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Oxidation properties of "Solar Salt"

Wassila BENAISSA
INERIS
Parc Technologique Alata BP 2, F-60550 Verneuil-en-Halatte
Wassila.Benaissa@ineris.fr

Douglas CARSON
INERIS

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Abstract

Solar Salt is a name sometimes given to a molten salt mixture made up of about 60% of sodium nitrate ($NaNO_3$) and 40% of potassium nitrate (KNO_3). This composition is near the eutectic point and is thermally stable until 600°C. It is popular in Industrial Solar Energy Projects and is used for storing energy in the form of heat to smooth out the peaks in electricity production. However for some technologies, combustible substances, like a thermal fluid for example, may come into contact with the molten salt. The aim of the paper is then to study the oxidizing properties of the solar salt in order to estimate the energy released by a potential reaction between the salt and combustibles and estimate safety issues. In that purpose, four types of experiments were carried out: the standard UN O.1 test for solid oxidizers, the standard UN O.2 test for liquid oxidizers, differential scanning calorimetry (DSC) and isothermal calorimetry (C80). The experimental program demonstrates the oxidizing properties of the solar salt and shows that the reactivity of solar salt with other combustibles has to be taken into account in a global risk analysis of a Solar Energy Central.

1. Introduction

Regarding the potentially dramatic effects of climate change and the estimated diminution of available fossil fuels, the development of new renewable energies have became a priority in research and development in order to anticipate the energy supply solutions of the future. Solar power, allowing conversion of sunlight into electricity, can be seen as one of the most promising ways [1]. In particular, during the last decades, concentrating solar power (CSP) has shown very interesting potentialities, through different sustainable power generation applications at industry scale [2]. Four different technology approaches are currently used for concentrating solar power: sterling dish, linear reflector, parabolic trough and power tower. In each case, the heat source provided by the sunlight is captured then concentrated by mirrors. One of the largest advantages of CSP against other sources of renewable energy such as photovoltaic or wind is the capability to provide a more flexible repartition of the power: to do so, the solar energy can be stored in thermal reservoirs and released during periods of peak power demand, cloudy weather or even at night [3]. Storage technologies can be either "direct" or "indirect". Indirect means that the storage medium is not heated directly by the concentrators. Indirect systems use a heat transfer fluid instead, typically synthetic oil, which passes through a heat exchanger with the storage medium to heat it indirectly. Typically the transfer fluid is synthetic oil and the storage medium is molten salts, generally nitrates. A practical example of this technology named Andasol 1 and implemented in Spain in 2008, use cool tanks (about 290°C) and hot tanks (about 390°C) of molten salts, with about 29,000 tones in each tank. In this configuration the storage capacity is about 1100 MWh that means about 7.5 h of full-load production of electricity and a very interesting benefit in terms of power supply duration [4].
In the field of safety, one can ask the risks of storing such a quantity of chemical product on a same spot. Indeed, combustible substances, like a thermal fluid for example, may come into contact with the molten salt. The aim of the paper is to study the oxidizing properties of a solar salt in order to estimate the energy released by a potential reaction between the salt and combustibles and estimate safety issues. The molten salt chosen as a case study is a mixture made up of about 60% of sodium nitrate ($NaNO_3$) and 40% of potassium nitrate (KNO_3). Four types of experiments were carried out: the standard UN O.1 test for solid oxidizers, the standard UN O.2 test for liquid oxidizers, differential scanning calorimetry (DSC) and isothermal calorimetry (C80).

2. Literature overview for the oxidizing properties

2.1 Pure nitrates

As the solar salt is a mixture of potassium and sodium nitrate, the reactivity of these two pure products has to be analyzed to understand the behavior of the salt.
Potassium nitrate is an ionic salt, odorless and melting at 333°C. It is stable at ambient temperature and pressure and can safely be stored during a long period if protected from moisture. When heated, potassium nitrate produces oxygen (cf. Eq.1). This reaction is endothermic and reversible.

$$KNO_3 \leftrightarrow KNO_2 + \tfrac{1}{2}\, O_2 \quad \text{[Eq. 1]}$$

Ullmann's Encyclopedia [5] gives a decomposition temperature equal to 530°C but smaller values around 400°C have also been published [6, 7]. According to the Wiley Guide to Chemical Incompatibilities [8], potassium nitrate is noncombustible, but enhances the combustibility or oxidation rate of many materials and chemical reactions can cause fire and explosion.

