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Assessment of four main representative flint facies as alternative storage materials for concentrated solar power plants

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ABSTRACT

At present there is an intense research for developing alternative sensible heat storage materials, such as natural rocks and recycled ceramics, able to work in concentrated solar power plants at high temperatures. This work demonstrates the potential of flint rocks as an economic and efficient filler material to be used with air as heat transfer fluid in packed bed storage system. Four facies of flint rocks were collected from south of France. To predict the performance of the storage system, crystalline structure, thermo-physical and thermo-mechanical properties of the studied rocks have been identified. For this purpose, the candidate rocks were subjected to extensive experimental characterizations under a series of thermal cycles. XRD, SEM, DSC/TGA, pycnometer, LFA, dilatometer, high temperature ultrasonic testing and nano-indenter method have been used to analyze these samples. Consequently, the 400°C was identified as ideal temperature for the heat treatment process of flint. The obtained results from the four analyzed samples have been compared together and with currently used storage materials. The results gathered from this paper prove the potential of flint in terms of high density, good specific heat capacity and good thermal stability up to 400°C to be used as filler material in energy storage applications relevant for low and medium temperature solar power plants.

Keywords: Concentrated solar power, thermal storage, thermocline, packed bed, natural storage material, thermo-physical and mechanical properties of flint.

Nomenclature		Acronyms	
C_p	specific heat capacity (J/kg.K)	CSP	concentrated solar power
λ	thermal conductivity (W/m.K)	TES	thermal energy storage
T	temperature (°C)	IEA	International energy agency
α	thermal diffusivity (m ² /s)	HTF	heat transfer fluid
ρ	bulk density (kg/m ³)	XRD	X-ray diffraction
ρ_0	bulk density at room temperature (kg/m ³)	DSC	differential scanning calorimeter
$\Delta L/L_0$	linear thermal expansion	TGA	thermogravimetric analysis

SEM	scanning electron microscope
LFA	laser flash analysis
EDS	energy dispersive spectroscopy

1. Introduction

Concentrated solar power (CSP) plants are promising means of generating electricity and they are experiencing strong growth in recent years. However, the solar energy is considered a variable source. Its availability is often inappropriate to the request of consumers. In fact, scaling up of a CSP plant to meet the peak demand leads to high costs [1]. Therefore, the thermal energy storage (TES) can improve the relevance of the solar power plant by providing the ability to match electricity production to the peak demand periods, and by feeding the power block with constant heat power level. Several thermal storage technologies are already available and related to CSP installations. The most mature storage system is the two-tanks molten salts system. However, in this type of storage the two tanks are not completely filled and the molten salts used have a relatively high cost (50% of the storage system). In addition, the molten salts have the largest contribution to the environmental impact of the storage system which presents 20% of the environmental footprint of the whole CSP plant [2]. According to the IEA (International Energy Agency) scenario, the world-wide annual production of molten salts will not be able to meet the development of CSP needs of the concerned material in 2050 [3,4]. Thus, thermocline concept can obviously offer a more economical storage system than conventional two-tanks [5]. This technology is based on the use of a single tank filled usually by molten salts or synthetic oils where the cold fluid remains at the bottom of the tank and the hot remains at the top due to the thermal stratification [6]. However, the molten salts are known to be corrosive media for tubes and pumps, the most critical challenge to limit their application [7]. Recently, using of solid filler materials in a thermocline system has drawn the attention of research laboratories as a cost-effective storage system. This technology is called packed bed/dual-media thermocline storage system [5]. In this concept, the solid filler media replaces a large amount of the fluid used (such as molten salts) and prevents convective mixing within the storage liquid [8]. In fact, wide range of solid materials can be used to store the thermal energy. The choice of the filler material is one of the key issues for an efficient storage, as well as to minimize the financial and the environmental impacts of the storage unit [9]. As a result, it has been identified a number of criteria required for the storage materials, namely [10]:

- high thermal storage capacity,
- mechanical and chemical stability,
- compatible with the heat transfer fluid (HTF),
- complete reversibility for a large number of charging/discharging cycles,
- abundantly available at low commercial cost with low environmental impact,
- stable under high-temperature conditions.

In this perspective, from the solid storage materials that have been tested are metals, bricks, sand, concrete and rocks which can be considered as available at low cost high temperature heat storage materials [11]. A sensible heat module made of high temperature concrete with an embedded heat exchanger through which the HTF will flow has been developed by German Aerospace Centre (DLR) [6,12]. Several thermal cycles were conducted on concrete module with success up to 390°C [3]. The concrete is a favorable storage material due to its low cost, high specific heat capacity at room temperature, availability, facility of processing and structural stability [1,13,14]. However, this material presents long term instability. When concrete is heated, a number of transformations take place and negatively affect on its characteristics [15]. Moreover, special care has to be given to the first heating cycle of concrete in order to avoid the formation of internal cracks resulting from the evaporation of its initial water content [3].

A great number of academic studies have been focused on innovative ceramics or refractory materials made from industrial wastes such as asbestos, slag or fly ashes [16]. These materials have been used as regenerators at temperatures of several hundred degrees Celsius. Despite the well adaptation for these materials in storage applications, some problems are still under investigation such as the large energy consumption during their elaboration to get homogeneous melting [17].

Rocks are considered as an essential candidate to make the solar system more efficient and reliable. They are applicable over a wide temperature range with limiting temperature given by the rock's melting point [18]. On the other hand, they do not require safety concerns, as is the case of high vapor pressure of thermal oil [19]. It should be noted that flint raw materials were intentionally heat-treated during the prehistoric age in order to facilitate the knapping of this type of rock during tools manufacturing [20]. Moreover, flint rocks were used to control the heat of fast burning fuels and to boil water, as well as to increase the effective heating

time of the fire place [3,21–23]. This finding led Schmidt et al. [24] to search about the consequences of heating on the structure of flint rocks.

In this regard, the most researches related to rock bed storage system focus only on modeling the thermocline system in order to predict the performance of the storage unit and evaluate its efficiency [25]. Few studies are interested in high temperature experimental characterization of physical and mechanical properties of rocks [25–29]. It is evident that the temperature plays an important role on the structural properties of rock [30,31], where some minerals contained in the rock can transit from phase to phase under the effect of heating, thus modifying the rock's properties [32]. Barbara et al. [33] conducted tests of compressive strength on heated and unheated flint rocks. Their results showed that when the samples were cooled gradually in the oven, they exhibited an increase in the strength of (25-40) % over the unheated samples. Thus, increasing the compressive strength due to heating is desirable feature for storage material in order to withstand the stress in the storage tank especially after the thermal expansion. In fact, adequate data on the physical and mechanical properties of flint rocks at high temperatures are missing.

