

## NewSOL Project (720985)

### Thermal properties

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“Thermal properties”

Internal Report on work developed by LNEG included in Subtask 5.1 “Thermocline concrete tank simulation” for partial fulfillment of deliverable D5.1 “System configuration for thermocline concrete tank”.

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## 1. Overview

In order to implement the simulation of a thermal process in a computational fluid dynamics application, it is needed to know the thermal properties of the involved chemical species, namely the density, the specific heat, the dynamic viscosity and the thermal conductivity. The experimental determination of the thermal properties for the molten salts and for the S. Domingos Mines ore were performed by, respectively, Yara and UEvora.

In Section 2, the determined thermal properties for both materials are presented; In Section 3, the thermal properties for the molten salts are assessed and adapted to the CFD application package; In Section 4, the same work is performed for the ore slurry; and in Section 5 some conclusions are disclosed.

## 2. Yara MOST thermal properties

The Yara Patent WO2014/044652 A1 describes the “Use of a Calcium Potassium Nitrate salt for the manufacture of a heat transfer fluid”. In this document, a weight composition of 42%  $\text{Ca}(\text{NO}_3)_2$ , 15%  $\text{NaNO}_3$  and 43%  $\text{KNO}_3$  for the Yara MOST was disclosed and a melting temperature of 131 °C was achieved.

The thermal properties needed to discretize the molten salts in a CFD application package with energy and turbulence calculations are the density, the specific heat, the thermal conductivity, the dynamic viscosity and mass diffusivity.

Yara (2018) answers to most of the questions with regard the thermal properties of the Yara MOST molten salts for modelling purposes. Moreover, all the presented properties by Yara are temperature dependent. Tables 1 and 2 present the disclosed data.

Table 1: Yara MOST specific heat.

Temperature [°C]	Specific heat [J/kg-K]
200 ± 10	1800 ± 50
216 ± 10	1791 ± 40
230 ± 10	1521 ± 60
250 ± 10	1490 ± 40
306 ± 10	1470 ± 75
400 ± 10	1450 ± 60

430 ± 10	1645 ± 30
480 ± 10	1515 ± 50
500 ± 10	1400 ± 50

Table 2: Yara MOST density, thermal conductivity (calc), dynamic viscosity and thermal diffusivity.

Temperature [°C]	Density [kg/m <sup>3</sup> ]	Thermal conductivity <sup>1</sup> [W/m-K]	Dynamic viscosity [mPa.s]	Thermal diffusivity [m <sup>2</sup> /s]
130	2250 ± 50		> 30	-
140	2240 ± 50		12,5 ± 0,1	-
150	2230 ± 50		7,8 ± 0,1	-
170	-		5,4 ± 0,1	-
200	2210 ± 50	0,5 ± 0,01	3,6 ± 0,1	1,26×10 <sup>-8</sup> ± 2×10 <sup>-9</sup>
205	-		3,6 ± 0,1	-
260	-		2,4 ± 0,1	-
300	2137 ± 50	0,55 ± 0,01	2,1 ± 0,1	1,23×10 <sup>-8</sup> ± 2×10 <sup>-9</sup>
400	2040 ± 50	0,55 ± 0,005	1,4 ± 0,1	1,86×10 <sup>-8</sup> ± 1,5×10 <sup>-9</sup>
460	-		1,1 ± 0,1	-
500	1885 ± 50	0,44 ± 0,005	1,1 ± 0,1	1,67×10 <sup>-8</sup> ± 1×10 <sup>-9</sup>

In the minutes of a bilateral meeting between LNEG and UEvora (in Annex), in January, 26<sup>th</sup>, UEvora referred that the behavior of the thermal energy storage tank should be simulated up until 525 °C. However, the available data only presents thermal properties ranging from 200 °C up until 500 °C.

Figures 1 to 5 depict the experimental data provided by Yara.

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<sup>1</sup> Calculated by Yara.