Sodium nitrate is an ionic salt, odorless and melting at 308°C. It is stable at ambient temperature and pressure and can be safely stored during a long period if protected from moisture. When heated, potassium nitrate produces oxygen (cf. Eq.1). This reaction is endothermic and reversible.

$$NaNO_3 \leftrightarrow NaNO_2 + \tfrac{1}{2} O_2 \quad [Eq.\ 2]$$

Ullmann's Encyclopedia [5] gives a decomposition temperature around 500°C but smaller values around 380°C have also been published [6, 7]. According to Wiley' Guide to Chemical Incompatibilities [8], sodium nitrate is non combustible, but enhances the combustibility or oxidation rate of many materials and chemical reactions can cause fire and explosion.

2.2 Classification

Potassium nitrate and sodium nitrate are classified 5.1 (oxidizing substances) by the "Recommendations on the Transport of Dangerous Goods" [9] and class 1 oxidizers by the U.S. *Hazardous Material Code*, NFPA 400, Chapter 15, Oxidizer Solids and Liquids [10]. The last classifies oxidizer materials according to their ability to cause spontaneous combustion and how much they can increase the burning rate. Of four classes, class 1 is the least dangerous and refers to substances which "slightly increase the burning rate of combustible materials" but "do not cause spontaneous ignition when they come in contact with them".
The sodium nitrate and potassium nitrate mixture is also clearly identified in the classification 5.1 and UN number 1499.

2.3 Solar salt

Solar salt is composed of two powerful oxidizers, both stable until 400°C. The mixture of these two salts without impurity gives a eutectic which melts at 219°C. From this point, the solar salt becomes a transparent liquid which can be used as a thermal fluid. Some industrial applications shows that the operating temperature of a solar central can reach 400°C for the hot storage, for a quantity more than 20,000 tones. Regarding safety, one can ask two questions: is the solar salt thermally stable and what are its oxidizing properties?

3. Experiments and results

3.1 Experimental approach

Two calorimetric devices and two tests from the Transport of Dangerous Goods Manual [11] have been used: differential scanning calorimetry (DSC), Calvet calorimeter, test O.1 for oxidizing solids and test O.2 for oxidizing liquids.

The calorimetric experiments are used to study the thermal stability of the solar salt and the reaction with combustibles.
One important constraint was met for the UN standards: the tests and criteria are significantly different for solid and liquid oxidizers. Depending on the temperature, the solar salt state can be one or another. Some modification was then made to manage the two states.

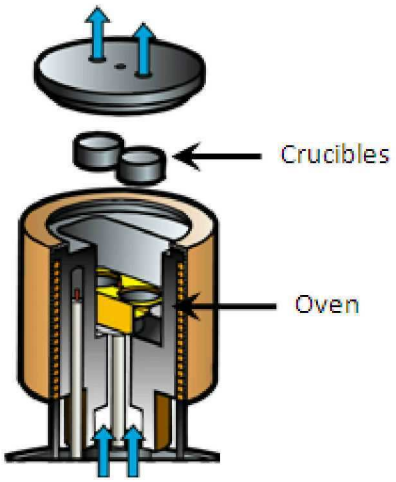
3.2 Chemicals

High purity (99.99%) sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3) were purchased separately from MERCK. At ambient temperature, these two products are generally white crystal powders. The solar salt is then prepared by mixing these two powders. The solar salt was ground to less than 100 µm and tested as such.
A combustible oil containing biphenyl has been chosen to represent the heat transfer fluid.
The characteristics of the cellulose used to perform the tests follow the recommendation of the manual of tests and criteria published by the United Nation for Transport of Dangerous Goods [11]. It is dried fibrous cellulose, with a fiber length between 50 and 250 µm and a mean diameter of 25 µm. It is dried in a layer no more than 25 mm thick at 105°C for 4 hours and kept in a desiccator until cool and needed for use. The water content is less than 0.5% by dry mass.
Pure potassium bromate has been used as reference for the O.1 test.

3.3 DSC experiments

The DSC is a micro-calorimetric technique which measures a heat flux difference between a few milligrams sample and a reference, placed in a same temperature control oven and following the same scan rate (cf. picture 1). It is used to detect all kind of exothermic and endothermic behavior: phase transitions, heat capacity, chemical reactions/decompositions, etc. The test gives access in thermal power and energy released by the sample [12].

Picture 1. DSC calorimeter



Each few milligrams sample is introduced at ambient temperature in a stainless steel crucible. The crucible is then sealed and put in an oven with an empty crucible as reference. The two crucibles are heated at 5 K/min from ambient temperature up to 700°C. The heat flux and the energy released are then measured (see figures 1 to 7). Table 1 summarizes the results.

