energies

Article

Research on Fresh and Hardened Sealing Slurries with the Addition of Magnesium Regarding Thermal Conductivity for Energy Piles and Borehole Heat Exchangers

Tomasz Sliwa *, Tomasz Kowalski, Dominik Cekus and Aneta Sapińska-Śliwa

Laboratory of Geoenergetics AGH, AGH University of Science and Technology in Krakow, al. Adama Mickiewicza 30, 30-059 Krakow, Poland; tkowal@agh.edu.pl (T.K.); dominik.cekus@gmail.com (D.C.); ans@agh.edu.pl (A.S.-Ś.)

* Correspondence: sliwa@agh.edu.pl; Tel.: +48-12-617-22-17

Abstract: Currently, renewable energy is increasingly important in the energy sector. One of the so-called renewable energy sources is geothermal energy. The most popular solution implemented by both small and large customers is the consumption of low-temperature geothermal energy using borehole heat exchanger (BHE) systems assisted by geothermal heat pumps. Such an installation can operate regardless of geological conditions, which makes it extremely universal. Borehole heat exchangers are the most important elements of this system, as their design determines the efficiency of the entire heating or heating-and-cooling system. Filling/sealing slurry is amongst the crucial structural elements. In borehole exchangers, reaching the highest possible thermal conductivity of the cement slurry endeavors to improve heat transfer between the rock mass and the heat carrier. The article presents a proposed design for such a sealing slurry. Powdered magnesium was used as an additive to the cement. The approximate cost of powdered magnesium is PLN 70–90 per kg (EUR 15–20/kg). Six different slurry formulations were tested. Magnesium flakes were used in designs A, B, C, and magnesium shavings in D, E and F. The samples differed in the powdered magnesium content BWOC (by weight of cement). The parameters of fresh and hardened sealing slurries were tested, focusing mainly on the thermal conductivity parameter. The highest thermal conductivity values were obtained in design C with the 45% addition of magnesium flakes BWOC.

Keywords: geothermal energy; cement slurry; borehole heat exchangers; sealing slurries

check for updates

Citation: Sliwa, T.; Kowalski, T.; Cekus, D.; Sapińska-Śliwa, A. Research on Fresh and Hardened Sealing Slurries with the Addition of Magnesium Regarding Thermal Conductivity for Energy Piles and Borehole Heat Exchangers. *Energies* **2021**, *14*, 5119. https://doi.org/10.3390/en14165119

Academic Editors: Carlo Roselli and Sherif L. Abdelaziz

Received: 23 May 2021
Accepted: 26 July 2021
Published: 19 August 2021

1. Introduction

An increased share of renewable energy in the total energy balance of European countries can be observed in recent years. This is mainly due to the new energy guidelines included in the 2018 Directive of the European Parliament and of the Council on the promotion of the use of energy from renewable sources. The Directive determines the share of renewable energy to be at least 32% of the European Union's total energy balance by 2030, referring to the need for reducing emissions related to fossil fuels combustion and the implementation of other environmental objectives [1].

The new energy policy of Poland described in the Annex to the Resolution No. 22/2021 of the Council of Ministers of 2 February 2021 entitled "Energy Policy of Poland until 2040" the so-called EPP2040 assumes the optimal, longest possible use of own energy resources through i.a. the development of renewable energy sources, as well as energy efficiency improvement. From the renewable energy perspective, particularly important are the provisions concerning the renewable energy sources share (RES) in the final gross energy consumption, which has to be at least 23% by 2030, and the reduction of greenhouse gas (GHG) emissions by approximately 30% in comparison to 1990, also until 2030. In addition, it is planned that by 2040 all households' thermal needs will be covered by system heat and by zero- or low-emission individual sources, e.g., heat pumps in individual heating and deep geothermal energy in system heating [2].

Geothermal energy is one of the so-called renewable energy sources. The basic methods of exploiting geothermal energy include the use of:

- Geothermal heat from natural intakes [3];
- The heat from geothermal waters by using boreholes [4–7];
- Groundwater [8,9];
- The heat from the rock mass by means of borehole heat exchangers [10–15] or energy piles [16–20];
- Hot Dry Rocks (HDR systems) [21–24] and Enhanced Geothermal System (EGS) [21,24–26];
- Salt domes [27,28];
- Water from drainage, e.g., underground or opencast mines [29–31];
- Closed mines [27,32];
- Waters accompanying the multi-phase exploitation of hydrocarbons [33].

The exploitation of geothermal water is the most effective method of heat extraction, but such a solution is strongly conditioned by the presence of aquifers with high water temperature. The most popular solution, available to everyone, which can be performed with any lithology, are borehole heat exchangers [12,34], as well as energy piles [16,35,36]. The so-called shallow geothermal energy has been described for a long time [10,37–40]. Borehole heat exchangers are undoubtedly an increasingly common method of obtaining energy from the rock mass. They enable heat provision to both large facilities (such as shopping centers, schools, office buildings) and small single-family houses, which enhances their multidimensional ability to operate. The greatest increase in the use of the described system is mainly observed in highly developed countries such as Sweden, Germany or Switzerland [41–47], but also in other countries [48]. In 2018 alone, around 23,500 geothermal heat pumps were sold in Germany [46]. This progress is also noticeable in Poland. Based on data from two drilling companies, the amount of borehole heat exchangers performed (in meters) increased from approx. 4000 m to over 60,000 m over the years 2004–2010 [41,49]. Moreover, as of 31 December 2018, there are estimated to be over 56,000 ground source heat pumps in Poland (with a heating capacity between 10 and 200 kW). Their total capacity was at least 650 MWt, and heat production was 3100 TJ/year [50]. Proposals for using various types of hybrid systems are also increasingly popular [51–53].

Borehole exchangers are made by placing an appropriate pipe structure (single U-tube, double U-tube, coaxial system) in boreholes specifically drilled for this purpose [14,41,54,55]. There are also analogous systems with three U-tubes [56]. Discussions on using multiple U-tubes (multi U-tube) in one borehole [57], or W-type and coil-type constructions in concrete energy piles [58] are presented in international publications.

It is common practice to construct installations in the form of U-tubes at depths up to 150 m [49] or even 200 m [59,60], and coaxial systems in deeper boreholes [59,60].

The amount of heat exchanged with the rock mass is mainly influenced by the thermal conductivity of rocks [61–63]. The presence of groundwater flow is also a very important element that influences the heat transfer in aquifer caused by the operation of a BHE [9]. Another very important element improving the heat transfer is the filling/sealing slurry with appropriate parameters [12,64,65]. The selection of the sealing slurry affects the efficiency of the borehole heat exchanger's operation. Currently, the slurry is selected based on four criteria [41]:

- Physicochemical compatibility with the environment (no negative impact on the natural environment);
- Appropriate rheological properties (the slurry can be pumped);
- Economic factors (minimization of slurry cost);
- Highest possible thermal conductivity.

Appropriately designing the slurry is not easy, it requires long and meticulous research in terms of both the additives used and the ingredients' proportions. The current state of the art includes the use of ready-made industrial mixtures, as well as cement with additives such as graphite, as sealing slurries for borehole heat exchangers [66–68]. According to the manufacturers, the thermal conductivity of ready-made industrial mixtures is approx. 2.0 $W \cdot K^{-1} \cdot m^{-1}$. However, they are expensive and therefore rarely used in Poland, hence the legitimacy of searching for alternative fillers.

