TECHNICAL REPORT

HAZARD ISSUES IN PARABOLIC TROUGH TECHNOLOGY USING MOLTEN SALT AND SYNTHETIC OIL WITH REGARD TO OXIDIZING AND TOXICITY PROPERTIES

Abstract

Synthetic oils and molten salts are the most commonly used working fluids in Concentrated Solar Power (CSP) plants, especially when combined with storage systems allowing the increase in electrical power dispatchability. However, when looking at French regulations, the 2001 incident at the AZF fertilizer factory near Toulouse has set a premise to strengthen policies related to nitrate-based products. Since then, these products are said to be negatively associated in the French public opinion. In 2007, during the development of the SOLENHA project, a 12 MW_e Parabolic Trough project located in the heart of the Alps, a detailed hazard study was handed over to the French public authorities to clarify the properties of the existing products associated with Parabolic Trough technology.

Keywords: hazard issues, pollution, toxicity, molten salts, heat-transfer fluids, parabolic trough

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Contact details

Solar Euromed SAS
3, Avenue de la Découverte
Parc Technologique
F-21000 Dijon – France
T: +33 380 380 000
F: +33 380 380 001
M: contact@solareuromed.com

All inquiries regarding this technical report shall be directed to :

Simon Benmarraze
Solar Euromed SAS
3, Avenue de la Découverte
Parc Technologique
F-21000 Dijon – France
M : simon.benmarraze@solareuromed.com

3 Avenue de la Découverte
Parc Technologique
2100 Dijon - France
Tél : +33 380 380 000
Fax : +33 380 380 001

1. Introduction

SOLENHA (fig. 1) was a projected 12 MW_e (80 ha) solar thermal power plant using the Parabolic Trough (PT) technology, located in Aspres-sur-Buëch (French Alps). It included a molten salt storage system designed to ensure a 12-hour storage (fig. 2).

FIGURE 1 - The SOLENHA project

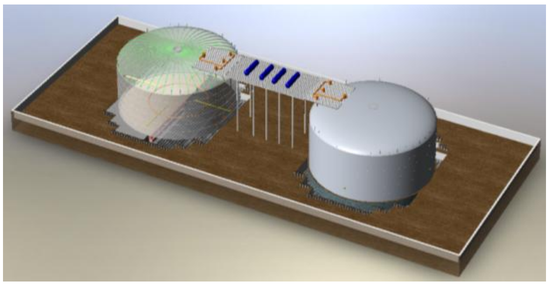

FIGURE 2 – Two-tank molten salt storage system envisioned

The project was the first of its type in France, and therefore used quantities of molten salt and synthetic oil that were unusually high for this country. All these novelties inferred a very careful and accurate analysis of the products and hazard risks of such a plant.

In order to respond to this request, the following studies were commisionned:

- The Molten Salts characterization [1] in collaboration with the French National Institute of Risk and Industrial Environment (INERIS)
- The hazard study [2] in collaboration with the oil and gas engineering company TECHNIP.

In parallel to these studies, the classification of the installation with regard to French and European regulations was also investigated.

2. Regulatory background

2.1. Classification rules

Following a series of industrial accidents that caused a lot of human and material damage, France adopted tools for classifying and controlling the industrial risks generated by operation of industrial installations (pollution, safety, health…). One of these tools is the ICPE regulation (Classified Installations for the Protection of the Environment, 1976), which was amended by the European so-called 'Seveso II' directive 96/82/EC in 1996 [3], and provides identification and classification for industries as a function of the chemical substances and/or activities on site. This classification ranks these facilities through thresholds, each corresponding to a level of dangerousness.