The originality of our work comes through that it is the very first project which demonstrates the behavior of four facies of flint rocks under the effect of heating to be used as storage material in packed bed storage system operated with the air as the HTF. Flint is a hard and compact rock and most often has a homogeneous aspect [8,34]. Due to its high silica content, flint rock has a thermal conductivity (3.5 W/m.K) rather higher than the current used TES materials, besides to its higher strength and hardness characteristics [35,36]. In this regard, four varieties of flint rocks were gathered from different regions in France in order to assess the effect of localization on their properties. The samples were subjected to various experimental characterizations to identify the chemical composition and the crystalline component of these rocks, as well as to study the effect of heating on their physical and mechanical properties, knowing that the rocks must withstand the repeated thermal cycles without any degradation or chemical instability. It is worth mentioning that this study will help also the archaeologists to identify the various stages of heating on archaeological pieces and to link them with either intentionally controlled heating or, on the contrary, with accidental heating by specifying the applied heating mod.

2. Materials and methods

2.1. Selected samples

As mentioned in the introduction, it has been selected the most four facies of flint rocks available in the south of France (see Figure 1) to be used as storage material. These facies had been used by prehistoric people due to their good quality. Each flint sample used in this study corresponds to a distinct formation that can be characterized by its mineralogical content and micro-texture. Consequently, the studied samples could have various physical and mechanical properties, making each sample react differently with heating. The primary position and preliminary macrotextural description of the studied samples are presented below:

- SA sample: From Salinelles (Gard), primary position, Oligocene facies.
Biomicrite silicification in lacustrine environment. Heterogeneous macrotexture.
- ML sample: From Saint Martin de Londres (Hérault), primary position, Lutetian facies.
Low fossiliferous mud clay silicification formed in evaporitic context. Heterogeneous macrotexture.
- CG sample: From Costières du Gard - St Gilles (Gard), secondary position on plio-
quaternary alluvial deposits.
Silicification of a low fossiliferous micrite in a reducing environment. Homogeneous
and very fine macrotexture.
- NS sample: From Narbonne Sigean - Doul peninsula (Aude), primary position,
Aquitanian facies.
Bio-microsparite silicification in brackish lacustrine environment. Heterogeneous
macrotexture.

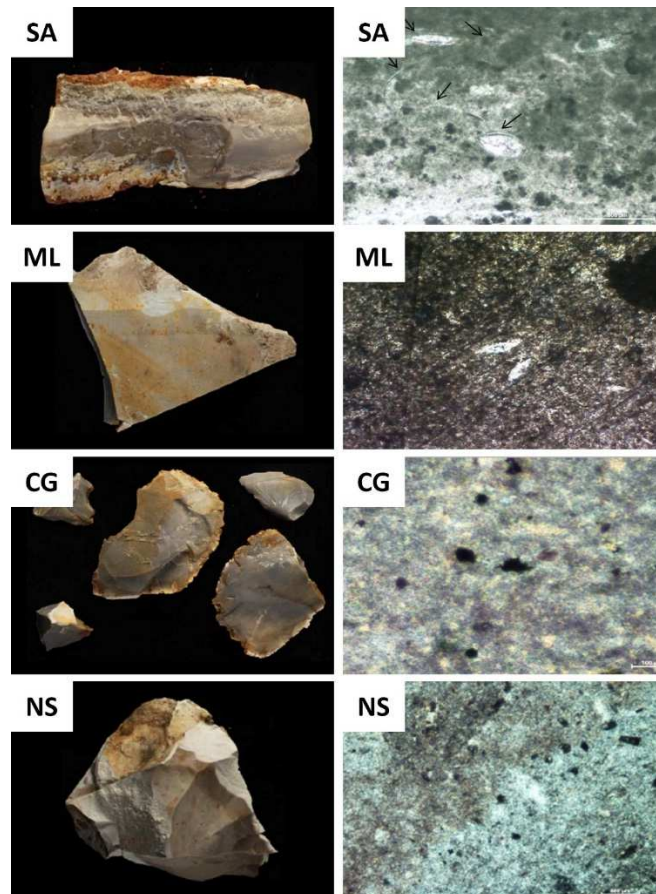


Figure 1 : Selected flint rocks with their corresponding micrographs

As shown in Figure 1, the micrograph of flint SA indicates the presence of ostracod remains in wackestone silica texture. Concerning the flint ML, it contains cryptocrystalline silica and gypsum crystals. While the flint CG has a silica mudstone texture with inclusions of automorphic quartz. Finally, the flint NS has microsparite silica and chalcedony.

2.2. Samples preparation

In fact, each experimental test requires a specific sample preparation. For XRD, DSC/TGA, SEM and C_p measurements, samples were crushed and sieved under $150\ \mu\text{m}$ to be transformed into fine powders, where others were cut to obtain square samples ($10 \times 10 \times 1.5\ \text{mm}$) for laser flash measurements. Besides, other samples with a dimension of $5 \times 5\ \text{mm}^2$ and length of 20 mm and 80 mm were shaped for dilatometer and Young's modulus characterizations, respectively.

Scanning Electron Microscope (SEM):

The chemical composition of powder samples was identified by using SEM Hitachi S-4500 equipped with energy dispersive spectroscopy (EDS). The instrument was operated with an accelerating voltage of 15 kV and a probe current of 50 mA.

X-Ray Diffractometer (XRD):

In order to define the effect of heating on the crystalline structure of the analyzed samples, XRD measurements were performed at room temperature by using PANalytical X-ray diffractometer on raw and heat-treated samples. The data were collected between 15 and 80 in 2θ , using $\text{CuK}_{\alpha 1,2}$ radiation.

Differential Scanning Calorimeter (DSC) and Thermo-Gravimetric (TG) analyzer:

This system has been used for identifying the characteristic temperatures of the studied samples in order to determine the proper maximum working temperature of flint rocks. Powder samples have been characterized by DSC/TG analyzer using a SETARAM Setsys Evolution TGA-DSC 1750 thermobalance. The samples were heated from room temperature to 1000°C during two thermal cycles with heating/cooling rate of 20 °C/min, under air atmosphere. While DSC 404 F1 Pegasus was used to measure the specific heat capacity values of the studied rocks in a temperature range of 20-400 °C, under air atmosphere. For each measurement, powder sample of 60 mg was used with a heating rate of 10 °C/min.

