Smartrec

H2020-EE-2016-2017

Grant Agreement Number: 723838

Developing a standard modularised solution for flexible and adaptive integration of heat recovery and thermal storage capable of recovery and management of waste heat.

Deliverable Number:	3.7
Title:	Summary Public Report of WP3
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Organisation:	CEA
Submitted Date:	23/04/2018
Due Date:	31/12/2017
Report Classification:	Public

HORIZON 2020

DOCUMENT CONTROL:

Document History [to be removed from the final approved version]	
Status & Version:	V1
Contractual Delivery Date:	31/12/2017
Actual Delivery Date:	24/04/2018
Deliverable Number:	3.7
Deliverable Name:	Summary public report of WP3
Internal Document ID:	

Approvals			
	Name:	Organisation:	Date:
WP Leader	S. Rougé	CEA	23/04/2018
Coordinator	A. Smith	ALTEK	24.4.2018

History			
Rev No.	Date:	Modifications:	Author *[name and Organisation]*
1	23/04/2018	Initial version TWI contribution missing	S. Rougé (CEA)
2	24.4.18	TWI contribution included	B. Robinson
3			

1. EXECUTIVE SUMMARY:

This deliverable provides a short summary of the work package WP3 devoted to the Dual Media Thermocline (DMT) heat storage system. CEA is leader of WP3, the other main contributors are TWI, SPIKE and INNORA.

WP3 was held from M1 to M16 and had the following objectives:

1. To develop a dynamic model of DMT
2. To select proper solid filler materials
3. To select proper heat transfer fluids (HTF), the main focus being molten salts
4. To identify the instrumentation and control requirement for DMT
5. To validate the dynamic model of DMT through experimental data
6. To develop a cost model of the DMT

Each objective corresponds to a deliverable D3.1 to D3.6 that details the work that was performed during this period. A milestone MS3 corresponding to the DMT technical and cost models achievement was included in WP3.

2. TABLE OF CONTENTS

3. WP3 OBJECTIVES AND RESULTS

WP3's objective is to perform the Dual Media Thermocline (DMT) storage module modelling and design. CEA is leader of this work package, the other main partners are TWI and SPIKE that contribute to the heat transfer fluid (HTF) and solid filler selections and INNORA that contributes to the DMT instrumentation and control requirements.

Objective 1: Modelling of DMT.

A dual-media packed bed is a finite volume in which the heat transfer fluid is flowing in the voids around the filler particles. The main thermal transfers during heat charges and discharges are done at the surface between the HTF and the solid material by convection and conduction, and by conduction inside the solid elements, the zone of intense transfer being in the thermocline gradient. If the transfers are mainly convective, the axial conduction in the bed and in the walls have to be taken into account, especially when the system is in stand-by between cycles of charge/discharge. The tank, even insulated, is submitted to heat losses with the ambient atmosphere (sides and top) or with the basement. This effect is more important for small scale DMT than for big ones.

1D models are generally in good agreement with experimental data because the behaviour is very 1D on the vertical axis. For the purpose of the Smartrec project, the main efforts have been put on a good representation of all the phases inside the DMT which was not existing yet in the models described in the literature. The Smartrec model is thus a transient 1D model with 3 phases: HTF, rocks gravels and walls. Sand can also be added to close the bed porosity, but it is then supposed in thermal equilibrium with the fluid and in that case there is a pseudo-phase formed by the fluid and the sand. For each phase an energy equation must be written and solved, that is why this model is referred as a '3 equation model' also.

The model was written under Matlab. The main program called Smartrec. M includes the input data and treats the results of calculation (curves for instance). This program calls a program 'Thermocline. M' in which the scientific calculations are done. The other functions provide:

- The thermal properties of the selected HTF (prop_f.m), solids (prop_s.m) and walls (prop_p.m)
- The correlations for the convective heat transfer (HTC.m) and for the bed effective conductivity (cond_eff.m)
- 2 methods of implicit resolution have been developed, one for the fluids (Cramer.m), the Cramer method, and the other one, a Newton-Raphton method, for gases (F.m, jacobFD.m) because the higher velocity would induce a very short time step of calculation and a very long time of calculation with a Cramer method.