Table 1. DSC test on Solar Salt, cellulose and thermal fluid

	Component A		Component B		Tonset (°C)	Enthalpy (J/g)	Enthalpy (J/g combustible)
DSC n°1	solar salt	100 %			stable	--------	--------
DSC n°2			cellulose	100 %	300	-588	-588
DSC n°3	solar salt	50 %	cellulose	50 %	240	-3054	-6108
DSC n°4			thermal fluid	100 %	610	-545	-545
DSC n°5	solar salt	85 %	thermal fluid	15 %	550	-707	-4799
DSC n°6	solar salt	45 %	thermal fluid	55 %	540	-2454	-4490
DSC n°7	potassium chloride	60 %	thermal fluid	40 %	stable	--------	--------

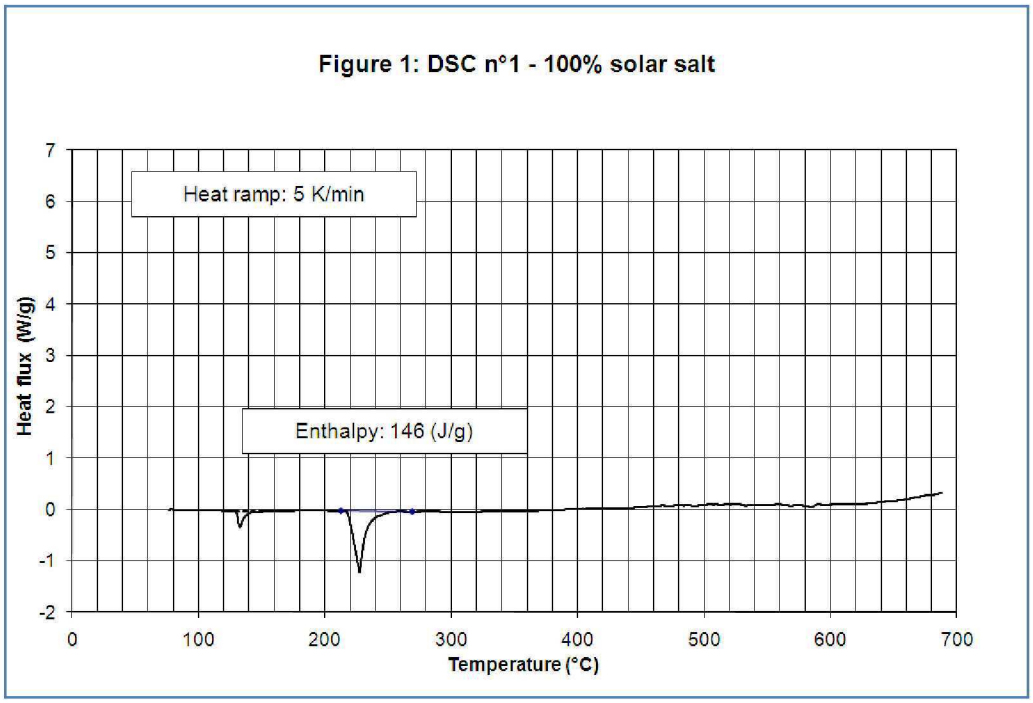


Figure 2: DSC n°2 - 100% cellulose

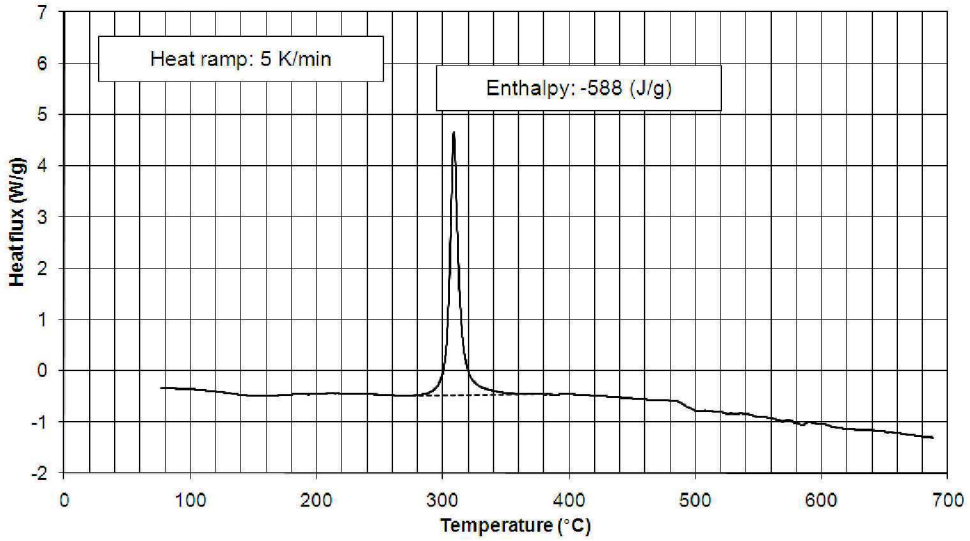


Figure 3: DSC n°3 - 50 % solar salt + 50 % cellulose

