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

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Abstract: Research carried out in the assessment of the possibilities of using chilled geothermal water which are classified as waste. Waste geothermal water can be purified by membrane processes (nanofiltration/reverse osmosis) and after that re-used as drinking water. The implementation of this solutions in industry scale would reduce the negative impact of discharge saline waste geothermal water to streams. Waste recycled in this way could be reused, what is very important especially in areas with problems of lack or deficit of water. The most important application of research is recycling waste of geothermal water and their valorisation due to specific micro- and macroelements content, good quality and lack of salinity components.

Keywords: zero-waste, waste geothermal water, medicinal raw material, drinking water, desalination

Introduction

In 2015 the United Nations adopted Sustainable Development Goals (SDG) which are the World challenge for the next 15 years. SDG target 6.3 requires to 2030 improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, having the proportion of untreated wastewater and increasing recycling [1]. The problem of waste and their 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 with wastewater will be widely discussed in special report [2]. According to the UN by 2050 nearly 70% of humanity will be living in urban areas [3], so it will be cause most important task for the future - preparing the appropriate infrastructure and tools to effectively and sustainably reduce solid- and wastewater. Some kind of this actions are known as „zero-waste initiatives”.

Apart from water and sewage management issues, the second major environmental goal is the 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, reduces greenhouse gas emissions and 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) - mainly vapour resources that are utilised, the Central European Basin (Denmark, the North German Basin in Germany, the Polish Basin (also called the Polish Lowland), the Pannonian Basin (Hungary, Slovakia, Serbia, Slovenia, Romania, Austria), the Inner Carpathians using the Mesozoic floor series of the tertiary basins surrounding the Tatra mountains (Poland, Slovakia) and several other areas (Slovakia), the Subalpine Molasse Basin (Germany), the Upper Rhine Graben (France, Germany, Switzerland), and other Alpine and older regions of Southern Europe (Italy, Bulgaria, Macedonia, Greece, 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 waters present in the structures examined exhibit different properties. There are both fresh waters, which total dissolved substances (TDS) are below 1.0 g/L, brackish waters (TDS from 1 to 10 g/L), saline waters (TDS from 10 to 30 g/L) and brine (TDS more than 30 g/L). Brine and saline geothermal waters are mostly used for heating purposes, but low mineral content and fresh geothermal waters are mostly made available for heating and leisure purposes [8]. Development and commercialization of geothermal waters as an 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 waters is determined by their temperature, variety of dissolved ions, gases and trace elements. In many countries, there are specific regulations and law rules used for the classification of groundwaters. In Poland, if groundwater is not contaminated and with natural variations in physical and chemical parameters and contains at least one specific pharmaco-dynamic component, and/or has a temperature above 20°C is then considered as therapeutic water [10]. Moreover, whole mineral water, which TDS is more than 1 g/L can be medicinal water, medicinal raw material, regardless of whether it contains specific components (Table 1).

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

Total dissolved solids (TDS)	Temperature [^oC]	Pharmaco-dynamic factors – specific components	Chemical type of water
≥ 1 g/L – mineral water < 1 g/L – slightly mineralized	> 20 - geothermal water < 20 - cold water	2 mg F^-	Fluoride
		1 mg I^-	Iodated
		1 mg S(II)	Sulfuric
		70 mg H_2SiO_3	Silica
		10 mg Fe(II)	Ironic
		74 Bq	Radon or radioactive
		250 mg free CO_2	Carbonate
		1000 mg free CO_2	CO_2-rich, carbonized

Medicinal and geothermal water are very wide used in spas for medical treatment in baths and swimming pools, drinking treatment (crenotherapy), inhalation, irrigation and rinsing [11-14]. In various papers have studied the effects of different types of thermo-mineral and geothermal waters used in spas in treatment purposes [15-19]. Some of them presents also the results of investigation to use in balneotherapy the combine the therapeutic effects of clays and mineral waters, known as pelotherapy [20-22].

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 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.

Material and methods

Raw geothermal water from particular wells has been selected to testing opportunities for the comprehensive utilisation of cooled geothermal water resources and the optimisation of the operation of existing geothermal systems. In this context membrane technologies has been supplied to examined opportunity to receive drinking water and also specific concentrate, as a source of medicinal raw material.