Under the 'Seveso II' directive, all facilities are subject to notification, and according to their level of dangerousness, can be:

- subject to notification (N) only
- subject to authorization (A - lower threshold)
- subject to encumbered authorization (AS - upper threshold)

3 Avenue de la Découverte
Parc Technologique
2100 Dijon - France
Tél : +33 380 380 000
Fax : +33 380 380 001

In the case of SOLENHA, the following classification was initially adopted for the two main products and the two main activities leading to regulatory concerns:

	Characteristics of the facility	ICPE section	Description of the section	Class
Chemicals	Therminol VP1® synthetic oil quantity > 400 tons	1173.2	Hazardous for the environment -B-, toxic for aquatic species. 2. quantity ≥ 200 t but < 500 t	A
Chemicals	Solar salt quantity > 15,000 tons	1200.2.a	Oxidizing agent. 2.a) quantity for use/storage ≥ 200 tons	AS
Activities	Solar salt storage in liquid phase volume : 8.6 x 106 L	2562.1	Heating and industrial treatment through molten salt baths. 1. volume of baths > 500 L	A
Activities	Use of synthetic oil above 110°C (flash point), with volume > 400 m^3	2915.1.a	Heating process using organic fuel as HTF 1. temperature above flash point a) quantity > 1,000 L	A

TABLE 1 - ICPE classification sections for SOLENHA

This classifying is done with regard to the physicochemical characteristics of the products used in the facility, which are usually well defined for conventional industries. It can be seen that the upper threshold Seveso (AS) was attributed to SOLENHA because of the quantity of solar salt on site. Although, SOLENHA being the first French project of its kind, it used chemicals that were unconventional and unspecified by the Directive. This observation led us to testing and characterizing the following chemicals :

- the heat-transfer fluid (HTF), known as Therminol VP1®, which is a eutectic mixture of 26% biphenyl - $(C_6H_5)_2$ - and 74% diphenyl ether - $O(C_6H_5)_2$. It has a flash point of 110°C, and was to be used in the process at temperatures ranging from 200 to 400°C, range in which it acts as a fuel.
- the storage fluid, a molten salt compound, eutectic mixture of 60% sodium nitrate – $NaNO_3$ – and 40% potassium nitrate – KNO_3. It decomposes at about 700°C, and was meant to be used at temperatures ranging from 292°C to 385°C, range in which it behaves as an oxidizing agent.

3. Working fluids' critical characteristics

As explained above, the absence of standardized testing procedures to assess oxidizing characteristics of liquid chemical compounds in France, led us to collaborate with INERIS to perform a study [1] of stability characteristics of the molten salt and heat-transfer oil compound, at normal operating temperatures.

3 Avenue de la Découverte
Parc Technologique
2100 Dijon - France
Tél : +33 380 380 000
Fax : +33 380 380 001

3.1. Molten salt

For reminders, here is a table of the decomposition temperatures of several molten nitrates:

	NaNO3	KNO3	Solar Salt
Decomposition T (°C)	500 [4]	530 [4]	700 [1]

TABLE 2 - Decomposition temperature of certain molten nitrate salts

The stability range of the solar salt has been inquired through the DSC (Differential Scanning Calorimetry) method, which consists in a gradual increase of temperature (5°C/min) of a sample of the product of interest in a high pressure sealed crucible (fig. 3), and the measure of the amount of heat needed to provide for this temperature difference.

The results of the calorimetry on a 6.75 mg solar salt sample are shown on fig. 4.

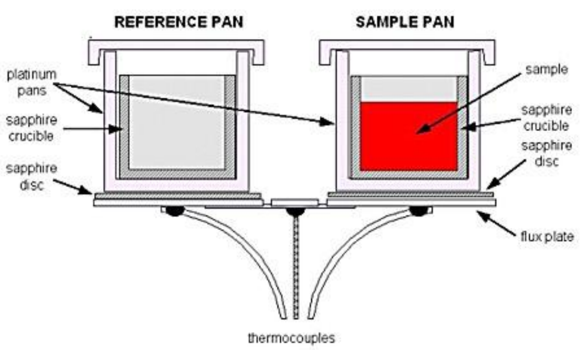

FIGURE 3 – Differential Scanning Calorimetry (DSC)