Dilatometer:

The operating temperature range of storage applications in CSP plants is rather wide. Thus, it would be important to take into account the rocks thermal expansion coefficient. This latter was measured using NETZSCH DIL402PC pushrod dilatometer. Samples having dimension of (5 × 5 × 20 mm) were heated to 400°C at 2.5 °C/min during three thermal cycles.

Ultrasonic measurement of Young's modulus in temperature:

The evolution of Young's modulus versus temperature has been measured by using high temperature ultrasonic technique. The measurements were performed with an original equipment developed by GEMH laboratory in 1980s to determine the elastic properties of the materials using the propagation of ultrasonic in a long bar mode [37]. The experimental procedure required an intermediate frequency about 130 kHz for a sample length of 80 mm

and cross section of 5×5 mm². The thermal program used in this analysis is identical to that used in dilatometer, namely 2.5 °C/min of heating and cooling rate over one thermal cycle.

Nano-indenter:

The hardness of original and thermally heated samples was characterized by using Nano-indenter II in order to determine the transformations of the mechanical properties of the studied samples due to the heat treatment. It has been done by using a Berkovich diamond indenter in the form of pyramid with a face angle of 65.27°.

Pycnometer:

The bulk density values of small unshaped solid pieces of flint samples (around 1 × 1 × 1 cm) were obtained at room temperature using a helium pycnometer AccuPyc1330, in which each recorded value is the average of 10 measurements.

Once the density at room temperature (ρ_0) is known, the density at high temperatures $\rho(T)$ is calculated by applying the Eq. 1; where $\Delta L/L_0$ is the linear thermal expansion:

$$\rho(T) = \frac{\rho_0}{\left(1 + \frac{1}{100} \frac{\Delta L(T)}{L_0}\right)^3} \quad \text{Eq. 1}$$

Laser flash:

The thermal diffusivity values of flint samples were measured by using square samples (10 × 10 × 1.5 mm) in NETZSCH LFA 457 instrument. The measurements were carried out under argon atmosphere with a heating rate of 2.5 °C/min, between (20-400) °C during five thermal cycles. Each presented experimental result represents the average of five measured values at the same temperature.

The thermal conductivity (λ) of the studied rocks was calculated by multiplying the thermal diffusivity (α) and the thermal capacity ($\rho \times C_p$) as a function of temperature (T) (see Eq. 2):

$$\lambda(T) = \alpha(T) \times \rho(T) \times C_p(T) \quad \text{Eq. 2}$$

3. Results and discussion

3.1. Mineralogical content and structural analysis

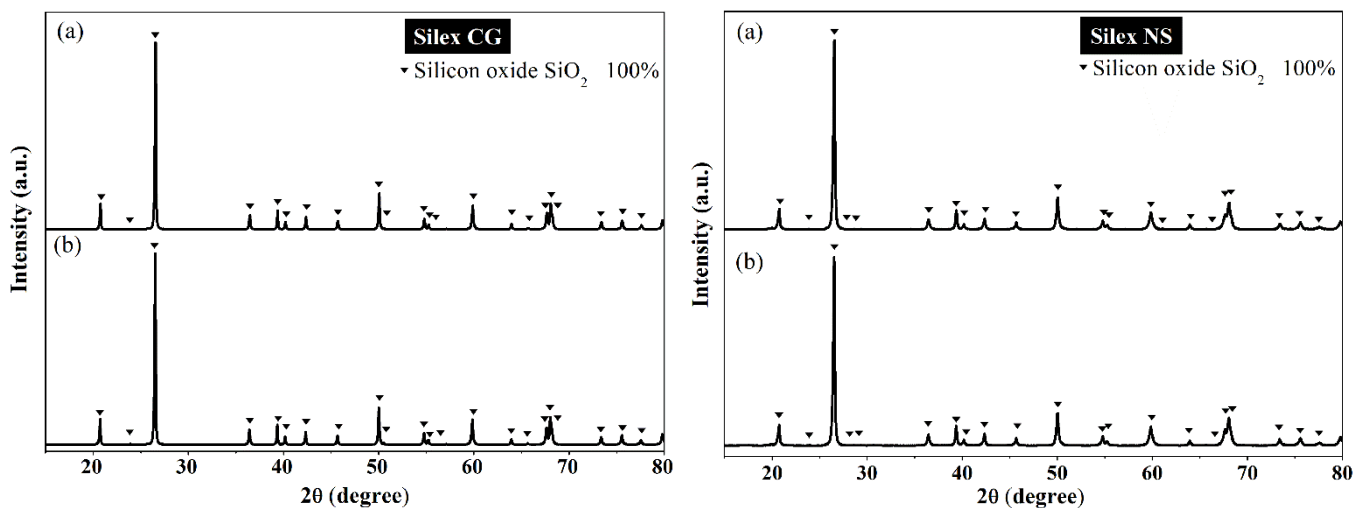
The chemical compositions of the raw flint samples are expressed in Table 1 in the form of oxide weight percent. It is observed that the most predominant constituent is the silicon oxide, as well as the presence of varying percentages of calcium and magnesium oxides in flint SA and ML.

(wt%)	SiO ₂	MgO	CaO
CG	100	-	-
SA	80	-	20
NS	100	-	-
ML	91.4	2.5	6.1

Table 1 : Chemical compositions of raw studied flint samples

In the literature it has already been published that, an increase in the amount of silicon oxide content in natural stones has notable effect on strength properties and microhardness [35]. This latter is very required in storage materials in order to avoid the crushing under repeated thermo-mechanical stress [38].

In order to identify the crystalline phases present in the four varieties of flint, the XRD analysis has been performed.