A schematic diagram of the apparatus used in test is shown in Figure 1. Experiments were conducted using the semi-industrial scale pilot installation, equipped with 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 hour/day) capacity was expected to be 1 m^3/h. The spiral wound DOW FILMTEC polyamide thin-film composite membranes type has been matched to raw water quality and content of microelements. The inorganic and radon concentrations of treated water (permeate) and concentrate has been analysed in accredited laboratories.

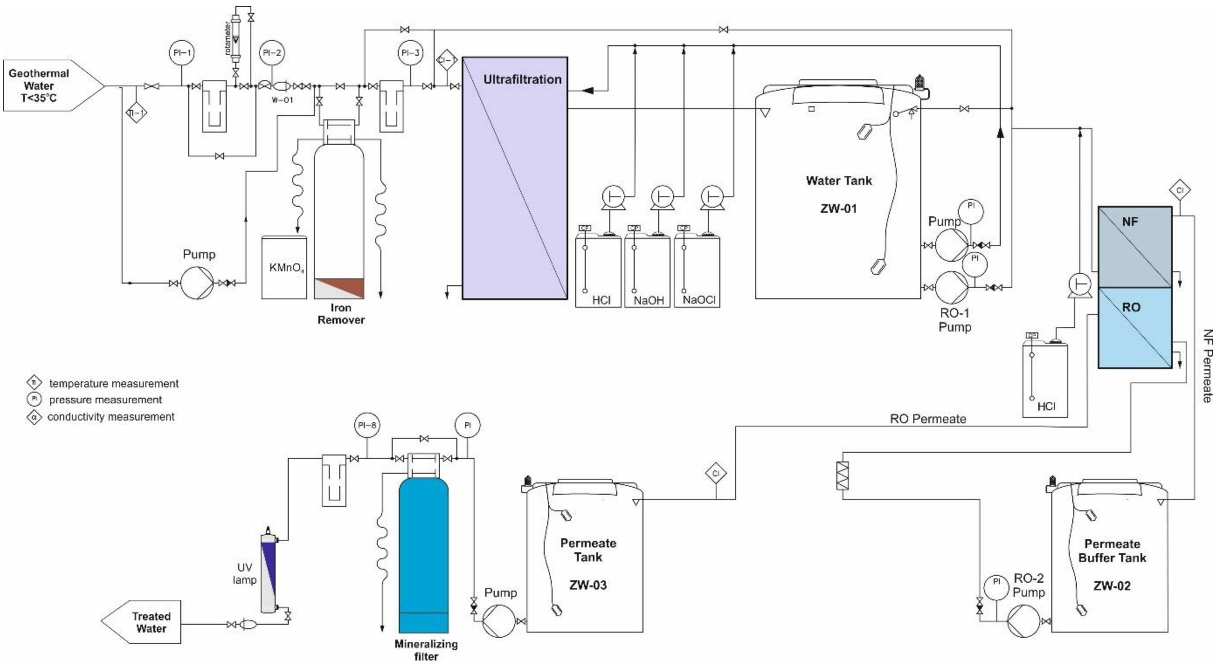

Figure 1. Process diagram of the geothermal water desalination facility.

Results

Exploitation of geothermal water in dublet or tripled system (with the production and the injection wells) is costly due to necessity of drilling two wells and/or risk of the corrosion or clogging in injection wells. Therefore entrepreneurs more likely implement solution with waste discharging into the stream or drains as long as the wastewater quality meet requirements of the law. Geothermal waters with mineralization below 1000 mg/L are consider as drinking water and can be used as a water supply for local community. This is the utilisation way of geothermal wastewater after using in heating processes in Mszczonow, a town in central Poland [4]. However, the large majority of companies operate high concentrated brine which must be subjected to processes of removal oversize concentrations of macro- and microelements.

The chemical composition of the waters tested are shown in Table 2. Geothermal waters from the Polish Lowlands and from two different geothermal systems were tested, i.e. the Lower Cretaceous (GT-1) and Lower Jurassic (GT-2). The total dissolved solids (TDS) ranged 6.16 g/L (GT-1) and 4.86 g/L (GT-2). The waters contain high concentrations of iron, silica, sulphates, strontium and carbonate, and in consequence may affect desalination using membranes due to membrane scaling. That is why, the pre-treatment process was equipped in iron-removal, ultrafiltration (UF) and nanofiltration (NF) (Fig. 1). Ultrafiltration membranes serve as a barrier to dispersed substances, including colloids and microorganisms. The NF membranes was used to soften water and to retain colloids, many low and medium molecular weight organic compounds and divalent ions [23]. In case of:

