



# Article Treatment of Waters Having Different Ionic Composition and pH with Natural Zeolites from Bulgaria

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**Abstract:** The migration of 32 elements from natural zeolitized tuffs from the Beli Plast and Golobradovo deposits (Bulgaria) was determined in ultrapure, tap, mineral, and coal mine waters in order to evaluate their desorption and adsorption properties. The tuffs are Ca-K-Na and contain clinoptilolite (90 and 78wt.%, respectively), plagioclase, sanidine, opal-CT, mica, quartz, montmorillonite, goethite, calcite, ankerite, apatite, and monazite. The desorption properties are best revealed during the treatment of ultrapure, tap, and mineral water, whereas the adsorption properties are best manifested in coal mine water treatment. The concentrations of Al, Si, Fe, Na, Mn, F, K, Pb, and U increase in the treated ultrapure, tap, and mineral water, while the content of K, Be, Pb, and F increase in the treated mine water. The tuffs show selective partial or complete adsorption of Na, Mg, Sr, Li, Be, Mn, Fe, Co, Ni, Cu, Zn, Al, Pb, U, and SO<sub>4</sub><sup>2–</sup>. They demonstrate the ability to neutralize acidic and alkaline pH. Sources of F are presumed to be clinoptilolite and montmorillonite. The usage of zeolitized tuffs for at-home drinking water treatment has to be performed with caution due to the migration of potentially toxic and toxic elements.

**Keywords:** natural clinoptilolitized tuffs; Bulgaria; mineral and chemical composition; trace elements; adsorption; desorption; water treatment

# 1. Introduction

The ion exchange, adsorption, and molecular sieve properties of natural, modified natural, and synthetic zeolite minerals, caused by the specifics of their crystal structure, determine their broad range of applications, such as industry (petroleum refining, petrochemical production, solar thermal collectors, gas separation including  $CO_2$  capture and conversion, and building industry), agriculture (livestock feeding additives, odor control, soil fertilizers, and remediation), environmental protection (water and wastewater purification and radioactive waste site remediation/decontamination), and human and veterinary medicine (nutrition supplements) [1–6]. Access to high-quality drinking water on a global scale is still limited [7]. This problem demands the usage of water (natural and waste), which needs prior purification from different impurities and contaminants (organic and inorganic substances), as well as microorganisms. There is an established methodology for water treatment in treatment plants to obtain safe drinking water depending on the original water source [8,9]. Despite the established methods for the purification of drinking waters, in some cases, modified natural and synthetic zeolites are used for the removal of heavy metals (Cu, Cd, Pb, and As), fluorine, and  $NH_4^+$  [10–13]. Since ancient times, zeolites were used for drinking water purification [14].

Recently, there has been a global trend to use natural zeolites for healthcare purposes (detoxification) at home. This trend includes 1) zeolite powder as a nutritional supplement for drinking; and 2) zeolite granules for table water improvement. Usually, the recommended usage of the sold granulated "zeolite supplements" is through soaking the



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**Copyright:** © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). zeolitized tuff particles of variable sizes in containers with high-quality water, while the powdered zeolite has to be consumed mixed in water or fresh fruit juice. In most cases, there is no info about the origin of the raw material and whether and how it has been modified. The state of zeolites as a nutritional supplement for human consumption is still not established. The European Union (EU) Regulation 651/2013 [15] authorizes the utilization of sedimentary clinoptilolite (clinoptilolite zeolitized tuff) as feed additive for all animal species if the natural zeolite raw material meets the requirements, i.e., clinoptilolite content  $\geq$ 80%, clay mineral content  $\leq$ 20%, and other silicate minerals (opal-CT, quartz, plagioclase, feldspar, and mica) with and overall content between 20 and 30%. The EU Regulation 744/2012 [16] defines the maximum permissible levels of hazardous inorganic components, such as lead, arsenic, mercury, and fluorine, in the zeolite raw material to be used as feed additives. Currently, there is no official authorization by the EU and respective EU countries' authorities (incl. Bulgaria) on whether clinoptilolite-containing or based materials can be safely introduced as novel food and food additives for human consumption.

In Bulgaria, thick successions of zeolitized pyroclastic rocks cover large areas in the Eastern Rhodopes (Southeastern Bulgaria) ([17–19], etc.) and host several zeolites (mainly clinoptilolite) deposits [20–22]. By origin, they are related to the proximal explosive products of the Early Oligocene acid volcanism that occurred in the area [23,24] and spread tephra across SE, S, and Central Europe [25]. In recent decades, they have been the subject of considerable interest, and new data is being published on their geological setting and conditions of formation [26,27], trace element geochemistry [28,29], the structure of natural and modified clinoptilolite [30,31], and various applications of Bulgarian zeolites ([32–39], etc.).

The aims of this study are (1) to test and confirm the desorption properties of natural zeolites in ultrapure water; (2) to study and evaluate the recent trend of usage of natural zeolites as water improvers with healing effects among the public; and (3) to study the sorption properties of natural zeolites for treatment of waste (mine) waters.

This study represents new and additional information on Bulgarian natural zeolitized tuffs used for the treatment of waters with different physicochemical parameters (pH and EC) and the chemical composition obtained using a set of mineralogical and geochemical methods.

# 2. Materials and Methods

Two 7–8 kg composite samples of Bulgarian zeolitized tuffs from deposits in Eastern Rhodopes were studied. The first one is collected from the Beli Plast quarry (BP) and the second one from an outcrop in the vicinity of the Golobradovo village (GB) (Figure 1, Table 1). The samples were crushed manually into particles with variable sizes (0.1–1.5 cm), as the fine powdery material was not removed. Both samples were quartered and 50 g portions of each were pulverized by a Fritsch planetary ball mill using agate grinding bowls and balls for mineralogical and geochemical studies.

Five different water media were used in this study (Figure 1, Table 1): ultrapure water (dw), tap water (tw), natural mineral (mw) and spring "zeolite" (zmw) waters, and mine water (trn1w). The zmw (mineral water from the area near Beli Plast quarry) was used just for comparison.

