

Speed Of Reaching The Full Potential Heat Capacity Of A Basalt Product: Experimental Results

Karin Rindt*

Department of Energy Engineering
Czech Technical University in Prague
Prague, Czech Republic
<https://orcid.org/0000-0002-2896-8377>
Karin.Edel@fs.cvut.cz

Lukáš Pilař

Department of Energy Engineering
Czech Technical University in Prague
Prague, Czech Republic
<https://orcid.org/0000-0002-5430-7054>

Frantisek Hrdlička

Department of Energy Engineering
Czech Technical University in Prague
Prague, Czech Republic
<https://orcid.org/0000-0003-0337-6292>

Abstract—Renewable Energy Sources naturally deliver energy intermittently, causing fluctuations in energy supply. The energy is therefore also not provided corresponding to the actual need, but according to the availability. Hence, the demand for energy storage is rising with the increasing utilization of renewable energy sources, tackling the difficulties coming along with it. Carnot-Batteries are one out of a few geographically independent storage possibilities for longer durations. The thermal energy storages employed in Carnot-Batteries vary from liquid molten salt storage with two-tanks or single-tank thermocline storage to packed bed configurations with encapsulated PCM or natural solid materials, like rocks. Storage materials, which are found plenty in nature, having nearly no direct impact on the environment, are water and rocks. Natural Rocks offer a greater temperature span for operation than water and are therefore suitable for a wider range of applications. A possible natural rock for use in thermal energy storage is volcanic material basalt. In this experimental work, basalt, after its usage in cast form as flue pipes in a power plant, is analyzed, focusing on its properties for energy storage applications. Using this product would offer the reuse of an otherwise not anymore useful, leftover product and provide a storage material without the need of taking it from nature. The experimental research to retrieve the speed of reaching the full potential heat capacity of this product is described. The samples of basalt and the basalt product are analyzed at different temperatures from 300°C to 750°C. Additionally, air cooling, from these temperatures down to 100°C, and surface structure changes are evaluated. Insights into important boundary conditions for employment as storage material are given. In future work, it is anticipated to use these results as the base for a charging model of the basalt product and its validation.

Index Terms—thermal energy storage (TES), Carnot-Batteries, power-to-heat-to-power (P2H2P), basalt, heat capacity

I. INTRODUCTION

With the increasing employment of Renewable Energy Sources (RES), improving its overall reliability is inevitable. Variable renewable energy sources (VRES)

like sun and wind make up a great part of renewable energy production and greatly impact the electric grid. As long as the maximum integration of VRES stays under 10 percent of the total energy production, no changes would be necessary [1]. However, many countries already exceed this limit, for instance Germany, which had 28 percent of combined on- and offshore wind and solar power production in 2019 from the total produced electricity. Besides the obvious problem of a lack of energy when the demand exceeds the production, overproduction can cause similar severe problems within and over the border of a country's own grid [2]. There are many possibilities to tackle these challenges, but all are footing on two basic principles: enhancing the electricity distribution and enlarging the storage capacities. Carnot-Batteries are one out of a few geographically independent storage possibilities for longer durations. In a Carnot-Battery, electricity is converted to heat as which it is stored and then converted back to electricity when needed. The principle, therefore, is also known as Power-To-Heat-To-Power or short P2H2P. If a heat pump accomplishes the conversion to heat, it is also called Pumped Thermal Energy Storage (PTES). The thermal energy storages employed in Carnot-Batteries vary from liquid molten salt storage with two-tanks or single-tank thermocline storage to packed bed configurations with encapsulated PCM or natural solid materials, like rocks. Thermal Energy storage isn't new technology, however, for the use as electricity storage, new requirements need to be taken into account, and the search for further possible storage materials goes on. One of the most important thermodynamic properties for solid materials in a heat storage is the heat capacity. Further, it is from value to know how fast the material can be charged and discharged, as well as how quickly it can be employed to

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the full extend. This paper analyses and compares the speed of reaching the full potential heat capacity of two possible storage materials, attempting to shed some light on their most important properties. Natural basalt, which is found plenty in nature, having nearly no direct impact on the environment, and a basalt product, which could get a chance for a second-life as storage material after its usage as flue gas pipes or heat insulating tiles.