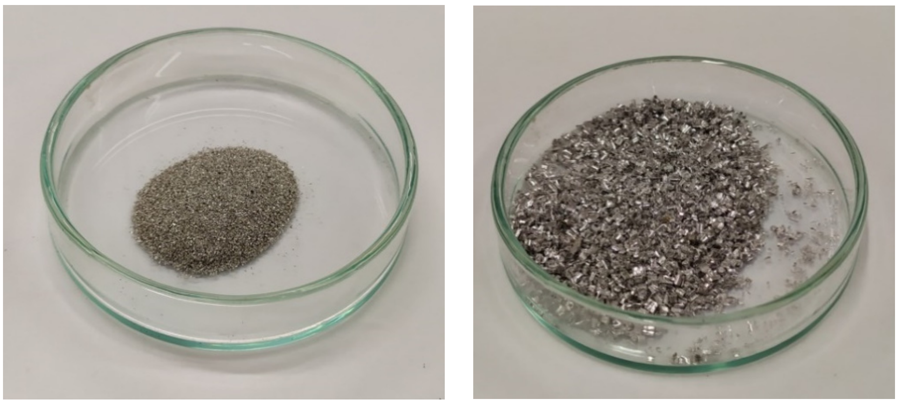
The research aims to design a sealing slurry with increased thermal conductivity, enabling more effective heat extraction from the rock mass. Powdered magnesium was selected for testing due to its high thermal conductivity. The thermal conductivity of magnesium at room temperature is approximately 156 $W \cdot K^{-1} \cdot m^{-1}$ [69]. The use of magnesium for energy exchange purposes is described, among others, by Tian et al. [70]. They describe the effect of magnesium addition on thermal conductivity and the upper temperature limit of thermal stability. They describe a highly thermally conductive composite phase change material created by mixing magnesium particles with a eutectic ternary carbonate salt (Li_2CO_3-Na_2CO_3-K_2CO_3). The designed material was used as a heat transfer medium and/or energy carrier in advanced high-temperature concentrating solar power plants [70]. The use of this material, but in the form of magnesium oxide, is reported by Du et al. [71]. They describe the Thermal Conductivity of Epoxy Resin Reinforced with Magnesium Oxide-Coated Multiwalled Carbon Nanotubes studies. Multiwalled carbon nanotubes coated with the magnesium oxide (MgO@MWNT) were fabricated and dispersed into an epoxy matrix. The thermal conductivity of the epoxy resin was increased due to the increased content of MgO@MWNT [71].

The use of such slurry in borehole heat exchangers will allow reduction in the number of exchangers in installations for facilities with high demand for heat or cold, while limiting the area of land required for drilling [72–75].

2. Research Methodology

The design was based on the common cement CEM I 42.5R according to the PN-EN 197-1: 2012 standard. The choice of the binder was dictated by good strength properties (high value of early strength, greater than or equal to 20 MPa after 2 days), high availability on the market and, above all, low price. CEM I cement consists of 95–100% Portland clinker with 0–5% of secondary component admixtures [76].

The tested cement additive is magnesium. It is a silver-grey alkaline earth metal, used for research in the solid-state, in the form of flakes with a grain size below 0.25 mm, and in the form of shavings (Figure 1). The approximate cost of powdered magnesium is PLN 70–90 per kg. PLN is the official currency and legal tender of Poland. According to the exchange rate from the National Bank of Poland as of 14 June 2021, one US dollar costs PLN 3.7185.



(**a**) (**b**)

Figure 1. (**a**) magnesium in flakes with a granulation <0.25 mm, (**b**) magnesium in shavings.

The material is chemically stable under normal environmental conditions (1 atm and 20 °C). According to the classification system of the Globally Harmonized System of Classification and Labelling of Chemicals (GHS), it is a flammable solid substance (hazard class and category—Flam. Sol. 2), and a substance which releases a flammable gas in contact with water (Water-react. 2). Considering the fact that one of the extinguishing agents in the event of the selected additive's ignition is cement, it can be assumed that the design based on cement, water and magnesium will not be flammable [77].

Analyzing the toxicological hazards, magnesium is not acute toxic and is not classified as a sensitizing, corrosive or irritant substance, and therefore no special precautions or protective clothing are required. According to Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 16 December 2008 on the classification, labelling and packaging of substances and mixtures, it is not classified as a substance hazardous to the aquatic environment. Despite that, it is recommended to prevent the substance from entering the sewage system, surface water and groundwater. Therefore, it is planned to perform a washout treatment in the future to reduce potential adverse effects [77].

The research on sealing slurries can be divided into two main categories: research on fresh slurries and on hardened ones [14]. Testing fresh slurry determined its liquidity, density, viscosity, and rheological parameters. For the hardened slurry, the most important parameter, its thermal conductivity, was investigated.

The FOX50 instrument (Figure 2) is designed to test the thermal conductivity of materials in the range from 0.1 to 10 $W{\cdot}K^{-1}{\cdot}m^{-1}$. It contains a set of two round plates covered from the outside with a cylinder equipped with an insulation layer. The instrument complies with the ISO 8301 standard for Thermal insulation—Determination of steady-state thermal resistance and related properties—Heat flow meter apparatus. The upper plate remains stationary, while the lower plate can move vertically due to the pneumatic mechanism. The instrument's body houses electronics, control devices and a liquid crystal display. Additionally, the device is equipped with a digital sample thickness reader with an accuracy of ±0.025 mm. The kit also includes a cooling module and a compressor (Figure 2). Thermal conductivity studies were based on Pyrex calibration to standardize the results [78].

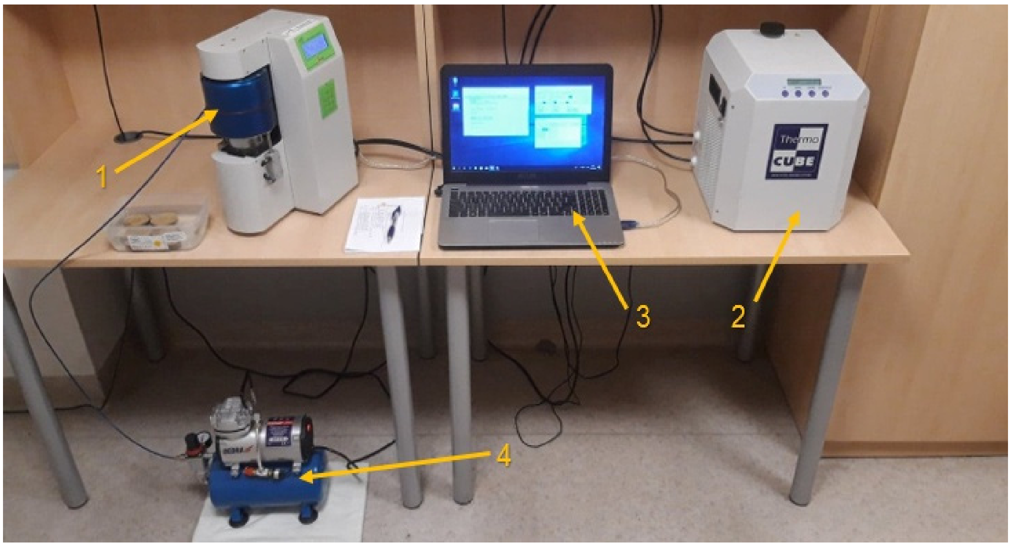


Figure 2. Measuring station, 1—FOX 50 Lambdameter by TA Instruments, 2—ThermoCube 200–500 thermoelectric recirculation cooler by Solid State Cooling System, 3—laptop with Win Therm50v2 software, 4—DED7472 compressor by Dedra.