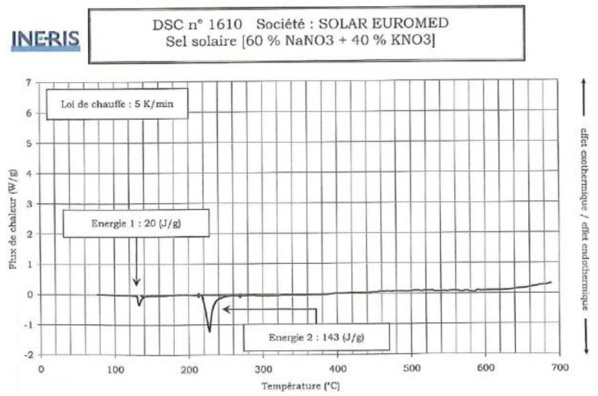

FIGURE 4 – DSC results for solar salt

These measurements show endothermic peaks corresponding respectively to the crystallization (~ 115°C) and fusion (~ 219°C) of the solar salt, and the thermal stability of the salt from ambient to 700°C approx.

3 Avenue de la Découverte
Parc Technologique
2100 Dijon - France
Tél : +33 380 380 000
Fax : +33 380 380 001

3.2. Synthetic oil

The same measurements have been made for the Therminol VP1® synthetic oil, which results are shown on fig. 5, and for a mixture of molten salt and synthetic oil (fig. 6), in order to be able to predict the behavior of such mixtures, which could appear in the case of a leakage in the heat exchanger.

It can be seen, for the oil itself, that an exothermic peak appears at about 580°C, corresponding to the decomposition of the substance.

When it comes to salt/oil mixtures, a strong reaction can be observed, which initiates around 500°C, and frees an amount of energy of 4800 kJ/kg_{oil}. This reaction takes place between sodium nitrate and biphenyl:

$$NaNO_3 + (C_6H_5)_2 \rightarrow NaNO_2, CO_2, H_2O, NO_x$$

and produces toxic molecules such as NO_x and maybe other toxic aromatic compounds.

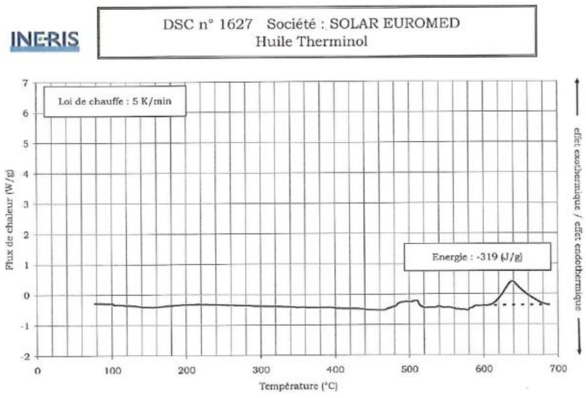

FIGURE 5 – DSC results for synthetic oil

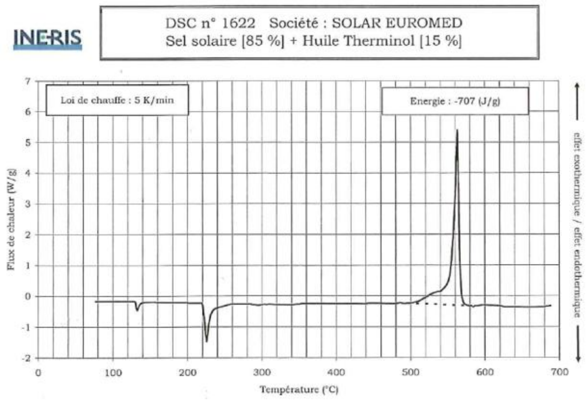

FIGURE 6 – DSC results for a mixture of 85% solar salt with 15% synthetic oil

In terms of the toxicity of the oil, data was retrieved from the Safety Datasheet for Therminol VP1® [5] elaborated by Solutia. The main data is given in the following table:

Type of toxicity	Test	Lower bound of toxicity
Oral	DL50, rat	2050 mg/kg
Inhalation	CL50, rat – 4 hours	5010 mg/kg
Dermal	DL50, rabbit – 24 hours	2.66 mg/L