II. EXPERIMENTAL PROCEDURE AND METHODOLOGY

Heat Q_r (1) is stored within a rock r with the mass m_r , when it is heated to a certain temperature. In this experiment, the initial temperature of the rocks is the room temperature (RT). With a furnace, they are heated to different temperatures denoted with $x^\circ\text{C}$, where they have the heat capacity $c_{p,r,x^\circ\text{C}}$. The heat stored in this way can be described as $\Delta Q_{r,(RT)to(x^\circ\text{C})}$ (2).

$$Q_r = \Delta Q_{r,(RT)to(x^\circ\text{C})} \quad (1)$$

$$\Delta Q_{r,(RT)to(x^\circ\text{C})} = m_r \cdot c_{p,r,(x^\circ\text{C})} \cdot \Delta T_{r,(RT)to(x^\circ\text{C})} \quad (2)$$

During the heat capacity measurement, the rock is releasing heat to the water of the calorimeter (3).

$$\Delta Q_{r,(w)} = \Delta Q_w \quad (3)$$

Together with the temperature difference of the water (after measuring) to the room temperature, the total heat stored in the rock over the charging time can be determined (4).

$$\Delta Q_{r,(RT)to(x^\circ\text{C})} = \Delta Q_{r,(w)} + \Delta Q_{r,(RT)} \quad (4)$$

The heat released to the water is

$$\Delta Q_w = m_w \cdot c_{p,w} \cdot (T_{w,ac} - T_{w,bc}) \quad (5)$$

with the mass m_w and the heat capacity $c_{p,w}$ of the water. The water temperature before cooling down the rock is $T_{w,bc}$, afterwards $T_{w,ac}$. The heat capacity of the water is approximated and assumed to be

$$c_{p,w} \approx 4182 \frac{\text{J}}{\text{kgK}} \quad (6)$$

for all temperatures. The remaining heat, stored due to the temperature difference of the water after the cooling ($T_{w,ac}$) to the room temperature $T_{(RT)}$, is denoted in the following as $\Delta Q_{r,(RT)}$.

$$\Delta Q_{r,(RT)} = m_r \cdot c_{p,r,(w,ac)} \cdot (T_{w,ac} - T_{(RT)}) \quad (7)$$

The true heat capacity of the rock at these temperatures is unknown as well but can be approximated with the heat capacity of the rock at 20°C by Waples and Waples [3].

This is acceptable as the variation of basalt heat capacity at the water temperatures is a few percent only, and because the influence on the overall result is minimal. With the basalt products composition being nearly the same as the raw basalt, this value is used as an approximation for also calculating the basalt products' heat capacity. However, it should be mentioned that the real heat capacity of the specific, analyzed basalt and basalt product must differ from this value according to the values determined in this paper's experimental work.

$$\begin{aligned} c_{p,r,(w,ac)} &\rightarrow c_{p,r,(20^\circ\text{C})} \\ c_{p,r,(20^\circ\text{C})} &= 898 \frac{\text{J}}{\text{kgK}} \end{aligned} \quad (8)$$

The heat capacity $c_{p,r,(x^\circ\text{C})}$ of the rock, at the temperature $x^\circ\text{C}$ is then calculated as

$$\begin{aligned} c_{p,r,(x^\circ\text{C})} &= \frac{Q_r}{m_r \cdot \Delta T_{r,(x^\circ\text{C})to(RT)}} \\ &= \frac{\Delta Q_w + \Delta Q_{r,(RT)}}{m_r \cdot \Delta T_{r,(x^\circ\text{C})to(RT)}} \end{aligned} \quad (9)$$