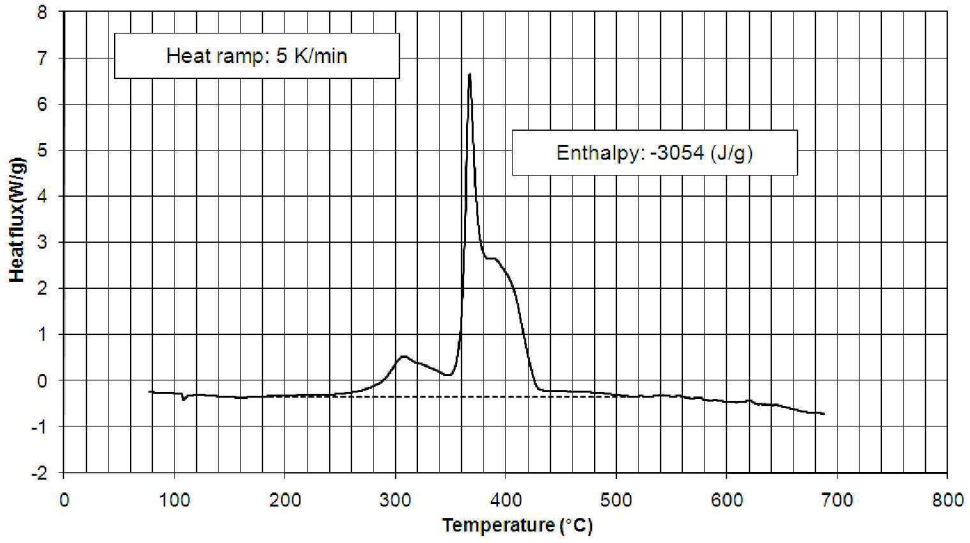


Figure 4: DSC n°4 - 100% thermal fluid

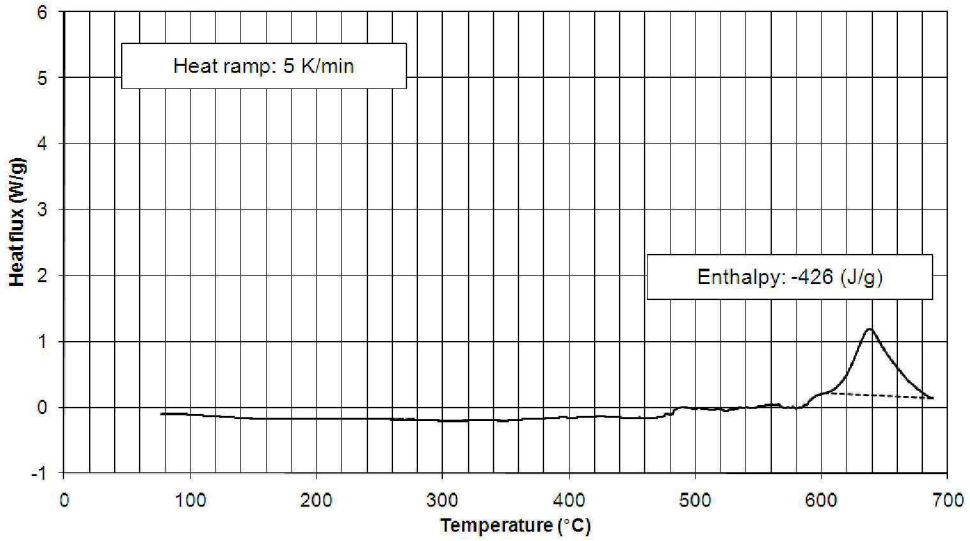


Figure 5: DSC n°5 - 85 % solar salt + 15 % thermal fluid

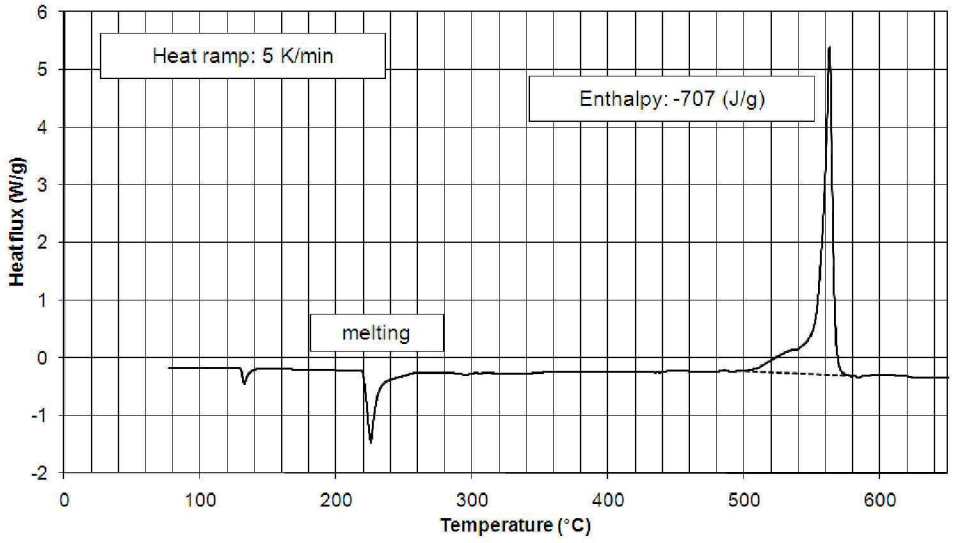


Figure 6: DSC n°6 - 45 % solar salt + 55 % thermal fluid

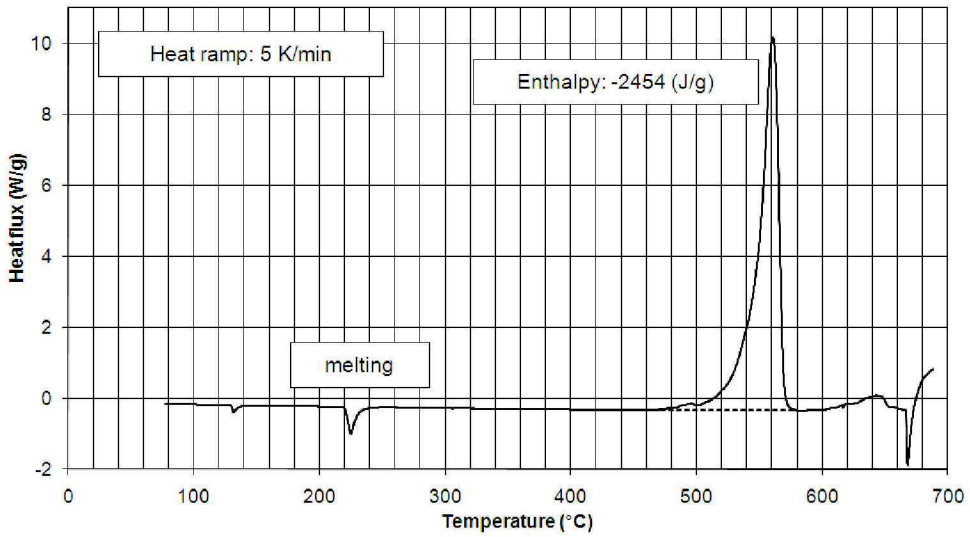
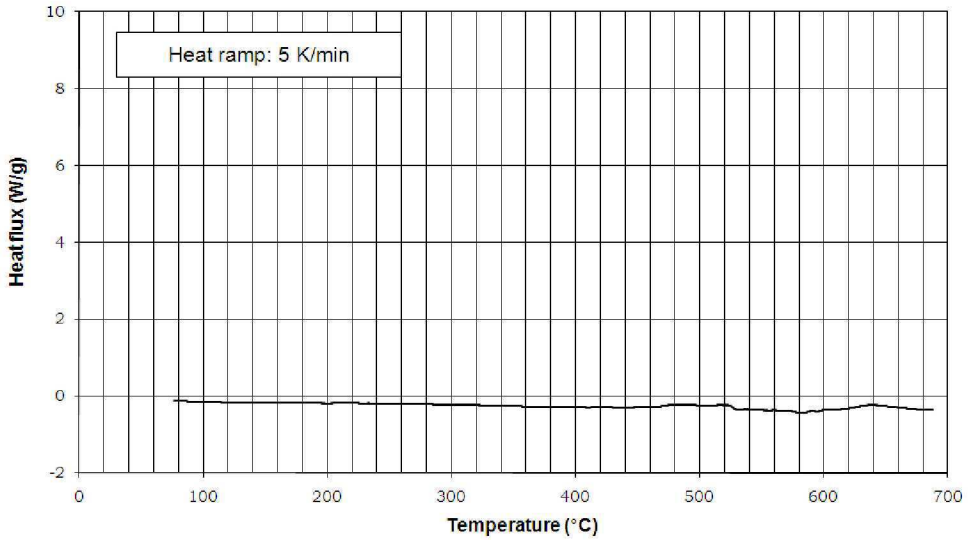