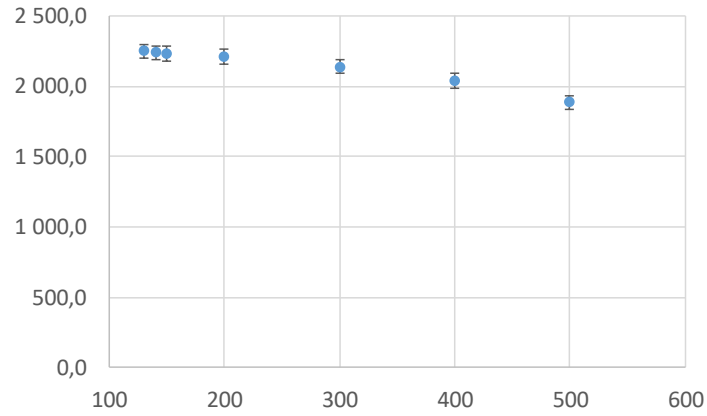


Figure 1: Yara MOST density, in kg/m<sup>3</sup>.

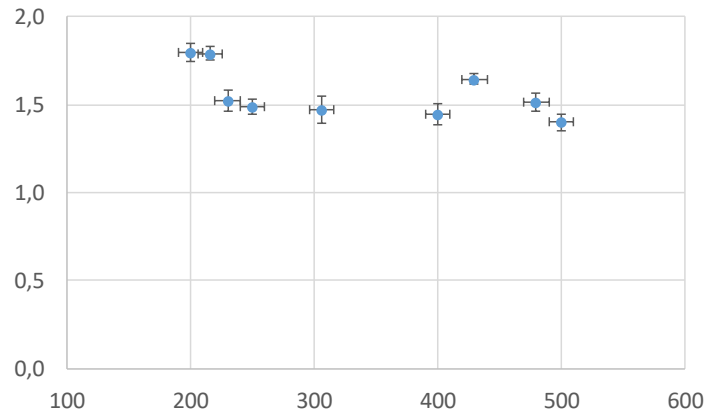


Figure 2: Yara MOST specific heat, in kJ/kg-K.

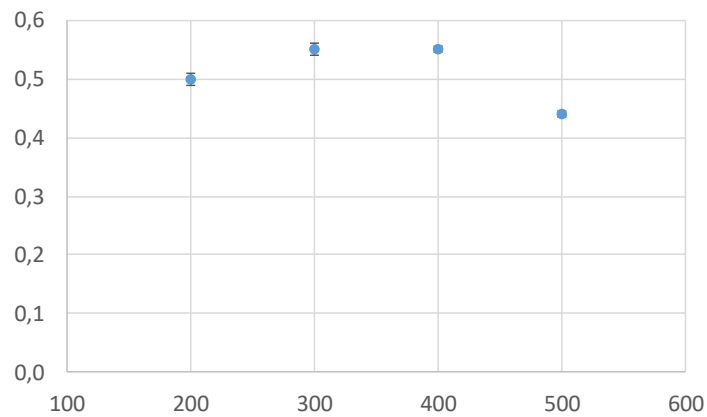


Figure 3: Yara MOST thermal conductivity, in W/m-K.

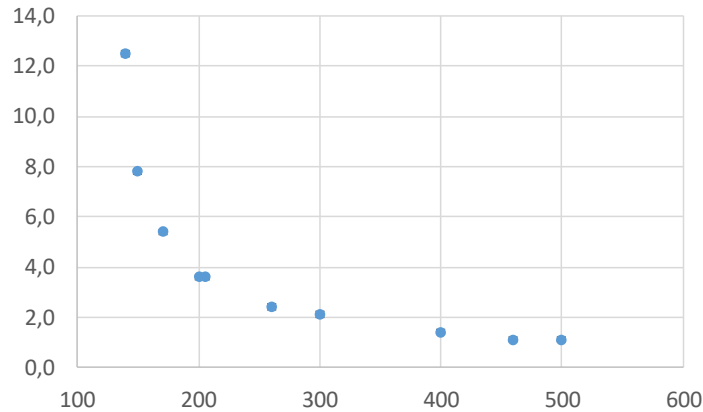


Figure 4: Yara MOST dynamic viscosity, in mPa.s.