Six different formulations of the sealing slurry were prepared based on the addition of magnesium in two granulations, CEM I 42.5 R cement, and water as a mixing liquid. The amount of the additive was selected in concentrations of 15%, 30% and 45% BWOC (by weight of cement—based on the dry weight of cement). This choice was dictated by previous research observations, in which various concentrations were tested (1%, 2%, 5%), but the results were not satisfactory. A constant water–mixture ratio (W/M) of 0.5 for each formula was established to eliminate the potential impact of changing the coefficient W/M on the obtained results. Sealing slurry samples were prepared in accordance with the applicable standard. For this purpose, cylinder-shaped molds with a diameter of 55 mm were prepared and filled with slurry. After hardening, the discs were stored completely immersed in water, which corresponds to the conditions present in the borehole heat exchangers. Figure 3 shows an exemplary test sample. The composition of individual designs is presented in Table 1.

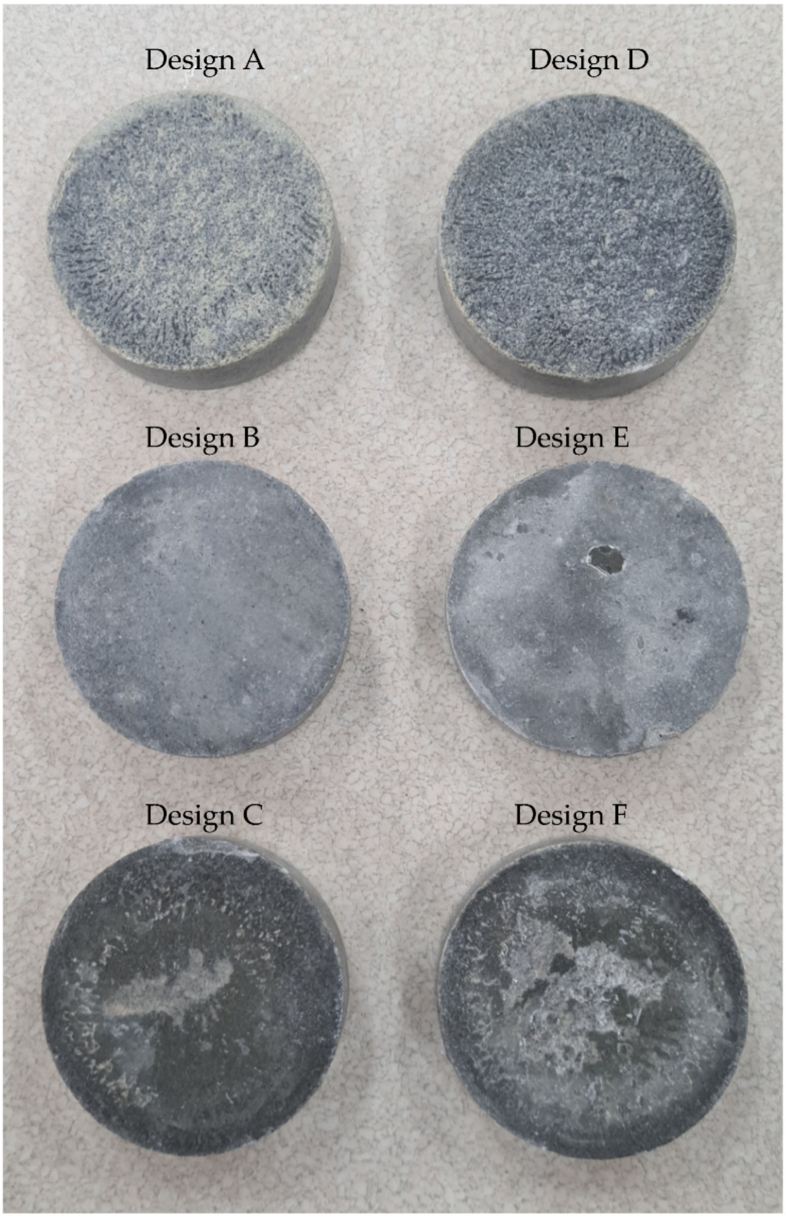


Figure 3. Sample prepared for thermal conductivity tests.

Table 1. Composition of individual designs.

Design Composition		Magnesium Flakes			Magnesium Shavings		
Design name		A	B	C	D	E	F
The percentage concentration of the additive	%	15	30	45	15	30	45
Cement	g	400	400	400	400	400	400
Additive	g	60	120	180	60	120	180
Mixing liquid (water)	g	230	260	290	230	260	290
W/M	-	0.5	0.5	0.5	0.5	0.5	0.5

Test results for the fresh sealing slurries are presented in Table 2.

Table 2. Parameters of fresh sealing slurries.

Magnesium Type and Design Name		Magnesium Flakes			Magnesium Shavings		
		A	B	C	D	E	F
Dynamic viscosity	mPas	55	83	not measurable	40	not measurable	not measurable
Liquidity	mm	195	195	140	245	235	195
Density	$g \cdot cm^{-3}$	1.77	1.75	1.64	1.79	1.71	1.63
Conventional viscosity	s	20	25	not measurable	11	not measurable	not measurable

An increase in the additive concentration causes a decrease in the sealing slurry density, as magnesium ($\rho \approx 1.74\ g \cdot cm^{-3}$) has a much lower density than cement ($\rho \approx 3.05\ g \cdot cm^{-3}$). The liquidity decreases with increasing additive concentration, which makes the slurry more difficult to pump. With the increase in magnesium concentration, the dynamic viscosity of the slurry increases. It should be noted that cement slurry is a complex system that changes its properties over time, under the influence of both internal and external factors. An increase in the slurry's viscosity may lead to difficulties related to its injection. Therefore, in the future, prior to the potential industrial application, it is planned to test the designs of slurries enriched with admixtures of agents regulating the slurry's viscosity and increasing its liquefaction.

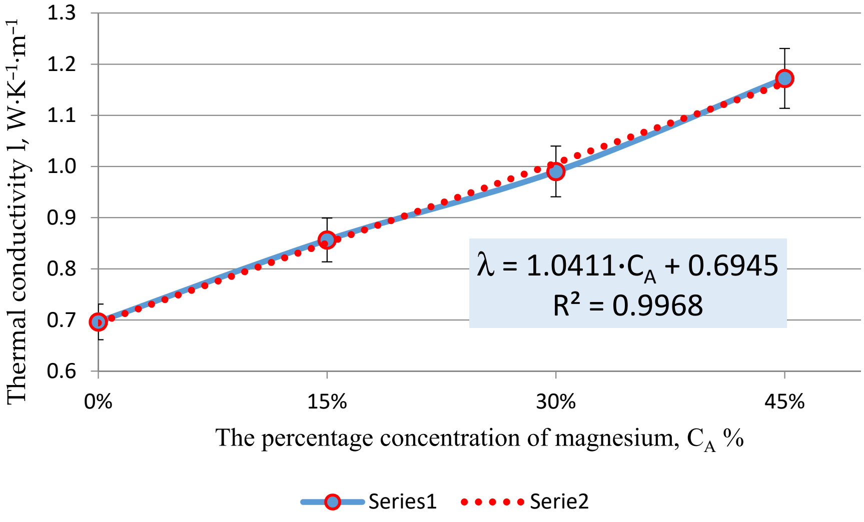
During the research practice, samples behaved differently from the moment they were prepared. For some additives, a height shrinkage (reduction of the sample height), while for others swelling, of even a few millimeters, was observed.