1) GT-1: the NF process was carried out at a transmembrane pressure of 1.0 MPa, NF permeate recovery of 70% and 30% of concentrate and in RO process the transmembrane pressure was 1.5 MPa, 67% of RO permeate and 33% of concentrate was obtained. Temperature of geothermal water tested was about 20^{o}C;
2) 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 RO process was carried out at a transmembrane pressure of 1.5 MPa, 72% of RO permeate and 28% of concentrate. Temperature of geothermal water tested was about 17^{o}C;

Table 2. Physical properties and chemical composition of the geothermal water tested

Element	GT-1*	GT-2*
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	2645.0

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_2SiO_3, [mg/L]	32.18	25.84
^{222}Rn, [Bq/L][1]	5.4	6.0

[*] - Average value

Cooled geothermal water and pre-filtered, was directed to the iron removal filter. Water at a pressure of ca. 0.3-0.5 MPa flowed through a catalyst bed layer, on the surface of which oxidized iron hydroxides were retained, precipitating as floccules 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 programmed. After filtering major contaminants and removing iron, the water was fed to the ultrafiltration module, which was an extension of water treatment prior to nanofiltration and reverse osmosis. Ultrafiltration membranes were used to remove micro suspensions that limited the possibility of feeding the water tested to the reverse osmosis stage. It was envisaged that after the ultrafiltration module, the SDI (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 m^3, and some of it was used to rinse UF membranes. Apart from water, hydrochloric acid and sodium hydroxide were also used during the washing of ultrafiltration membranes; these were supplied by independent dosing pumps. All processes related to the operation of the UF module were fully automated and proceeded according to the program.

After the intermediate tank, separate pumps for the water feeding the NF and RO stage were installed. To control the high feed water hardness its pH was brought down to 5±0.5 before NF. The permeate from the NF stage was fed to the RO station. Desalinated water was to be produced at the rate of 1 m^3/h in a continuous cycle, i.e. 12 h a day. In the same time, there were received about 0.5-0.6 m^3/h of NF concentrate and 0.4 - 0.45 m^3/h of RO concentrate. After subjecting desalinated water to subsequent processing (mineralization by filtering it through a dolomite bed and UV sterilization), the technological cycle was complete.

In both cases, as a result of the geothermal water treatment process high-quality permeate was obtained whose physical and chemical properties are presented in Table 3. The water was devoid of carbonate hardness as a result of the nanofiltration process applied that 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 ($CaMg(CO_3)_2$) bed. As a result, after additional UV sterilisation, high-quality water was obtained from geothermal water that met the requirements for drinking water. It has thus been demonstrated that geothermal water is a renewable energy carrier that can also be perceived as a raw material, i.e. water than can be used for commercial purposes.

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

Element	GT-1[**]		GT-2[**]	
	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_2SiO_3, [mg/L]	8.39	0.34	12.34	1.24
^{222}Rn, [Bq/L]	2.4	1.4	3.0	1.8

** - Average value

Numerous studies on geothermal systems demonstrate that the ability to dispose of chilled geothermal waters, which are treated as waste, is an extremely important factor affecting the amount of energy that can be extracted from the water [24]. Owing to geological and hydrogeological conditions, primarily in the case of reservoirs located outside seismic and volcanic activity zones, geothermal waters are present at considerable depths of more than 1,500–2,000 metres below ground level. This results in their elevated TDS levels. The tests presented in this paper were conducted on waters extracted from Lower Cretaceous and Lower Jurassic formations in the Polish Lowlands. The aquifers present in these geological structures exhibit high reservoir parameters, which means that the capacity of geothermal wells tends to be high (from 25 to more than 200 m^3/h) [24, 25]. The Lower Cretaceous reservoir, which occupies ca. 115,521 km^2 [24], consists of complexes of discontinuous, interspersed sandy, sandy-marly and sandy-mudstone layers with thicknesses ranging from a few to 300 m. In its central area, water temperature ranges from 20 to 40^oC [24,25]. On the other hand, the Lower Jurassic geothermal reservoir occupies ca. 158,600 km^2 (almost 51% of country area) and consists of a fine and mixed grain-size sand and sandstone layer from 10 to 650 m thick; depending on the depth, the geothermal water within the reservoir exhibits TDS levels ranging from 0.5 to over 100 g/L and its temperature ranges from 40 to 90^oC [8, 24]. The active zone from which water is supplied to the GT-1 geothermal spans from 1,892 to 2,025 m below ground level; for the GT-2 well, it spans from 1,489 to 1,620 m below ground level. In the case of water extracted from such depths, the most appropriate method of disposal is considered to be the re-injection of chilled waste water back into the reservoir [8]. This method of water disposal usually generates high investment expenditure associated with the construction of the required number of absorption wells as well as operating costs resulting from the need to pump considerable amounts of water at pressures of up to 40–50 MPa. Thus it is typically replaced by injecting part of the water and/or discharging part or all of the water into surface receiving waters. The proposed method of waste geothermal water treatment and the use of desalinated water for commercial purposes is certainly a more rational solution. Therefore specialists in the field of environmental engineering increasingly undertake research and conduct experiments that enable the efficient utilisation of chilled waste geothermal waters [26-28]. In the light of the global water shortage, searching for alternative water resources is an important challenge. Gude [29] lists many solutions to this problem and applications for such water worldwide, while stressing that a suitable combination of a desalination process and a geothermal source should be identified with a preliminary assessment and evaluation procedure. The economics and environmental impacts of the desalination plants should be assessed with site-specific information to eliminate future failures.