The mineral and phase composition was determined using powder X-ray diffraction (XRD) and scanning electron microscopy in conjunction with energy-dispersive X-ray spectroscopy (SEM-EDS). Powder diffraction measurements were carried out using HUBER Guinier Image Plate Camera G670 (Geological Institute, BAS, Sofia, Bulgaria), working in an asymmetric transmission mode, equipped with Ge monochromator on the primary beam, and providing pure Cu K $\alpha$ 1 radiation ( $\lambda$  = 1.540598 Å). X-ray diffraction patterns were collected in the range of 4 to 100° 2 $\theta$  with a step size of 0.005° 2 $\theta$ , simultaneously. The XRD data were processed with Match! software package for phase identification (v. 3.15 and 3.16, Crystal Impact, Bonn, Germany) [40]. A qualitative and semi-quantitative phase analysis was performed using the reference patterns in the Powder Diffraction File database of the International Center for Diffraction Data (ICDD PDF-2) and the Crystallography Open

Database (COD). LaB<sub>6</sub> NIST 660a standard was used to track the instrumental bias in intensity and peak positions. SEM-EDS analyses were carried out using ZEISS EVO 25 LS with an EDAX Trident system (Institute of Mineralogy and Crystallography, BAS, Sofia, Bulgaria), at an accelerating voltage of 15 keV and a beam current of 1 nA.



**Figure 1.** Location of the studied samples. Legend: green stars—water samples; red stars—zeolitized tuffs.

Major element oxide contents (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, Na<sub>2</sub>O, K<sub>2</sub>O, MnO, P<sub>2</sub>O<sub>5</sub>, and SO<sub>3</sub>) in zeolite tuffs were determined using Malvern Panalytical Epsilon 3<sup>XLE</sup> energy-dispersive X-ray fluorescence spectrometer (EDXRF) on fused Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub> pellets made in Pt-Au (95% Pt and 5% Au) crucibles at 1050 °C in the Geochemistry laboratory at the Faculty of Geology and Geography, Sofia University. The same fused pellets were further used for a trace element content measurement using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) using a PerkinElmer ELAN DRC-e ICP-MS equipped with a New Wave UP193-FX excimer laser system (Geological Institute, BAS, Sofia, Bulgaria). The analyses were carried out in four 100 µm diameter spots in each fused pellet at a 10 Hz repetition rate and a 9–10 J/cm<sup>2</sup> homogeneous energy density on the sample. A total of 53 isotope masses were measured throughout the experiment using ICP-MS. External standardization was performed using NIST SRM 610 glass. Data reductions of the analyses were performed using SILLS ver. 1.1.0 software [41] and SiO<sub>2</sub> content (measured by EDXRF) as the internal standard. The reported concentrations for each sample are average values from the four measurements performed on the pellet.

Laboratory water leachates were generated by soaking 100 g portions of the granular samples (BP and GB) in 400 mL of ultrapure water with a pH of 7.5 and mine water with a pH of 2.87 for six days, at room temperature, with single daily stirring for the first four days. In addition, the sample from the Beli Plast (BP) quarry, which is well-known and easily accessible to the public, was also used for the treatment of tap (tw) and natural mineral water (mw) from the Sofia area (Table 1). Some of the water leachates contained suspended material (fine fraction). The water leachates were decanted and then filtrated using paper filters. The 100 mL quantities of each water and leachate filtrated through membrane filters were analyzed for major anion and trace element composition and physicochemical parameters at the Aquaterratest certified laboratory according to the relevant EN and ISO standards. The residual quantities of the filtrated leachates and the

mine water were evaporated at room temperature (~30  $^{\circ}$ C) to dry residue and studied using XRD and SEM-EDS.

Table 1. List of studied samples, sampling locations, and description.

Sample Name	Sample Type	Place of Sampling and Description
BP	Zeolitized tuff (cream-white color)	Samples were collected from the Beli Plast quarry, located to the north of Beli Plast village, 20 km N-NE away from Kardzhali town (Figure 1). The clinoptilolitized pyroclastics belong to the first Early Oligocene acid phase. The samples (~8 kg) were provided by the chief geologist of the quarry operated by Imerys Minerals Bulgaria JSC.
GB	Zeolitized tuff (pale green color)	Samples (~7 kg) were collected from an outcrop located 750 m southeast of the Golobradovo village, 45 km E away from Kardzhali town (Figure 1). The clinoptilolitized pyroclastics belong to the first Early Oligocene acid phase.
dw	Ultrapure water	Produced by Thermo ScientificTM BarnsteadTM Smart2PureTM water purification system.
tw	Tap/drinking water	Drinking water supplied from the Iskar reservoir, Sofia.
mw	Mineral water	Mineral water from springs in the SW area of Sofia with a temperature of 19 °C. Its lithology is related to Late Cretaceous andesitic rocks [42,43].
zmw	Spring water	Spring water, known as "zeolite" water, is water from a borehole with a depth of 170 m, located 500 m NW from the Beli Plast zeolitized tuff quarry. The source lithology is presumed to be Eocene-Early Oligocene volcanic and pyroclastic rocks [44].
trn1w	Mine water	Water taken from the mining area of Troyanovo North mine, Maritsa East, lignite basin. It is formed by precipitation (rain, snow) draining into ditches and other low areas in the open-pit mine and interacts with the organic and mineral matter (coal and clay partings).
BPdw	Water leachate	Water leachate produced by the treatment of ultrapure water with Beli Plast zeolitized tuffs.
GBdw	Water leachate	Water leachate produced by the treatment of ultrapure water with Golobradovo zeolitized tuffs.
BPtw	Water leachate	Water leachate produced by the treatment of tap water with Beli Plast zeolitized tuffs.
BPmw	Water leachate	Water leachate produced by the treatment of mineral spring water from the SW area of Sofia with Beli Plast zeolitized tuffs.
BPtrn1w	Water leachate	Water leachate produced by the treatment of mine water from the Maritsa East lignite basin with Beli Plast zeolitized tuffs.
GBtrn1w	Water leachate	Water leachate produced by the treatment of mine water from the Maritsa East lignite basin with Golobradovo zeolitized tuffs.

# 3. Results

3.1. Mineralogy

3.1.1. Mineral Composition of Zeolitized Tuffs

A major component of the zeolitized tuffs (BP and GB) is clinoptilolite (Table 2, Figures 2 and 3A) as its BP content is higher by 12%. Other minerals characteristic of both tuffs are plagioclase, sanidine, quartz, and opal-cristobalite-tridymite (O-CT), as GB contains more O-CT and sanidine. Celadonite, calcite (Figures 2 and 3B), goethite, and ankerite were identified in GB. Montmorillonite was detected in the fine fractions of the treated ultrapure water samples, which means that in the untreated samples, the clay content is undetectable by XRD. Apatite (Figure 3C) occurs in BP tuff, while monazite occurs mostly as grains with sizes ~1–3  $\mu$ m, rarely up to 20  $\mu$ m in both tuffs (Figure 3D).