To determine the speed of reaching the full potential heat capacity, ten rock patterns (Fig. 1) are put into a furnace at 300°C to 750°C (Fig. 2). One pattern is removed and placed in the calorimeter (Fig. 3) every 3 minutes with the help of a metal claw (also in Fig. 3), and the heat capacity is calculated based on the waters temperature rise. The calorimeter consists of an insulated steel bucket filled with 3,5l to 4l water and is topped with an insulating lid to prevent temperature exchange with the environment, keeping the effect of the partial boiling of the water to a minimum. Two RTD sensors are immersed in the water at two different heights to measure the temperature rise of the water and to detect temperature stratification within the tank (Fig. 4). To prevent temperature stratification in the first place and speed up the rock's cooling in the water, a stirrer is installed. A third RTD is measuring the room temperature and is fixed to the top of the laboratory stand. All data is acquired by a National Instruments Module (9226), processed with a National Instruments Compact DAQ Chassis (cDAQ 9185), and evaluated in LabVIEW.



Fig. 1. Layout of rock patters for heating in the furnace.



Fig. 2. Furnace for heating up the rock patterns.



Fig. 3. Calorimeter and measurement set-up.

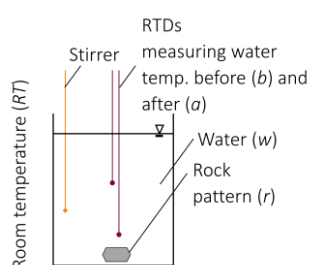


Fig. 4. Scheme of calorimeter and measurement set-up.

III. CHARACTERIZATION OF NATURAL BASALT AND THE CAST BASALT PRODUCT

Basalt is a volcanic rock with good abrasion resistance and a low tendency to corrosion [4]. The rock analyzed in this paper is quarried in Slapany u Chebu in the west of the Czech Republic. The raw rock is further denoted as natural basalt (Fig. 5). The basalt product (Fig. 6) is produced by the company EUTIT s. r. o. in Stara Voda (Cheb, Czech Republic), close to the stone' quarry. The first step of the production process is the melting of the rock at 1280°C and casting it in the form of molds and cylinders. Those castings will then be placed in kilns at 850°C. This heat treatment forces the basalt to recrystallize and changes its properties. Compared to the natural basalt, the cast basalt product is now inert, homogeneous, denser, non-porous, resistant to many

chemicals, and highly abrasionresistant. It can withstand temperatures of 450°C. The cast basalt is used in various applications like flue gas pipes, iron slurries, coal pipes, or hoppers. The chemical composition of natural basalt and the cast basalt product from EUTIT are shown in table 1 and compared graphically in Fig. 7.



Fig. 5. Piece of natural basalt.



Fig. 6. Piece of the basalt product.

TABLE I
CHEMICAL COMPOSITION OF NATURAL BASALT AND THE CAST BASALT PRODUCT [4].

Name	Chemical formula	Natural Basalt	Basalt product
Silicon dioxide	SiO_2	45.95%	45.33%
Aluminium oxide	Al_2O_3	12.74%	12.44%
Magnesium oxide	MgO	12.9%	12.39%
Calcium oxide	CaO	11.22%	11.38%
Iron(III) oxide	Na_2O	2.98%	2.96%
Sodium oxide	TiO_2	12.9%	12.39%
Titanium dioxide	MgO	2.05%	2.10%
Potassium oxide	K_2O	1.03%	0.94%
Loss on ignition	-	0.58%	1.09%

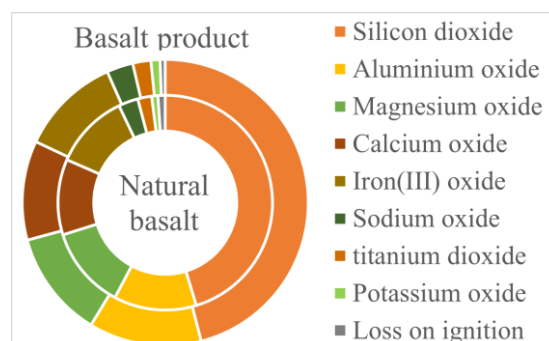


Fig. 7. Graphic comparison of the chemical composition of natural basalt and the cast basalt product [4]