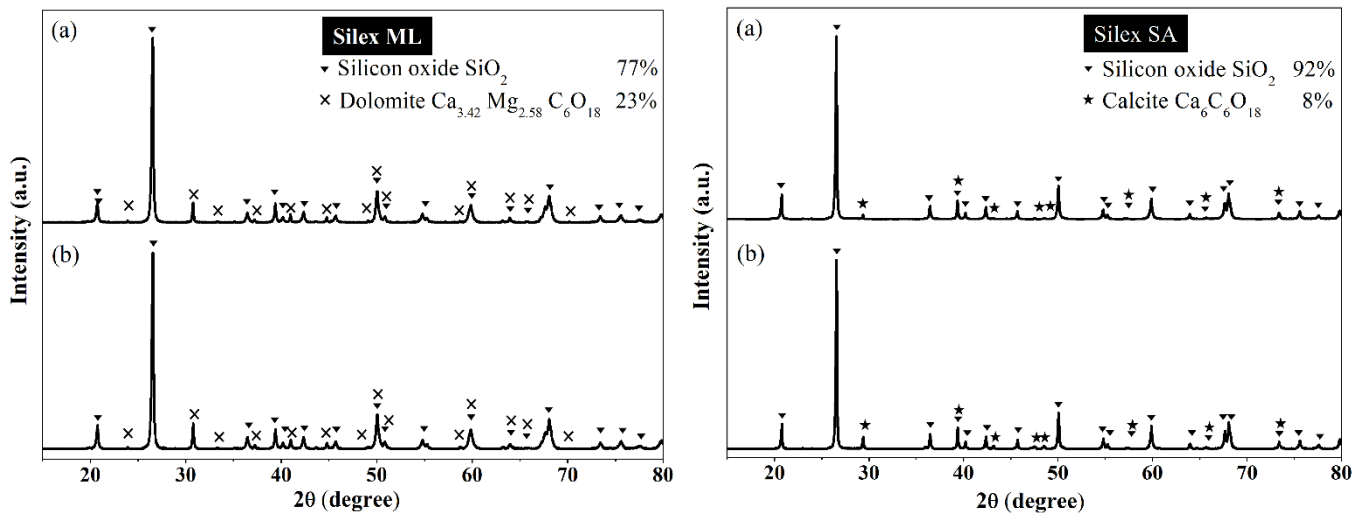


Figure 2 : Experimental X-ray powder diffraction profile of four flint rocks at room temperature: a) raw, b) heat-treated up to 400°C

The diffractograms of the studied rocks (see Figure 2) show the presence of silicon oxide as predominate crystalline phase, coupled with a small percentage of dolomite in flint ML and calcite in flint SA. We do not observe any broad contribution corresponding to amorphous phase, which would indicate that the samples are, essentially, totally crystallized and contain considerable amount of quartz. According to a study made by Faik et al. [16], the crystallized materials are more suitable for storage applications at medium temperatures (below 500°C) than at high temperatures.

3.2. Proper working temperature range

As it is known, the CSP plants have several operating temperature ranges depending upon the solar concentrating ratio: linear Fresnel and parabolic trough collectors almost up to 400°C, solar power towers up to 600°C and parabolic dish collectors up to 1000°C [1,39]. Therefore, in order to determine for which CSP approach our samples could be suggested as successful storage material, the proper maximum working temperature of the studied samples should be approximately determined. Consequently, flint rocks can be used without excessive changes in their chemical and mechanical properties up to this target temperature. The assessment of the thermal behavior of flint samples has been carried out by DSC/TG analysis. Corresponding weight losses under temperature change were recorded during two successive thermal cycles using a rate of 20 °C/min up to 1000°C.

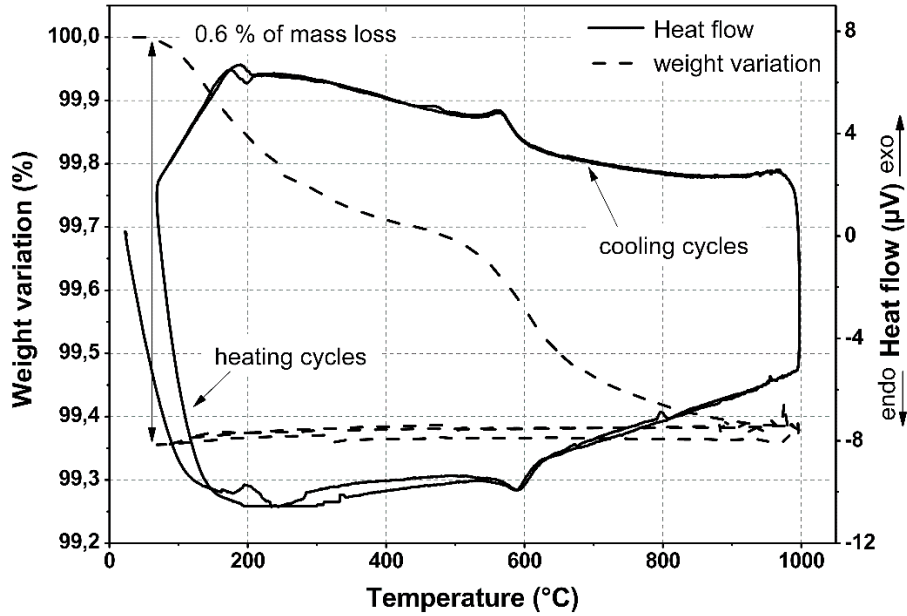
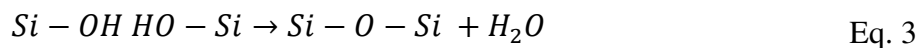


Figure 3 : DSC/TG analysis of raw flint CG, two thermal cycles up to 1000°C, 20 °C/min

The resulting curve of mass loss is shown as a function of temperature in the case of flint CG (the dashed line in Figure 3). It should be noted that as long as the four varieties showed almost similar behavior, they haven't been presented all here in order not to overload the figures. Since the samples are mainly composed of quartz, the amount of water contained within their structures is very small (about 0.6%) and its loss would be unlikely to affect significantly on their mechanical properties. The obtained result is in agreement with the data reported in the literature [40]. In fact, the obtained curve of the mass loss indicates the presence of three temperature intervals:

- below 200°C, represents the loss of water molecules held in the interconnected open pores,
- between 300°C and 550°C, the silanol transforms and new bridging of Si-O-Si reduce the surface of the open pores according to the reaction:



- above 550°C, the vapor pressure of water, resulting from Eq. 3 and trapped in the closed pores, increases and eventually causes the internal fractures in the rock [24,41].