The above statement also involves the issue of disposing of the concentrate obtained in membrane processes [30,31]. The physical and chemical properties of the concentrate are affected by factors such as the physical and chemical properties of raw water (the feedwater supplied to the desalination plant), the recovery rate of treated water, retention levels of individual components, the preliminary desalination methods used, the amounts and types of chemicals used in the desalination process, etc. The concentrate must be disposed of in an environmentally safe manner. Where it can be sold as a raw material, it is an additional advantage. Owing to its salinity and environmental considerations, the concentrate must not be discharged into surface waters. Therefore, apart from the 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 re-injected into the rock formation or – even better – utilised for industrial purposes. Earlier work by the authors, which concerned geothermal waters obtained from carbonate formations within the framework of the Podhale geothermal system [32-35] threw light on the possible commercial use of concentrate ingredients. 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 applicable to balneological products. It was checked whether 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 filtration of

geothermal water through the nanofiltration 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 in the technological arrangement considered, the evaluation of properties of concentrates after the NF process is of key importance.
The geothermal water concentrates obtained after the NF process from the GT-1 and GT-2 wells exhibited TDS values of 12.5 g/L 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), metasilicic 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 of respectively 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).

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 waters pursuant to the regulation of the Minister of Health [36].

Element	GT-1*		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	2349.0	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_2SiO_3, [mg/L]	93.73	26.12	73.48	54.10	-	-	-
^{222}Rn, [Bq/L]	<0.5	<0.5	<0.5	<0.5	-	-	-

* - Average value

The production of concentrates for therapeutic and/or balneological purposes is justified for Cl-Na waters with a TDS above 1,000 mg/L and as high I^- ion concentrations as possible. In the cases considered, the concentrate is a Cl-Na water, but I^- ion content did not reach 2 mg/L, which results directly from the relatively low concentrations of iodides in the feedwater (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, Sb). A comparison of analysis results of the concentrate (Tab. 4) obtained as a result of the desalination of water from the wells under consideration with the aforementioned guidelines demonstrates that the concentrate meets the expected parameters for waters used externally. In this both cases, no substances were found that would prevent the utilisation of the concentrate for external use. On the other hand, considering the increased concentrations of the metasilicic ion in the concentrates tested, they may be considered useful for cosmetic purposes.

Conclusion

Waste geothermal water can be purified by membrane processes (nanofiltration/reverse osmosis) and after that re-used as drinking water. The implementation of this solutions in industry scale would reduce the negative impact of discharge saline waste geothermal water to streams. Waste recycled in this way could be reused, what is very important especially in areas with problems of lack or deficit of water. The most important application of research is recycling waste of geothermal water and their valorisation due to specific micro- and macroelements content, good quality and lack of salinity components.

The results of inorganic components tests and organic and radioactive showed compatibility between parameters of received concentrate and requirements of Polish national criteria for the assessment of the medicinal raw materials. In turn the treated water (permeate) can be used as a drinking water or other useful purposes.

Nowadays, when the World common problem is a shortage of drinking water, a very important role play research for better utilisation of geothermal water and their waste. Geothermal water can be firstly energy source but after membrane processes can be using as a source of drinking water or/and medicinal raw material and balneological products.

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