IV. RESULTS AND DISCUSSION

A. Heating

For the experiment, samples of natural basalt weighting 46g to 73g and samples of the basalt product weighting similar 43g to 64g were compared. The natural basalt's full potential heat capacity is reached after 24 minutes at 300°C and 400°C. With increasing heating temperature, the full potential heat capacity is reached faster – 12 minutes at 500°C, 600°C, 700°C and 15 minutes at 750°C. Fig. 8 shows the change of heat capacity of the natural basalt over time for temperatures from 300°C to 750°C. The speed of reaching the full potential heat capacity is increasing from 0.50 (J/(kg*K))/s at 300°C until 1.35 at 600°C to 750°C (Fig. 11). The basalt product, on the other hand, reaches its full potential heat capacity already after 21 minutes at 300°C, 18 minutes at 400°C and 500°C, 15 minutes at 600°C, 12 minutes at 700°C, and 9 minutes at 750°C (Fig. 9). Up to 500°C, the speed of reaching the full potential heat capacity is higher for the cast basalt than for the raw rock. Between 500°C and 700°C, the speed of reaching the full potential heat capacity is higher for the natural basalt. Above 700°C, the speed of reaching the full potential heat capacity is again higher for the basalt product. Generally, the speed of reaching the full potential heat capacity increases with higher temperatures. At 300°C the speed is 0.66 (J/(kg*K))/s, increasing up to 1.82 (J/(kg*K))/s at 750°C (Fig. 11). This shows that the speed of reaching the full potential heat capacity is higher for the basalt product than for the natural basalt. A second batch of natural basalt, with patterns weighting less than the mainly analyzed batch, 18g to 38g, was included in this analysis and showed that the speed of heat capacity is also dependent on the size of the rock pieces (Fig. 10, Fig. 11).

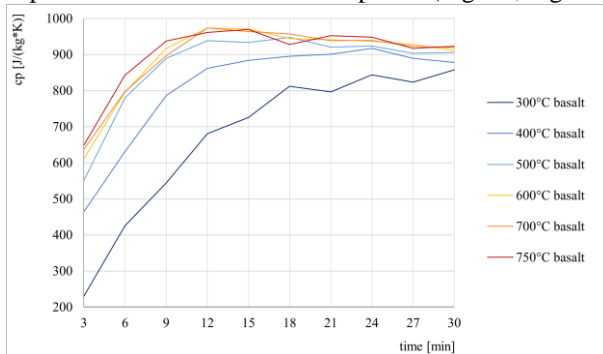


Fig. 8. Static change of the natural basalts heat capacity (samples 46g – 73g).

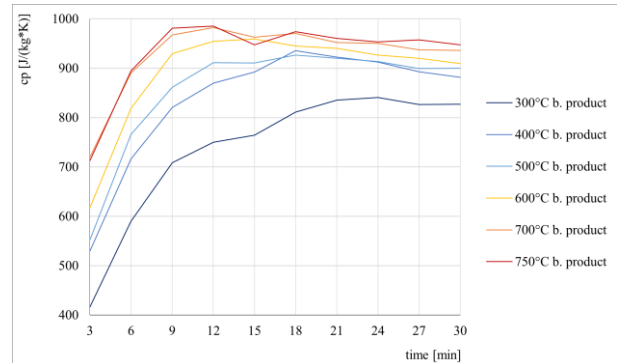


Fig. 9. Static change of the basalt products heat capacity (samples 43g – 64g).

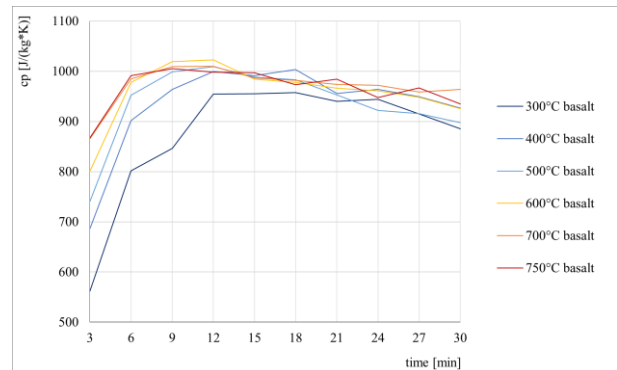


Fig. 10. Static change of the naturals basalt heat capacity (samples 18g – 38g).

