

## CARBON MATERIALS FOR SOLAR THERMAL ENERGY

Badenhorst H.  
Department of Chemical Engineering,  
South African Research Chairs Initiative: Chair for carbon materials and technology  
University of Pretoria,  
Pretoria, 0002,  
South Africa,  
E-mail: [carbon@up.ac.za](mailto:carbon@up.ac.za)

### ABSTRACT

Cost-effective capture and storage of solar energy still remains a challenge facing broad-based implementation of this renewable technology. Work at the South African Research Chairs Initiatives (SARChI), Chair in Carbon Materials and Technology at the University of Pretoria is aimed at developing materials from cheap, local carbon sources for solar thermal applications. The focus is split on developing composites for both solar energy capture and thermal energy storage.

Preliminary investigations are based on systems designed to provide heating needs like hot water through solar energy. Two different approaches to the capture of solar energy were explored. Firstly the use of carbon black and expanded graphite pressed discs and secondly the production of mesophase based graphitic foams.

The carbon black discs demonstrated the ability to reach a peak collector temperature of around 70 °C whilst providing approximately 4 kW.hr per m<sup>2</sup> per day. The foam with the best capture had an efficiency calculated at around 95%. This is based on measured incoming radiation converted into sensible heating of the water.

Phase change materials present an efficient and innovative solution to the problem of thermal energy storage. These materials suffer from a major drawback due to their low thermal conductivity. Two alternatives were explored for enhancing this property. Firstly the direct incorporation of phase change material into expanded graphite was tested. A variety of loadings were explored. It was found that at low concentrations of 6 mass % the time required for the sample to undergo the phase transition could be reduced by 70% for heating and 85% for cooling. Beyond this point the decrease in phase transition time diminishes.

Ongoing work is also being done to explore the use of highly conductive sheets manufactured from roller-pressed expanded graphite. Unfortunately these sheets suffer from structural integrity issues which are being optimized.

### INTRODUCTION

It is widely accepted that a worldwide transition towards a more sustainable blend of energy resources is required [1]. This necessitates the addition of renewable energy to the collection of fossil fuel supplies. In addition, evidence is growing to support the significance of atmospheric carbon dioxide as a contributing factor to a potential change in the global climate [2]. These factors are driving governments to incorporate renewables into their energy policy and South Africa is no exception [3, 4].

South Africa has some of the highest solar fluxes on earth [1, 5, 6] making solar energy a prime candidate for renewable energy generation in this country. In conventional energy networks the energy must be transmitted along long distances of high-voltage transmission lines which results in significant losses [7]. A key to addressing this problem is the use of demand side measures to directly supply users' energy requirements. This is especially true in Africa where a large portion of the population still does not have access to the main energy grid [4]. Without decentralized energy supply significant installation costs will be required.

To support this model it is critical to cheaply supply secondary energy needs like heating, without the need for intermediate conversion to another form. This will offset the costs of installing large energy generation facilities to provide all the energy needs through electricity. As such the monetary and social benefits of utilizing solar energy for water heating applications in rural or low income areas have been well established [8]. However, there is still significant room for improvement to make existing systems cheaper and more efficient.

The South African government has recently implemented an Integrated Industry Waste Tyre Management Plan [9]. In accordance with this directive thousands of tons of scrap tyres will be recycled. Thus South Africa has a cheap and readily available resource for carbon black as a by-product of the recycling process. This material contains significant amounts of

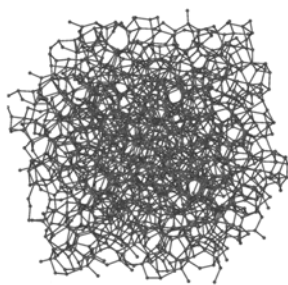
ash and would require expensive processing for most re-use applications. Carbon black, an amorphous form of pure carbon, has excellent absorption properties in the wavelength range associated with solar radiation [10]. Hence, this would not only be a feasible supply of highly absorbent material for solar energy capture but would also have the benefit of removing a major waste problem.

