23,24]. On the other hand, the Lower Jurassic geothermal reservoir has a surface of ca. 158,600 km² (almost 51% of the area of Poland) and consists of a fine and mixed grain-size sand and sandstone layer from 10 to 650 m thick. Depending on the depth, geothermal water in the reservoirs exhibits TDS levels ranging from 0.5 to over 100 g/L and has a temperature ranging from 40°C to 90°C [8,23]. The active zone at which geothermal water occurs in borehole GT-1 stretches in the range from 1,892 to 2,025 m below ground level. In the well GT-2, the active zone runs from 1,489 to 1,620 m below ground level.

The most appropriate method of disposal of highly mineralised geothermal water is reinjection of wastewater back into the reservoir [8]. This method usually generates high investment costs related to the construction of the required number of absorption wells and also operating costs arising due to the pumping of considerable amounts of water at pressures of up to 40–50 MPa. Usually, the problem of discharging wastewater is solved by injecting part of the water back into the reservoir and/or discharging the rest or all of the wastewater into a surface receiver. The proposed method for the treatment of waste geothermal water and the use of desalinated water for commercial purposes is certainly a more rational solution. In the context of the global water shortage, searching for alternative water resources is a very important challenge. Therefore, specialists in the field of environmental engineering increasingly undertake research and conduct experiments which enable the efficient utilisation of chilled waste geothermal water [25]. Arar et al. [26,27] present the results of research related to the demineralisation of geothermal water by RO and electrodeionisation. Gude [28] highlighted that a preliminary assessment and evaluation procedure of desalination processes and geothermal sources should be identified. The economic and environmental impacts of the desalination plants should also be assessed with site-specific information to eliminate future failures.

An important statement involves the issue of disposing of the concentrate obtained in the membrane processes [29,30]. The physical and chemical properties of the concentrate are determined by factors such as the physical and chemical properties of raw water (the feed water supplied to the desalination plant), the recovery rate of treated water, retention level of individual components, use of preliminary desalination methods, amounts and types of chemicals using in the desalination process, etc. The concentrate must be disposed of in an

Table 3
Physical and chemical properties of permeate after NF and RO

Element	GT-1 ^a		GT-2 ^a	
	NF permeate	RO permeate	NF permeate	RO permeate
TDS (mg/L)	2,525.0	91.0	2,554.9	170.8
Total hardness (mg CaCO ₃ /L)	8.6	0.9	183.0	0.7
Carbonate hardness (mg CaCO ₃ /L)	8.6	0.9	18.9	0.0
Na (mg/L)	950.3	34.06	901.18	68.97
K (mg/L)	12.67	1.22	13.47	5.39
Ca (mg/L)	2.74	0.30	50.90	0.27
Mg (mg/L)	0.436	0.045	13.615	<0.1
Cl (mg/L)	1,532.0	40.7	1,510.0	76.6
SO ₄ (mg/L)	1.33	0.49	37.81	<3.0
I (mg/L)	0.24	0.059	0.03	0.12
As (mg/L)	0.010	0.005	0.004	0.001
F (mg/L)	0.43	0.14	0.20	0.039
Cr (mg/L)	0.005	<0.005	0.008	<0.005
Cd (mg/L)	<0.0003	<0.0003	<0.0003	<0.0003
Ni (mg/L)	<0.001	<0.001	<0.001	<0.001
Pb (mg/L)	0.0024	0.0005	0.0006	0.0016
Hg (mg/L)	<0.0001	<0.0001	0.0003	<0.0001
Al (mg/L)	<0.005	<0.005	<0.005	<0.005
Mn (mg/L)	0.017	<0.005	0.022	<0.005
Fe (mg/L)	<0.01	<0.01	0.05	0.03
Sr (mg/L)	<0.20	<0.20	1.24	<0.2
H ₂ SiO ₃ (mg/L)	8.39	0.34	12.34	1.24
²²² Rn (Bq/L)	2.4	1.4	3.0	1.8

^aAverage value.

environmentally safe manner. This is an additional advantage in the case where the concentrate can be sold as a raw material. Due to salinity and environmental considerations, the concentrate could not be discharged into surface water. Therefore, apart from factors related to the efficiency of producing desalinated water that meets the requirements for water intended for human consumption, the operation of the water treatment plant must be optimised in order to produce just a small stream of concentrate that could be reinjected into the rock formation or – even better – utilised for industrial purposes.

Some earlier work related to geothermal water obtained from carbonate formations in the Podhale geothermal system [31–34] threw a positive light on the possibility of commercial use of the concentrates. The physical and chemical properties of the concentrates obtained during the desalination of water from the GT-1 and GT-2 wells were also evaluated in terms of the requirements for balneological products. It was checked that the concentrates obtained contained no potentially toxic components that would prevent their commercial use. Table 4 summarises the results of the tests conducted for the concentrates after the NF and RO processes. The concentrates obtained as a result of the filtration of geothermal water through the NF membrane exhibit significantly higher TDS

values than concentrates after the RO process (Table 4). This result is obvious because softened geothermal water with already reduced solute content was fed to the RO membrane (Table 2). Therefore, the technological arrangement considered the most important is the evaluation of the properties of concentrates after the NF process.