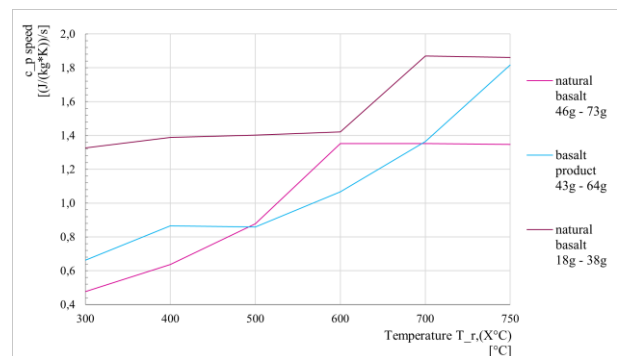


Fig. 11. Speed of reaching the full potential heat capacity.

Even though the limit of the material, guaranteed by EUTIT for their product, is 450°C, no significant difference was found for the heat capacity. After reaching its maximum, the heat capacity starts decreasing again for both the natural basalt and the basalt product. This might be partially explained through water evaporating from the pores of the rock, which might slightly increase the heat capacity in the first minutes of the measurement as the heat capacity of water is several times higher than the heat capacity of the rock (noting that the waters heat capacity

is also exponentially increasing at temperatures greater 200°C [5]). However, the greater influence on the actual, measured heat capacity seems to be the composition of the individual rock, as the same behavior can be seen after 30 and 60 minutes of heating in advance of determining the heat capacity (analyzing the heat capacity for 33 to 60 and 63 to 90 minutes) which can be seen in Fig. 12. While looking at Fig. 12 it is also interesting to see that already at the third time heating the rock at the same temperature, the heat capacity decreases. This effect of the unstable and decreasing heat capacity is greater for smaller rock samples, which also backs the thesis that the exact rock composition greatly influences the true heat capacity.

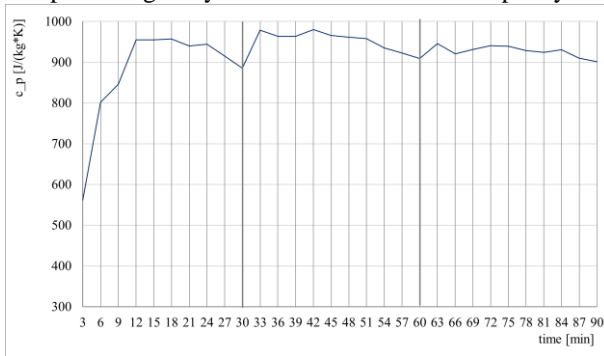


Fig. 12. Static change of the natural basalt's heat capacity over a period of 90 minute at 300°C (samples 18g – 38g).

Generally, the reached full potential heat capacity is quite similar for all temperatures. The final full potential heat capacity (after 30 min) varies less than 13% for the basalt product and less than 7% for the natural basalt. Besides the heat capacity determination, weight and surface changes were observed during the experiments. White parts of the rock surface turned red for both materials after the first heating (Fig. 13 natural basalt, Fig. 14 basalt product). This change is most likely some light corrosion and connected to the loss of weight of the material. The natural basalt has a weight loss during the first heating cycle of 1.5% and the basalt product of 0.06%. However, the color is further changing redder, with an increasing number of cycles, indicating that the tendency to corrosion might not be as low, as expected by the companies claims. It might turn out that there's a negative impact on a storage life-time by corrosion or other decaying processes. The most important conclusion of the heating experiment is that the speed of reaching the full heat capacity of both materials is high (fast charging) and that the temperature doesn't have a very big influence on the heat capacity of the basalt product while having an even lower influence on the heat capacity of the natural basalt.