Mineral	Zeolitiz	ed Tuffs	Fine-grained Material of Zeolitized Tuffs After Treatment						
-	BP	GB	BPdw	GBdw	BPtw	BPmw			
Clinoptilolite	M (90)	M (78)	M (45)	M (59)	M (67)	M (78)			
Plagioclase	m (1)	m (2.8)							
Sanidine	m (2)	M (3.3)							
Quartz	m (1)	m (1.6)				m (1.3)			
Opal-Cristobalite-Tridymite (O-CT)	M (6.4)	M (7.6)	M (16.4)	M (12)	M (15.7)	M (9.2)			
Mica (Celadonite)		M (3.1)	M (7)	M (13.7)					
Montmorillonite	а	а	M (32)	M (10.3)					
Goethite	а	m (1)							
Calcite		m (1.7)							
Ankerite		а							
Monazite *	а	а	а						
Apatite *	а								

**Table 2.** Semi-quantitative mineralogical composition of samples determined by XRD (in wt.%) and SEM-EDS: major (>3%)—M; minor (1–3%)—m; and accessory minerals (<1%)—a.

\* minerals identified only by SEM-EDS.



**Figure 2.** Powder diffraction patterns of zeolitized tuffs. Abbreviations: Cpt, clinoptilolite; Sa, sanidine; Pl, plagioclase; Qz, quartz; O-CT, opal-cristobalite-tridymite; Cal, calcite; Ank, ankerite; Gth, goethite.



**Figure 3.** SEM back-scattered (BSEI) and secondary electron (SEI) images of (**A**) clinoptilolite crystals filling hollow of a glass shard (SEI, GB); (**B**) clinoptilolite containing calcite with traces of partial dissolution (BSEI, GB); (**C**) apatite crystal and fine clinoptilolite grains associated with gypsum in the filtrated dry residue (BSEI, BPtrn1w); (**D**) monazite crystals and clinoptilolite grains in the filtrated dry residue (BSEI, GBtrn1w). Abbreviations: Cpt, clinoptilolite; Cal, calcite; Ap, apatite; Mnz, monazite; Gp, gypsum.

### 3.1.2. Mineral Composition of Dry Residues

During filtration, micro-sized particles/crystals of the rock-forming and accessory minerals passed through the filter paper into the leachates. This explains their occurrence in the dry residues (Table 2). The major newly formed phases identified in the dry residues from leachates, produced with ultrapure water, are halite and calcite, as calcite has a higher quantity in the Golobradovo leachate (GBdw), whereas halite is more abundant in the Beli Plast leachate (BPdw) (Figure 4A,B). The same minerals were found in the dry residues from the tap and mineral spring waters in larger quantities. Eugsterite occurs in BPmw dry residue (Figure 4B). Discrete phases of Fe and Fe>>Cu were observed in BPdw and GBdw, whereas the Cu>>Sn phase was found in GBdw (Figure 4C) and BPmw.

The dry residue produced from the coal mine water contains a large variety of sulfates (Na–Mg-, Na–Al-, Na–Ca-, Na-, Ca-, Mg-, and Sr-), halite, and sylvite, which form well-shaped crystal aggregates (Table 3, Figures 5–7).



**Figure 4.** SEM back-scattered (BSEI) images of newly formed minerals. (**A**) Calcite crystals among fine clinoptilolite (BPmw); (**B**) calcite and needle-shaped eugsterite crystals in fine clinoptilolite (BPmw); (**C**) discrete Cu>>Sn phase over fine clinoptilolite (GBdw). Abbreviations: Egt, eugsterite; Cal, calcite; Cpt, clinoptilolite.

**Table 3.** Semi-quantitative mineralogical composition of dry residues from mine water and mine water-produced leachates determined using XRD (in wt.%) and SEM-EDS: major (>3%)—M; minor (1–3%)—m; and accessory minerals (<1%)—a.

	Water	Water L	eachates
Mineral	TrN1	BPtrn1w	GBtrn1w
Löweite Na <sub>12</sub> Mg <sub>7</sub> (SO <sub>4</sub> ) <sub>13</sub> ·15H <sub>2</sub> O	M (36.3)	M (16.9)	M (52)
Blödite Na <sub>2</sub> Mg(SO <sub>4</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	M (29.3)	M (12.2)	m (7.7)
Alum-(Na) NaAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O	M (1.9)	m (1.4)	
Tamarugite NaAl(SO <sub>4</sub> )₂·6H <sub>2</sub> O	M (8.5)	M (3.1)	
Cesanite Na <sub>3</sub> Ca <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> OH	M (3.4)		M (4.5)
Eugsterite Na <sub>4</sub> Ca(SO <sub>4</sub> ) <sub>3</sub> ·2H <sub>2</sub> O		M (10.1)	
Glauberite Na <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub>	M (3.7)		
Hexahydrite MgSO <sub>4</sub> ·6H <sub>2</sub> O	M (4.4)	M (36.3)	M (14.8)
Mirabilite Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	M (3.5)		
Gypsum CaSO <sub>4</sub> ·2H <sub>2</sub> O	M (7.6)	M (19.6)	M (16)
Celestine SrSO <sub>4</sub> *	а		
Halite NaCl	m (1.4)	a (0.3)	m (1.2)
Sylvite KCl *	a		
Cu phase *		а	

\* Minerals identified only by SEM-EDS.



2Θ Cu Kα

**Figure 5.** Powder diffraction patterns of dry residues from mine water and mine water-produced leachates.



Figure 6. Cont.



**Figure 6.** SEM back-scattered (BSEI) and secondary electron (SEI) images of sulfates crystalized from coal mine water trn1w. (**A**) Intergrown crystal aggregates of löweite, blödite, cesanite, tamarugite, and mirabilite (BSEI); (**B**) crystals of Alum-(Na) among intergrown aggregates of tamarugite and hexahydrite (BSEI); (**C**) rhombohedral crystal aggregates overgrown by mirabilite and tamarugite (SEI); (**D**) flake-shaped tamarugite aggregates and rounded mirabilite overgrowing prismatic blödite (SEI); (**E**) crust of löweite and tamarugite intergrown crystal aggregates with encrustation of halite (white) (BSEI); (**F**) blödite prismatic aggregates intergrown with gypsum crystals with encrustations of skeletal halite, and individual crystals of sylvite and celestine (BSEI). Abbreviations: Löw, löweite; Blö, blödite; Aum-Na, alum-(Na); Tmr, tamarugite; Csa, cesanite; Mrb, mirabilite; Hhy, hexahydrite; Gp, gypsum; Hl, halite; Clt, celestine; Syl, sylvite.