During the cooling segment and the second heating cycle, no remarkable loss of mass is observed, which indicates the stability of the studied rock after the first heating cycle. The

DSC chart (the solid line in Figure 3) shows only one prominent event at 590°C, which is the characteristic of quartz phase transition from alpha to beta. Hence, the ideal heat treatment temperature is a compromise between the production of exhaustive silanol transformations and the prevention of accidental fractures. Therefore, according to this primary test, the 400°C could be considered as a proper maximum working temperature of flint rocks to be used as TES material. However, this conclusion needed to be confirmed by additional measurements. It is for this reason that the observation of the microtexture of the raw and thermally heated samples (for five thermal cycles up to 400°C at 2.5 °C/min) has been done by polarized light microscope. As shown in Figure 4, the heat treatment of flint rocks in the medium temperature range (below 400°C) induces no cracks on the microscope scale.

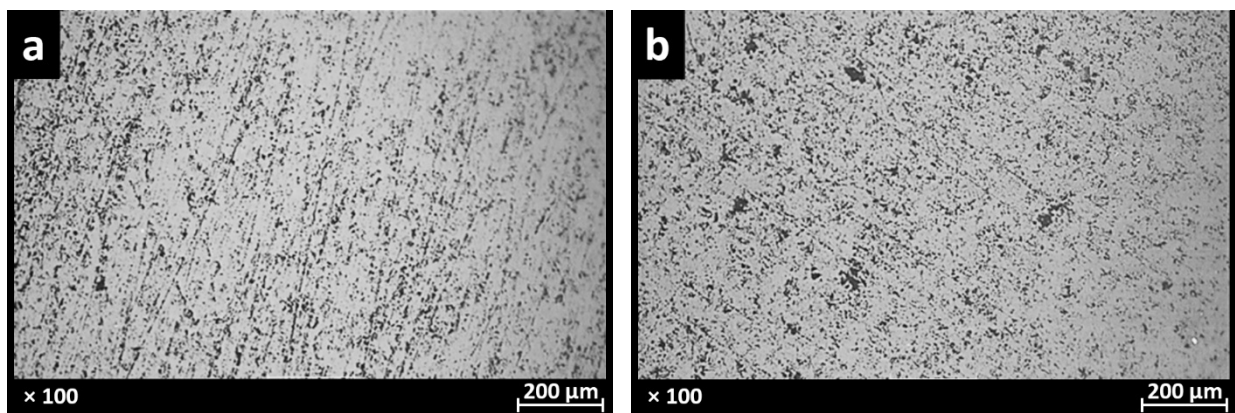


Figure 4 : Optical micrographs: a) raw flint CG, b) 5 cycles heat-treated flint CG

Moreover, our proposal for 400°C as a safe limit temperature for flint rocks was also supported by conducting the thermal expansion measurements analysis up to 1000°C, during three successive thermal cycles with a heating and cooling rate of 2.5 °C/min.

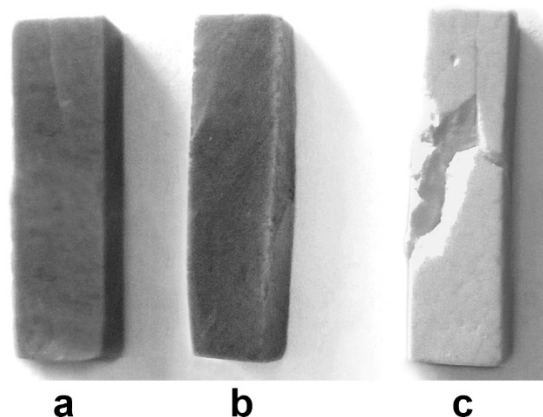


Figure 5 : Degradation of flint CG: a) raw, b) heated up to 400°C, c) heated up to 1000°C

As shown in Figure 5, by heating the flint rock up to 1000°C, the finished product became brittle and markedly shattered. This phenomenon refers to occurrence of very large irreversible deformations within the material due to excessive heating (above 400°C). The stability of the studied samples over the temperature range of 400°C is expected where no significant difference in diffractograms between the raw and the heat-treated samples is observed (see Figure 2).

Depending on the above, the ideal temperature range for flint rocks to be used as TES material is up to 400°C. This latter was also proposed in the previous studies [23,42] which revealed that microcrystalline siliceous samples almost all show a marked reduction in fracture toughness and suffer no or little damage when heated up to 400°C [43].

3.3. Thermo-mechanical characterization

Indeed, in order to validate the long-term use of storage material in high-temperature storage application, it is necessary to evaluate its expansion coefficient, Young's modulus and the hardness under repeated thermal cycles to which it will have to be subjected during its use.

3.3.1. Thermal expansion

This parameter is particularly needed for storage applications in order to take into account the effect of heating on the storage material with respect to the storage tank. The change in sample length as a function of temperature is illustrated in Figure 6 in the case of flint CG for three successive thermal cycles up to 400°C. During the heating cycles, the rise in temperature increases the length of the sample continuously till the maximum temperature, followed by a decrease in sample's length in the cooling cycles until reaching to the ambient temperature. The obtained result illustrates that the curves have rather regular behavior and they are nearly congruent and overlap each other with a very slight deviation. The rest of the samples followed the same expansion curve up to the target temperature, and they showed almost constant thermal expansion coefficients. These latter represent the slope of the curves which varied between $16 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ and $18.42 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ in the studied samples. However, it is relatively high, higher than that of concrete $13 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ [44]. The absence of significant change in the tendency during the heat treatment indicates the capability of flint rocks to withstand thermal cycling up to 400°C without the risk of cracking.

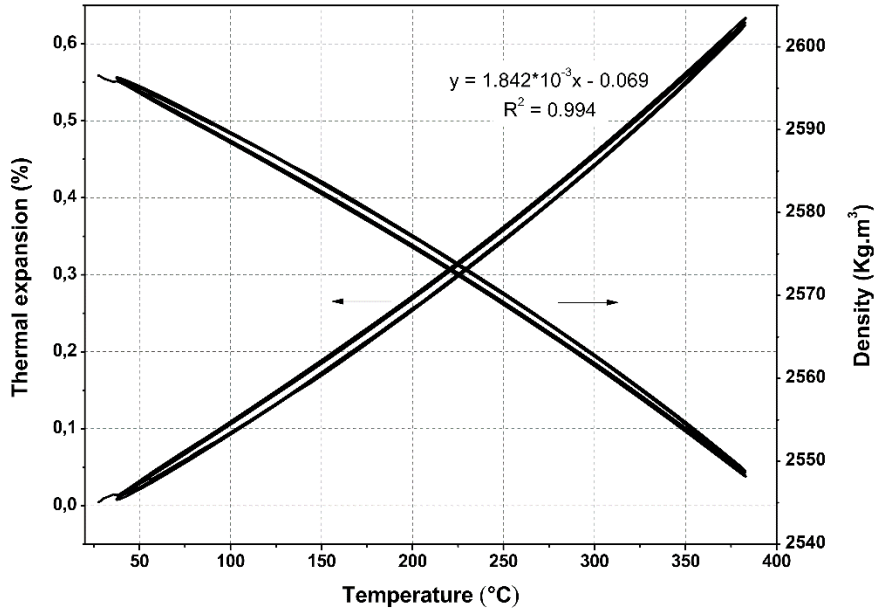


Figure 6 : Evolution of thermal expansion and density of flint CG up to 400°C, 2.5 °C/min, 3 successive heating cycles