One of the most effective ways of storing collected thermal energy is through the use of phase change materials (PCMs) [11]. These materials have a high energy storage density and near isothermal operation since energy is stored as latent heat. However, a major drawback facing the implementation of these materials is their low thermal conductivity [12]. Graphite, a crystalline form of pure carbon, has excellent thermal conductivity [13] and could be utilized as an additive to enhance the thermal properties of PCMs. In addition South Africa has a readily available source of graphite in neighbouring Zimbabwe where the mineral is mined [14].

Thus carbon, in these two different forms, has the potential to be used as a low cost, locally available additive for the capture and storage of solar thermal energy. This manuscript presents four novel carbon composites, two in each of the two applications respectively, which have been developed and tested at the SARChI Chair for carbon materials and technology at the University of Pretoria.

### SOLAR ENERGY CAPTURE – CARBON BLACK

A general group of carbon materials exist which may be broadly labelled as amorphous carbons. This group includes char, coal, anthracite, activated carbon, vitreous carbon, etc. Superficially these carbons may be classified as amorphous due to their lack of long range order and having a molecular structure related to either diamond or graphite or some combination of the two. This results in the complex structures shown conceptually in Figure 1. Their actual structure is still poorly understood despite numerous investigations into a wide variety of these materials [3,4].

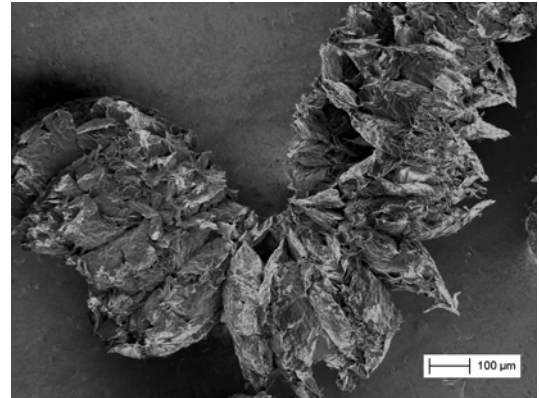


**Figure 1** Amorphous carbon

Carbon black (CB) is one example of amorphous carbon relevant to energy capture. It has a well-established absorption spectra across the entire range of solar radiation [5]. It is so effective as an electromagnetic wave absorber that it is employed in stealth aircraft to reduce the planes' radar signature. As mentioned earlier, South Africa has a cheap and readily available source of carbon black in the form of recycled

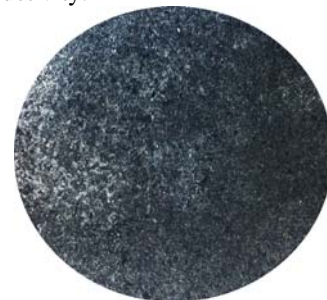
scrap tyres. The tyres with any metal removed are pyrolyzed producing a gas, some oil and a granular powder form of CB. Unfortunately the powder when pressed is very brittle and the forms easily disintegrate. To overcome this, a second form of carbon was used: expanded graphite.

Graphite has a layered hexagonal (or honeycomb) structure. The in-plane atoms are linked with strong covalent bonds, giving graphite its excellent in-plane thermal conductivity. Adjacent planes on the other hand are held together by weak van der Waals forces. This gives graphite a low shear strength and also allows the intercalation, or insertion, of foreign atoms in between the layers. Intercalated graphite (ES 250 B5) is available commercially from the Qingdao Kropfmuehl Graphite company. Upon heating, these hetero-atoms are liberated into the gas phase, forcing adjacent graphite layers apart. This results in a very low density, porous material, with the concertina-like structure, called expanded graphite (EG) shown in Figure 2.



