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THE IMPACT OF GRAPHITE ON THE THERMAL CONDUCTIVITY OF SOLIDIFIED GROUT**

1. INTRODUCTION

Geothermal energy is a constantly developing science which is concerned about taking heat from inside the Earth and converting it into energy. (The most significant factor of the increased interest in this field of studies are the growing prices of fossil fuels and the dangers that fossil fuels can cause. Geothermal energy can be defined by enthalpy. There is low-enthalpy geothermal energy and high-enthalpy geothermal energy. Nowadays the low-temperature geothermal energy has become more popular due to the utilization of borehole heat exchangers which makes the heat intake less independent of geological structures [2].

Vertical borehole heat exchangers are increasingly popular because they need a small surface area in which to operate. Another advantage of borehole heat exchangers is the more stable temperature at greater depths. It is necessary to drill a well or adjust the old one to install a borehole heat exchanger. The depth and the amount of borehole heat exchangers is dependent on the demand for heating power. It is really important to know the parameters of the rock, such as type, thermal resistance, volumetric heat capacity or hydrogeological parameters [2, 3].

There are a few types of borehole heat exchangers: single U-tubes (Fig. 1a), double U-tubes (Fig. 1b), triple U-tubes and coaxial borehole heat exchangers (Fig. 1c).The first type is suitable to depths of 150 m, the second kind is for deeper wells. The construction of borehole heat exchangers requires the selection of a proper sealing grout [3, 8, 9].

Sealing grout is an important part of the installation as it can guarantee the proper working of the borehole heat exchanger. The main task for the grout is that it tightly fill the space between the walls of the well and heat exchanger and also supports heat transfer between the rock mass and the medium circulating in the borehole heat exchanger [3].

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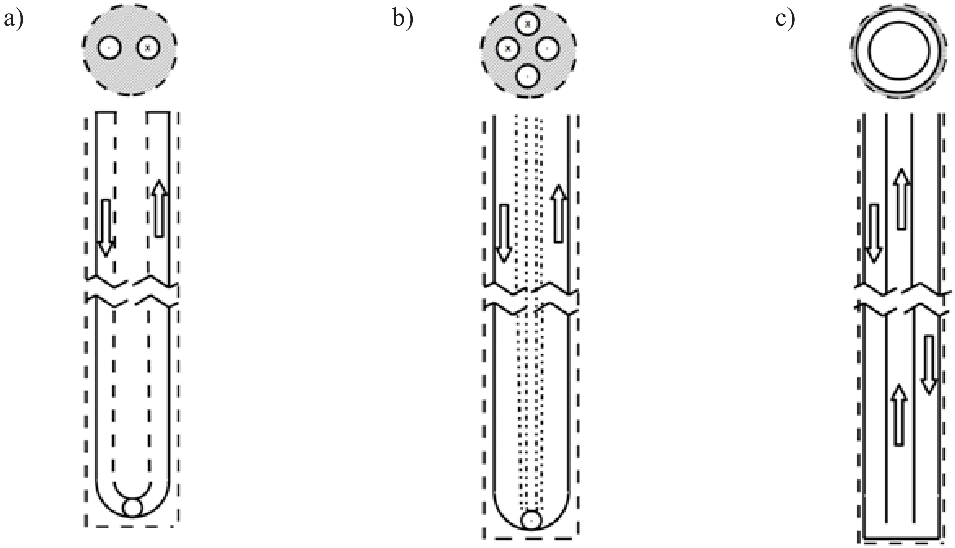


Fig. 1. Schemes of borehole heat exchangers [3]:
a) single U-tube; b) double U-tube; c) coaxial system

The grout used to install a borehole heat exchanger should be easily pumped and have a good workability. It should have increased thermal conductivity paired with low permeability [4]. What is more, the grout should be able to isolate aquifers to protect them from pollution [7].

There are many grouts with increased thermal conductivity and proper parameters on the market. For example: Calidutherm–Terra Calidus, Hekoterm–Hekobentonity, Raugeotherm–Rehau, Stüwa Therm–Stüwa oraz ThermoCem Plus–Górażdże. Their biggest disadvantage is their high price, especially on the Polish market. Research was focused on finding proper admixtures added to grout which can improve the thermal properties. This paper contains the description of the influence of graphite on (blast furnace cement) CEM III/B-V 32.5R.

The goal of the paper is the examination of graphite influence on the thermal conductivity of solidified grout. The grouts which contain graphite should have better thermal conductivity than grouts made without this admixture.

2. GRAPHITE

This research concerns the usage of graphite flakes from the SINOGRAF SA company. It is one of the natural types of graphite which itself is one of the native element minerals. It was created in the same manner as coal, by means of the metamorphosis of organic substances which contained large amounts of carbon. It is characterized by an ordered crystal structure and a distinctive metallic sheen. Flake graphite is also called silvery graphite or crystalline graphite [8, 10].