In the material properties functions have been programmed all the materials needed for Smartrec but also all the materials used in the publications of the literature that were used for the model validation. Other materials could be added in the future if necessary.

The model includes the possibility to degrade the number of phases, assuming that some phases are in thermal equilibrium at the same temperature. For instance, if the fluid and the walls are in thermal equilibrium, 2 energy equations are required only and we will speak of a '2 equations model'. If the fluid, the walls and the gravels are at the same temperature, the model will simplify in a '1 equation model'. These simplifications are based on the assumption that the fluid, solid and wall temperature spatial and temporal derivatives are similar, which is true very often. The advantage is to speed the calculation time, but of course some informations are missing in that case, for instance the difference of temperature between the fluid and the gravels.

For the pilot model needs that is developed in the work package WP4, the set of equations of the simplified 1D-1equation model is provided because it should be sufficient and runs much faster. This 1-equation model is also used for the design of the Smartrec DMT.

For the validation on the Smartrec experimental results the refined 1D-3 equations model will be used.

The thermohydraulique model is described in the deliverable D3.1 The advances on a thermomechanical model of a DMT are also presented in the deliverable D3.1 and the 'Ratcheting' phenomena is explained. This thermomechanical model is not necessary for the DMT design but will provide simple rules of design.

Objective 2: Selection of filler material

The main interest of adding a solid filler in a thermocline heat storage system is to displace an expensive heat transfer fluid (HTF) volume by a cheaper solid volume. The solid filler should of course have a storage volumetric density similar to the HTF, which is the case in general. The solid filler has also the advantage to decrease the risks of natural convection in the tank.

The main questions for the choice of the solid filler are **chemical**: is the solid and the HTF compatible with no degradation of the solid and HTF properties with time? and **economical**: is the solid filler less expensive by a factor of 5 to 10 than the HTF on a storage density basis? The methods to answer in the frame of the Smartrec project are several:

- A list of solid material families appropriate for the range of Smartrec temperatures (CEA)
- An extensive review of the existing knowledge of chemical compatibility between solid materials and molten salts at high temperature when the publication exist which is rare, or at least their stability in hot air. (CEA)
- A quotation for all the solid materials of interest (CEA)
- Static tests of solid-HTF chemical compatibility on the TWI set-ups.
- Dynamic tests of solid-HTF chemical compatibility on the SPIKE set-up.

The solid filler materials of interest for a high temperature DMT belongs to 2 main families, the glass and ceramics materials, and the composites materials (including manufactured composite, waste, natural rocks).

The glass and ceramic family is very wide and includes products that could sustain high temperature and that could probably be compatible with molten salts even if the state of the art in this field is very limited. The main constraint of this family is the cost. Ideally, the storage solid should be less expensive than the molten salt it displaces by a factor 5 at least. Common molten salts have an energetic cost in the range 10-30 €/kWh (on the basis of a DT=100°C), whereas the glass and ceramic family are in the range 50-500 €/kWh, and are therefore not good candidates for the filler material apart if the HTF itself is very expensive.

In this family, the only promising approach is the research from John et al[1]. on Ordinary Portland Cement (OPC) with fine aggregates and polypropylene fibres, 2 concretes of this kind were tested successfully in Solar Salt up to 585°C. But as it would be difficult and expensive to manufacture and mould this concrete in balls or slates in small quantities for the purpose of the Smartrec DMT, this product is therefore not selected in the top list of solid filler materials.

Industrial waste is a very wide and promising field of research but also very complex because waste composition and properties can vary. As a consequence, the few existing results of compatibility with molten salts show large discrepancies, a huge amount of work should be done to confirm that some of these products could be used in a DMT. Even if they can be tested at lab-scale in the Smartrec project, they should not be selected for the pilot.

The results obtained on vitrified asbestos with the commercial name of COFALIT® are more consistent but it was not possible to purchase this product in the frame of the project.

Some natural rocks, quartzite and basalt mainly, seem at the actual state of the art the best choice for the DMT. These rocks are common, have a low cost and have been successfully tested in one or two molten salts (HITEC XL and/or Solar Salt) as high as 560°C[2],[3].

For a temperature lower than 500°C, quartzite is the best solid filler and is selected for the Smartrec DMT.