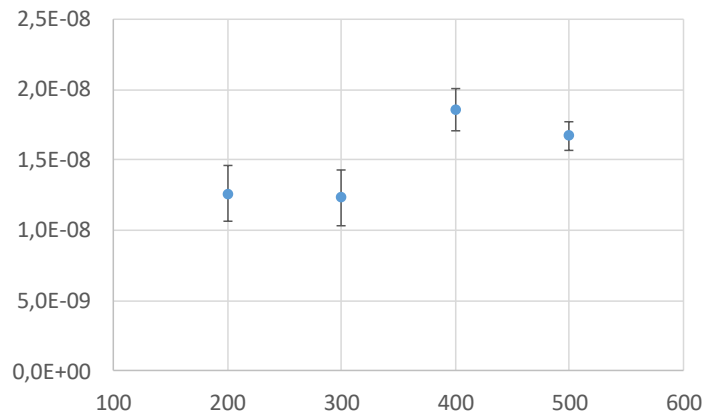


Figure 5: Yara MOST thermal diffusivity, in m<sup>2</sup>/s.

### 3. Yara MOST regressions

In order to use the material thermal properties in the CFD package, several possibilities exist. However, besides the constant properties (independent from temperature), the most common function to define the thermal properties is a 1<sup>st</sup> order polynomial function or, alternatively, a piecewise-linear function.

In order to compare the thermal properties provided by Yara, the reference properties for Hitec XL were considered, due to the same chemical composition. Hitec XL is also a ternary mixture of molten salts and its constitution is identical to Yara MOST, thus it would be expected to have an identical specific heat formulation.

Unfortunately, the thermal properties for Hitec XL available in the literature are not completely clear. As Yara denotes in the patent application (Obrestad *et al.*, 2013), there is a Hitec XL with the same composition of the Yara MOST (42% Ca(NO<sub>3</sub>)<sub>2</sub>, 15% NaNO<sub>3</sub> and 43% KNO<sub>3</sub>) as described by

Pacheco *et al.* (2001) and there is also described another Hitec XL with 48%  $\text{Ca}(\text{NO}_3)_2$ , 7%  $\text{NaNO}_3$  and 45%  $\text{KNO}_3$  as described by Kearney *et al.* (2003).

Moreover, Gomez *et al.* (2013) studied the composition problem of different molten salts Hitec XL type and reported 6 different compositions. Hence, most of the publications reporting Hitec XL thermal properties don't report the MS mass composition. Therefore, the thermal properties available in the literature are not clearly linked to a particular composition.

Equations 1 to 4 represent the polynomial functions considered to represent the Yara MOST thermal properties in the CFD package. The dynamic viscosity will be defined by a piecewise-linear function.

$$\rho(T) = -0,91987.T + 2380,9 \quad (1)$$

$$Cp(T) = -0,70121.T + 1799,3 \quad (2)$$

$$k(T) = -4,0 \times 10^{-6}.T^2 + 2,62 \times 10^{-3}.T + 0,133 \quad (3)$$

$$\alpha(T) = -4,0 \times 10^{-14}.T^2 + 4,66 \times 10^{-11}.T + 4,14 \times 10^{-9} \quad (4)$$

The adjustment of the polynomial function for density to the experimental data provided by Yara is in good agreement ( $R^2 = 0,967$ ) with experimental data. The 1<sup>st</sup> order polynomial regression presents an identical slope to the polynomial function for the Hitec XL (Figure 6).

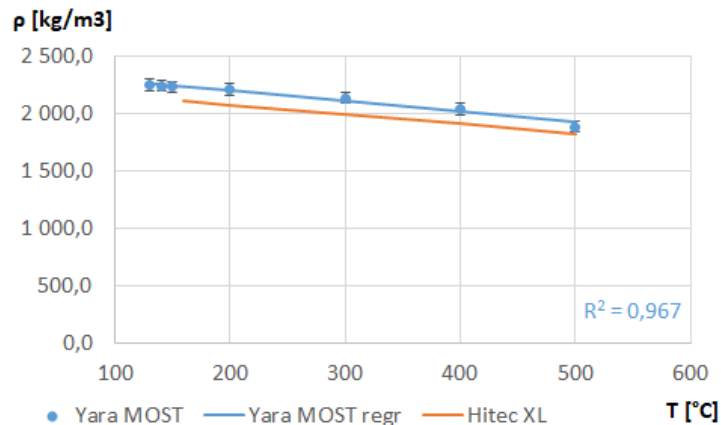


Figure 6: Comparison between Yara MOST's density regression and Hitec XL.