**Figure 7.** SEM back-scattered (BSEI) images of (**A**) halite cubes in hexahydrite fine matrix (GBtrn1w); (**B**) long prismatic gypsum aggregates among fine-grained clinoptilolite (BPtrn1w); (**C**) crust of anhedral or rounded mirabilite with gypsum crystals (GBtrn1w); (**D**) discrete Cu phase precipitated on gypsum crystal face (BPtrn1w). Abbreviations: Hhy, hexahydrite; Mrb, mirabilite; Gp, gypsum; Hl, halite; Cpt, clinoptilolite; Cu, Cu phase.

The most abundant sulfates are löweite and blödite, occurring mostly as intergrown twinned aggregates of rhombohedral (löweite) and prismatic or anhedral (blödite) crystals (Figure 6A,C–F). They are overgrown by less abundant flake-shaped tamarugite (Figure 6A–E), platy-shaped cesanite (Figure 6A), cube-trisoctahedron-dodecahedral crystals of Alum-(Na) (Figure 6B), rounded aggregates of mirabilite (Figure 6C,D), prismatic crystals of hexahydrite (Figure 6B), prismatic gypsum (Figure 6E), and glauberite. Halite, sylvite, and celestine occur in the smallest quantity as overgrowing encrustations (halite) (Figure 6E,F) and individual crystals (celestine and sylvite) (Figure 6F).

The phases crystallized in dry residues from the treated mine water with zeolite tuffs are less in number and there is a distinct difference among their diversity (Table 3, Figures 5 and 7), which is probably due to precipitation/crystallization from waters with different pH, i.e., acidic (BPtrn1w) and neutral (GBtrn1w), as well as the impact of the used zeolitized tuffs for treatment with relatively different chemical and mineral composition. Except for löweite, blödite, hexahydrite, gypsum, and halite (Figure 7A,B), which occur in different quantities compared to the trn1w dry residue, the other minerals of tamarugite, cesanite, mirabilite (Figure 7C), and alum-(Na) are determined only in one of the two dry residues, as glauberite is not formed. Instead of glauberite, another Na–Ca sulfate occurs, i.e., eugsterite as a major constituent. Discrete Cu phases are found using SEM-EDS in BPtrn1w (Figure 7D).

### 3.2. Geochemistry

### 3.2.1. Chemical Composition of Zeolitized Tuffs

The contents of 52 elements were determined in the BP and GB (Table 4). The concentrations of most elements in both samples are relatively similar. However, the GB sample is enriched in Na, Ca, Ba, LREE, Gd, W, Mn, Co, and Pb, whereas BP is enriched in K, Sr, Sb, and U. Based on the major alkaline and alkaline earth elements content, the studied zeolitized tuffs are K-Ca-Na (Beli Plast) and Ca-K-Na (Golobradovo). Both samples were compared to the upper continental crust (UCC) [45] to reveal any specific geochemical signatures inferred by the established coefficient of enrichment (CE). The following elements were found with CE > 1.5: 1) BP—Ag<sub>17.7</sub> > Cs<sub>5.3</sub> > U<sub>5.0</sub> > Bi<sub>4.2</sub> > S<sub>3.7</sub> > Rb<sub>3.1</sub> > In<sub>3.0</sub> > Sn<sub>2.8</sub> >  $Sb_{2.5} > (Pb, Th)_{2.3} > Nb_{1.9} > P_{1.6} > Ta_{1.5}; 2) GB - Cs_{5.1} > Bi_{4.1} > In_{3.8} > U_{3.4} > Pb_{3.3} > Sn_{3.1} > Cs_{5.1} > Bi_{4.1} > In_{3.8} > U_{3.4} > Pb_{3.3} > Sn_{3.1} > Cs_{5.1} > Bi_{4.1} > In_{3.8} > U_{3.4} > Pb_{3.3} > Sn_{3.1} > Cs_{5.1} > Bi_{4.1} > In_{3.8} > U_{3.4} > Pb_{3.3} > Sn_{3.1} > Cs_{5.1} > Bi_{4.1} > In_{5.1} > I$  $S_{2,6} > (Rb, Th)_{2,4} > P_{1,9} > Nb_{1,8} > (W, Sb)_{1,7}$ . The normalized patterns of rare earth elements and yttrium (REY) to UCC [46] show very distinct negative Eu/Eu\* anomaly (0.5-0.7), slight LREE enrichment ( $La_N/Sm_N$ —1.7–1.9,) in both samples, but a lower LREE in BP compared to GB, weak positive  $Y/Y^*$  anomaly (1.1) in BP, and relative Tm, Yb, and Lu enrichment in BP. The zeolitized tuffs have different concentrations of REY, BP-83 ppm, and GB—133 ppm. They are incorporated mostly in silicate minerals (plagioclase, sanidine, mica, clinoptilolite, O-CT, and in accessory minerals (apatite, monazite)).

### 3.2.2. Chemical Composition of Waters Used for Treatment

The drinking waters (tw and mw) used to treat the zeolitized tuffs have low mineralization (EC  $\leq$  500), as the tap water has a neutral pH, while mineral water (mw) has an alkaline pH (Table 5). According to the major ion components, tap water can be classified as a bicarbonate-calcium type. Both mineral waters can be classified as a bicarbonate-sulfate-sodium type [42]. The zmw contains twice as much sodium and nearly three times as much bicarbonate and carbonate ions, as well as a significantly higher content of fluorine than mw (1.1 mg/dm<sup>3</sup>), but has a lower content of nitrates, sulfates, potassium, calcium, and magnesium. Compared to the requirements listed in Regulation No. 9 [47], all these waters are suitable for drinking.