Objective 3: Selection of HTF

Following completion of the selection process the following candidate HTFs were highlighted (in order of priority):

- NaOH/KOH eutectic (assuming corrosion issues are not prohibitive)
- Solar Salt (60% $NaNO_3$-40%KNO_3) or Hitec (7% $NaNO_3$, 53% KNO_3, 40%$NaNO_2$) assuming Tmax can be reduced to ~450°C
- Caesium Acetate (assuming that a less expensive supplier can be located)
- Sn-Bi eutectic (outside of cost per unit volume criteria)

[1] John E., Hale M., Selvam P., Concrete as a thermal energy storage medium for thermocline solar energy storage systems, Solar Energy 96 (2013) 194-204

[2] Brosseau D.A., Hlava P.F., Kelly M.J., Testing thermocline filler materials and molten-salt heat transfer fluids for thermal energy storage systems used in parabolic trough solar power plants, SAND2004-3207.

[3] Martin C., Breidenbach N., Eck M., Screening and analysis of potential filler materials for molten salt thermocline storages, ES2014-6493.

Of these materials only sodium hydroxide/potassium hydroxide eutectic met the criteria for use in the high temperature application (≥600°C) while being both readily available and low cost. However, the corrosivity of this environment is not fully understood, though the literature available does suggest it to be high and to increase at temperature above ca. 500°C[4].

Following this material, Solar Salt (60% $NaNO_3$-40%KNO_3) or Hitec (7%$NaNO_3$-53%KNO_3-40%$NaNO_2$) were highlighted as potential HTFs. However, these materials begin to degrade at temperatures greater than approximately 450°C making them unstable for a high temperature application. Solar Salt and Hitec are also commercial products and as such their physical properties and corrosively are largely understood making testing unnecessary, provided a suitable literature review has been performed. Other options such as caesium acetate and Sn-Bi eutectic, while have suitable physical properties, are limited by cost and supply chain.

As such, testing in this work package 3 would focus on testing of sodium hydroxide/potassium hydroxide eutectic. Should this material prove inappropriate Solar Salt or Hitec would be selected. To supplement this information additional testing, at a later date, would also be carried out to assess more exotic potential HTFs such as liquid metals in order to provide a data on potential HTFs for higher temperature applications including the nuclear sector.

Corrosion Testing and Salt Selection

Welded and parent material samples of three different stainless steels (304, 310 and 316) were tested in sodium hydroxide/potassium hydroxide eutectic at two temperatures, 450°C and 600°C. Three potential filler materials for the DMT were also tested at in the salt at 450°C:

- Pea gravel - quartz – SiO2
- River sand - quartz – SiO2
- Basalt - SiO_2/Al_2O_3/Oxides

Results of these corrosion tests showed extensive corrosion of the stainless steels at both temperatures, though to a greater extent at the greater temperature, and dissolution of the filler materials.

Dissolution of the filler materials was attributed to the attack of the silicon dioxide, present in all the filler material tested, by the alkali molten salts resulting in the formation of soluble silicates (e.g. Na_2SiO_3, K_2SiO_3). This was an expected outcome of the testing and so was only performed at the lower temperature condition. This effect, in itself, is not a significant barrier to the use of NaOH/KOH as a HTF. Filler materials are largely used to bulk out the DMT in order to reduce the volume of the HTF required. This is a particularly beneficial approach if the filler material is significantly cheaper than the HTF in question. However, the lower cost of NaOH/KOH (€320 per tonne) means that any benefit from the utilisation of filler materials would be minimal, particularly if exotic/costly materials were required.

[4]Lai, 2007

Results gathered regarding the testing of the stainless steels in NaOH/KOH eutectic were largely in agreement with the limited available literature. There is a significant increase in the corrosivity of the candidate HTF with increasing temperature. The most significant advantage of NaOH/KOH as a HTF relative to Hitec or other nitrates is its higher thermal stability. However, at 600°C this molten salt has been observed to be incompatible with stainless steel 304, 310 and 316. While less corrosion occurred during testing at 450°C notable corrosion still occurred and long term testing (>30 days) would be required to determine if NaOH/KOH may be used as a HTF at this lower temperature. Therefore, apart from the low cost (€320 per tonne,), NaOH/KOH does not provide any significant advantage over Hitec or other nitrate based HTFs which are stable up to 450°C.