TABLE 3 - Toxic characteristics of Therminol VP1®

3 Avenue de la Découverte
Parc Technologique
2100 Dijon - France
Tél : +33 380 380 000
Fax : +33 380 380 001

4. Hazard study

The hazard study for SOLENHA [2] was performed by Technip. It describes the potential dangers caused by the installation, and the risks it breeds for the environment and the neighboring population. It identifies the different dangers to which the facility could be confronted to, taking into account:

- the probability of occurrence of a given event,
- the kinetics and potential seriousness of a given event.
- the efficiency of the prevention and protection measures taken by the operator,

4.1. Probability of events

The quantitative and qualitative definition of each probability class is as follows:

Class	A	B	C	D	E
Definition	*frequent*	*probable*	*improbable*	*highly improbable*	*extremely improbable*
Probability /yr	10^{-2}	10^{-3}	10^{-4}	10^{-5}	

TABLE 4 - Classes of probability for hazardous events

4.2. Seriousness of events

The delimitation of the danger zones for a given incident is determined by three thresholds:

- the Irreversible Effects' Threshold (SEI)
- the Lethal Effects' Threshold (SEL)
- the Significantly Lethal Effect's Threshold (SELS)

These thresholds were defined for several effects in the case of SOLENHA:

Effect	SEI	SEL	SELS	Comment
Toxicity	43 ppm	-	-	For 30 min of exposure to Therminol VP1®
Thermal flow	3 kW/m²	5 kW/m²	8 kW/m²	For 2 min of exposure
Pressure wave	5 kPa	14 kPa	20 kPa	At maximal amplitude of the wave

TABLE 5 – Main hazardous events with their thresholds

Each event is then evaluated for its degree of dangerousness, in terms of exposed persons[1] according to a scale from the French Ministry of Ecology (MEEDDM) [2]:

Seriousness of consequences	Danger zone delimitated by SELS	Danger zone delimitated by SEL	Danger zone delimitated by SEI
Disastrous (D)	Between 10 and 100 persons	Between 100 and 1000 persons	> 1000 persons
Catastrophic (C)	Between 1 and 10 persons	Between 10 and 100 persons	Between 100 and 1000 persons
Important (I)	≤ 1 person	Between 1 and 10 persons	Between 10 and 100 persons
Serious (S)	Nobody	≤ 1 person	Between 1 and 10 persons
Moderated (M)	No lethality zone out of the facility		≤ 1 person
(1) Exposed person : taking into account, if applicable, the construction measures meant to protect people against certain effects , and the possibility of sheltering people in case of an occurrence of a dangerous phenomenon, if its kinetics and propagation allow it.			

TABLE 6 - Scale of seriousness

3 Avenue de la Découverte
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2100 Dijon - France
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4.3. Dangerous Phenomena

4.3.1. Nomenclature

126 events were identified for SOLENHA, which could seriously impact the surroundings of the installation, and which were called Dangerous Phenomena (DPh). These were mitigated by Measures for Mastering the Risks (MMR). Each of these events is classified and given an acronym in the following manner:

Information	Position of breach	Leakage	# of unavailable MMRs	DPh
Possible value	*BF* – Cold Collector *BI* – Intermediate Collector *BC* – Hot Collector *CSO1,2,3,4* – Hot Solar Field (southwest) *CSE1,2,3* – Hot Solar Field (southeast) *CNE1,2* – Hot Solar Field (northeast) *CNO1,2,3,4,5* - Hot Solar Field (northwest) *FSO1,2,3,4,5* - Cold Solar Field (southwest) *FSE1,2* - Cold Solar Field (southeast) *FNE1,2* – Cold Solar Field (northeast) *FNO1,2,3,4,5*- Cold Solar Field (northwest)	*F* – 10% of nmfr* *B* – 30% of nmfr *G* – 100% of nmfr *nmfr : nominal mass flow rate	*M0, M1, M2…*	*TX* – toxic *JE* – flame jet *EX* – vapor cloud explosion *FN* – pool fire *BLEV* – BLEVE** **BLEVE: Boiling Liquid Expanding Vapor Explosion

Table 7 - Nomenclature of Dangerous Phenomena (DPh)

For example, BF|F|M1|JE corresponds to an event initiated at all cold collector points, with a 10% leakage, with one unavailable MMR, and for the flame jet phenomenon.