**Figure 2** Expanded Graphite

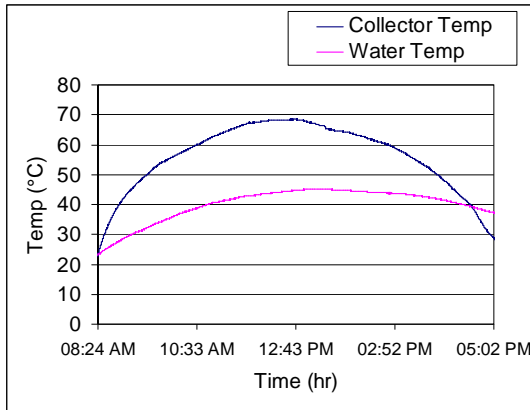
Since the planes have been in essence only pushed apart, they remain largely intact. Thus the resulting material still retains the high thermal conductivity of graphite. To provide structural support for the CB, it is mixed with EG and pressed into flat sheets or discs. These discs, see Figure 3, remain a very dark matt black which is ideal for solar radiation absorption but have the added advantage of increased strength and thermal conductivity.



**Figure 3** Pressed CB/EG disc

Several ratios of CB to EG were tested and it was found that above a CB content of 70% the material integrity was compromised and the discs could not maintain their shape.

These discs were tested in a simple flat plate collector shielded from wind via a glass box. The discs were placed on top of a copper disc attached to a copper rod, placed inside an insulated container filled with water. The discs were horizontal and no attempt was made to optimize orientation with respect to the sun, given the initial status of the testing. During the day peak collector temperatures of around 70 °C were achieved, as shown in Figure 4.



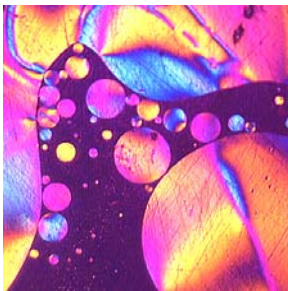
**Figure 4** Collector and geyser temperatures

The preliminary results were encouraging indicating that approximately 4 kW.hr was harvested per m<sup>2</sup> per day. Given the average solar radiation for this location during the period of testing is 5.67 kW.hr per m<sup>2</sup> per day [15], an approximate efficiency of 70% is obtained. This is lower than commercial flat plate systems which achieve around 80% but higher than evacuated tube systems at 60% [16].

Given the early stage of development and lack of insulation it is expected that this figure can be improved. Work is ongoing to reformulate the carbon black into a paint, which will be used to coat the collector of a small scale parabolic trough system.

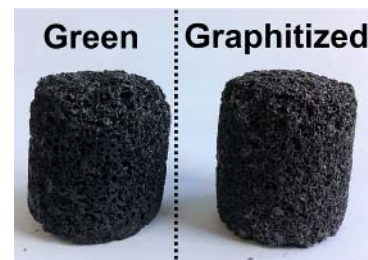
### SOLAR ENERGY CAPTURE – MESOPHASE FOAM

During the production of synthetic graphite, a discotic nematic liquid crystal, known as mesophase, is formed. This is the main precursor for graphite. A polarized light microscope allows regions of parallel orientation to exhibit the same colour, as can be seen in Figure 5.