Figure 7: DSC n°7 - 60 % potassium chloride + 40 % thermal fluid



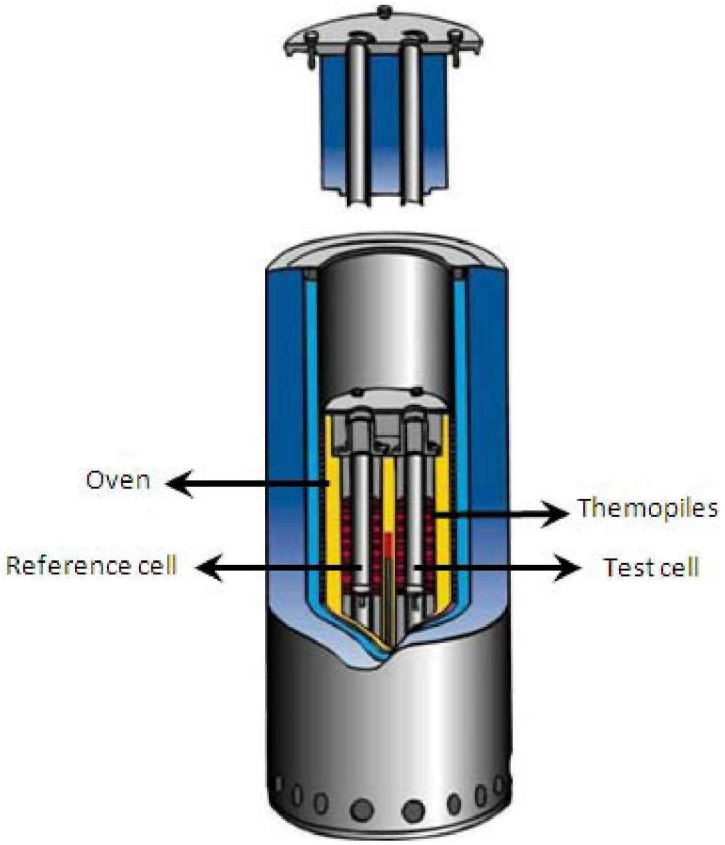
On figure n°1, the endothermic peak is characteristic of the melting point of the solar salt and it is thermally stable up to 650°C (cf. figure 1).
The cellulose decomposes at 300°C with an enthalpy of -588 J/g (cf. figure 2). When solar salt is mixed to cellulose, we observe a significant difference: the onset temperature is much less and the enthalpy is almost ten times larger. It seems that the solar salt enhances the decomposition of the cellulose (cf. figure 3).

We can reach a similar conclusion for the thermal fluid (cf. figure 4). The last is very stable until 545°C. When mixed with solar salt, the initial temperature decrease around 500°C and the enthalpy is also almost ten times larger (cf. figure 5 and 6). The figure 7 confirms that with another inert product, no thermal activity is detected.
These results illustrate the influence of solar salt acting like a typical oxidizer i.e. it increases the reactivity of a combustible substance when both are thoroughly mixed.

3.4 C80 experiments

The Calvet calorimeter is also a differential calorimeter that may be operated isothermally or in the scanning mode as a DSC. It allows working with larger sample volumes (few grams) and shows a higher sensitivity (around 0,1 $W.kg^{-1}$) essentially due to the measurement principal, based on a array of thermocouples totally surrounding the cells (sample and reference) (cf. picture 2). As in the DSC, the test gives thermal power and energy released by the sample and allows detecting exothermic activity [13].