3 Avenue de la Découverte
Parc Technologique
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Fax : +33 380 380 001

4.3.2. MMR Matrix

These events fall into three categories, according to both their probability (from A to E) and their importance (from 'Moderate' to 'Disastrous'). The three categories are:

- **acceptable risk (green – OK zone)**
- **intermediate risk (yellow – MMR zone)**
- **inacceptable risk (orange – NO zone)**

These categories and the zone they cover are shown in the following table, which synthesizes the probability of the 126 DPh encountered in the hazard study for SOLENHA, along with their seriousness, in a matrix (called the MMR matrix):

		Probability of the DPh				
		E $p < 10^{-5}$	D $10^{-5} \le p < 10^{-4}$	C $10^{-4} \le p < 10^{-3}$	B $10^{-3} \le p < 10^{-2}$	A $p > 10^{-2}$
Seriousness of the consequences	Disastrous SELS > 10 p SEL > 100 p SEI > 1.000 p	MMR rank 2	NO rank 1	NO rank 2	NO rank 3	NO rank 4
	Catastrophic SELS < 10 p $10 \le$ SEL ≤ 100 p $100 \le$ SEI ≤ 1.000 p	MMR rank 1 *2 DPh*	MMR rank 2 *1 DPh*	NO rank 1	NO rank 2	NO rank 3
	Important SELS ≤ 1 p $1 <$ SEL ≤ 10 p $10 \le$ SEI ≤ 1.000 p	MMR rank 1 *38 DPh*	MMR rank 1 *13 DPh*	MMR rank 2 *9 DPh*	NO rank 1 *4 DPh*	NO rank 2
	Serious SELS = 0 p SEL ≤ 1 p SEI < 10 p	OK *27 DPh*	OK *6 DPh*	MMR rank 1	MMR rank 2	NO rank 1
	Moderate SEI < 1 p	OK *8 DPh*	OK *11 DPh*	OK *3 DPh*	OK *2 DPh*	MMR rank 1

TABLE 8 - MMR Matrix

3 Avenue de la Découverte
Parc Technologique
2100 Dijon - France
Tél : +33 380 380 000
Fax : +33 380 380 001

All of the four phenomena that fall into the NO category are related to toxic events, which are detailed below:

Designation	Leakage	Point	DPh	P	SELS (m)	SEL (m)	SEI (m)	Seriousness
BFFMOTX	10%	BF	Toxic	B	-	-	750	Important
*BFFMOTX**	10%	BF west	Toxic	B	-	-	543	Important
BFBMOTX	30%	BF	Toxic	B	-	-	592	Important
*BFBMOTX**	30%	BF west	Toxic	B	-	-	556	Important

TABLE 9 - List of events with inacceptable risk

For instance, the first of these DPh has a yearly probability of 3 x 10^{-3} (B) and a SEI of 750m. A hostel-farmhouse and an individual house having a lower distance to the leakage points, and hosting at most 20 people, this event fell in the 'Important' category (10 ≤ SEI ≤ 100). Some events would have had a catastrophic impact (namely FSO5FTX, FNE2BTX and FNO3BTX), but their classification is mitigated by their very low probability (respectively E, E and D). Reversely, some events (namely BCFMOTX and BCFMOTX*) had a relatively high probability of occurrence (B), but their effect would have been only moderate.

4.3.3. Map of impacted areas

As an example, the map of the would-be impacted area for event BFBM0TX (toxic dispersion for a 30% leakage on the cold collector parts, with a duration of 600 seconds before isolating the site) is shown below. The dotted black line is the limit of the plant site, whereas the orange line corresponds to the limit of the SEI (i.e. the line where the aerial concentration of Therminol VP1® is equal to 43 ppm) after 10 minutes of uncontrolled dispersion. The points of origin of the leakage are represented by the blue dots.