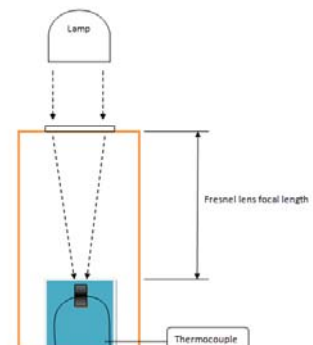
**Figure 5** Mesophase pitch

Mesophase is generally derived from coal-tar or petroleum based pitch which is of very high quality. It is possible to heat-treat this mesophase to produce a highly porous foam. This foam can subsequently be graphitized at very high temperatures to produce a highly conductive three dimensional structure. However, these foams are expensive to manufacture, due to the specific type of pitch and strenuous processing conditions required. A cheaper alternative may be possible by using lower grade pitch material mixed with intercalated graphite. When heated the pitch melts and the intercalated graphite expands to form a porous foam structure. Low quality coal tar pitch was sourced from the ArcelorMittal steel production facility in South Africa where it is an unwanted by-product. This pitch was heat-treated at 437 °C for 6 hours to transform some of the material into mesophase while maintaining the liquids rheological properties to allow foaming. The partially transformed pitch was mixed with intercalated graphite and foamed at 460 °C followed by stabilisation in air at 250 °C for 24 hours. The resulting foam structure was carbonized and graphitized by slow heating to 2750 °C in a TTI furnace (Model: 1000–2560–FP20), both can be seen in Figure 6.



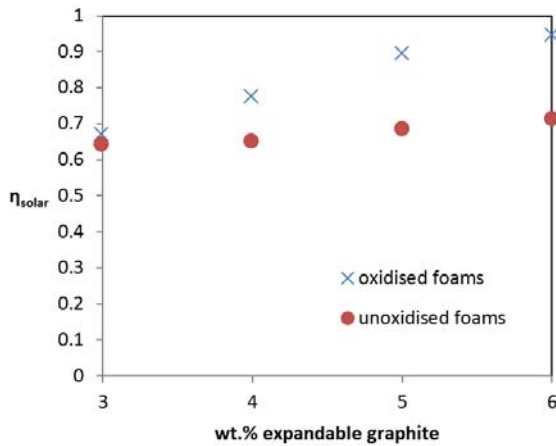
**Figure 6** Graphite foams

A more detailed description of the foam production process is provided elsewhere [17]. To test the foams they were placed in an insulated container filled with water and a transparent lid. A small scale solar simulator was built using a Phillips MASTER MHN-SE 2000W metal halide lamp. Light from the lamp was focused onto the foam using a small Fresnel lens, a schematic of the setup is given in Figure 7.



**Figure 7** Testing rig for graphite foams

A range of intercalated graphite loadings were tested, ranging from 3 to 6%. Above and below these levels the material would either not foam to a noticeable extent or produce an extremely brittle and porous foam. In addition it was found the foams contained a significant amount of closed porosity. The pores were opened by oxidation in air at 750 °C up to approximately 5% mass loss. The rate at which the water was heated was used to calculate the thermal efficiency of the foam, defined as the heating rate of the water divided by the light radiation incident on the foam (as measured by a spectrophotometer). The results are shown in Figure 8.



**Figure 8** Graphite foam water heating results

The results are very promising, indicating excellent transfer of the incident radiation to water. As expected the foam with the highest percentage of intercalated graphite has the highest efficiency, at around 95%, as it is the most porous structure and hence the largest area for heat transfer. In the future the geometry of the foams will be modified to determine the optimal depth to exposed top area, as well as exploring alternative production methods to lower costs.

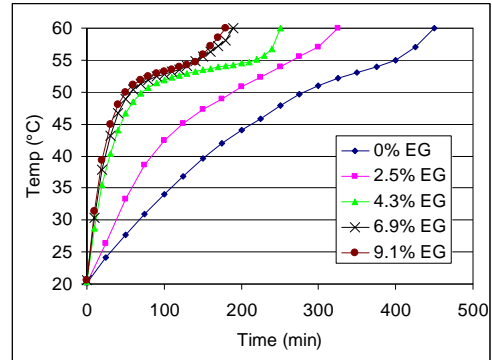
### SOLAR ENERGY STORAGE – EXPANDED GRAPHITE

Phase change materials (PCMs) present an efficient and innovative solution to the problem of thermal energy storage. These materials suffer from a major drawback since they generally have a very low thermal conductivity. Graphite is a well-known additive for the enhancement of thermal conductivity. As mentioned earlier, expanded graphite (EG) still contains virtually intact graphite sheets. However, these have now been swollen into large empty cavities, giving a porous material ideal for impregnation with PCMs.