The geothermal water concentrates obtained after the NF process from the GT-1 and GT-2 wells exhibited TDS values of 12.5 and 10.5 g/L, respectively, and also elevated levels of fluoride – 1.4 mg/L (GT-1) and 1.3 mg/L (GT-2), meta-silicic acid – 93.7 mg/L (GT-1) and 73.5 mg/L (GT-2) and iodides – 1.41 mg/L (GT-1) and 0.065 mg/L (GT-2). On the other hand, no elevated radon concentrations were found; the gas most probably evaporated during the oxidation of water in the iron removal plant and in buffer tanks. The geothermal water concentrate obtained after RO is also highly mineralised water, with a TDS, respectively, of 6.3 g/L (GT-1) and 4.6 g/L (GT-2). However, it does not exhibit elevated concentrations of specific ingredients with potentially therapeutic value (Table 4).

The production of concentrates for therapeutic and/or balneological purposes is justified for Cl–Na water with a TDS above 1,000 mg/L and as high as possible I⁻ ion concentrations. In the cases analysed, the concentrate is a Cl–Na

Table 4

Comparison of concentrate analysis results with the highest admissible concentration of ingredients that are undesirable in excessive amounts and toxic ingredients in therapeutic water pursuant to the regulation of the Polish Minister of Health [35]

Element	GT-1 ^a		GT-2		The highest admissible concentration		
	NF concentrate	RO concentrate	NF concentrate	RO concentrate	Drinking cure	Inhalation	Bathing
TDS (mg/L)	12,792.9	6,289.7	10,498.5	4,628.2	–	–	–
Total hardness (mg CaCO ₃ /L)	1,083.8	51.9	910.2	703.5	–	–	–
Carbonate hardness (mg CaCO ₃ /L)	84.0	51.9	128.5	0.0	–	–	–
Na (mg/L)	4,327.0	2,349.0	3,699.15	1,417.80	–	–	–
K (mg/L)	41.46	37.57	51.98	39.80	–	–	–
Ca (mg/L)	333.8	16.27	245.48	207.46	–	–	–
Mg (mg/L)	60.98	2.749	72.341	45.167	–	–	–
Cl (mg/L)	7,490.0	3,752.0	6,002.0	2,520.0	–	–	–
SO ₄ (mg/L)	316.6	41.03	260.95	316.95	–	–	–
I (mg/L)	1.41	0.034	0.06	0.13	–	–	–
As (mg/L)	0.029	0.020	0.020	0.012	–	–	–
F (mg/L)	1.4	1.2	0.065	0.15	–	–	–
Cr (mg/L)	0.019	0.011	0.024	0.027	0.01	0.01	–
Cd (mg/L)	<0.0003	<0.0003	<0.0003	<0.0003	0.003	0.003	–
Ni (mg/L)	0.003	0.002	0.003	0.050	0.03	0.03	–
Pb (mg/L)	0.0085	0.0018	0.0048	0.0214	0.01	0.01	–
Hg (mg/L)	<0.0001	<0.0001	0.0004	0.0003	0.001	0.001	–
Al (mg/L)	<0.005	0.009	<0.005	0.006	0.1	0.1	–
Mn (mg/L)	3.444	0.241	0.119	0.299	–	–	–
Fe (mg/L)	1.83	0.07	0.13	1.02	–	–	–
Sr (mg/L)	12.97	0.56	6.18	5.17	–	–	–
H ₂ SiO ₃ (mg/L)	93.73	26.12	73.48	54.10	–	–	–
²²² Rn (Bq/L)	<0.5	<0.5	<0.5	<0.5	–	–	–

^aAverage value.

water but the I⁻ ion content did not reach 2 mg/L because of low concentrations of iodides in the feed water (geothermal water). A potential factor restricting the commercial use of concentrates may be their content of organic and/or petroleum substances, radioactive elements or potentially toxic elements (Cd, As, Hg and Sb). A comparison of analysis results of the concentrate (Table 4) obtained as a result of the desalination of water from the wells taking consideration of the aforementioned guidelines demonstrates that the concentrate meets the expected parameters for water used externally. In both these cases, no substances were found that would prevent the utilisation of the concentrate for external use.

On the other hand, they may be considered useful for cosmetic purposes, if one considers an increase in concentrations of metasilicic acid in the concentrates.

4. Conclusion

Geothermal water resources are important energy and water solutions. Our experimental research done on a semi-production scale showed that waste geothermal

water, used for heating purposes can be purified by membrane processes (NF/RO) and after that reused as drinking water. The implementation of this idea on an industrial scale could improve geothermal water management and use. Also in many cases, it can reduce the negative impact of the discharge of saline waste geothermal water to streams. Waste recycled in this way could be reused, which is very important especially in areas with problems of a lack or deficit of freshwater. On the other hand, the waste stream obtained during the procedure for geothermal water treatment, the concentrate, may be useful as a new product for therapeutic and/or balneological purposes. In our cases, the results of inorganic and radioactive component analyses showed compatibility with Polish national criteria for the assessment of medicinal raw materials. The mining of zero-waste initiative waste geothermal water can be a source of medicinal raw materials. Nowadays, when a shortage of drinking water is a common problem in the world, research plays a very important role in the better utilisation of geothermal water and energy. Geothermal water can be firstly an energy source, but after the application of treatment processes can be used as a source

of freshwater or/and medicinal raw material – balneological products.

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