		~ )	211101															
Elements																		
Ref./Sample	Na %	Mg %	A1 %	K %	Ca %	Rb	Sr	Ŷ	Zr	Nb	Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
UCC	2.42	1.50	8.15	2.32	2.56	84	320	21	193	12	4.9	624	31	63	7.1	27	4.7	1.0
BP (mean)	0.62	0.40	6.45	2.70	1.89	259	243	13.6	94.5	22.6	26.2	21.5	16.5	31.2	2.9	9.0	1.4	0.22
BP (SD)						1.3	4.7	0.5	1.4	0.8	0.4	1.1	0.5	0.8	0.2	0.3	0.2	0.01 <sup>a</sup>
GB (mean)	1.13	0.57	6.35	1.79	2.78	203	161	14.6	105.7	21.3	24.8	57.3	29.4	55.5	5.3	16.3	2.3	0.25
GB (SD)						5.4	1.8	0.3	0.9	0.8	0.8	3.3	0.7	0.8	0.1	1.3	0.4	0.02 <sup>a</sup>
Elements																		
Ref./Sample	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Hf	Ta	W	Si %	Р	S	Sc	Ti	V	Cr
UCC	4.0	0.7	3.9	0.83	2.3	0.30	2.0	0.31	5.3	0.9	1.9	31.1	200	621	14.0	3800	97	92
BP (mean)	1.4	0.3	2.2	0.40	1.4	0.28	2.1	0.27	3.4	1.3	< 0.4	30.74	318	2516	3.96	640	9.4	36.8
BP (SD)	0.3	0.02	0.06	0.02	0.2	0.05	0.2	0.03	0.2	0.1			43.9	276	0.4	13.1	0.7	5.8
GB (mean)	2.4	0.3	2.4	0.56	1.5	0.22	1.5	0.29	3.6	1.3	3.1	30.08	386	1603	4.02	762	12.9	34.7
GB (SD)	0.8	0.03	0.4	0.06	0.3	0.02	0.2	0.04	0.4	0.1	1.0		40	273	0.4	17.1	0.8	7.6
Elements																		
Ref./Sample	Ν	/In	Fe %	Со	Ni	Cu	Zn	Ga	As	In	Sn	Tl	Pb	Bi	Th	U	Ag	LOI %
UCC	19	000	3.91	17.3	47	28	67	17.5	4.8	0.056	2.1	0.9	17	0.16	10.5	2.7	0.053	
BP (mean)	2	07	0.55	< 0.5	5.4	10.4	37.9	16.5	3.7	0.17	5.8	0.8	38	0.67	24.5	13.6	0.94	13.13
BP (SD)	6	5.0			1.2 <sup>a</sup>	1.9	6.4	1.1	0.3 <sup>a</sup>	0.02	0.6	0.04	0.8	0.05	0.6	0.2	0.2 <sup>a</sup>	
GB (mean)	3	49	0.60	0.9	5.7	12.2	36.4	14.2	<3.9	<0.21	6.6	0.6	57	0.65	24.7	9.1	<0.76	14.09
GB (SD)	8	3.8		0.3 <sup>a</sup>	0.3 <sup>a</sup>	1.9	2.4	0.9			0.5	0.1	1.3	0.07	1.2	0.4		

**Table 4.** Chemical composition of the zeolitized tuffs (in ppm, except otherwise cited). Major elements (wt.%) are analyzed by XRF while trace elements are analyzed by LA-ICP-MS.

UCC—upper continental crust chemical composition [45]. SD—standard deviation calculated based on four measurements. SD is not calculated for major elements, which have only one measurement. <sup>a</sup>—standard deviation calculated based on two or three measurements.

		Regulations			Wa	ters				Lead	chates		
Elements/Ions	[47]	[48]	[49]	tw	mw	zmw	trn1w	BPdw	GBdw	BPtw	BPmw	BPtrn1w	GBtrn1w
						Lithoph	nile						
Li			0.0011	< 0.05	< 0.05	< 0.05	0.45	< 0.05	< 0.05	< 0.05	< 0.05	0.32	0.27
Be		0.0002	0.001	< 0.01	< 0.01	< 0.01	0.052	< 0.01	< 0.01	< 0.01	< 0.01	0.17	< 0.01
Na	200		6.30	5.80	54.23	127	3029	16.05	42.7	22.9	42.4	1320	1386
Mg	80		4.10	2.47	1.12	0.21	876	12.99	4.10	1.28	0.26	554	600
AĬ	0.2		0.24	0.031	0.021	< 0.05	77.8	29.26	19.0	3.62	0.024	63	< 0.01
Κ			2.30	3.43	3.42	0.55	1.76	13.02	11.5	5.23	7.10	59	24
Ca	150		15.00	11.8	6.04	1.09	441	11.73	9.10	3.84	10.3	465	444
Sr			0.08	0.070	0.07	0.023	10.25	0.055	0.03	0.01	0.008	0.955	0.632
Ba		1.0	0.054	0.009	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.013
						Non-me	tals						
В	1.0	1.0	0.0130	< 0.05	< 0.05	0.20	2.18	< 0.05	< 0.05	< 0.05	< 0.05	2.08	1.88
С			11.00	11.7	12.9	45.8	<bdl< td=""><td>7.03</td><td>23.43</td><td>11.75</td><td>11.71</td><td><bdl< td=""><td>11.71</td></bdl<></td></bdl<>	7.03	23.43	11.75	11.71	<bdl< td=""><td>11.71</td></bdl<>	11.71
$HCO_3^-$				59.5	65.4	184.1	<10.0	35.7	119	59.7	59.5	<10.0	59.50
$CO_{3}^{2-}$				<10.0	<10.0	48.02	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0	<10.0
N			0.23	0.19	3.33	0.08	2.98	0.18	0.30	0.41	3.78	7.84	6.48
$NO_3^-$	50	50.0		0.84	14.77	0.35	nd	0.78	1.32	1.80	16.76	33.0	26.53
$NH_4^+$	0.5	4.0		< 0.01	< 0.01	< 0.01	3.84	< 0.01	< 0.01	< 0.01	< 0.01	0.53	0.63
F-	1.5	1.7	0.09	< 0.1	0.11	1.10	3.30	0.39	0.14	0.37	0.33	1.35	18.31
Si			6.50	0.70	14.65	18.66	54.71	168.9	125.7	36.35	21.98	58.76	7.07
S			3.70	3.39	16.31	7.16	3685	13.4	0.32	4.31	16.98	1965	1988
$SO_4^{2-}$	250	250		10.13	48.78	21.40	11018	40.07	0.95	12.90	50.78	5874	5944
Cl	250	200	7.80	9.37	28.01	11.08	200	1.43	2.57	7.99	28.07	221	230
						Siderop	hile						
V		0.01	0.0010	< 0.01	< 0.01	< 0.01	0.062	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Cr	0.05	0.05	0.0002	< 0.01	< 0.01	< 0.01	0.023	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Mn	0.05	1.0	0.0120	< 0.01	0.025	< 0.01	38.26	0.861	0.149	0.085	< 0.01	19.23	21.69
Fe	0.20	1.0	0.67	0.052	< 0.005	< 0.005	167	25.25	14.31	2.79	0.175	1.71	0.089
Со		0.02	0.0009	< 0.01	< 0.01	< 0.01	0.001	< 0.01	< 0.01	< 0.01	< 0.01	0.576	0.353
Ni	0.02	0.02	0.01	< 0.01	< 0.01	< 0.01	3.27	< 0.01	< 0.01	< 0.01	< 0.01	2.75	1.04