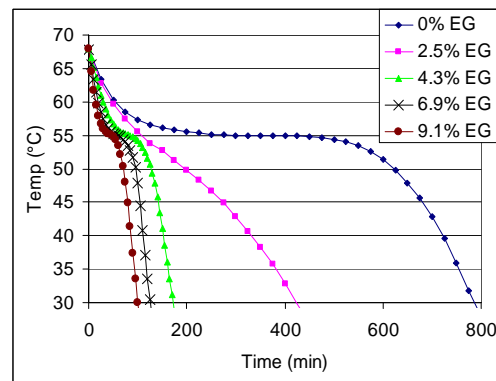
Stearic acid supplied by Pan Century Oleochemicals Sdn. Bhd was chosen as the PCM suitable for storing solar energy and releasing it at a temperature suitable for hot water generation. It has a melting temperature of 55 °C and a heat of fusion of around 200 kJ/kg as measured by a PerkinElmer DSC 4000. The stearic acid was mixed with increasing amounts of expanded graphite. The mixed samples were placed in glass test

tubes and heated or cooled in an oil or ice-water bath respectively.

The results for the phase transition measurements on the PCM/EG composite material are shown in Fig. 9 and 10 for heating and cooling respectively.

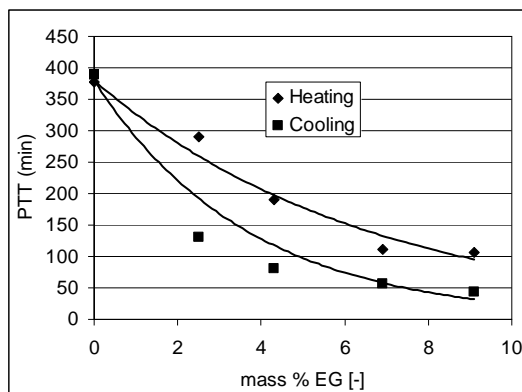


**Figure 9** PCM/EG composite - heating



**Figure 10** PCM/EG composite - cooling

For comparative purposes the peak transition time (PTT) may be used to assess the influence of the EG on the phase transition. For heating this may be defined as the minima in the derivative of the temperature as a function of time, i.e. the point of inflection in the measured temperature during melting. This is the point where latent heat uptake is starting to diminish as sensible heat storage is beginning to increase. The time taken to reach this point is an indication of how thermally conductive the sample is, i.e. the speed of melting or solidification. Similarly the point of inflection during cooling is given by the maxima in the derivative of the temperature for the PTT. These are plotted in Fig. 11.



**Figure 11** Graphite foam water heating results

The trends for the two phase transition times are quite similar. They both indicate that beyond EG concentrations of 6 mass %, there is no further significant decrease in the time required to achieve phase transition. The time reduction for achieving the phase transition is remarkable. At low concentrations of just 6 mass % the time required for the sample to undergo the phase transition is reduced by 70% for heating and 85% for cooling. Clearly the addition of the expanded graphite has a tremendous impact on the thermal conductivity of the composite.

#### SOLAR ENERGY STORAGE – GRAPHITE SHEETS

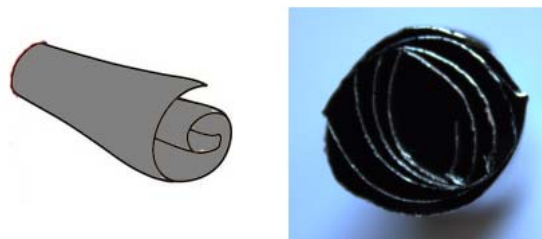
In addition to the direct incorporation of the EG into a PCM composite, it may be used in a more traditional fashion for heat exchange. The highly porous EG powder can be flattened into sheets which can then be further compacted in a roller-press, to produce a graphitic sheet similar to paper (physical properties can be found in [18]), as shown in Figure 12.