3. Results and Discussion

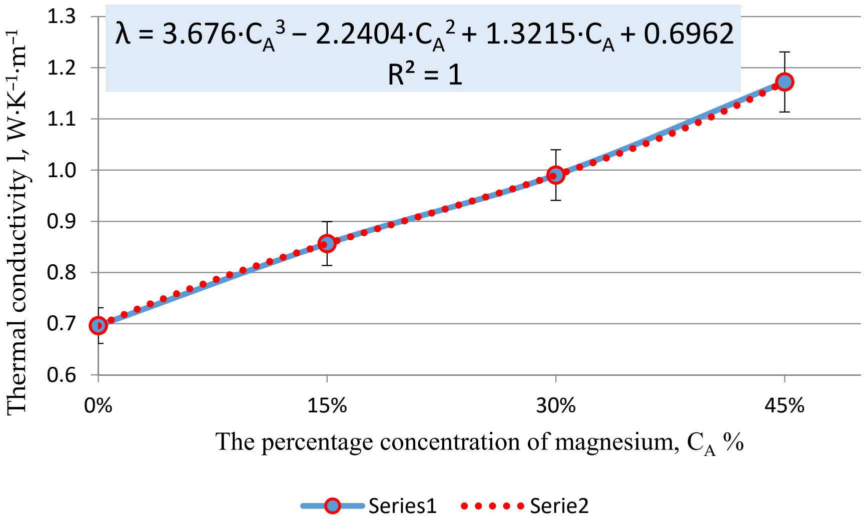
Each design was tested at least five times on a Pyrex calibration, and baseline descriptive statistics for the thermal conductivity and thickness were assessed for the individual tests. Table 3 presents the measured values of the thermal conductivity for the base sample, consisting only of cement and water with w/c = 0.5. Table 4 presents the results for designs A, B, and C. Figure 4 shows the effect of magnesium flakes concentration on the sample's average thermal conductivity value.

Based on the results, a linear relationship between the additive concentration and the slurry's thermal conductivity was determined. Additionally, in comparison to the base sample, for design A there was a 23% increase in thermal conductivity, for design B—42%, and for design C—as much as 68%. More detailed studies on the pumpability of slurries with the 30–45% magnesium addition should be carried out. The recommendation results from Table 2 data, where the slurry with the addition of 30% magnesium is pumpable, while the slurry with the addition of 45% magnesium is not.

Table 5 presents the results for designs D, E, and F. Figure 5 shows the effect of magnesium shavings concentration on the average thermal conductivity values.



(**a**)



(**b**)

Figure 4. The influence of the magnesium flakes concentration on the sample's average thermal conductivity values: (**a**) trend line as a linear function, (**b**) trend line as a polynomial function; Series 1—graph based on the measurement results, Serie 2—trend line.

Table 3. Thermal conductivity test results for the base sample.

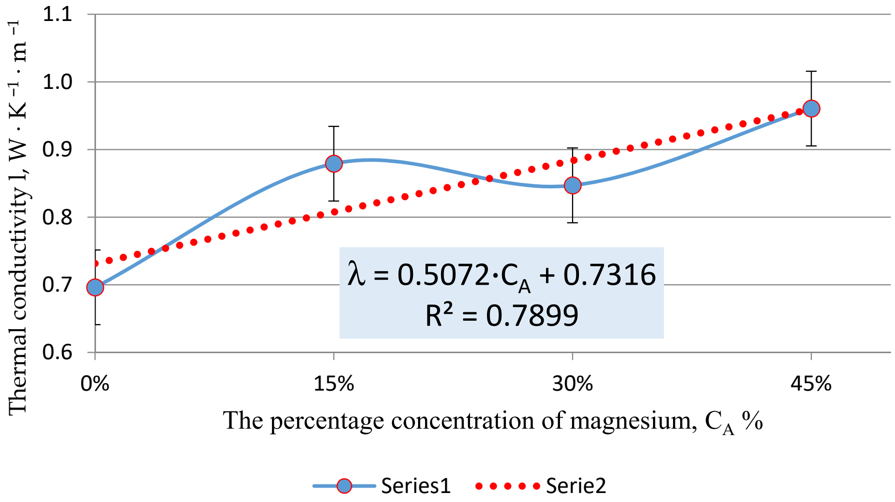
Test	Thermal Conductivity	Thickness
no.	$W \cdot K^{-1} \cdot m^{-1}$	mm
1	0.707	18.01
2	0.698	18.14
3	0.696	18.29
4	0.682	18.03
5	0.698	18.06
Descriptive statistics		
Average	0.696	18.11
Median	0.698	18.06
Standard deviation	0.00907	0.11
The range of variation	0.025	0.28
Minimum	0.682	18.01
Maximum	0.707	18.29

Table 4. Thermal conductivity test results for designs A, B and C.

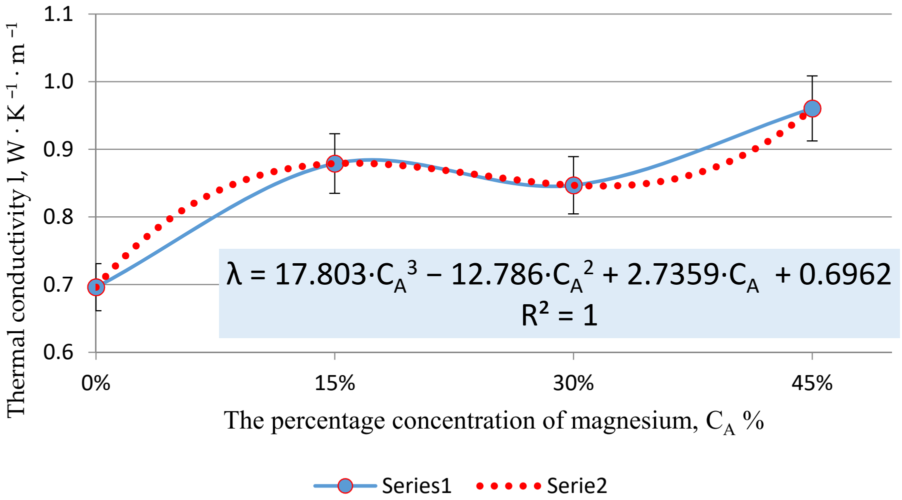
Test	Thermal Conductivity	Thickness	Thermal Conductivity	Thickness	Thermal Conductivity	Thickness
No.	$W{\cdot}K^{-1}{\cdot}m^{-1}$	mm	$W{\cdot}K^{-1}{\cdot}m^{-1}$	mm	$W{\cdot}K^{-1}{\cdot}m^{-1}$	mm
	Design A		Design B		Design C	
1	0.890	17.73	0.893	18.04	1.105	18.41
2	0.788	17.81	0.994	17.88	1.213	18.57
3	0.820	17.70	0.935	17.88	1.216	18.75
4	0.889	17.70	1.085	18.03	1.169	18.41
5	0.895	17.70	1.044	16.97	1.158	18.85
			Descriptive statistics			
Average	0.856	17.73	0.990	17.76	1.172	18.60
Median	0.889	17.70	0.994	17.88	1.169	18.57
Standard deviation	0.0493	0.048	0.0779	0.45	0.0456	0.20
The range of variation	0.11	0.11	0.192	1.07	0.111	0.44
Minimum	0.788	17.70	0.893	16.97	1.105	18.41
Maximum	0.895	17.81	1.085	18.04	1.216	18.85