Picture 2. C80 calorimeter



Two tests were carried out. Firstly, the cellulose is put in a closed cell and tested in DS mode at 0.5 K/min from ambient temperature to 300°C (cf. figure 8). Secondly a cell constructed of two compartments separated by a membrane is used: 300 mg of cellulose is introduced in the first

compartment and 300 mg of solar salt is introduced in the second. During a first step, the two products are heated separately until 300°C. When the heat flux is stabilized, the membrane is broken and the two products mixed (cf. figure 9). When the mixing occurs, a highly exothermic reaction can be observed that is not detected when the cellulose is pure.

Figure 8: C80 n°1 - 100 % cellulose

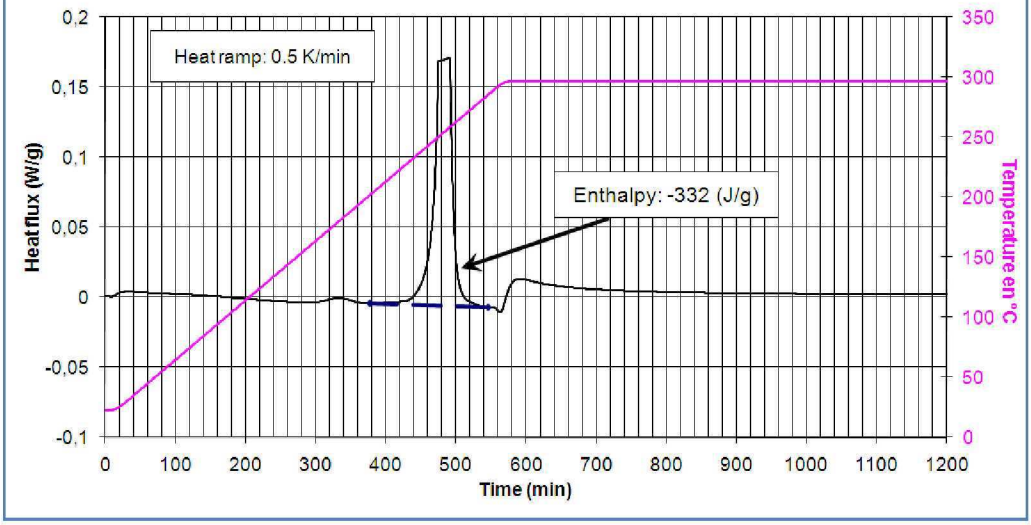
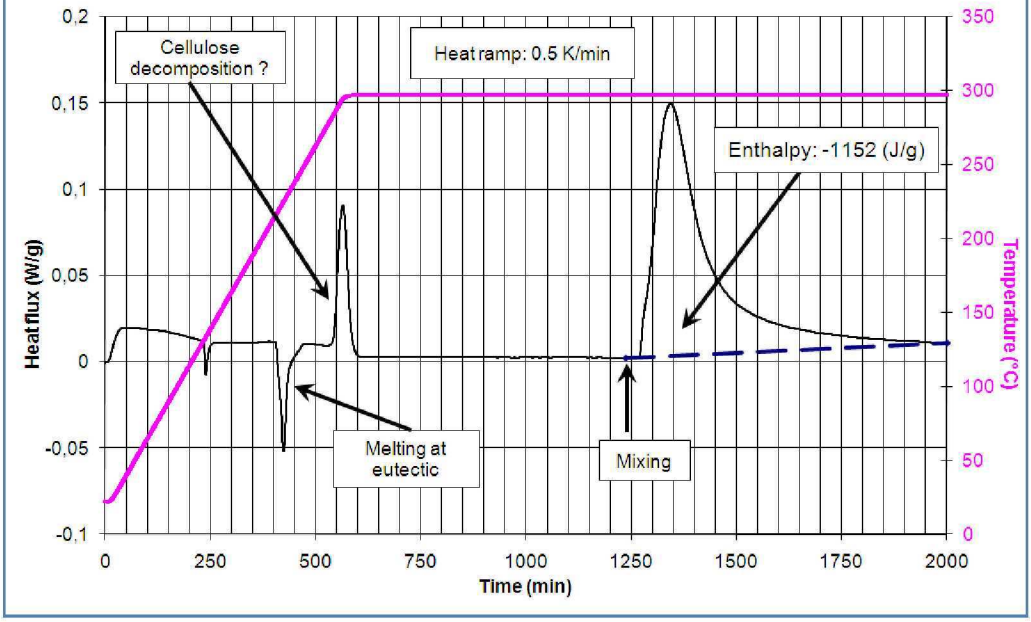


Figure 9: C80 n°2 - 50 % solar salt + 50 % cellulose



3.5 O.1 test

The UN manual defines the O.1 test as a method to measure the potential for a solid substance to increase the burning rate or burning intensity of a combustible substance when the two are thoroughly mixed (cf. picture 3). For the O.2 test, a liquid is also considered as an oxidizer if the mixture made with the combustible substance can spontaneously ignite.

