THERMAL STORAGE FOR SOLAR POWER PLANTS BASED ON LOW COST RECYCLED MATERIAL

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ABSTRACT
Thermal storage is a key technology needed for both the optimal integration of industrial thermodynamic solar power plants to the grid and the reduction in size and optimization of the working conditions of the power block. According to today constraints, the storage approaches developed during the eighties do not match all the current environmental, technical and regulation standards. Concerning the storage of large amount of heat, thousands of tonnes of material are needed inducing too important investment costs and large potential environmental impact. In the present study, a low-cost material (8 euros/t) inherited from the industrial vitrification of Asbestos is considered. This end-of-life and low-cost material presents no environmental hazard and interesting thermophysical properties. In the present paper are gathered preliminary characterizations of such ceramics which are compared to more conventional storage materials.

1. BACKGROUND

At an industrial scale, thermodynamic solar power plants are based upon two different major technologies [Ecostar 2004] related to their concentrating solar flux systems: (1) the solar trough leading to 200 to 400°C temperature range or (2) the central receiver towers leading potentially to higher temperature range up to 800°C. For almost thirty years, the first technology has been already tested with success industrially in the US and is today acknowledged as the most mature one. Large scale industrial plants of 50 to 300 MW\(e\) are expected, under construction or just achieved in US, North Africa or Spain. The other technology has been first tested at pilot scales during the eighties (Solar One in USA, Themis in France, Solar Two in USA, CESA in Spain) and has been only very recently applied at industrial scale but at rather low temperature level of 250°C (PS10 and PS20 Abengoa-Solar plants of Sevilla Spain).

In all cases those solar power plants are subject to both the intermittencies of the source (predictable and unpredictable) and to the shift between the electrical needs and the solar availability.

If not managed, the variations of the solar source would induce major lowering of the power block performances, lowering in life time expectancy of the related equipments, increase in needed maintenance, overscaling of the equipments to fit the energy peak. All those consequences would lead to an increase in initial financial investments as well as to a low commercial value of an unpredictable electric production.

Then, two different approaches have been already developed to solve those major drawbacks: the hybridization of the solar process with a fossil source like gas or the use of thermal storage.
The growing scarcity of the fossil resources imposes even more than before the use of thermal storage technologies. Those available today are mostly inherited from the eighties and based on sensible heat systems in which a large amount of storage material is needed.

The leading technique is the so called “two tanks molten salt” one [Pacheco 2002, Herrmann et al. 2004] in which a mixture of nitrate salts (NaNO$_3$/KNO$_3$ or NaNO$_3$/KNO$_3$/NaNO$_2$) in the liquid state is flowed alternatively from a “low” temperature level tank to a “high” temperature level one through a heat exchanger in which alternatively the heat transfer fluid of the solar field heats it or the production of water steam for the power block cools it. The major advantages of this technology are: the storage media is also used as heat transfer fluid, the sensible heat of the molten salts is high, the chemical and metallurgy industries use it for years and molten salts are rather stable and cheap. The major drawbacks are related to corrosion, to possible plugging due to the rather high solidification temperature (142 to 250°C), the market competition with other uses in industry or agriculture. In the very recent 50MW$_e$ Andasol solar trough power plant of Granada based on such a technology, the 6.5 h of thermal storage require 28,000 tonnes of nitrate molten salt.

In an other approach, solid storage media can be used and according to their usually low thermal conductivity, the heat transfer fluid (primary or secondary) needs extended heat transfer interface area. For temperatures lower than 400°C, high temperature concrete (HTC) modules are under current development at the DLR [Laing et al. 2006]. The advantage is the availability and rather low cost of the raw material and the easiness of its use. Nevertheless, the life time expectancy of the system is estimated today at 10 years and the low thermal conductivity of the concrete ($1 \text{ W} \times \text{m}^{-1} \times \text{K}^{-1}$) imposes the need of an embedded extended costly metallic heat exchanger.

An other solid-media approach has been tested in Solar One or by the Sandia laboratory during the eighties: the use of beds made of natural particles like quartzite, granite, sand,….through which molten salt or solar oil flow to exchange heat. In this case, the storage material is very cheap and easily available but the contained impurities can enhance the degradation of the heat transfer fluid. Up to now, this technique has not been used in any industrial solar power plant.

Then, today there is a need in alternative thermal storage approaches focussed on the following major properties: low cost, high availability, life time expectancy of 20-30 years under thermal cycling, thermal stability up to 800°C, large storage capacity similar to HTC, good thermal conductivity (larger than 1), easy use, low CO$_2$ and unrenewable energy content.

In the present paper, a material industrially recycled from Asbestos-containing wastes is analysed as a good candidate. Main thermophysical properties are presented and compared to already acknowledged storage materials.