3.3.2. Young's modulus and hardness

Figure 7 displays the evolution of the Young's modulus and the thermal expansion of the studied CG sample as a function of temperature during one thermal cycle.

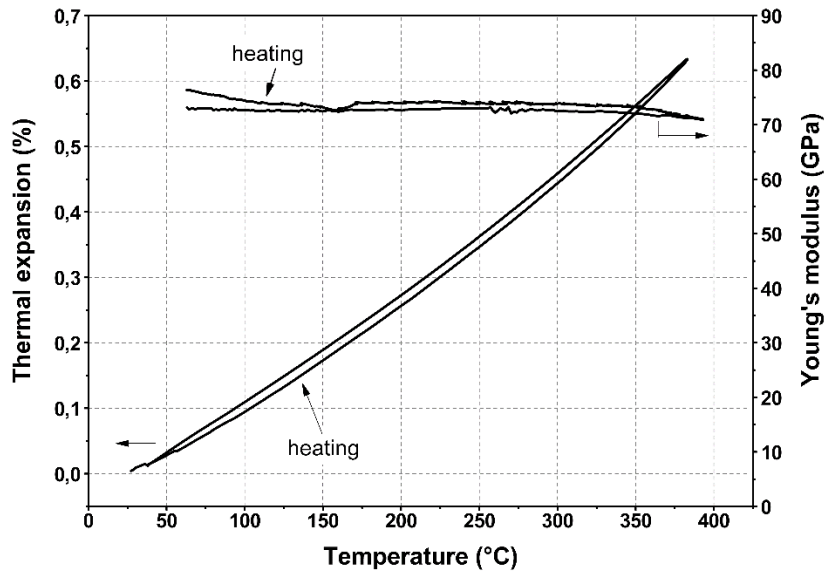


Figure 7 : Evolution of thermal expansion and Young's modulus of flint CG with temperature, 2.5 °C/min

The evolution of Young's modulus of flint CG (also the case in the rest of the studied samples) shows almost a constant value (about 80 GPa) and decreases slightly at high temperatures (this is always the case since the strength of the chemical bonds decreases with

temperature [45]). This stability of Young's modulus up to the target temperature is very interesting for storage applications.

Concerning the hardness measurements, Table 2 represents the values of hardness for the raw studied samples and the thermally heated up to 400°C. Each reported data in this table is the mean value of 10 successive measurements. In fact, generally, several natural crystals show hardening caused by heat treatment at temperature of 600°C or higher. This phenomenon can be attributed to the fact that the loss of silanol during heating causes the healing of defects sites within the crystals and closing the rock's pores. Since our study was conducted up to 400°C, the correlation between heating and hardness is not existed exactly.

Samples	Hardness (GPa)	
	raw	treated to 400°C
CG	10.89	10.32
SA	9.89	10.36
NS	10.06	9.82
ML	9.37	10.66

Table 2 : Results of the nano-hardness measurements for the four facies of flint

3.4. Thermo-physical characterization

3.4.1. Density

Room temperature density values of the studied samples are presented in Table 3 with other main physical properties. Moreover, this table reports a comparison between experimentally measured physical properties of the studied rocks with other available storage materials. As set out in this table, no significant difference is observed in the density values between the four varieties, and the average values lie in the range (2514-2596) kg/m³ at room temperature. The flint sample with a density value of 2596 kg/m³ (the lowest value among the studied samples) is slightly below the concrete and about 25% below the elaborated ceramics.

Samples	Density kg/m ³	Specific heat capacity J/kg.K	Thermal capacity MJ/m ³ .K	Diffusivity mm ² /s	Thermal conductivity W/m.K
CG	2596	750	1.95	2.94	5.72

SA	2572	760	1.95	2.03	3.97
NS	2514	740	1.86	1.78	3.31
ML	2567	770	1.98	1.5	2.96
Flint [46]	2600	740	1.92	1.82	3.5
Molten salts [47]	900-2600	1500	1.35-3.9	0.11-0.51	0.15-2
Cofalit [48]	3120	800-1034	2.5-3.22	0.84	1.4-2.1
Castable ceramics [49]	3500	866	3.03	0.44	1.35
HT Concrete [14,49]	2750	916	2.52	0.36-0.51	1

Table 3 : Experimentally measured physical properties of the studied rocks at room temperature compared with other storage materials

Once the density at room temperature is known, the density at elevated temperatures is calculated by applying Eq. 1. Figure 6 shows the change of the density of flint CG as a function of temperature, which decreases from 2596 Kg/m³ to 2548 kg/m³ as a result of heating from room temperature to 400°C. As expected, this parameter decreased slightly (1.8% in flint CG) under heating. In the same context, the values of the density for the rest of the samples decreased by heating about 1.8%, 1.8% and 1.7% in SA, NS and ML respectively.

3.4.2. Thermal capacity

From Table 3, the measured specific heat capacity values of the studied rocks at room temperature are in good agreement with data found in the literature [46]. The influence of temperature variation on the specific heat capacity values of tested samples up to 400°C is presented in Figure 8. It can be observed that the four samples follow a similar behavior, where the specific heat capacity increases substantially with temperature (31%, 38%, 39% and 40% in NS, ML, SA and CG respectively).