Picture 3. UN O.1 disposal



O.1 tests have been conducted on the solar salt mixed with dry fibrous cellulose in mixing ratio of 1:1 and 4:1, by mass of sample to cellulose. The burning characteristics of the mixture are compared with the standard 3:7 mixture (around 100 s), by mass of potassium bromate to cellulose. If the burning time is equal to or less than this standard mixture, the burning times should be compared with those from the packing group I or II reference standards, 2:3 (around 54 s) and 3:2 (around 4 s) ratios, by mass of potassium bromate to cellulose respectively. The results are summarized in table 1.

Table 2. UN O.1 test on Solar Salt

	Classification limits	Mixture	Molar ratio	Reaction time (s)					
				N°1	N°2	N°3	N°4	N°5	Average
Solar Salt		24 g solar salt / 6 g cellulose	4:1	7	8	7	9	8	7.8
		15 g solar salt / 15 g cellulose	1:1	20	19	20	21	19	19.8
Reference mixtures	Packing Group I limit	18 g potassium bromate / 12 g cellulose	3:2	6	5	6	6	7	6.0
	Packing Group II limit	12 g potassium bromate / 18 g cellulose	2:3	63	69	59	65	63	63.8
	Packing Group III limit	9 g potassium bromate / 21 g cellulose	3:7	115	112	118	123	120	117.6

The solar salt as tested is assigned to the class 5 (oxidizing substances and organic compounds), division 5.1 (oxidizing substances) and packaging group II (substances presenting medium danger), borderline packaging group I (substances presenting high danger). According to this test and criteria of the United Nation Manual, the solar salt has to be considered as a strong oxidizer.

4.1 O.2 test

According to the O.2 tests procedure, the liquid to be tested is mixed to 1:1 ratio, by mass, with fibrous cellulose, poured into a pressure vessel with an exposed electric heating coil. The mixture heated (by action of the heating coil) in a pressure vessel and the rate of pressure rise is compared with those of reference substances. Since solar salt is a powder mixture at ambient temperature, the procedure had to be slightly adjusted:

- the pressure vessel was placed empty in an oven at 250°C overnight,
- a mixture of 2.5 g of solar salt with 2.5 g of cellulose was then prepared in a glass container.
- the pressure vessel was filled with the mixture to cover the ignition coil,
- the pressure was vessel was covered with aluminum foil and placed in the oven for 30 more minutes,
- the pressure vessel was taken out of the oven and closed according to conventional procedure,
- the heating coil was energized.

To complete the approach, two other mixtures were tested in the exact same conditions: a mixture of solar salt and an inert powder, a mixture of solar salt and an inert liquid. Since the operating temperature is much higher than the conventional one, it is important to verify that the cellulose thermal behavior doesn't influence the results. Table 2 summarized the pressure rise obtained. Perchloric acid solution (55%) has been chosen as a typical reference for a solution classified 5.1 (oxidizing substances) and packaging group I: the mean pressure rise time for a 1:1 mixture with cellulose is 59 ms.

Table 3. UN O.2 test on Solar Salt

Component A	Component B	Test n°1	Test n°2
Perchloric acid (55%)	cellulose	59 ms (typical time taken from the UN manual. Solution 5.1 packaging group I)	
Solar salt	cellulose	23 ms	30 ms
Solar salt	Inert powder	No significant pressure rise	No significant pressure rise
Inert mineral oil	cellulose	No significant pressure rise	No significant pressure rise

Since the tests have not been carried out in the exact same condition as the one described in the UN manual, it is not possible to directly extrapolate the classification of the molten solar salt. However, the result shows a significant reaction when the solar salt and the combustible are mixed showing a potential influence of the salt on the combustion.

4. Conclusion

Despite the good knowledge of the hazard characteristics of the pure components of the solar salt, the oxidizing characteristics of the mixture were not clearly identified. The experimental program has demonstrated the oxidizing properties of the solar salt and shows that there is a potential important reactivity of solar salt with other combustibles. Since it is one of the technical options used in the solar centrals using concentrated solar power, this property has to be taken into account in a global risk analysis of a Solar Energy Central.

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