**Figure 12** Roller-pressed EG sheet

These sheets can then be placed between alternating layers of PCM to form a sandwiched structure similar to a plate and frame heat exchanger. However, this approach suffers from a drawback due to the anisotropic nature of graphite. During pressing the graphite platelets are aligned perpendicular to the pressing direction. Whilst graphite has excellent in-plane conductivity, across plane it is a fairly good insulator. The thermal conductivity in these respective directions can vary by more than an order of magnitude.

To overcome this issue, an approach is being developed with a design more similar to the conventional annular arrangement. In this case the EG sheets are rolled into “scrolls”, depicted in Figure 13. The spaces between the scrolls are then filled with PCM.



**Figure 13** EG “scrolls”

These scrolls can either be wrapped around an inner tube through which the heat transfer fluid is passed, or alternatively these can be placed into the inner tube whilst the heat transfer fluid flows through the outer annulus. Thus instead of acting as a barrier, heat is conducted through the sheet in a spiralling radial direction.

Despite the fact that these sheets are fairly malleable, they can easily fracture if excessive bending stresses are applied. The thicker the sheets become, the more prone they are to breaking. At the moment work is focused on finding the optimal thickness of the sheets to provide sufficient strength whilst still maximising the heat transfer.

In addition a variety of techniques are being explored to find cost-effective ways of manufacturing intercalated graphite and hence EG sheets from natural graphite locally sourced from mining activities in Zimbabwe.

#### CONCLUSIONS

All over the world renewable energy is being incorporated into the existing energy supply mix. Since South Africa has some of the highest solar fluxes on earth it makes sense to utilize this abundant natural resource. The monetary and social benefits of utilizing solar energy for water heating applications in rural or low income areas has been well established. However significant room for cost and efficiency improvement of the currently available systems exists.

Carbon and graphite materials find several applications in this system due to its unique properties. South Africa has a readily available source of cheap carbon black from recycled waste tyres which could be used as a solar collector with the added benefit of removing a major waste problem. In addition, a convenient supply of mined natural graphite is accessible in nearby regions. This material has excellent thermal conductivity which can be used as an additive and structural component.

With the purpose of developing a solar water heating system for household applications, two aspects of the design were tested for feasibility: capture and storage. Two different approaches to the capture of solar energy were explored. Firstly

the use of carbon black and expanded graphite pressed discs. These were linked to a water reservoir and demonstrated the ability to reach a peak collector temperature of around 70 °C whilst providing approximately 4 kW.hr per m<sup>2</sup> per day.

The second approach involved the production of mesophase based graphitic foams. In this case a poor quality, local sourced coal tar pitch was used as the starting material, together with intercalated graphite to produce highly conductive porous foams. A variety of loadings were tried but foam integrity limited this to a range of between 3 and 6% expanded graphite.

The foams were suspended in water while light from a lamp was focused onto them using a small Fresnel lens. It was found that a small amount of oxidation was needed up to a burn-off of 5% to fully open the porous structure. In this case the material with the highest expanded graphite loading and hence the largest surface area demonstrated the best capture efficiency of around 95%.

Phase change materials present an efficient and innovative solution to the problem of thermal energy storage. These materials suffer from a major drawback through their low thermal conductivity. Two alternatives were explored for enhancing this property. Firstly the direct incorporation of phase change material into expanded graphite was tested. A variety of loadings were explored. It was found that at low concentrations of 6 mass % the time required for the sample to undergo the phase transition could be reduced by 70% for heating and 85% for cooling. Beyond this point the decrease in phase transition time dwindles.

On-going work is also being done to explore the use of highly conductive sheets manufactured from roller-pressed expanded graphite. These sheets can be rolled into a scroll shape and incorporated into a traditional annular heat exchanger along with the phase change material. Unfortunately the sheets can be brittle and fracture under bending stress. Currently the optimal thickness is being determined to provide sufficient strength whilst still providing significant thermal conductivity enhancement.

