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Heat Recovery at High Temperature by Molten Salts for High Temperature Processing Industries

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Abstract. Waste heat is a problem common to high temperature processing industries as a significantly underused resource, often due to challenges in economic heat valorization. Secondary aluminum recycling and ceramic processing were identified as key examples with economically recoverable waste heat. Several challenges are inherent; these processes are batch-based rather than continuous with corrosive particulate-laden flue gas over a wide temperature range. The EU H2020 Smartrec project aims to develop a technology capable to recover heat at high temperature from industrial processes. It is being coordinated by UK-based company ALTEK, with the rest of the consortium being made up of companies from EU countries. The Smartrec project is aimed at developing a modularized standard heat recovery solution integrated with thermal energy storage (TES) and a knowledge-based software tool. Smartrec has been designed for industrial applications such as secondary aluminum (furnace), ceramic (kiln), cement (kiln) and flat glass (furnace) industries with a very harsh and corrosive environment.

The concept of Smartrec is based on the utilization of a Heat Transfer Fluid (HTF) stable at high temperature ($\geq 600^{\circ}$ C) such as molten salts. Through a Heat Pipe Heat Exchanger (HPHE) the heat at the exit of heat source is transferred to the Heat Transfer Fluid (HTF) which is circulating within the Smartrec loop. When the input waste heat source is available, HTF will simultaneously transfer heat to the user end process via a user end heat exchanger (HX) or to a thermal energy storage (TES). When the exhaust stream is unavailable, the TES will supply the needed thermal energy to the HTF which in turn will transfer it to the user end PX.

The validation at industrial level of the abovementioned technology is currently ongoing as part of the Smartrec project.

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INTRODUCTION

The worldwide effort to achieve a more environmentally friendly and sustainable energy system is mostly involving the industrial sector, in order to reduce CO_2 emissions.

The recovery of waste heat from industrial processes is a great way to improve energy efficiency. The EU2020 Smartrec project is focused on Heat Recovery (HR) from industrial processes. The structure of this technology and the selection of the Heat Transfer Fluid (HTF) are influenced by the heat source (batch or continuous) and the end user requirements, which were investigated by the authors in the previous activity. In addition, a numerical model of the Smartrec system was developed in order to guide the design of the piping system and insulations.

HPHE PRINCIPLE

The implementation of heat pipe technologies is vast with a range of applications and temperatures ranging from cryogenics to high temperatures experienced in metallurgy and ceramic processes [1] [2] [3]. Regardless of the temperature range, the success of the heat pipe is primarily due to the fundamental two phase process occurring within the heat pipe during operation. The technology primarily exists as two versions: a thermosyphon and a heat pipe. The application of a thermosyphon relies on gravity to return the condensate to the evaporator. The heat pipe works on the similar principle but relies on a wick to return the condensate back to the evaporator. The utilisation of wicks is strictly limited to complex pipe geometries where the evaporator is above the condenser, or in anti-gravity applications [1]. Both heat pipe and thermosyphon exist as a hermetically sealed tube with an adiabatic, condenser and evaporator containing a small amount of working fluid. When a heat source is applied to the evaporator, the working fluid starts to boil, and the vapour travels up to the condenser section which is located in a cooler stream. The vapour releases its latent heat, with the liquid condensate travelling back down to the condenser with the assistance of gravity or wick. The two phase cycle is continuous, resulting in a near isothermal wall temperature allowing for heat to be transported at any length [4]. The implementation of thermosyphon and heat pipes being applied and developed into the form of heat exchangers is desirable in multiple industries due to their flexible passive nature, low maintenance and low risk of cross contamination. The operation of heat pipe heat exchangers in comparison to shell and tube highlight an increased reliability, as each heat pipe is effectively a single entity and unaffected by the other pipes. The failure of one heat pipe will not halt the operation of the heat exchanger, unlike more traditional heat exchangers.