**Table 5.** Physicochemical parameters, chemical composition of waters, and water leachates (mg/dm<sup>3</sup>).

		Regulations			Waters				Leachates					
Elements/Ions	[47]	[48]	[49]	tw	mw	zmw	trn1w	BPdw	GBdw	BPtw	BPmw	BPtrn1w	GBtrn1w	
						Chalcop	hile							
Cu	2.0	1.0	0.01	< 0.01	< 0.01	0.019	0.557	< 0.01	< 0.01	< 0.01	< 0.01	0.132	0.019	
Zn	4.0	5.0	0.01	0.015	< 0.01	< 0.01	3.52	0.114	0.058	0.019	< 0.01	1.07	0.146	
As	0.01	0.10	0.0004	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.009	< 0.01	< 0.01	< 0.01	< 0.01	
Cd	0.01	0.005	0.08	< 0.01	< 0.01	< 0.01	0.016	< 0.01	< 0.01	< 0.01	< 0.01	0.012	< 0.01	
Sn			0.00004	< 0.01	< 0.01	< 0.01	< 0.01	0.016	0.009	< 0.01	< 0.01	< 0.01	< 0.01	
Pb	0.01	0.05	0.005	< 0.01	< 0.01	< 0.01	0.019	0.039	0.037	0.008	< 0.01	0.032	< 0.01	
						Radioac	tive							
U	0.03	0.03 *	0.001	< 0.01	<0.01	< 0.01	0.119	0.030	< 0.01	<0.01	< 0.01	0.098	< 0.01	
						Other	ſS							
pН	6.5–9.5	5.5–9.0		7.64	9.55	8.85	2.87	7.63	7.39	7.72	7.66	3.40	7.34	
Dry residue (mg/dm <sup>3</sup> )				84	178	200	13650	44	84	56	152	7830	8010	
EC ( $\mu$ S/cm)	2000	1000		112	279	500	14470	137	191	138	282	8730	9170	

Table 5. Cont.

\* The value is from [47] because there is no value for U in [48]. nd, not determined. < bdl, below detection limits.

According to the major ion content, the mine water is the sulfate-sodium type with a pH of 2.87 and EC of 14,470  $\mu$ S/cm. The water also contains Mg and Ca in high quantities, as well as NH<sub>4</sub>, Si, and Cl. Compared to the third category surface water [48], the mine water contains the following elements with inflated values (times of increase as subscript value): Be<sub>261</sub> > Fe<sub>167</sub> > Ni<sub>164</sub> > Co<sub>51</sub> > (SO<sub>4</sub><sup>2-</sup>)<sub>44</sub> > Mn<sub>38</sub> > V<sub>6.2</sub> > U<sub>4</sub> > Cd<sub>3.2</sub> > B<sub>2.2</sub> > F<sub>1.9</sub>. Compared to the average element contents of surface water [49], the values of most ions are elevated, as the highest contents are for S<sub>996</sub> < Co<sub>1133</sub> < Mn<sub>3190</sub>.

# 3.2.3. Chemical Composition of Water Leachates (Treated Waters)

Both leachates from ultrapure water (BPdw and GBdw) retain neutral pH (7.4–7.6) and show an increase of EC (137 and 191  $\mu$ S/cm) and dry residue, respectively (Table 5). Increased concentrations of Al, Mn, Fe, and Pb are found in the leachates in comparison to Regulation No. 9 and Fe in comparison to Regulation No. 12 (Figure 8A); whereas the comparison with average contents of surface waters [49] reveals raised contents of more elements, such as Al, Si, Sn, Mn, Fe, F, Zn, As, U, and others.

The leachates produced by the treatment of tap water (tw) and mineral water (mw) model use natural zeolites as a water purifier and improver for domestic purposes (drinking). They show insignificant changes in the EC and decreases in the mineral water pH to neutral. However, considerable migration of Al, Si, Fe, and Na from the tuff is detected in the tap water leachate (BPtw), whereas in mineral water leachate (BPmw), only F and K and, to a lesser extent Ca and Si, have elevated contents.

The comparison with Regulation No. 9 shows that the contents are within the maximum permissible levels in BPmw, whereas in BPtw, Al, Fe, and Mn have exceeded contents. However, this increased mineralization will not be observed when the tuff is soaked in a larger volume as it is performed at home (Figure 8B,C).

The treated with natural zeolitized tuffs mine water show a significant decrease in most element concentrations (Na, Mg, Al, Sr, S, and others), but the degree of content decrease among BPtrn1w and GBtrn1w is different. An increase of K is determined in both leachates after treatment, as in BPtrn1w is higher. Furthermore, Be and Pb also increase in BPtrn1w, whereas F increases in GBtrn1w. The NO<sub>3</sub><sup>-</sup> ion is detected in both treated waters, which can be related either to tuffs or air influence. The pH of treated waters (leachates) changes differently from neutral after treatment with Golobradovo zeolitized tuff to very weakly increased to 3.40 with Beli Plast zeolitized tuff. Compared to Regulation No. 12 (Figure 9) in BPtrn1w, the content of sulfates, Mn, and Co decreased twice; the content of Fe was almost completely removed; V was not detected; and the Ni, Cd, and U content slightly decreased, but the content of Be increased. In GBtrn1w, the Fe content is within permissible levels, and U, Cd, V, and Be are completely removed, but F increases. Compared to the average element contents of sulface water [49], the trend of element content decreases. Additionally, the increase of K in BPtrn1w and F in GBtrn1w is also confirmed.



Figure 8. Cont.



**Figure 8.** Behavior of zeolitized tuffs in different water media. (A) Desorption properties in ultrapure water; (B) adsorption and desorption in tap water; and (C) adsorption and desorption in mineral water.



Figure 9. Behavior of zeolitized tuffs in mine water with acidic pH.

### 4. Discussion

# 4.1. Natural Zeolites as Desorbents in Ultrapure Water

The content of the alkaline and alkaline-earth elements (exchangeable ions) in the zeolitized tuffs in Bulgaria vary laterally and vertically in the deposits [20,21,31,50]. Among all four studied zeolitized tuffs (this study and Yossifova et al. [51]), Golobradovo tuffs have the highest Na content, 1.13 wt.%, whereas the dominant element content of the Most zeolitized tuffs and the zeolite supplements is K–Ca–Na. According to recent mi-

croprobe data [29], the clinoptilolite from the Beli Plast and Golobradovo deposits have a predominant Ca-K content, whereas Na is below 0.3 apfu.