The main properties of graphite are: high thermal and electrical conductivity, high thermal and chemical resistance, low rate of thermal expansion and very good lubricity. The plate/flake graphite is used in molding, the refractories, for the production of lubricants, brake linings, for the production of paints and anti-corrosion coatings, or cores in the production of batteries, electrodes and electrical accessories [10].

The research on grouts with graphite was made in Poland [8, 10]. The usage of graphite to improve the thermal conductivity of grout as also been described by foreign scientists, for example Delaleux and Lee [1, 5].

3. DESCRIPTION OF THE RESEARCH

In the following section there is a description of the test kit, measurement methodology and samples which were used to conduct the research.

The test kit

The test kit contains: an insulation board with stands, solidified grout samples, a heating device, a thermal imaging camera (Flir) and a thermometer (Flir). The insulation board (Fig. 2) was made with two shields of beaverboard filled with insulating foam. There is a hole cut in the middle of the board where samples can be placed. In the case of clearances between the board and the sample, there was a gasket around the sample to fill the whole surface.

Fig. 2. The insulation board with the sample holder

The solidified grout samples was placed in the insulation board and heated with a heating device, namely a hairdryer by Remington (Fig. 3). The dryer was turned on 30 s before the measurement. This action was made to ensure the air flow is uniform during the entire measurement.

Fig. 3. Heating device – dryer (Remington)

The measurement of the surfaces of samples was made by a thermal imaging camera (Flir) (Fig. 4) and then by a thermometer (Flir) (Fig. 5). The samples were measured with a constant distance between samples and the thermometer/thermal imaging camera.

Fig. 4. Thermal imaging camera

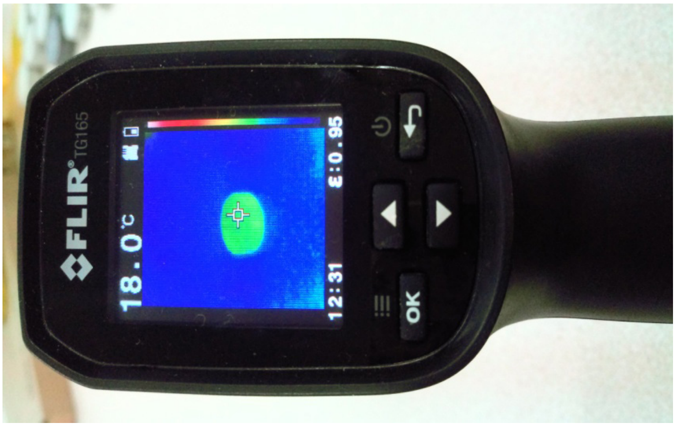


Fig. 5. Contactless thermometer

Methods of measurement

The manner of measurement and the elements of the test kit are experimental and they are about finding cheaper alternatives to measure thermal conductivity. The survey is a measurement of the temperature of both sides of the samples of solidified grout with various admixtures of graphite (according to diatomite samples). The research was made in the Laboratory of Geoenergetics Faculty of Drilling, Oil and Gas, AGH UST Stanisława Staszica in Krakow.

The measurement of every sample took 10 min. Longer measurement was impossible because of the low power of the heating device and a longer measurement could have had a negative influence on the results. The temperature of both sides of the sample was measured before heating. Then – during the heating – measurements were made of the temperature of both sides of the sample every 2 min. The results are presented in a table, where the temperature difference between the sides of the sample is calculated at every time interval and denoted as ΔT – equation (1):

$$\Delta T = T_{heated} - T_{opposite} \tag{1}$$

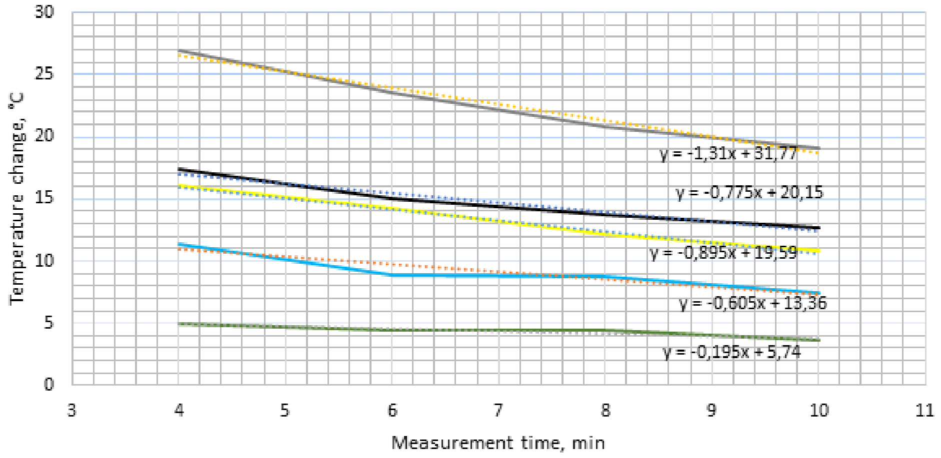
where:

ΔT – the temperature difference [°C],
T_{heated} – the temperature of the directly heated side [°C],
$T_{opposite}$ – the temperature of the opposite side [°C].