Hitec, with a lower melting point than Solar Salt, was therefore selected as the HTF for the Smartrec system.

Novel High temperature HTFs

The results of WP3 have demonstrated that there is no suitable HTF that meets all of the criteria set by the consortium/application. This is largely due to the cost limitations. As part of the salt selection process discussed in D1.3 a number of alternative HTF were highlighted however, these substances were rejected due to their high inherit cost and the cost of the required materials combination. While the use of these materials is not suitable in this application, these material combinations present an opportunity for significant energy saving in high temperature/high value industries such as nuclear power. Therefore, resource will be directed toward assessment of these materials.

A high temperature application means that liquid metal candidates become a more attractive option relative to molten salts due to their high stability. Liquid metals have a notable challenge when considering compatibility with construction materials, namely liquid melt embrittlement. As such the combination of parent materials and liquid metals must be carefully considered. The following table highlights some potential liquid metal HTF which could be tested as part of this project[5], although obviously their extremely high cost (and that of the construction materials required to contain and pump them) limits potential areas of application to exotic situations where extremely wide liquid ranges, low vapour pressures and very high boiling points are required.

Table 1. Potential HTFs.

Liquid Metal	Melting point / °C	Boiling point / °C	Cost / € per tonne
Gallium	30	2400	234000
Tin/bismuth eutectic	138	1564	25000

TWI will therefore continue to perform corrosion/embrittlement testing of liquid metal HTF candidate for a high temperature application >600°C as part of the Smartrec project.

[5]Smither et al. 1987

Objective 4: DMT Instrumentation and control requirement

CEA proposed 2 scheme of integration of the DMT in the whole Smartrec pilot plant, one with the DMT in parallel to the end-user and one with the DMT in series with the end user. Apart from the storage system, the Smartrec loop includes as main components a Heat-Pipe Heat-Exchanger (HPHE) in which the waste heat is collected from the loaded industrial flue gas and an air cooler that simulates the end-user.

The parallel configuration is more complex but is more flexible as the HPHE, DMT and end-user powers can be different. This configuration is more realistic and close to an industrial application, the scheme is depicted on the following Figure:

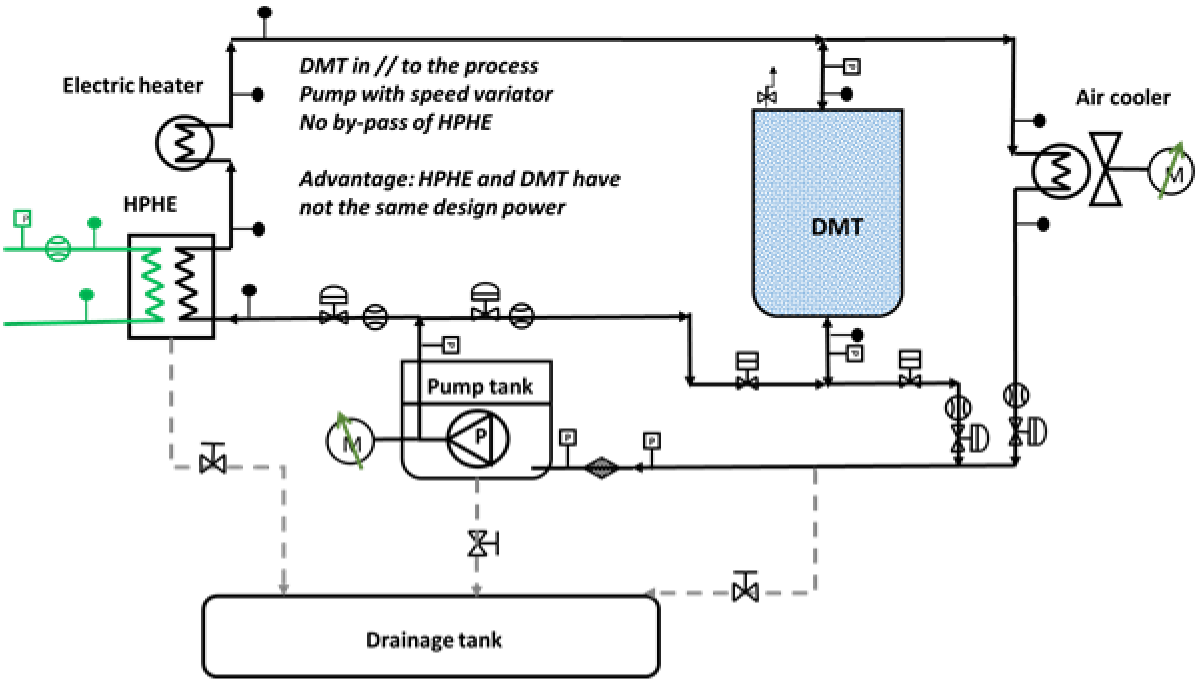

Figure 1. Scheme of the SMARTREC pilot plant with the DMT in parallel to the process

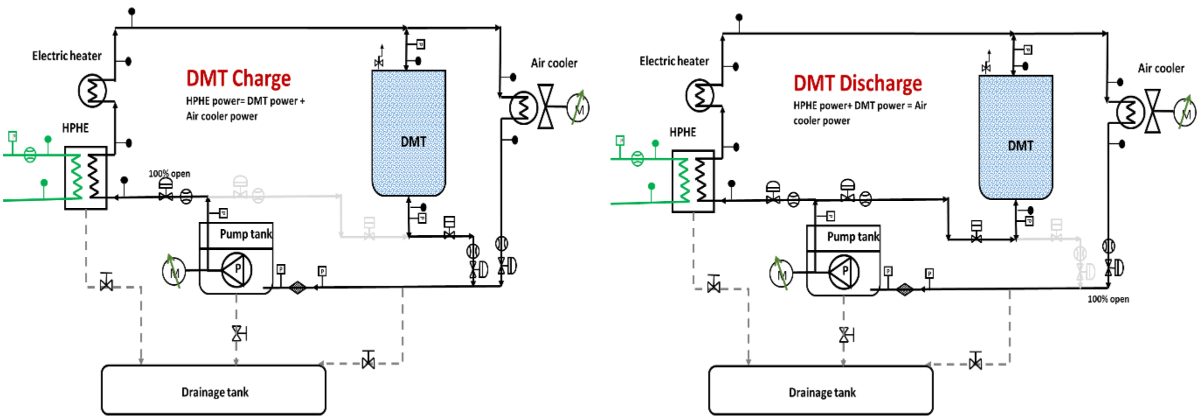

Figure 2. DMT charge and discharge for a parallel configuration

The DMT instrumentation will serve for control but also for the scientific purpose of the DMT model validation, it will include:

- Measures of flowrate, pressure and temperature at the inlet and outlet of the tank (control and thermal model validation)
- Measures of temperatures inside the tank in the HTF and the gravels and on the tank walls (110 TC in total, thermal model validation)
- Strain gauges on the height of the tank if this is possible, strain gauges are very sensitive to temperature gradients and the measure might be difficult (mechanical model validation).
- Electric heaters on the outside of the tank (control, to prevent salt freezing and to preheat before salt filling) associated with regulation and safety thermocouples (3 TC per heaters).

The DMT is by nature a passive system controlled by the whole system needs and economic optimization. The only main requirement is to provide a steady temperature at the inlet of the DMT, both in charge and in discharge, this is achieved thanks to the HPHE module regulation during charges and thanks to the air cooler during discharges.

Objective 5: DMT model validation

The thermal DMT model developed in Smartrec can only be validated on existing data of the literature at the moment as no Smartrec data exist yet. The objective is to show that the 1D-3 phases model fits well with the data, no need of a 2D or 3D model, and that the simplification to 2 phases or 1 phase does not degrade the performance in most cases. The advantage of using data from the literature is to validate the model on a large range of HTF (thermal oils, molten salts, air), solid materials and DMT sizes (from 10 kWh to 10 MWh), the main drawbacks is that some important informations are often missing in the publications. An extensive review of existing data has been done for the project and the best publications have been compared to the model:

- Results from Hallet and Gervais (1977)[6]: DMT with thermal oil, river gravels and silica sand
- Results from Pacheco et al (2002)[7]: DMT with molten salt HITEC XL, quartzite rocks and silica sand. The only previous DMT with molten salts.
- Results from Bruch et al (2017)[8]: DMT with thermal oil, silica gravels and sand (CEA DMT)
- Results from Cascetta et al (2015, 2016)[9,10]: DMT with air and alumina beads

Concerning the thermomechanical model, there is a real lack of reliable experimental data to validate such a model. One objective of the project will be to implement some strain gauges

[6] Hallet, R.W.Jr., Gervais, R.L., 1977. Central receiver solar thermal power system - Phase 1 - CDRL ITEM 2 - Pilot Plant Preliminary Design Report - Vol V - Thermal Storage Subsystem, SAN/1108-8/5

[7] Pacheco, J.E., Showalter, S.K., Kolb, W.J., 2002. Development of a molten-salt thermocline thermal storage system for parabolic trough plants, J Sol Energy Eng Trans ASME, vol. 124, 153 - 159.

[8] Bruch, A., Molina, S., Esence, T., Fourmigué, J.F., Couturier, R., 2017. Experimental investigation of cycling behaviour of pilot-scale thermal oil packed-bed thermal storage system, Renewable Energy, vol. 103, 277 - 285

[9] Cascetta, M., Cau, G., Puddu, P., Serra, F., 2015. Experimental investigation of a packed bed thermal energy storage system, J.Phys.Conf.Ser., vol. 655

[10] Cascetta, M., Cau, G., Puddu, P., Serra, F., 2016. A comparison between CFD simulation and experimental investigation of a packed-bed thermal energy storage system, Appl Therm Eng, vol. 98, 1263 - 1272

on the DMT walls with the help of TWI, a main difficulty being the deviation under temperature gradient of such sensors.

Objective 6: Cost modelling of DMT

The objective is to estimate the cost of a Dual Media Thermocline (DMT) module ready for operation, the reference size is a functional unit of 1 MWh. The Smartrec cost model is valid for a large range of energies, 100 kWh to 1GWh (10^6 kWh) and covers a large range of temperatures from 80 to 600°C.

For practical reasons the model is limited up to now to 5 fluids (water, Therminol 66, HITEC salt, Solar Salt, air), 3 solids (Quartzite, Basalt, Quartz sand) and 4 metallic alloys (1 standard carbon steel, 2 low-alloy carbon steel, 1 stainless steel). Other materials could be added in the future.

The model is limited to above ground metallic tank DMT, pits or concrete volumes are not included.

The cost model is based on the "pre-estimate" method developed in the seventies for the petroleum industry and that was mainly dedicated to the cost evaluation of tanks, reactors, heat-exchangers, pumps and compressors. This method can be applied to a DMT because it is mainly a metallic tank. This methods allows to calculate the weight of the tank and to deduce its cost through some corrective factors. The cost of the components linked to the DMT tank – site preparation, pipes, valves, instrumentation and control, insulation- are simply calculated by an average percentage of the tank cost.

The method was not fitted specifically on DMTs, there is a certain uncertainty on the absolute DMT cost, and the only way to improve the method is to have real costs of DMT in the future.

This method has also some limitations and cannot take into account the cost of the filling materials, solids or fluids, and the cost of the filling procedure.

For the solid materials and the liquid fluids, direct quotations have been done thanks to the main suppliers, and when possible, extrapolated to large quantities even if the decrease of cost for large quantities is rather minor in general.

The solid filling procedure cost was estimated on the basis of the CEA feedback for small scale DMT, this cost model is perfectible for large scale DMT. The molten salt filling procedure cost was estimated on the basis of the CEA feedback for small quantities, this cost model is perfectible too.

Even if the DMT cost model needs some validation, it allows to compare different technologies costs between themselves. The cost model was applied for 3 range of temperatures, 80-150°C, 150-400°C and 400-600°C. On the range 80-150°C, single phase pressurised water thermoclines seem the best technology. On the range 150-400°C, HITEC is more performant than Therminol 66 especially at large scale. The bed porosity must be as small as possible because HITEC is rather expensive. On the range 400-550°C, Solar salt can be preferred to air, there is no real need to add sand in that case because the salt is rather cheap. Above 550°C, there is no other solution than air at the moment, the NaOH-KOH eutectic is too corrosive.