The disturbance of the linear trend may be related to the uneven additive distribution in the sample, as well as a different thickness of the samples (shrinkage) compared to the others. Moreover, in comparison to the base sample, for design D there was a 26% increase in thermal conductivity, for design E—22%, and for design F—38%.

Comparing Figures 4 and 5, it can be seen that with the same percentages of additives BWOC (30% and 45%), the higher thermal conductivity values were obtained for magnesium flakes. For a 15% BWOC addition, magnesium shavings resulted in a higher thermal conductivity value. For Designs A and D, which had the same BWOC content (15%) but different types of magnesium, similar thermal conductivity results were obtained. In the case of Designs B and E, as well as C and F, with the same BWOC content (30 and 45%) but different types of magnesium, these values are not similar. The results indicate that the form of the additive (either shavings or flakes) influence the thermal conductivity value of the tested samples. Figures 4 and 5 present the equations describing the studied phenomena, taking into account the coefficient of determination (R^2) as the relationship between the regression model and the studied phenomenon. For both additives, the polynomial function is a better description, as the coefficient of determination for the model is equal to one. In the case of the linear equation, a much better fit occurs in the case of magnesium flakes (R^2 = 0.9968) than in the case of magnesium shavings (R^2 = 0.7899). According to the literature [79], the stepwise regression family is not suitable for the approximation of thermal conductivity, which was confirmed by the conducted calculations. The linear regression has a much lower R^2 value compared to the polynomial regression. Other regression methods can also be applied, such as the regression based on artificial neural network or group method of data handling. Regression models always require validation, and the test of R^2 is most often used for this purpose. The higher value of R^2 indicates that the empirical model is highly prognostic for the original model [79]. In many fields of science, various regression models are developed and applied with the use of analytical data [80]. The authors used the most popular method for determining the correlation of the interdependence of phenomena. With polynomial regression, a functional correlation (R^2 = 1) was obtained due to the small number of variants of the examined slurry recipes.



(**a**)



(**b**)

Figure 5. The influence of magnesium shavings concentration on the average thermal conductivity values: (**a**) trend line as a linear function, (**b**) trend line as a polynomial function; Series 1—graph based on the measurement results, Serie 2—trend line.

Table 5. Thermal conductivity test results for designs D, E and F.

Test	**Thermal Conductivity**	**Thickness**	**Thermal Conductivity**	**Thickness**	**Thermal Conductivity**	**Thickness**
No.	**W·K^{-1}·m^{-1}**	**mm**	**W·K^{-1}·m^{-1}**	**mm**	**W·K^{-1}·m^{-1}**	**mm**
	Design D		**Design E**		**Design F**	
1	0.896	18.95	0.773	16.00	0.9818	19.38
2	0.926	18.92	0.860	16.86	1.1640	22.15
3	0.827	17.32	0.892	16.94	0.8724	16.54
4	0.917	19.53	0.823	15.82	0.8388	16.51
5	0.829	18.69	0.887	16.94	0.9456	15.72
			Descriptive statistics			
Average	0.879	18.68	0.847	16.51	0.961	18.06
Median	0.896	18.92	0.860	16.86	0.946	16.54
Standard deviation	0.0480	0.82	0.0495	0.55	0.127	2.68
The range of variation	0.099	2.21	0.118	1.12	0.325	6.43
Minimum	0.827	17.32	0.773	15.82	0.839	15.72
Maximum	0.926	19.53	0.892	16.94	1.164	22.15

4. Conclusions

The research aimed to find a cement slurry with the highest possible thermal conductivity while maintaining the lowest possible production costs. The use of a sealing slurry with an increased thermal conductivity improves the heat exchange with the rock mass. The innovation in the study was the addition of magnesium in the form of flakes and shavings. The addition of magnesium lowers the slurry's density but increases its viscosity. Magnesium tends to slightly increase in volume during the setting of the slurry in comparison to its fresh state.

An important factor influencing the results is the thorough mixing of the additive in the slurry, and the distribution of the additive particles in the hardened sample. The samples were tested on both sides in order to eliminate the influence of the uneven mixing, and the distribution of the additive in the hardened sealing slurry, on the thermal conductivity results. Thermal conductivity is strongly dependent on environmental conditions (including temperature and humidity). The humidity of the tested samples was at maximum due to the maturation conditions—full immersion in water as an environment similar to borehole conditions was assumed.

For slurries with the magnesium flakes addition, the thermal conductivity of the tested samples increases together with the percentage of additive in the sample, relative to the weight of dry cement. The highest thermal conductivity values were obtained for design C, where the thermal conductivity increased by 68% in relation to the base sample made of cement alone. For design A, a 23% increase was noted, and for design B—42%. In the case of samples with magnesium shavings addition, the highest increase in thermal conductivity compared to the base sample was recorded for design F (by 38%). For design E, it increased by 22%, while for design D by 26%.

In the future, it is planned to test samples with lower humidity and at different temperatures. The operation of a borehole heat exchanger, as well as an energy pile, can cause drying of the hardened sealing slurry, and can take place in a fairly wide temperature range, usually from −5 to +35 °C.

Author Contributions: Conceptualization, T.S. and T.K.; methodology, T.S.; software, D.C.; validation, A.S.-Ś., D.C. and T.K.; formal analysis, T.K.; investigation, D.C.; resources, T.K.; data curation, D.C.; writing—original draft preparation, D.C.; writing—review and editing, A.S.-Ś.; visualization, D.C.; supervision, T.S.; project administration, A.S.-Ś.; funding acquisition, T.S. All authors have read and agreed to the published version of the manuscript.