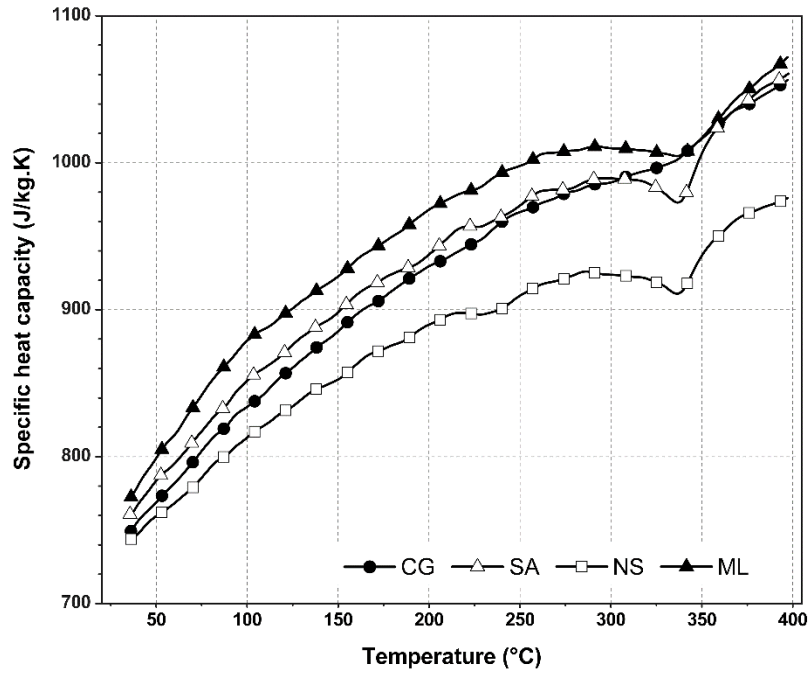


Figure 8 : Specific heat capacity of studied flint samples, 10 °C/min

In flint CG, the specific heat capacity rises from 750 J/kg.K at 20°C to reach a maximum value of 1050 J/kg.K at 400°C. The minimum value observed about (300-350) °C could correspond to the silanol transformation. However, this value is more distinctive in NS, SA and ML samples compared to flint CG, that could be probably related to its firm and fine macrotexture, where the evaporation of the water from its structure will be slow and difficult.

It is worth mentioning that, when the results obtained were compared with rhyolite, which has been identified as suitable storage material by Tiskatine et al. [50], the tested flint samples presented specific heat capacity values almost similar to that in rhyolite (see Table 4). In addition, Saxena et al. [51] proposed desert sand as a good sensible storage medium, thanks to its low cost and high availability. However, the specific heat capacity of aforementioned material is lower than those measured in our study, where its average value between 150°C and 1100°C is about 870 J/kg.K [52].

Samples	Flint CG	Flint SA	Flint NS	Flint ML	Rhyolite
C_p at 25°C [J/kg.K]	750	760	740	770	780

Table 4 : Specific heat capacity of studied flint samples compared with rhyolite at room temperature

In fact, the thermal capacity is the physical property with the most pronounced effect on the amount of the stored energy [53]. Considering that the density varies during heating, the

thermal capacity of each rock has been calculated as the product of density and specific heat capacity.

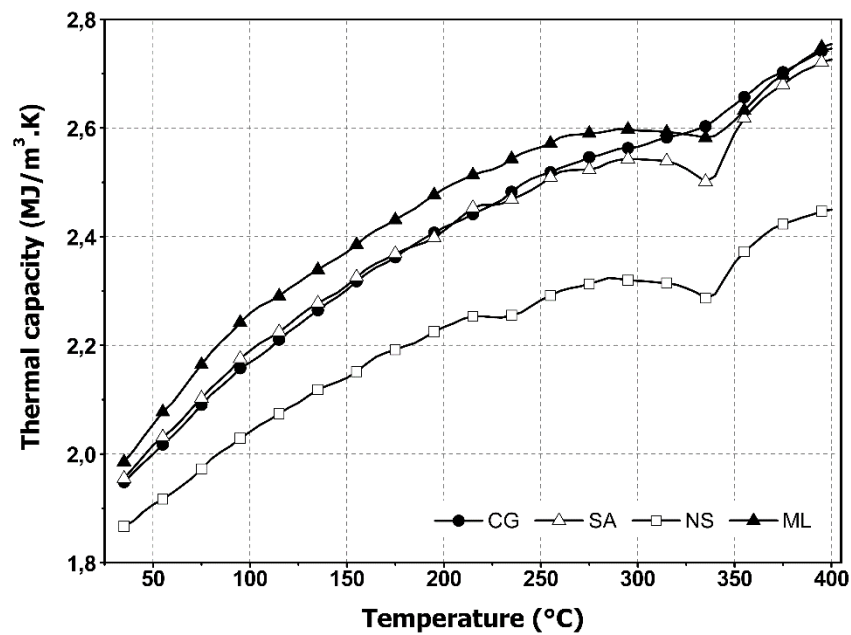


Figure 9 : Thermal capacity of studied flint rocks

From Figure 9, the similarity of the thermal capacity curves between the four varieties of flint are evident. Between 35°C and 400°C the thermal capacity increases with increasing the temperature. The average values vary from (2.45-2.75) MJ/m³.K at 400°C. According to the results obtained, NS sample presents the lowest capacity among the studied samples. This may be due to its heterogeneous macrotexture, while the rest of the studied samples showed homogeneity in their structures. At 300°C, flint seems to have higher thermal capacity (2.54 MJ/m³.K for SA, 2.56 MJ/m³.K for CG and 2.6 for ML) than hornfels, granite, marble and quartzite rocks characterized by Grirate et al. [9] and suggested as thermal storage materials.

3.4.3. Thermal diffusivity and thermal conductivity

This parameter determines the rate at which the heat can be stored and recovered, where the larger thermal diffusivity value refers to the faster propagation of the heat into the medium [15]. In fact, the diffusivity strongly depends on the chemical bonds between atoms and the presence of the impurities in crystals. The graph in Figure 10 represents the thermal diffusivity measurements of four flint samples heated up to 400°C, over five thermal cycles. The main behavior of this parameter is to decrease with increasing the temperature. This decrease was previously observed in the study made by Gibert et al. [54] on quartz polycrystalline aggregates. However, each studied sample is characterized by its own values

where the highest values are observed in flint CG. During the first heating process, it is noted that the diffusivity value of flint CG decreases from almost 2.93 mm²/s to 1.32 mm²/s with temperature rise (20-400) °C, which represents a decrease of 54 %. In the case of flint SA, the diffusivity values vary between 2.02 mm²/s at room temperature and 1.16 mm²/s at 400°C (a decrease of 42 %), while in flint NS and ML the diffusivity decreases by 38% and 34% from room temperature up to 400°C respectively. It can be noticed that for the temperatures above 200°C the obtained values from the four samples become closer. No noticeable changes are observed between the first and the fifth heating cycles, where the stabilization of the samples is expected. By comparing the values of the available storage materials at room temperature with flint rocks (see Table 3), this latter shows the highest thermal diffusivity [14,47–49]. This can be attributed to the fact that the rocks with high quartz content tend to have high thermal diffusivity, since the quartz has the highest diffusivity value of the commonly existing major minerals (3.8 mm²/s) [55].