In conclusion carbon and graphite based composites show promise for the effective capture and efficient storage of solar energy. It is hoped that in future the operating range of these additives and composite can be extended to higher temperatures for industrial applications such as electricity generation.

## REFERENCES

- [1] Heller L, Gauché P. Modeling of the rock bed thermal energy storage system of a combined cycle solar thermal power plant in South Africa. *Solar Energy*. 2013;93:345-56.
- [2] Lacis AA, Schmidt GA, Rind D, Ruedy RA. Atmospheric CO<sub>2</sub>: principal control knob governing Earth's temperature. *Science*. 2010;330(6002):356-9.
- [3] Winkler H. Renewable energy policy in South Africa: policy options for renewable electricity. *Energy Policy*. 2005;33(1):27-38.
- [4] Bugaje IM. Renewable energy for sustainable development in Africa: a review. *Renewable and Sustainable Energy Reviews*. 2006;10(6):603-12.
- [5] Dekker J, Nthontho M, Chowdhury S, Chowdhury SP. Investigating the effects of solar modelling using different solar irradiation data sets and sources within South Africa. *Solar Energy*. 2012;86(9):2354-65.
- [6] Fluri TP. The potential of concentrating solar power in South Africa. *Energy Policy*. 2009;37(12):5075-80.
- [7] Romm JJ. *The hype about hydrogen: Fact and fiction in the race to save the climate*. Washington DC: Island Press; 2004.
- [8] Donev G, van Sark WJHM, Blok K, Dintchev O. Solar water heating potential in South Africa in dynamic energy market conditions. *Renewable and Sustainable Energy Reviews*. 2012;16(5):3002-13.
- [9] Molewa, E. Minister of Water and Environmental Affairs, South African Government Gazette No 34796 of 28 November 2011, last access 06/09/2013: <http://www.sanews.gov.za/south-africa/waste-tyre-management-plan-gazetted>
- [10] Han D, Meng Z, Wu D, Zhang C, Zhu H. Thermal properties of carbon black aqueous nanofluids for solar absorption. *Nanoscale Res Lett*. 2011;6:457.
- [11] Zhang Z, Zhang N, Peng J, Fang X, Gao X, Fang Y. Preparation and thermal energy storage properties of paraffin/expanded graphite composite phase change material. *Applied Energy*. 2012;91(1):426-31.
- [12] Li M, Wu Z, Tan J. Properties of form-stable paraffin/silicon dioxide/expanded graphite phase change composites prepared by sol-gel method. *Applied Energy*. 2012;92:456-61.
- [13] Pierson HO. *Handbook of carbon, graphite, diamond and fullerenes. Properties, processing and applications*. New Jersey, USA: Noyes Publications; 1993.
- [14] Feytis A. The bright side of graphite. *Industrial Minerals* 2010;7:31-39.
- [15] Dekker J, Nthontho M, Chowdhury S and Chowdhury SP. Investigating the effects of solar modeling using different solar irradiation data sets and sources within South Africa. *Solar Energy* 2012;86:2354-2365.
- [16] Pluta Z. Evacuated tubular or classical flat plate solar collectors? *Journal of Power Technologies* 91:158-164.
- [17] Walter W Focke, Heinrich Badenhorst, Shatish Ramjee, Hermanus Joachim Kruger, Riaan Van Schalkwyk, Brian Rand. Graphite foam from pitch and expandable graphite. *Carbon* 73 (2014) 41–50.
- [18] Graftech International. Technical data sheet 321 "eGRAF Spreadershield" [www.graftech.com/eGRAF/eGRAF-Technical-Documents.aspx](http://www.graftech.com/eGRAF/eGRAF-Technical-Documents.aspx) (Jan 2015).