Funding: The research leading to these results has received funding from the Norway Grants 2014–2021 via the National Centre for Research and Development in Warsaw.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Directive (EU) 2018/2001 of the European Parliament and of the Council of 11 December 2018 on the Promotion of the Use of Energy from Renewable Sources. Available online: https://www.legislation.gov.uk/eudr/2018/2001 (accessed on 27 July 2021).
2. *Polityka Energetyczna Polski do 2040 r.—Załącznik do Uchwały nr 22/2021 Rady Ministrów z dnia 2 lutego 2021 r*; Ministry of Climate and Environment: Warsaw, Poland, 2021. (In Polish)
3. Sala, K. Przemysłowe wykorzystanie energii geotermalnej w Polsce na przykładzie geotermalnego zakładu ciepłowniczego w Bańskiej Niżnej (Industrial Use of Geothermal Energy in Poland Based on the Example of a Geothermal Heating Plant in Bańska Niżna). *Stud. Ind. Geogr. Comm. Pol. Geogr. Soc.* **2018**, *32*, 73–82. [CrossRef]
4. Sapińska-Śliwa, A.; Wiglusz, T.; Kruszewski, M.; Sliwa, T.; Kowalski, T. *Wiercenia Geotermalne. Doświadczenia Techniczne i Technologiczne (Geothermal Drilling: Techniques and Side Aspects)*; Laboratory of Geoenergetics Book Series Volume 3; Drilling, Oil and Gas Foundation: Krakow, Poland, 2017. (In Polish)
5. Sowizdzal, A. Geothermal energy resources in Poland—Overview of the current state of knowledge. *Renew. Sustain. Energy Rev.* **2018**, *82*, 4020–4027. [CrossRef]

6. Operacz, A.; Bielec, B.; Tomaszewska, B.; Kaczmarczyk, M. Physicochemical Composition Variability and Hydraulic Conditions in a Geothermal Borehole—The Latest Study in Podhale Basin, Poland. *Energies* **2020**, *13*, 3882. [CrossRef]
7. Bujakowski, W.; Bielec, B.; Miecznik, M.; Pająk, L. Reconstruction of geothermal boreholes in Poland. *Geotherm. Energy* **2020**, *8*, 10. [CrossRef]
8. Mazurkiewicz, J.; Kmiecnik, E.; Tomaszewska, B. Analiza możliwości wykorzystania wód podziemnych z utworów czwartorzędowych w systemach geotermii niskotemperaturowej na obszarze Małopolski. Część I (Analysis of the possibility to use the quaternary groundwater in the low-temperature geothermal systems in Małopolska. Part I). *Prz. Geol.* **2015**, *63*, 926–930. (In Polish)
9. Antelmi, M.; Alberti, L.; Angelotti, A.; Zille, A. Thermal and hydrogeological aquifers characterization by coupling depth-resolved thermal response test with moving line source analysis. *Energy Convers. Manag.* **2020**, *225*, 113400. [CrossRef]
10. Ingersoll, L.R.; Adler, F.T.; Plass, H.J.; Ingersoll, A.C. Theory of earth heat exchangers for the heat pump. *ASHVE Trans.* **1950**, *56*, 167–188.
11. Luo, J.; Rohn, J.; Bayer, M.; Priess, A. Thermal Efficiency Comparison of Borehole Heat Exchangers with Different Drillhole Diameters. *Energies* **2013**, *6*, 4187–4206. [CrossRef]
12. Sliwa, T.; Sapińska-Śliwa, A.; Knez, D.; Bieda, A.; Kowalski, T.; Złotkowski, A. *Borehole Heat Exchangers: Production and Storage of Heat in the Rock Mass*; Laboratory of Geoenergetics Book Series Volume 2; Drilling, Oil and Gas Foundation: Krakow, Poland, 2016.
13. Quaggiotto, D.; Zarrella, A.; Emmi, G.; De Carli, M.; Pockelé, L.; Vercruysse, J.; Psyk, M.; Righini, D.; Galgaro, A.; Mendrinos, D.; et al. Simulation-Based Comparison between the Thermal Behavior of Coaxial and Double U-Tube Borehole Heat Exchangers. *Energies* **2019**, *12*, 2321. [CrossRef]
14. Sliwa, T.; Jarosz, K.; Rosen, M.A.; Sojczyńska, A.; Sapińska-Śliwa, A.; Gonet, A.; Fąfera, K.; Kowalski, T.; Ciepielowska, M. Influence of Rotation Speed and Air Pressure on the Down the Hole Drilling Velocity for Borehole Heat Exchanger Installation. *Energies* **2020**, *13*, 2716. [CrossRef]
15. Boban, L.; Miše, D.; Herceg, S.; Soldo, V. Application and Design Aspects of Ground Heat Exchangers. *Energies* **2021**, *14*, 2134. [CrossRef]
16. Koene, F.G.H.; van Helden, W.G.J.; Romer, J.C. Energy piles as cost effective ground heat exchangers. In Proceedings of the TERRASTOCK 2000, Stuttgart, Germany, 28 August–1 September 2000.
17. Schröder, B.; Hanschke, T. Energiepfhähle—Umweltfreundliches Heizen und Kühlen mit geothermisch aktivierten Stahlbetonfertigpfählen. *Bautechnik* **2003**, *80*, 925–927. (In German) [CrossRef]
18. Brandl, H. Energy foundations and other thermo-active ground structures. *Géotechnique* **2006**, *56*, 81–122. [CrossRef]
19. Mousa, M.M.; Bayomy, A.M.; Saghir, M.Z. Experimental and Numerical Study on Energy Piles with Phase Change Materials. *Energies* **2020**, *13*, 4699. [CrossRef]
20. Sliwa, T.; Sapińska-Śliwa, A.; Wysogląd, T.; Kowalski, T.; Konopka, I. Strength Tests of Hardened Cement Slurries for Energy Piles, with the Addition of Graphite and Graphene, in Terms of Increasing the Heat Transfer Efficiency. *Energies* **2021**, *14*, 1190. [CrossRef]
21. Tester, J.W.; Brown, D.W.; Potter, R.M. *Hot Dry Rock Geothermal Energy—A New Energy Agenda for the 21st Century*; Los Alamos National Laboratory Report LA-11514-MS; US Department of Energy: Washington, DC, USA, 1989.
22. Tenzer, H. Development of hot dry rock technology. *GHC Bull.* **2001**, *12*, 14–22.
23. Wójcicki, A.; Sowiżdżał, A.; Bujakowski, W.; Szewczyk, J. *Ocena Potencjału, Bilansu Cieplnego i Perspektywicznych Struktur Geologicznych Dla Potrzeb Zamkniętych Systemów Geotermicznych (Hot Dry Rocks) w Polsce*; Ministry of Environment: Kraków, Poland, 2013. (In Polish)
24. Sapińska-Śliwa, A.; Kowalski, T.; Knez, D.; Sliwa, T.; Gonet, A.; Bieda, A. Geological and drilling aspects of construction and exploitation geothermal systems HDR/EGS. *AGH Drill. Oil Gas* **2015**, *32*, 49–63. [CrossRef]
25. Breede, K.; Dzebisashvili, K.; Liu, X.; Falcone, G. A systematic review of enhanced (or engineered) geothermal systems: Past, present and future. *Geotherm. Energy* **2013**, *1*, 4. [CrossRef]
26. Li, L.; Guo, X.; Zhou, M.; Xiang, G.; Zhang, N.; Wang, Y.; Wang, S.; Pagou, A.L. The Investigation of Fracture Networks on Heat Extraction Performance for an Enhanced Geothermal System. *Energies* **2021**, *14*, 1635. [CrossRef]
27. Kępińska, B. Geothermal Energy Use in Europe. In Proceedings of the GEOTHERMAL TRAINING PROGRAMME 30th Anniversary Workshop Orkustofnun, Reykjavík, Iceland, 26–27 August 2008.
28. Pająk, L.; Gonet, A.; Śliwa, T.; Knez, D. Analiza możliwości wykorzystania magazynów ciekłego propanu, lokowanych w strefie kawern wysadów solnych, do produkcji energii (Analysis of Energy Production Possibilities from Liquid Propane Storage in Salt Domes Cavities). *Wiert. Naft. Gaz* **2010**, *27*, 657–667. (In Polish)
29. Solik-Heliasz, E.; Małolepszy, Z. Możliwości wykorzystania energii geotermalnej z wód kopalnianych w Górnośląskim Zagłębiu Węglowym (The possibilities of utilisation of geothermal energy from mine waters in the Upper Silesian Coal Basin). In Proceedings of the International Scientific Conference Geothermal Energy in Underground Mines, Ustroń, Polska, 21–23 November 2001.
30. Solik-Heliasz, E. Ocena możliwości odzysku ciepła z wód pompowanych z kopalń węgla kamiennego (Assessment of possibility of heat recovery from waters pumped from hard coal mines). *Pr. Nauk. GIG Górnictwo Sr.* **2002**, *2*, 17–24. (In Polish)
31. Namysłowska-Wilczyńska, B.; Wilczyński, A.; Wojciechowski, H. Możliwości wykorzystania zasobów wodnych i energetycznych w podziemnych kopalniach surowców mineralnych (Possibilities of the utilization of water and Energy in undeground mineral resources mines). *Zesz. Nauk. Inst. Gospod. Surowcami Miner. Energią Pol. Akad.* **2016**, *95*, 47–58. (In Polish)