Fig. 13. Surface changes of natural basalt (FLTR: before, after one, and after many heating cycles).



Fig. 14. Surface changes of the basalt product (FLTR: before, after one, and after many heating cycles).

B. Cooling

It takes 21 to 27 minutes to naturally cool down the basalt product to about 100°C oven temperature (Fig. 15). On the other hand, the heat capacity falls in less than 3 minutes to the heat capacity the pattern has at 100°C (Fig. 16). The natural basalt needs 21 to 30 min to cool down to about 110°C oven temperature (Fig. 17). The oven used for keeping the 100°C is an older model of dryer, which is why the temperature was hard to set exactly to 100°C. However, this doesn't influence the experiment's conclusion significantly and is, therefore, an accepted inaccuracy. The heat capacity of the natural basalt is falling slower than for the basalt product. It takes 12 minutes until the value is at the rock's heat capacity at 100°C (Fig. 18). As can be seen in Fig. 15 to Fig. 18, the heat capacity is again fluctuating around a median value as also for the heating process, illustrated in the last subchapter. This again indicates that the specific rock composition and size have the greatest influence on the heat capacity. It can be summarised that the cooling (discharge) of the rocks, especially the cast basalt product, is relatively fast, which indicates an effective discharge of stored heat.

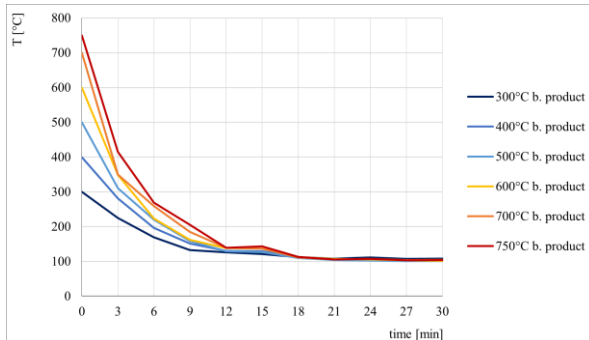


Fig. 15. Basalt product temperature during cooling (samples 28g – 44g).

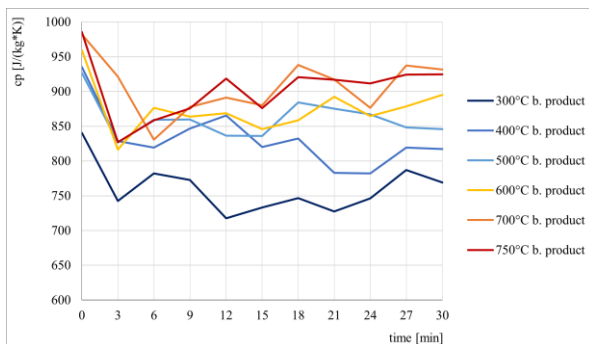


Fig. 16. Basalt product heat capacity during cooling (samples 28g – 44g).

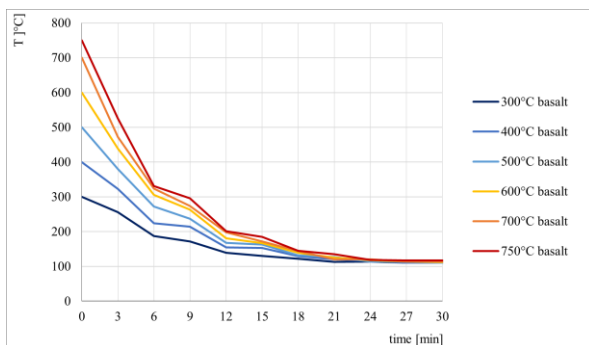


Fig. 17. Natural basalt temperature during cooling (samples 72g – 103g).