The adjustment of the polynomial function for specific heat to the experimental data provided by Yara is not in good agreement ( $R^2 = 0,323$ ) with experimental data. Moreover, the 1<sup>st</sup> order polynomial regression presents a different slope and intercept from the polynomial function for the Hitec XL (as described in SAM, 2008) (Figure 7).

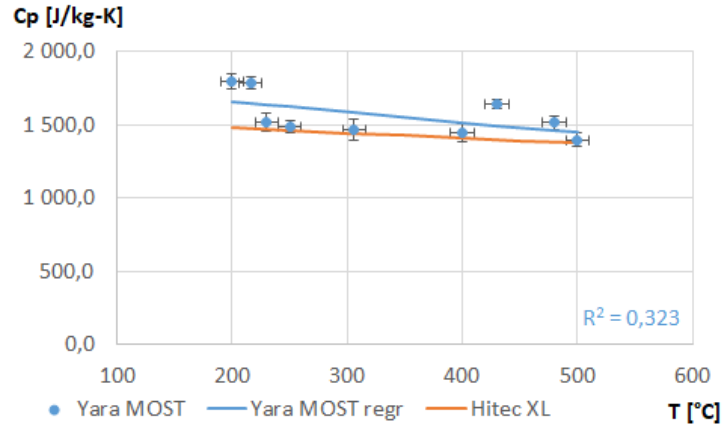


Figure 7: Comparison of specific heat between Yara MOST's regression and Hitec XL.

The specific heat polynomial function as defined in SAM (2008) is presented in equation (5). The Yara MOST variation with regard to Hitec XL starts on 200 °C with 12,2% and ends at 500 °C with 5,3%.

$$Cp(T)_{Hitec\ XL} = -1,139 \times 10^{-4} \cdot T^2 - 2,624 \times 10^{-1} \cdot T + 1,536 \times 10^3 \quad (5)$$

Considering that the porosity “in situ” will present a major contribution to the thermal properties of the heat storage tank, namely the specific heat, it turns out that the influence of porosity is much higher than the influence of molten salts specific heat.

With regard to thermal conductivity, Yara (2018) does not provide measured values. The values provided by Yara were calculated, possibly by equation (6):

$$\alpha = \frac{k}{\rho \cdot Cp} \quad (6)$$

Where,

$\alpha$ : Thermal diffusivity [m<sup>2</sup>/s];

$\rho$ : Density [kg/m<sup>3</sup>]; and

$Cp$ : Specific heat [J/kg-K].

As a reference, the thermal conductivity of Hitec XL, as defined in SAM (2011), is considered independent from the temperature with a constant value of 0,519 W/m-K but the temperature dependent thermal conductivity calculated by Yara (2018) yielded results with some agreement with SAM (2011). Figure 8 depicts those results.

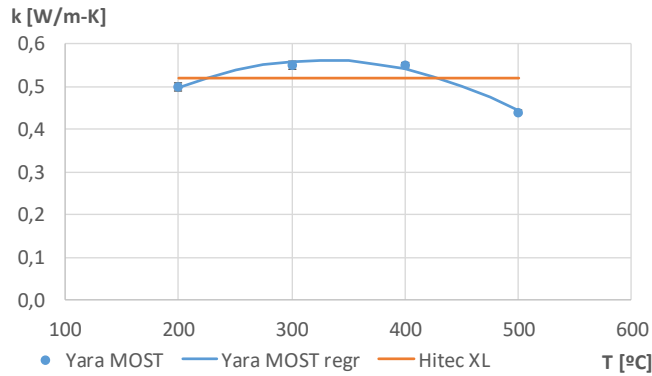


Figure 8: Comparison of thermal conductivity between Yara MOST's calculation and SAM's Hitec XL (2011).

Figure 9 depicts the thermal diffusivity experimental data provided by Yara (2018) against the SAM (2011) calculated thermal diffusivity, using equation (6).