2. MATERIALS AND CHARACTERIZATIONS

Selected storage material

According to the above constraints, the material selection was focused on recycled materials produced by industrial vitrification of wastes or other initially hazardous materials. In this field, Asbestos ceramics and glass are currently produced by industrial thermal treatments of corresponding wastes inhibiting irreversibly their hazardous character due to the initial microfibrous nature of the mater [Thompson et al. 2002].
Even very low concentrations of Asbestos fibres can induce fatal pulmonary disease. The Asbestos containing wastes can be immobilised by use of cements or polymeric resins or better definitely transformed by vitrification based on plasma [Gomez et al. 2009] or microwave processes [Gualtieri et al. 2000]. Plasma or microwave treatments convert Asbestos into a rocklike structure (hardness of 6 Mohs) with volume and weight reductions of 51 and 70% respectively [Gomez et al. 2009]. Depending upon the thermal conditions of cooling treatment, glass or ceramic structures are obtained.

The materials used in the present study have been kindly supplied by the company Inertam France [Inertam]. This company uses a plasma torch treatment at 1400°C to vitrify 6000 t/year of Asbestos containing wastes, and then to produce the corresponding amount of inert material of interest commercially called Cofalit®. The initial wastes come from various demolishing source representing currently in France 250.000 t/year which are thermally treated or placed in double bags stored in hazardous waste land disposal units. Therefore, a huge potential of material production can be considered.

Up to now, a sole commercial application of low value has been found for the Cofalit®: it is currently used as under-layer material to build roads. Then its commercial price is as low as 8 euros per tonne while the cost of its treatment by plasma torch is as high as 1200 euros per tonne. This high treatment cost as to be compared to the price for waste land disposal units, from 120 to 700 euros/t, which is still a temporary solution before the needed definitive treatment.

![Figure 1. as-received ceramic Cofalit®](image1.png) ![Figure 2. as-received glassy Cofalit®](image2.png)

During the industrial vitrification process, the molten product experiences various thermal cooling rates leading to different structural configurations from ceramics (Figure 1) to glassy materials (Figure 2). Then it is possible to produce any kind of intermediate product ranging between the ceramic and the glass. Taking into account the fact that the thermophysical properties of the material should depend upon this structural parameter, separate studies will be done for ceramic and glass materials as well as for intermediate ones.

In the present study only properties of mainly ceramic material is presented.

### 3. PROPERTIES

The raw as-received Cofalit® has been first observed by SEM microscopy in order to check the efficiency of the thermal treatment of vitrification with respect to the hazardous fibrous stucture.

As illustrated in the corresponding Figure 3 and 4 for both the ceramic and glassy materials, no fibrous structure can be seen any more. Then the vitrification treatment has removed all
hazardous character of the material. The Cofalit® commercial product has been officially acknowledged as inert material with no ecotoxicity and no lixiviation effect.

![SEM picture of ceramic Cofalit®](image1)

*Figure 3. SEM picture of ceramic Cofalit® side = 27 µm*

![SEM picture of glassy Cofalit®](image2)

*Figure 4. SEM picture of glassy Cofalit® side = 27 µm*

Then the ceramic has been thermally tested in ADT/DSC in order to observe any possible transformation or reactivity from room temperature up to 1200°C. As illustrated in Figure 5, in the whole thermal range potentially concerned by the solar power plants (from 200 up to 1000°C) no thermal effect was observed. Consequently, the raw Cofalit® can be considered as very stable under heating and can be probably used as thermal storage media for both the solar trough and the central receiver based power plants. Nevertheless, those preliminary results have to be extended to glassy materials and to samples having experienced cumulated thermal cycles within the thermal range of the application. This work will be done further.

![Graph of heat flow](image3)

*Figure 5. heat flow measured in a Setsys Cetaram thermobalance on the raw Cofalit®.*

**Thermal storage properties**

The media will be potentially used as sensible heat storage material. Then, its density and its specific heat have been measured by means of an Acupyc Setaram and a C80 calorimeter respectively.
The measured density is 3120 kg/m$^3$ which is in very good agreement with the range proposed by Inertam [Inertam] from 3000 to 3500. The specific heat measured by calorimetry is 860 J/(kg×K), a value very similar to those encountered for usual commercial glass. This point is rather reasonable considering the mean composition of the various Asbestos [Thompson et al. 2002] or the Cofalit which is mainly composed of SiO$_2$ and CaO at 75%wt [Inertam].

**Heat transfer properties**

The heat transfer properties of a sensible heat storage material are mainly concerned by two aspects: its thermal conductivity and its specific surface area and surface geometry to exchange heat with a working fluid.

*Thermal conductivity*

The thermal conductivity of the ceramic has been measured by using the steady state macroscopic method already detailed in previous studies [Touloukian et al. 1970, Py et al. 2001]. A cylindrical sample (25 mm in diameter and 50 mm in length, Figure 7) is placed between two standards of similar geometry but known conductivity. Three K thermocouples are placed axially at the center of each cylinder. The whole cylinder composed of the three materials is placed in an electrical oven in order to impose the temperature level. A thermal gradient is established at the two extreme surfaces of the two standards using a cooling and a heating sources. When the steady state is obtained, the thermal gradient is recorded and the thermal conductivity of the sample identified. Each measurement is repeated several times in order to check its relevance.