32. Małolepszy, Z. Man-made, low-temperature geothermal reservoirs in abandoned workings of underground mines on example of coal mines, Poland. In Proceedings of the IGC2003 Conference Multiple Integrated Uses of Geothermal Resources, Reykjavik, Iceland, 14–17 September 2003.
33. Warnecki, M. *Analiza Możliwości Pozyskiwania Pozabilansowych Zasobów Gazu Ziemnego z Nasyconych Poziomów Solankowych w Procesach Sekwestracji* CO_2 *(Analysis of Additional Gas Production Possibility from Deep Saline Aquifers in the Process of* CO_2 *Sequestration)*; Instytut Nafty i Gazu—Państwowy Instytut Badawczy: Kraków, Poland, 2016.
34. Bertani, R. *Geothermal Energy: An Overview on Resources and Potential*; Session 1, Geothermal Electricity Production: Possibilities, Technical and Economic Feasibility in Central European Region; International Geothermal Days, Conference & Summer School: Bratislava, Slovakia, 2009.
35. Vasilescu, A.R. Design and Execution of Energy Piles: Validation by In-Situ and Laboratory Experiments. Doctorate Thesis, L'École Centrale de Nantes, Nantes, France, 2019. Available online: https://tel.archives-ouvertes.fr/tel-02395284/document (accessed on 27 July 2021).
36. Lyu, W.; Pu, H.; Chen, J. Thermal Performance of an Energy Pile Group with a Deeply Penetrating U-shaped Heat Exchanger. *Energies* **2020**, *13*, 5822. [CrossRef]
37. Crandall, A.C. House Heating with Earth Heat Pump. *Electr. World* **1946**, *126*, 94–95.
38. Kemler, E.N. Methods of Earth Heat Recovery for the Heat Pump. *Heat. Vent.* **1947**, *9*, 69–72.
39. Sliwa, T. Wybrane systemy geotermalne w skałach suchych (Chosen geothermal systems in dry rocks). In Proceedings of the Conference on Current State and Development Prospects of Mining in the Aspect of Environmental Protection, Proceedings Dniepropietrowsk, Dnipropetrovsk, Ukraine, 13–14 May 1996.
40. Sliwa, T. Wybrane systemy geotermalne w aspekcie warunków geologicznych (Chosen geotermic systems in aspect of geology). *Zesz. Nauk. AGH Wiert. Naft. Gaz* **1998**, *15*, 199–208.
41. Gonet, A.; Sliwa, T.; Stryczek, S.; Sapińska-Śliwa, A.; Jaszczur, M.; Pająk, L.; Złotkowski, A. *Metodyka Identyfikacji Potencjału Cieplnego Górotworu Wraz z Technologią Wykonywania i Eksploatacji Otworowych Wymienników Ciepła (Methodology for the Identification of Potential Heat of the Rock Mass along with Technology Implementation and Operation of the Borehole Heat Exchangers)*; Wydawnictwa AGH: Kraków, Poland, 2011. (In Polish)
42. Gehlin, S.; Andersson, O. Geothermal Energy Use, Country Update for Sweden. In Proceedings of the European Geothermal Congress 2016, Strasbourg, France, 19–23 September 2016.
43. Perego, R.; Pera, S.; Galgaro, A. Techno-Economic Mapping for the Improvement of Shallow Geothermal Management in Southern Switzerland. *Energies* **2019**, *12*, 279. [CrossRef]
44. Gehlin, S.; Andersson, O.; Rosberg, J.E. Country Update for Sweden 2020. In Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland, 26 April–2 May 2020.
45. Link, K.; Lupi, N.; Siddiqi, G. Geothermal Energy in Switzerland Country Update 2015–2020. In Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland, 26 April–2 May 2020.
46. Lund, J.W.; Toth, A.N. Direct Utilization of Geothermal Energy 2020 Worldwide Review. In Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland, 26 April–2 May 2020.
47. Weber, J.; Born, H.; Pester, S.; Moeck, I. Geothermal Energy Use in Germany, Country Update 2015–2019. In Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland, 26 April–2 May 2020.
48. Shrestha, G.; Yoshioka, M.; Fujii, H.; Uchida, Y. Evaluation of Suitable Areas to Introduce a Closed-Loop Ground Source Heat Pump System in the Case of a Standard Japanese Detached Residence. *Energies* **2020**, *13*, 4294. [CrossRef]
49. Sliwa, T.; Gonet, A. Analiza efektywności wymiany ciepła w wymiennikach otworowych o różnej konstrukcji (Heat transfer efficiency analysis in different constructions of borehole heat exchangers). *Wiert. Naft. Gaz* **2011**, *28*, 555–570. (In Polish)
50. Kępińska, B. Geothermal Energy Country Update Report from Poland, 2015–2019. In Proceedings of the World Geothermal Congress 2020, Reykjavik, Iceland, 26 April–2 May 2020.
51. Bae, S.; Nam, Y.; da Cunha, I. Economic Solution of the Tri-Generation System Using Photovoltaic-Thermal and Ground Source Heat Pump for Zero Energy Building (ZEB) Realization. *Energies* **2019**, *12*, 3304. [CrossRef]
52. Hałaj, E.; Kotyza, J.; Hajto, M.; Pełka, G.; Luboń, W.; Jastrzębski, P. Upgrading a District Heating System by Means of the Integration of Modular Heat Pumps, Geothermal Waters, and PVs for Resilient and Sustainable Urban Energy. *Energies* **2021**, *14*, 2347. [CrossRef]
53. Palomba, V.; Bonanno, A.; Brunaccini, G.; Aloisio, D.; Sergi, F.; Dino, G.E.; Varvaggiannis, E.; Karellas, S.; Nitsch, B.; Strehlow, A.; et al. Hybrid Cascade Heat Pump and Thermal-Electric Energy Storage System for Residential Buildings: Experimental Testing and Performance Analysis. *Energies* **2021**, *14*, 2580. [CrossRef]
54. Bieda, A.; Kowalski, T.; Sliwa, T.; Skowroński, D.; Kowalska-Kubsik, I.; Rado, R. Udarowo-obrotowa metoda wiercenia otworowych wymienników ciepła jako alternatywa wiertnicza przyjazna środowisku (Rotary-percussion drilling for borehole heat exchangers as an environmentally friendly drilling alternative). *Przemysł Chem.* **2018**, *97*, 864–986. (In German) [CrossRef]
55. Zhou, A.; Huang, X.; Wang, W.; Jiang, P.; Li, X. Thermo-Hydraulic Performance of U-Tube Borehole Heat Exchanger with Different Cross-Sections. *Sustainability* **2021**, *13*, 3255. [CrossRef]
56. Kovacevic, M.S.; Bacic, M.; Arapov, I. Possibilities of underground engineering for the use of shallow geothermal Energy. *Gradevinar* **2012**, *12*, 1019–1028.