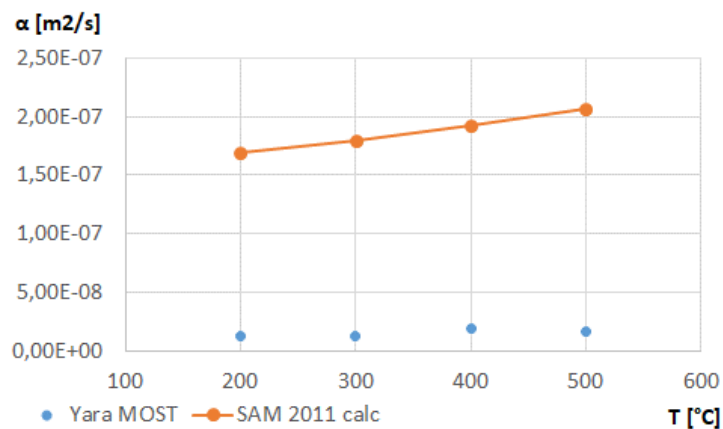


Figure 9: Comparison of thermal diffusivity between Yara MOST and SAM's Hitec XL (2011) calculation.

Finally, some differences also occur between Yara MOST's experimental data on dynamic viscosity and Hitec XL's data from SAM (2011). Figure 10 depicts the

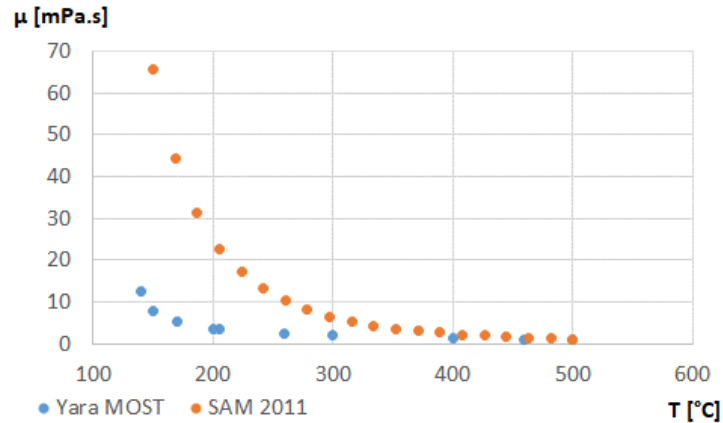


Figure 10: Comparison of dynamic viscosity between Yara MOST and SAM’s Hitec XL (2011).

## 4. Slag thermal properties

The most common way to represent a packed bed in CFD calculations is to define the filler material as a porous material. Thus, the void space in the material packed bed is an important parameter of the material and it represented as a porosity. The porosity will represent the part of the tank volume that will be filled by molten salts. Hence, the properties of the filler material will largely influence the behavior of the thermal energy storage tank, namely, the storage heat capacity, due to the large difference of specific heats between both molten salts and filler material.

In the abovementioned bilateral meeting between LNEG and UEvora, UEvora disclosed some properties for the slag from S. Domingos’ mines that will be used as filler material. Table 3 presents the disclosed data about the filler material.

Table 3: Slag thermal properties.

Property	Units	Value
Porosity	-	50%
Density	[kg/m <sup>3</sup> ]	3600
Specific heat (Cp)	[kJ/kg-K]	0,444
Thermal conductivity	[W/m-K]	1,7

In computational solutions of partial differential equations, meshing is a discrete representation of the geometry that is involved in the problem. Essentially, a mesh is the partition of space into elements (or cells) over which the equations can be approximated.

Zone boundaries can be free to create computationally best shaped zones, or they can be fixed to represent internal or external boundaries within a model.

## 5. Comments

The Yara MOST thermal properties were already disclosed by Yara (2018). Although the disclosed data presented several discrepancies from the available thermal properties for Hitec XL, regressions were performed for the disclosed data. In most of the cases the regressions yielded good adjustments to the experimental data.

However, some verifications must yet be done by Yara, namely the high scattering of the specific heat experimental data with very low uncertainty, the thermal diffusivity experimental data eventually leading to some discrepancies in the thermal conductivity calculations.

Finally, the dynamic viscosity should also be checked.

## 6. References

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