In the particular case of ceramic like Cofalit®, thermal conductivities have been measured between 150 and 300°C. The obtained results are illustrated in Figure 6.

![Figure 6: thermal conductivity of ceramic like Cofalit.](image)

In the experimented temperature range, the thermal conductivity decreases slightly from 3.6 at 140°C to 2.7 at 270°C but can be considered as rather stable and equal to 2.7.
This value is of particular interest: it will impose the thickness of storage material allowed for a needed mean heat exchange power for a specific thermal gradient. Then, a low thermal conductivity would impose a need of very extensive specific thermal interface to exchange the heat with the working fluid. Such surface area presents a cost in initial investment to build the storage module, a decrease in overall compactness of the storage unit and generally an increased pressure drop on the working fluid side. Complementary measurements will be done on glassy Cofalit® and all those measurements extended to higher temperatures up to 1000°C.

*Heat transfer interface*

The use of the obtained treated waste as storage material suppose to manage the heat transfer with the working fluids of the process and consequently to shape the media in a relevant form. Concerning this particular point, two different approaches can be considered:

1. the storage material can be potentially shaped directly at the outlet of the Asbestos treatment process by moulding of the molten product in the form of plates, cylinders or any other needed geometry. The commercial product is already proposed today for pavements.

2. the solid product can be also mechanically shaped as illustrated in Figure 7-8. Cylindrical ores of 25 mm in diameters (Figure 7) needed for thermal conductivity measurements have been easily obtained and the corresponding holes (Figure 8) in the block present also very good appearance.

Then, conventional heat exchanger geometries like multitubular ones can be obtained. Further work will be done in this field in order to realize and test a cylindrical shaped storage module.

![Figure 7. cylinder of Cofalit®](image1)

![Figure 8. holes in Cofalit®](image2)

*Thermal expansion*

If the proposed storage material is used in the form of dense blocks, connections with tubing will be necessary. Then, the thermal expansion of it is also an important property. This characterization has been done using a Netzsch DIL-402C apparatus on ceramic Cofalit® samples in parallelelipedic shape (5×5×30 mm³) from room temperature up to 900°C. The obtained curves were very reproductible and linear, the corresponding mean thermal expansion coefficient is equal to $8.8 \times 10^{-6}$/K.

4. DISCUSSION OF RESULTS

The obtained preliminary properties of the Cofalit® are gathered in Table 1 for comparison with sensible heat storage materials proposed today for solar power plants.
Table 1. Comparison of Cofalit® properties to those of other sensible heat storage materials.

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<tr>
<td>density [kg/m$^3$]</td>
<td>1870</td>
<td>3500</td>
<td>2750</td>
<td>3120</td>
</tr>
<tr>
<td>Cp [J/(kg×K)]</td>
<td>1600</td>
<td>866</td>
<td>916</td>
<td>860</td>
</tr>
<tr>
<td>$\rho \times$Cp [MJ/(m$^3$×K)]</td>
<td>2.99</td>
<td>3.031</td>
<td>2.519</td>
<td>2.683</td>
</tr>
<tr>
<td>$\lambda$ [W/(m×K)]</td>
<td>~ 0.8</td>
<td>1.35</td>
<td>1.0</td>
<td>2.7</td>
</tr>
<tr>
<td>thermal expansion [$10^{-6}$/K]</td>
<td>11.8</td>
<td>9.3</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>price [euros/tonne]</td>
<td>300</td>
<td>4500</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>price/$\rho \times$Cp</td>
<td>100</td>
<td>1480</td>
<td>32</td>
<td>3</td>
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The thermal capacity is presented both in term of mass and volume: the corresponding investment cost is usually based on weight while the corresponding volume is of great interest for the storage unit design.

From the Table 1, we can easily observe that the Cofalit® ceramics presents thermal storage capacities just in between the high temperature concrete and the castable ceramics or the solar salt, the highest thermal conductivity, the lowest thermal expansion but similar to those of the two other solid media and a very low cost (10 to 500 times lower to the other ones).

Those preliminary results demonstrate the high potential of such ceramics.

Moreover, the end-of-life character of the material should be very favourable in term of life cycle assessment applied to a whole solar power plant in which tens of thousands of tonnes of such storage materials are needed.

Those preliminary results have to be extended to glassy materials and more, the ageing effects under thermal cycling analysed. Those complementary characterizations are under progress and pilot tests on macroscopic storage modules will be realized.

6. CONCLUSIONS

Industrial ceramics produced by plasma treatment of Asbestos containing wastes have been considered as candidate to alternative thermal storage material for solar power plants. Preliminary characterizations have demonstrated their high potential: thermal storage capacities similar to high temperature concrete (HTC) and close to solar salts, thermal conductivities three times higher than HTC, similar thermal expansion and a very low cost of 8 euros/tonne. Moreover, the product is very stable under heat treatment up to 1200°C and then can be considered as alternative thermal storage media for both the solar trough based and the central receiver tower based power plants. Further work will be focussed on thermal cycling effects, properties of glassy products and thermal storage pilot tests.

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