The results obtained in the present treatment of ultrapure water with natural zeolitized tuffs confirm the results reported previously by Yossifova et al. [51]; although the pH of the ultrapure water was slightly acidic (pH = 5) and the samples were different, one from the Most deposit and one sold as zeolite supplement. Current results confirm the migration of Si, Al, Na, K, and Ca. Sr, Mg, Fe, Mn, Zn, and S in ultrapure water as the contents are higher (Figure 8A), and other elements also occur—F, Sn, Pb, and U. This could be a result of the difference in mineral and chemical composition of the zeolitized tuffs and pH of the ultrapure water, which is neutral in this study.

During treatment of ultrapure water, the zeolitized tuffs behave as desorbent because the ions in ultrapure water, which can be adsorbed, are H<sup>+</sup> and OH<sup>-</sup>, and all detected ions of elements in the leachates may come from the tuffs. Since clinoptilolite is a major mineral in the tuffs, such migration of ions is probably related to decationization [52,53], which apparently also occurs on a small scale together with desilication and dealuminization at neutral pH [54–56]. The Si content in BPdw and GBdw is higher than "zeolite" water and the leachates produced with ultrapure water reported in Yossifova et al. [51], which is due to the neutral pH of the ultrapure water (pH = 7.0) because Si migrates easier in neutral aqueous media [57]. The presence of other ions such as  $NO_3^-$  and  $HCO_3^-$  (probably dissolved from the air) and  $F^-$  may facilitate the migration of Si. Unlike Si, Al migrates better in acidic media (pH  $\leq$  5), as reported in [57] and this corresponds to dealumination. The higher rate of migration of Al in neutral media in this case is related to the higher rate of migration of Si. Although the Na<sup>+</sup>,  $HCO_3^-$ , and  $SO_4^{2-}$  content is higher in "zeolite" water (zmw), in comparison to BPdw and GBdw, the bulk ionic composition of the leachates is relatively similar. Possible sources for migrated elements could be (1) clinoptilolite (Na, K, Ca, Mg, Sr, Al, Si, and Fe); (2) clay minerals (all aforementioned elements, Mn, Zn, S, F, U, and Pb); (3) amorphous to micro-crystalline phase (O-CT) (Fe, Mn, Si, Al, Mg) [58]; (4) calcite and ankerite (Ca, Mg, Mn, Fe, and Sr); (5) geothite (Fe, Mn); and (6) efflorescent sulfates, chlorides (Na, Ca, Mg, Cl, and F).

Fluorine was detected in preserved volcanic glass in tuffs related to the same volcanic eruption, where its concentration varies between 0.08 and 0.14 wt.% (personal communication Prof. Peter Marchev, [59]). Clinoptilolite and montmorillonite crystallize from the volcanic ash glass. Thus, it can be assumed that F is included in the crystal lattice of these minerals. According to Pulido et al. [60] and Fischer [61], fluoride anions are incorporated in small cages, forming  $[SiO_4F]^-$  trigonal bipyramids. In montmorillonite, fluoride anion occurs as adsorbed species in the interlayer together with other anions (OH<sup>-</sup> and Cl<sup>-</sup>) and water molecules. Thus, it can be more easily desorbed in water media. Since weak decationization and dealumination are presumed to occur in natural zeolites treated with ultrapure water, they are accompanied by some desilication in neutral conditions. These processes are relatively weaker in GBdw compared to BPdw, which might be due to the higher Si/Al in GB clinoptilolite [29]. When desilication affects such [SiO<sub>4</sub>F]<sup>-</sup> polyhedron from the framework in the near-surface area, then  $F^-$  would be released together with Si. It is more likely to assume that F<sup>-</sup> migrates from clinoptilolite rather than montmorillonite because it is a major mineral in the tuffs, unlike montmorillonite. On the other hand, the clay minerals and amorphous phases would more easily desorb the  $F^-$  in water media, replacing it with  $OH^{-}$  and  $H_{2}O$  molecules.

Chemical analyses of clinoptilolite from both deposits report the presence of Fe in varying quantities [26,31,50], which occurs as Fe<sup>3+</sup> in the position of Al<sup>3+</sup>. Other sources of Fe could be montmorillonite, goethite, carbonates (calcite, ankerite), and opal. Manganese is rarely detected in clinoptilolite [62]. However, it occurs in the clay minerals, carbonates, goethite, and manganese oxide-hydroxides in the zeolitized tuff.

#### 4.2. Natural Zeolites as Sorbents for Drinking Water Purification and Quality Improvement at Home

The migration behavior of elements from the zeolitized tuffs during the treatment of drinking water (mineral and tap water), which contains dissociated ions, is different compared to ultrapure water treatment. Since the tap water has very low mineralization (Table 5), its behavior as desorption eluent during treatment is somewhat similar to the ultrapure water, although weaker. The mineralization of the original tap water after treatment weakly increases, especially Al, Si, Fe, and Na. However, the content of Al and Fe becomes higher than the permissible levels listed in Regulation No. 9 [47] (Figure 8B). Still, their contents are lower than those in BPdw and GBdw, which proves that the decationization process is limited by the presence of other cations in the aqueous media. The total cation and anion content of the BPtw becomes close to the original mineral water mw (also with low mineralization) (Table 5) used in the treatment. On the other hand, the total mineralization of the mineral water after treatment with the zeolitized tuff is preserved with insignificant variations of the ionic content (Figure 8C). It is important to note, however, that as a result of this treatment, the water is enriched in K and F, whereas Mg and Sr are adsorbed. The pH of the treated mineral water neutralizes (Table 5) similarly to the experiment of Philippidis and Kantiranis [63], even when the natural zeolites are not pretreated. Since the waters in different regions of the country have a different composition (hard, with a higher content of calcium and bicarbonates), the results after their treatment with natural zeolites would be different from those presented in this work. The mineral water used in this experiment is widely available among people in Sofia and its surroundings.

# 4.3. Natural Zeolites for Coal Mine Water Treatment

One of the fundamental applications of natural zeolites is their usage for wastewater treatment for the removal of  $NH_4^+$ , metalloids  $(As^{3+/5+}, Sb^{3+})$ , transition metals  $(Cu^{2+}, Ag^+, Zn^{2+}, Cd^{2+}, Hg^{2+}, Pb^{2+}, Cr^{3+}, Mo^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+})$ , radioactive Sr, Cs, and U [3,5,6,10,64–66]. Research on the application of Bulgarian natural zeolites as wastewater/industrial water treatment agents is published in [32,36,37,39,62].