The methodology is based on the Fourier heat conduction equation (2):

$$q = -\lambda \cdot \operatorname{grad} T \tag{2}$$

The next step was finding an interval in which the temperature difference ΔT stopped rising and start to tend towards zero. It can be seen that the directly heated side starts to transfer more heat to the opposite side. The phenomenon usually persisted until the end of measurement or shortly before it ended. The entire time interval when the temperature difference is decreasing is presented on a graph and it is close to a linear function (Fig. 6). In this way, we put all the samples on the chart, together with the base samples of known thermal conductivity. The most important thing is the angle of inclination of the function to the axis 0X. If we know the thermal conductivity and the angle of inclination of the base samples, we are able to determine the range of the thermal conductivity of the tested solidified grout samples by entering their angle of inclination between the angles of the base samples, which are considered angle limits for conductivity data.



Polyethylene 12 mm
Glass 12 mm
Fine-grained sandstone (12 mm)
Cement without admixture w/c 0.8
Cement with graphite 20% w/c 1.0
Linear Regression (Polyethylene 12 mm)
Linear Regression (Glass 12 mm)
Linear Regression (Fine-grained sandstone (12 mm)
Linear Regression (Cement without admixture w/c 0.8)
Linear Regression (Cement with graphite 20% w/c 1.0)

Fig. 6. A plot of temperature change of the measurement time

Test samples and base samples

The solidified grout samples (Fig. 7) were made according to the applicable standard PN-EN ISO 10426-2 [6]. They were stored in three different ways:

– at a temperature of 25°C (sample A),
– under water (sample B),
– in an oven heated to 80°C (sample C).

The rings were made with a thickness of 12 mm and 18 mm, but the calculations were made only for a thickness of 12 mm. All samples were made from metallurgical cement CEM III/B-V 32.5 R, with different contents of graphite and having different water-cement ratios (Tab. 1). In addition, the research used a base sample of known thermal conductivity, which were used to determine the scope of the thermal conductivity of the test samples.

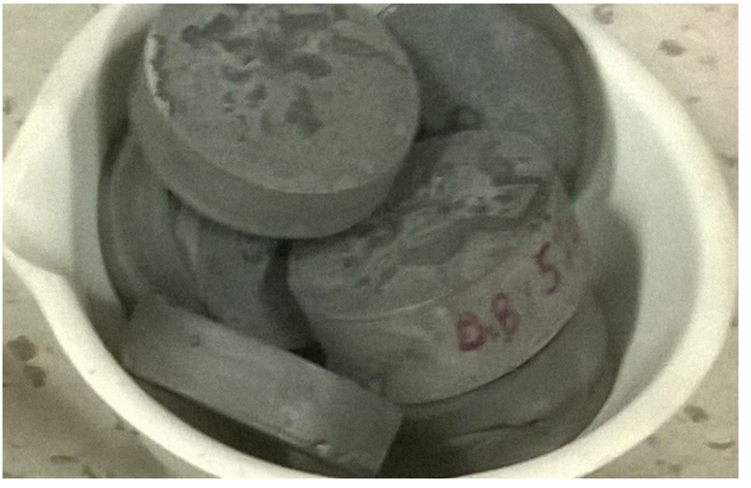


Fig. 7. The samples used for testing

Table 1
List of parameters of samples used for testing

The type of the cement	Water-cement ratio (w/c)	The percentage of the additive of graphite in the sample [%]
CEM III/B-V 32.5 R	0.8	5
CEM III/B-V 32.5 R	0.8	10
CEM III/B-V 32.5 R	0.8	15
CEM III/B-V 32.5 R	1.0	10
CEM III/B-V 32.5 R	1.0	20
CEM III/B-V 32.5 R	1.0	30
CEM III/B-V 32.5 R	1.2	10
CEM III/B-V 32.5 R	1.2	20

The measurement of the base samples were made in the Oil and Gas Institute (Krakow, Bagrowa 1) and in the Laboratory of Geoenergetics (Faculty of Drilling, Oil and Gas, AGH UST Krakow). The thermal conductivity was measured for five base samples:
- cement CEM III/B-V 32.5 R without admixture, w/c 0.7 and thickness 12 mm;
- fine-grained sandstone, thickness 12 mm;
- cement CEM III/B-V 32.5 R with graphite 20%, w/c 1.0 and thickness 12 mm;
- glass, thickness 12 mm;
- polyethylene, thickness 12 mm.