The DMT cost model was programmed under Matlab and calls 2 functions, one gives the material properties on the range of temperature and the second one the cost of the materials, this cost can vary with the number of tons that must be supplied.

For all the cases the main design and cost parameter is the difference of temperature between the charge and the discharge. For a DT of 150°C, cost in the range of 30-35 €/kWh can be obtained for large scale DMT and cheap HTFs such as Solar salt.

4 DMT DESIGN

The DMT design was done with the help of the DMT model and with the following specifications:

- Solid filler: quartzite gravels, mean diameter 20-40 mm. No sand. Bed porosity ~40%.
- Molten salt: HITEC salt ($NaNO_3$-$NaNO_2$-KNO_3 eutectic)
- The salt flowrate or the heat power: 4900 kg/h corresponding to a power of 200 kWh
- The duration of charge: 2 hours, corresponding to a heat energy of 400 kWh.
- The maximal temperature of charge Tmax: 300°C
- The minimal temperature of discharge Tmin: 200°C
- The maximal increase of temperature of the outlet fluid at the end of charge: 20% of the difference of temperature between Tmax and Tmin, in other words the outlet temperature will be 200°C during most of the charge and will be 220°C at the end of charge.
- The maximal decrease of temperature of the outlet fluid at the end of discharge: 20% of the difference of temperature between Tmax and Tmin, in other words the outlet temperature will be 300°C during most of the discharge and will be 280°C at the end of discharge.

For these parameters, the Smartrec DMT model gives an energy capacity ratio of 72% (ratio between the maximal storable energy and the true stored energy) and a bed volume of 7.6 m^3. The diameter and the height are chosen in order to have a height as high as possible and a diameter easing the solid filling procedure (a man can work inside). The general features of the DMT are:

- Bed diameter: 1.8 m
- Bed height: 3 m
- Fluid mass: ~7 tons
- Rocks mass: ~12 tons
- Tank mass:~2 to 3 tons

The general aspect of the DMT is given on the following Figure:

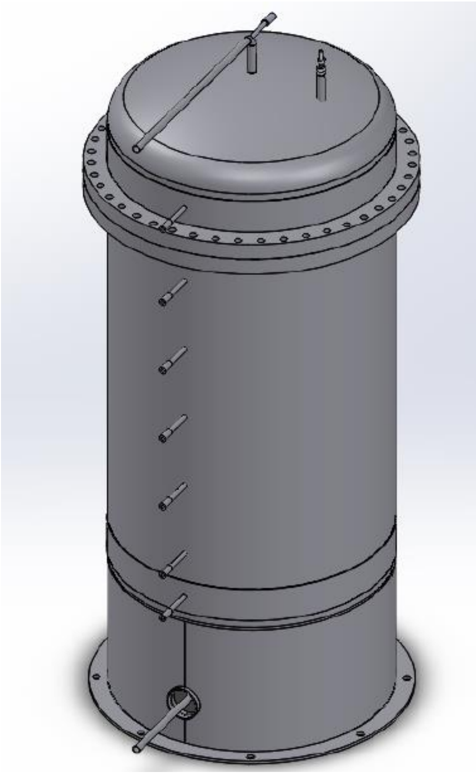

Figure 3. DMT tank and support skirt general view

5 WP3 PROGRESS

The following deliverables have been submitted:

Deliverable	Title	Main author	Type
D3.1	Model of DMT ready	CEA	Confidential report + thermal model (Matlab)
D3.2	Report on the selection of filler material	CEA	Confidential report
D3.3	Report on the selection of HTF	TWI + SPIKE	Confidential report
D3.4	Report on the instrumentation and control requirement of DMT	CEA	Confidential report
D3.5	Report on the DMT model validation	CEA	Confidential report
D3.6	Report on the DMT cost model	CEA	Confidential report + cost model (Matlab)

The following milestone has been achieved:

Milestone	Title	Main author
MS3	Model of DMT validated and cost modelling of DMT performed	CEA