In this study, the wastewater is a natural product formed in the coal mine from precipitation and is acidic with a high content of sulfates. The results after treatment of such water show the natural capacity of the zeolitized tuffs as sorbent without any pretreatment/activation for specific utilization. The trn1w contains NH4<sup>+</sup> and Na<sup>+</sup>, which are usually used as reagents during an ion exchange capacity estimation. In this case, they are readily adsorbed to various degrees (partially to completely) together with Li, Na, Mg, Sr, S, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and U (Figure 9). It should be noted that zeolite from Golobradovo completely adsorbed Be, Al, V, Cr, Cd, Pb, and U and almost completely adsorbed Sr, Fe, Cu, Zn, Co, Ni, Si, and Li. One of the reasons for this is probably related to the change in pH in the water media from 2.87 to 7.34, which, respectively, changes the migration ability of the ions. This change in pH is supposedly related to the partial dissolution of calcite (1.7% in Golobradovo, Table 2, Figure 3B) from the acidic water and the appearance of  $HCO_3^{-}$  in GBtrn1w. The neutralization of the water leachate marks the complete adsorption of U because, at  $pH \ge 5$ , the U is completely adsorbed as reported by [5,67–69]. Unlike the leachate from Golobradovo, the pH of Beli Plast (BPtrn1w) did not change much and remained acidic (pH = 3.40), which explains why U and the other transition metals (Cu<sup>2+</sup>, Zn<sup>2+</sup>, Cd<sup>2+</sup>, Pb<sup>2+</sup>, Fe<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup>) remain in the leachate at a higher content. On the other hand, K<sup>+</sup> and NO<sub>3</sub><sup>-</sup> are released in the leachates from both tuffs, Be<sup>2+</sup> and Pb<sup>+</sup> (from Beli Plast) and F<sup>-</sup> (from Golobradovo.) So far, zeolites have only been considered as possible sorbents of fluorides from fluoride-rich waters (purification) [12,13,70,71], but not as a possible source. Our study shows that  $F^-$  can be exchanged/desorbed from the tuffs into the aqueous media. As suggested in 4.1, the sources for F<sup>-</sup> migration could be clinoptilolite, clay minerals (montmorillonite), and amorphous phases. Adsorption of Al and Si, and release of F<sup>-</sup> are observed in the GBtrn1w which could suggest an extraction of  $F^-$  from the framework ([SiO<sub>4</sub>F]<sup>-</sup>) and replacement with Al<sup>3+</sup> and Si<sup>4+</sup>, which stabilize the framework. Fluoride is also included in apatite and mica

(celadonite), but it is less likely for  $F^-$  to be extracted from apatite in such aqueous media. However, since trn1w is from the coal mine, it may contain fulvic and humic organic acids (yellowish-rusty color of the water), which can promote some  $F^-$  leaching from celadonite (up to 3.1% in Golobradovo zeolitized tuff). This could explain the increase of  $F^-$  in GBtrn1w compared to BPtrn1w where its content decreased, e.g., adsorbed by BP zeolite.

The increase of  $Be^{2+}$  content in BPtrn1w can be explained with a better migration of Be in the acidic aqueous media (pH < 4) enriched with Na and sulfates and suitable desorbing host minerals in the tuffs, such as montmorillonite and goethite. The desorption of NO<sub>3</sub><sup>-</sup> ions occurs in all leachates (Table 5). However, the highest rate of desorption is determined in BPtrn1w and GBtrn1w. It is probably related to the sulfate-rich aqueous solution independently from the pH of the media. The desorption of K<sup>+</sup> is observed in all leachates, but higher contents are detected in the BPtrn1w, which is due to the higher content of K in Beli Plast tuff and the acidic pH of the leachate.

Both zeolitized tuffs (Beli Plast and Golobradovo) are reported to have the highest cation-exchange capacity (149.2 and 152.4 meq/100 g), as Golobradovo tuffs have a larger specific surface, adsorption, and pore volume than Beli Plast tuffs; thus more suitable for adsorbing radionuclides [22]. According to previous researchers [22,32], both tuffs are also suitable for waste/industrial water purification.

### 4.4. Ion Incorporation in Newly Formed Minerals

All leachates produce dry residues after water evaporation (at room temperature). A lower content of dry residues is formed from the treated ultrapure and drinking waters and is represented by halite and calcite (Figure 4). The highest content of dry residue is produced from the mine water, followed by the mine water-produced leachates (Tables 3 and 5, Figures 5–7). Dominant minerals among the newly formed phases are sulfates of the main cations Na–Mg, Na–Ca, Na–Al, Ca–, and Mg–. Halite is formed in much smaller quantities. The discrete phases with Fe–, Cu–, Fe>>Cu–, and Cu>>Sn– composition found in this study were also reported in the previous study of Yossifova et al. [51]. These minerals incorporate other ions from the aqueous solutions, which are in much lower content and may fit in the respective crystal lattice based on their oxidation state.

# 5. Conclusions

The investigated natural inactivated zeolitized tuffs, besides being sorbents with specific characteristics (different for BP and GB), are also desorbents. These properties are determined by their mineral and chemical composition. Their desorption properties are best manifested in the treatment of ultrapure water, which mineralizes as a result of desilication, dealuminization, and decationization of clinoptilolite. The desorption and adsorption properties also stand out in their interaction with waters of different pH and ionic compositions. The obtained results justify the use of natural zeolites in everyday life as sorbents-improvers of low-mineralized drinking water, but their use should be moderate and cautious considering the fact that the treated water is additionally mineralized. With long-term use of such waters, Al, Si, Fe, Mn, Pb, U, and F will regularly enter the human body, regardless of the fact that they will be in low concentrations. On the other hand, the direct consumption of finely ground zeolitized tuffs is not recommended due to the presence of other minerals (quartz, opal-CT, feldspar, plagioclase, clay minerals, and mica). This should also be taken into account when using them as a food supplement in animal husbandry. In regards to drinking water, in tap water, the Beli Plast zeolitized tuffs adsorbed Mg, Sr, and Ca, whereas in mineral water, they absorbed Mg, Sr, and Na. In the treated mine water, both zeolitized tuffs show adsorption selectivity towards Na, Mg, Sr, Li, Mn, Fe, Co, Ni, Cu, Zn,  $SO_4^{2-}$ . Golobradovo zeolitized tuff completely adsorbed Be, Al, Pb, and U. Both zeolitized tuffs neutralize the pH of the waters. The Golobradovo zeolitized tuff increases the pH of the mine water, whereas Beli Plast zeolitized tuff decreases the pH of the mineral water. The present study recommends further investigation of the mineral and chemical composition of the zeolitized tuffs, particularly with regard to F

concentrations and their migration behavior. Both zeolitized tuffs can be used for coal mine water treatment. They could be a potential source for Si and Al extraction in the future.

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