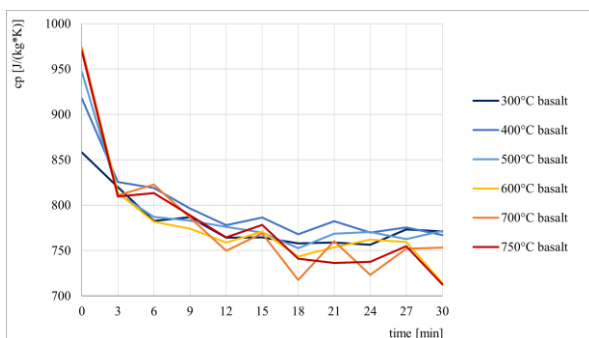


Fig. 18. Natural basalt heat capacity during cooling (samples 72g – 103g).

C. Validation and outlook

To validate the experiment methods, the results of the reached maximum potential heat capacity of natural basalt were compared to other experimental and theoretical research in Fig. 19. In the visualized experiments ([7-9]), comparable heat capacities were measured while also similar effects, like a dropping heat capacity at higher temperatures, can be identified ([7]). The authors of the respective paper, i.e. Martin et al. [7], don't explain the gap between their different measurement series but work with the average, acknowledging that it exists. The visible differences in the behavior of the heat capacity and the drop at higher temperatures in other works support the thesis in chapter IV.A that the composition of the individual rock greatly affects the heat capacity and its development. The similar results of other publications further prove and validate the experiment.

In Fig. 19 can also be seen that the theoretical works estimate much higher values, which shows the lack of accurate theoretical models of the heat capacity of basalt. In future work, a mathematical model of the speed of reaching the full potential heat capacity of the basalt product is going to be created and validated with the experimental results. Next to that, further thermodynamic properties will be analyzed and presented.

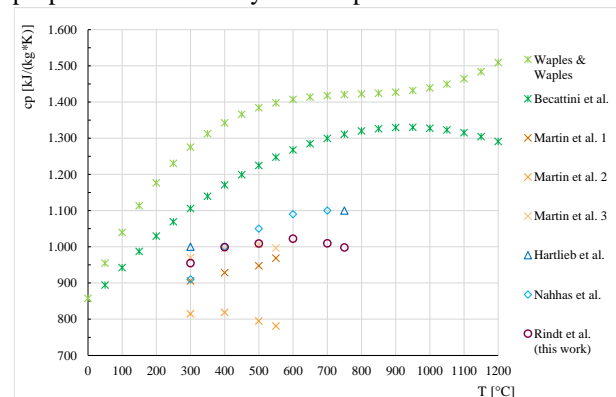


Fig. 19. Heat capacity of basalt rock – comparison with other experimental research and theoretical calculations [3] [6] [7] [8] [9].

V. CONCLUSION

This paper shows experimental work on the thermal capacity of natural basalt and a cast basalt product. It analyses the speed of reaching the full potential heat capacity of both materials and what affects it. Further, the process of cooling down to 100°C and general effects on the material through usage under thermal conditions, like e. g. surface changes, are evaluated. All experiments have

been conducted under laboratory conditions. The rock patterns were heated from room temperature to 300°C to 750°C with a furnace. The heat capacity was then determined with a calorimeter, measuring the temperature rise of the water. Additionally, the patterns were weighted between each heating or cooling, and the surface changes were evaluated visually. The speed of reaching the full potential heat capacity increases with higher temperatures. Simultaneously, the basalt product has a higher maximum speed of reaching the full potential heat capacity than the comparable basalt patterns. The heat capacity itself is increasing like a logarithmic function for both materials, and the full potential is reached in maximum 24 minutes. The final full potential heat capacity for temperatures of 300°C to 750°C after 30 minutes of heating varies less than 13% for the basalt product and less than 7% for the natural basalt. Important factors for the heat capacity behavior are the mass of the patterns, the influence of the material's inhomogeneity and possibly the humidity of the rocks, and the number of repetitions (visible and measurable changes in the first cycles).

Cooling the rock patterns takes less than 30 minutes, with the heat capacity falling in a logarithmic way. It can be concluded that the charging and discharging behavior is, as expected, dependent on the temperature, but not exclusively and that the full charging and discharging of individual pieces of rock can be completed in less than 30 minutes.

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