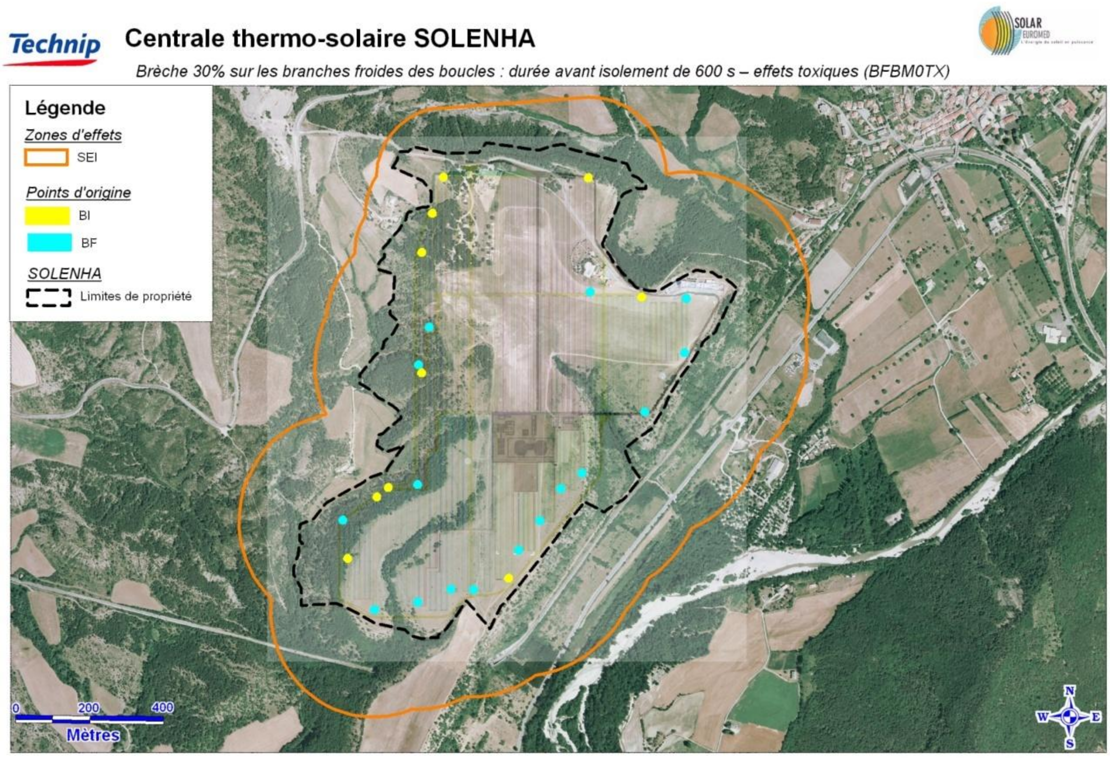

FIGURE 7 - Map of impacted area for event BFB0MTX

5. Conclusion

Although the administrative classification (ICPE) of our power plant as upper threshold Seveso was due to the use of the solar salt as a storage medium, the hazard study showed that risks mainly came from the use of synthetic oil Therminol VP1® above its flash point, which caused both thermal instability and toxicity issues.

Given the operating conditions of the power plant (between 200°C and 400°C for the HTF), reactivity issues of the synthetic oil and its highly improbable mixture with solar salt was not the main concern in the hazard study, which showed that toxicity was the most serious issue.

As a consequence of the various potential risks incurred by the use of this fluid in SOLENHA power plant, along with the resulting worries among the population, we moved to another type of solution, eliminating the need for salt and oil, and valued by the French Ministry of Ecology and Energy ([6]) as an evolution of PT systems: the Compact Linear Fresnel Reflectors (CLFR), associated to Direct Steam Generation (DSG).

3 Avenue de la Découverte
Parc Technologique
2100 Dijon - France
Tél : +33 380 380 000
Fax : +33 380 380 001

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