The results of the measurement of base samples conductivity is presented in Table 2.

Table 2
Thermal conductivity of base samples

Sign of the base sample	Name of the base sample	Thermal conductivity, λ, [$W \cdot m^{-1} \cdot K^{-1}$]
1	Cement CEM III/B-V 32.5 R without admixture, w/c 0.7 and thickness 12 mm	0.37
2	Fine-grained sandstone, thickness 12 mm	2.55
3	Cement CEM III/B-V 32.5 R with graphite 20%, w/c 1.0 and thickness 12 mm	0.54
4	Glass, thickness 12 mm	0.91
5	Polyethylene, thickness 12 mm	0.40

From these measurements, it shows that sandstone has the highest conductivity, and the smallest is cement without additives. The very low conductivity of both neat cement and the admixtured cement may be caused by the high porosity of samples.

The results

The base samples (unlike the test samples) were stored only at room temperature. Table 3 shows the thermal conductivity of the base samples with the corresponding angles (Fig. 8).

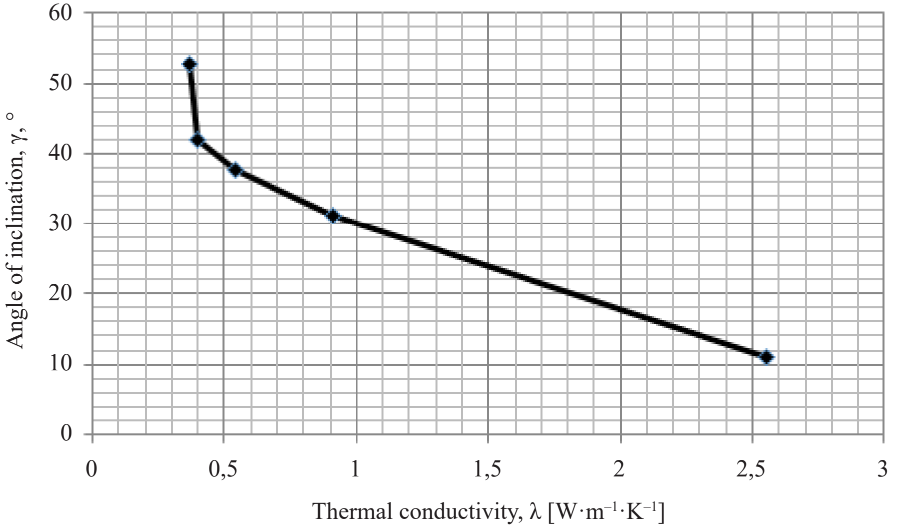


Fig. 8. A plot of the inclination angle of the heat conductivity of the test samples

Table 3
The thermal conductivity of the base samples with the corresponding angles

Sign of base samples	Thermal conductivity, λ [W·m^{-1}·K^{-1}]	Angle of inclination, γ [°]
1	0.37	52.64
5	0.40	41.83
3	0.54	37.78
4	0.91	31.17
2	2.55	11.03

From the above table, it can be concluded that the smaller the angle of the slope, the higher the thermal conductivity of the sample.

Table 4 shows the final results on the range of thermal conductivity for the analysed samples based on the inclination angles of samples in comparison to the angles of inclination base samples.

Table 4
The average values of the thermal conductivity of the test samples

	Thermal conductivity, λ [W·m^{-1}·K^{-1}]		
	temperature 25°C, sample A	water, sample B	oven, sample C
Without additions w/c 0.7	0.370	0.415	0.497
Without additions w/c 0.8	0.381	0.638	0.485
With 5% of graphite w/c 0.8	0.395	–	0.571
With 10% of graphite w/c 0.8	0.852	1.032	0.496
With 20% of graphite w/c 0.8	0.605	0.928	0.452
With 10% of graphite w/c 1.0	0.451	1.360	0.672
With 20% of graphite w/c 1.0	0.539	2.750	0.521
With 30% of graphite w/c 1.0	0.728	2.133	1.175
With 10% of graphite w/c 1.2	1.175	2.850	0.927
With 20% of graphite w/c 1.2	0.840	1.322	0.898

4. CONCLUSIONS

1) The addition of graphite increases the thermal conductivity of most solidified grout samples.
2) The best combination is 10% of graphite with a water-cement ratio 1.2, regardless of the place of storage (room temperature, water, the oven) and the combination of 20% of graphite with a water-cement ratio 1.0 for the sample which was kept in water.

3) Conditions of the storage of samples influenced thermal conductivity. A significant increase in thermal conductivity can be observed for the samples held in water compared to the samples stored at 25°C. When comparing samples with the same w/c (w/c = 0.8) it can be concluded that the samples with the addition of graphite in all conditions have a higher conductivity than those without additives.

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