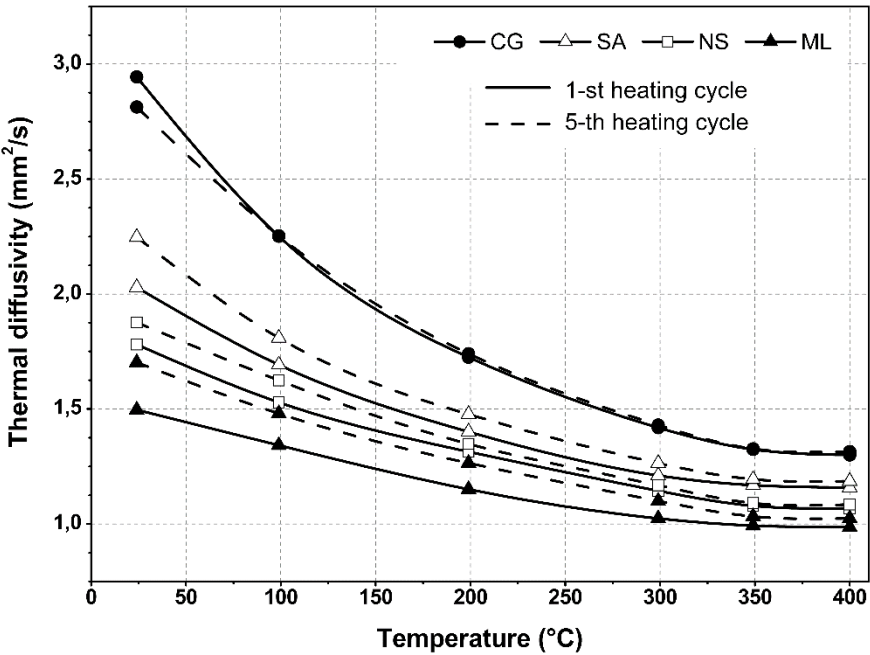


Figure 10 : Thermal diffusivity of studied flint rocks, solid line refers to 1st heating segment, dashed line refers to 5th heating segment, 2.5 °C/min

The thermal conductivity of the analyzed rocks has been calculated every 100°C from the measured density, specific heat capacity and thermal diffusivity values. The obtained results for flint samples are presented in Table 5 as a function of temperature. The thermal conductivities of the samples decreased with temperature where the average values lie in the range (3.56-2.6) W/m.K at 400°C. This decrease could be explained that number of phonon-

phonon collisions increases under heating, which leads to a decrease in the mean free path of phonons. According to the obtained results, it is obvious that CG and NS samples have the same chemical composition and diffraction profile, but their physical properties are quite different. This might be attributed to their formation mode and conditions, where flint CG is characterized by its homogeneous and very fine macrotexture, as opposed to flint NS which exhibits a heterogeneous macrotexture (mentioned previously).

Samples	λ (W/m.K)				
	35°C	100°C	200°C	300°C	400°C
CG	5.73	4.86	4.13	3.59	3.56
SA	3.95	3.7	3.35	3.04	3.13
NS	3.31	3.12	2.92	2.62	2.6
ML	2.97	3.02	2.84	2.62	2.7

Table 5 : Thermal conductivity of the four varieties of flint

The results calculated at room temperature are in accordance with values reported in the literature [46]. By comparing with other available storage materials, the flint samples proved much higher values of thermal conductivity [14,47–49] (see Table 3). This could be attributed to the fact that rock with high content of quartz is known to exhibit a high value of conductivity at room temperature. At 20°C, flint rocks present thermal conductivities higher than that of rhyolite (2.3 W/m.K) [50]. At high temperatures, the analyzed flint samples show higher thermal conductivity values compared to HT ceramics (1.35 W/m.K at 350°C) and concrete (1 W/m.K at 200°C and 1.1 W/m.K at 332.5°C) [29,56,57]. In conclusion, the described rocks in this paper could be used in parabolic trough CSP plants which use air as heat transfer fluid such as Ait-Baha pilot plant (3.9 MW_{th}) in Morocco where the packed bed of rocks is used as thermal energy storage system [58].

4. Conclusion

This work aims to study the potential of flint rocks as candidate storage material for CSP plants. Experimental study has been done of thermo-physical and thermo-mechanical properties of four facies of flint rocks by using several techniques. The obtained results showed that the studied rocks can be used as TES material for a medium temperature CSP process (up to 400°C). The flint rocks demonstrated good thermal stability over the entire range of targeted temperature, and physical properties similar or even higher to those of storage materials which are used or studied at present nevertheless with much lower cost.

Based on this study, the XRD analyses showed that the samples are completely crystallized and rich in quartz. DSC/TG measurements indicated that the major transformation occurring between 300°C and 550°C is the loss of silanol, and the peak at 590°C is characteristic of the quartz phase transition. The analyses of the physical properties of the studied samples demonstrated high density values compared to the molten salts. The mean values of the thermal capacity lie in the range (1.86-1.98) MJ/m.K at room temperature, while the thermal conductivity is between (2.97-5.73) W/m.K. Based on the obtained results, it seems that flint CG is the most recommended candidate for thermal storage applications. It has a density of about 2596 kg/m³, a specific heat capacity of 750 J/kg.K and a thermal conductivity of 5.72 W/m.K at ambient temperature. Its thermal capacity and thermal conductivity at 400°C is 2.75 MJ/m³.K and 3.56 W/m.K, respectively. From the thermo-mechanical point of view, the thermal expansion coefficient of flint CG is about $18.42 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ and the Young's modulus showed almost stable behavior under the effect of heating (about 80 GPa), which make it possible to assume a long service life. Finally, the data included in this work can be successfully used in numerical modeling in order to predict the performance of the storage system, as well as to estimate the physical properties of flint rocks from other locations by taking into account the similarity in the formation conditions, the microtexture and the crystalline structure.

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