57. Aydin, M.; Sisman, A. Experimental and computational investigation of multi U-tube boreholes. *Appl. Energy* **2015**, *145*, 163–171. [CrossRef]
58. Yoon, S.; Lee, S.R.; Xue, J.; Zosseder, K.; Go, G.H.; Park, H. Evaluation of the Thermal Efficiency and a Costanalysis of Different Types of Ground Heat Exchangers in Energy Piles. *Energy Convers. Manag.* **2015**, *105*, 393–402. [CrossRef]
59. Sliwa, T.; Nowosiad, T.; Vytyaz, O.; Sapińska-Śliwa, A. Study on the efficiency of deep borehole heat exchangers. *SOCAR Proc.* **2016**, *2*, 29–42. [CrossRef]
60. Sliwa, T.; Kruszewski, M.; Zare, A.; Assadi, M.; Sapińska-Śliwa, A. Potential application of vacuum insulated tubing for deep borehole heat exchangers. *Geothermics* **2018**, *75*, 58–67. [CrossRef]
61. Rybach, L. Geothermal Heat Pumps. In *Encyclopedia of Solid Earth Geophysic*; Gupta, H.K., Ed.; Springer: Dordrecht, The Netherlands, 2011; pp. 411–415.
62. Lee, S.-R.; Yoon, S.; Go, G.-H.; Kang, H.-B.; Park, D.-W. Evaluation of Heat Exchange Rate for Different Types of Ground Heat Exchangers. In Proceedings of the International Offshore and Polar Engineering Conference, Anchorage, AK, USA, 30 June–5 July 2013.
63. Fouché, O.; Soussi, C.; Bracq, G.; Minec, S. Seasonal Storage of Sensible Heat in Tunnel-Surrounding Rocks. In Proceedings of the ISRM 1st International Conference on Advances in Rock Mechanics, Hammamet, Tunisia, 29–31 March 2018.
64. Lund, J.; Sanner, B.; Rybach, L.; Curtis, S.; Hellstrom, G. Ground source heat pumps—A world review. *GHC Bull.* **2004**, *8*, 1–10.
65. Alberti, L.; Angelotti, A.; Antelmi, M.; La Licata, I. A Numerical Study on the Impact of Grouting Material on Borehole Heat Exchangers Performance in Aquifers. *Energies* **2017**, *10*, 703. [CrossRef]
66. Delaleux, F.; Py, X.; Olives, R.; Dominguez, R. Enhancement of geothermal borehole heat exchangers performances by improvement of bentonite grouts conductivity. *Appl. Therm. Eng.* **2012**, *33–34*, 92–99. [CrossRef]
67. Sliwa, T.; Sowa, M.; Stryczek, S.; Gonet, A.; Złotkowski, A.; Sapińska-Śliwa, A.; Knez, D. Badania stwardniałych zaczynów cementowych z dodatkiem grafitu (The study of hardened cement slurries with addition of graphite). *Wiert. Naft. Gaz* **2011**, *28*, 571–585. (In Polish)
68. Berktas, I.; Nejad Ghafar, A.; Fontana, P.; Caputcu, A.; Menceloglu, Y.; Saner Okan, B. Synergistic Effect of Expanded Graphite-Silane Functionalized Silica as a Hybrid Additive in Improving the Thermal Conductivity of Cementitious Grouts with Controllable Water Uptake. *Energies* **2020**, *13*, 3561. [CrossRef]
69. Dziadoń, A. *Magnez i Jego Stopy*; Monografie, Studia, Rozprawy, M28; Wydawnictwo Politechniki Świętokrzyskiej: Kielce, Poland, 2012. (In Polish)
70. Tian, H.; Du, L.; Wei, X.; Deng, S.; Wang, W.; Ding, J. Enhanced thermal conductivity of ternary carbonate salt phase change material with Mg particles for solar thermal energy storage. *Appl. Energy* **2017**, *204*, 525–530. [CrossRef]
71. Du, F.P.; Tang, H.; Huang, D.Y. Thermal conductivity of epoxy resin reinforced with magnesium oxide coated multiwalled carbon nanotubes. *Int. J. Polym. Sci.* **2013**, *2013*, 541823. [CrossRef]
72. Sliwa, T.; Sapińska-Śliwa, A.; Gonet, A.; Kowalski, T.; Sojczyńska, A. Geothermal Boreholes in Poland—Overview of the Current State of Knowledge. *Energies* **2021**, *14*, 3251. [CrossRef]
73. Lee, S.-M.; Park, S.-H.; Jang, Y.-S.; Kim, E.-J. Proposition of Design Capacity of Borehole Heat Exchangers for Use in the Schematic-Design Stage. *Energies* **2021**, *14*, 822. [CrossRef]
74. Robert, F.; Gosselin, L. New methodology to design ground coupled heat pump systems based on total cost minimization. *Appl. Therm. Eng.* **2014**, *62*, 481–491. [CrossRef]
75. Li, C.; Mao, J.; Zhang, H.; Li, Y.; Xing, Z.; Zhu, G. Effects of load optimization and geometric arrangement on the thermal performance of borehole heat exchanger fields. *Sustain. Cities Soc.* **2017**, *35*, 25–35. [CrossRef]
76. *"Cement, Kruszywa, Beton" w Ofercie Grupy Górażdże, Rodzaje, Właściwości, Zastosowanie*; Grupa Górażdże: Chorula, Poland, 2016.
77. *Karta Charakterystyki Magnezu—Karta Charakterystyki Magnez Wiórki Firmy Carlroth Zgodnie z Rozporządzeniem (WE) nr 1907/2006 (REACH), Zmienionej 2015/830/UE Sporządzona 23.01.2017 r*; Carl Roth: Karlsruhe, Germany, 2017.
78. *FOX 50 110 °C Instrument Manual, LaserComp—TA Instruments 2002–2016*; LaserComp–TA Instruments: Wakefield, MA, USA, 2016.
79. Tariq, R.; Hussain, Y.; Sheikh, N.A.; Afaq, K.; Ali, H.M. Regression-based empirical modeling of thermal conductivity of CuOwater nanofluid using data-driven techniques. *Int. J. Thermophys.* **2020**, *41*, 43. [CrossRef]
80. Qian, X.; Lee, S.; Soto, A.-M.; Chen, G. Regression Model to Predict the Higher Heating Value of Poultry Waste from Proximate Analysis. *Resources* **2018**, *7*, 39. [CrossRef]