HPHE Working Fluid and Casing Material Selection

The selection of working fluids is entirely dependent on the application, temperature range and composition of both hot exhaust streams and condenser streams. As the heat pipe contains both liquid and vapour phases, the temperature range should be within a liquids critical point and freezing condition. A working fluid with higher surface tension is more favourable to achieve a higher capillary force, enabling a better wetting of the wick and pipe wall material; the flow resistance can then be reduced by selecting a working fluid which has a lower viscosity. However, selecting a working fluid with higher latent heat of vaporization minimises the required amount of working fluid, leading to a reduction in the pressure drop through the heat pipe [4] [5].

However, there are some limitations for the operation of heat pipes such as continuum flow limit, sonic limit, capillary limit, entrainment limit, viscous limit and boiling limit, which need to be taken into consideration during the design process of the heat pipe. One of the challenges of high temperature heat pipes is the corrosion which occurs as a result of the incompatibility between the working fluid and the shell case material. This incompatibility results in a chemical reaction, resulting in the production of non-condensable gases that dramatically affect the thermal performance of the heat pipe. The production of non-condensable gases can further accelerate the effects of corrosion, which reduces the life span of the heat pipe. The presence of non-condensable gases can be due to many factors such as inappropriate manufacturing methods. It is highly recommended to perform a high vacuum value when charging the heat pipe to prevent the presence of the oxygen gas and expand the life span of the heat pipe[5].

Fluid	Symbol/ Formula	Melting Point, (°C)	Normal Boiling Temp (°C)	Critical Temp (°C)	Useful Range (°C)	Compatible Materials
Acetone	C ₃ H ₆ O	-94.3	56.1	235	0 to 120	Aluminium* Copper Stainless Steel, Ferritic Steels Polymers (PTFE, PA, PP)
Methanol	CH₃OH	-97.6	64.7	240	10 to 130	Copper Stainless Steel Ferritic Steels Silicone Polymers (PTFE, PA, PP)
Ethanol	C ₂ H ₆ O	-114.35	78.35	241	0 to 130	Aluminium Copper Stainless Steel Ferritic Steels Silicone
Water	H ₂ O	0	100	373.95	10 to 287	Copper Stainless steel
Toluene	C ₇ H ₈	-95	111	318.64	50 to 200	Aluminium Copper Stainless Steel Ferritic Steels Polymers (PTFE, PA, PP)
Dowtherm A		12	257.1	497	150 to 395	Stainless Steel, Aluminium, Titanium
Naphthalene	C10H8	80.26	217	475	135 to 350	Aluminium, Stainless Steel, Steel, Titanium, Nickel based alloys
Caesium	Cs	28.44	671	1664.85	450 to 900	Titanium, Niobium, Stainless steel, Nickel based super alloys
Potassium	K	63.38	759	1949.85	500 to 1000	Stainless Steel
Sodium	Na	97.72	883	2299.85	600 to 1200	Stainless Steel, Nickel, Inconel
Silver	Ag	961.78	2212	N/A	1800 to 2300	Tungsten, Tantalum

*if used with pure substance

TABLE 1: HPHE working fluid and shell material compatibility for Mid-High Temperature Ranges [1],[6-11]

HPHE Modelling and Design

The HPHE design was conducted by ECONOTHERM to build an innovative unit compatible with the corrosive heat sink fluid of molten salt in the application of challenging exhaust compositions. The development of two units allowed innovative heat pipe heat exchangers to be developed and manufactured for both the heat recovery from aluminium furnaces and ceramic kilns. The development of the HPHE model is based on multiple conditions including the requirements of the end user.

The basic principle of the design is to consider the parallel thermal connection of the heat pipes to calculate the combined resistance and logarithmic temperature difference between hot and cold streams through the unit [4].

HPHE Design and Manufacture

Ceramic Industry

The primary aim of the Smartrec unit is to recover heat from a full-scale ceramic kiln—although there have been recent developments for waste heat recovery in the ceramic industry. The Smartrec unit is a breakthrough in HPHE design, highlighting the operation of a vertical unit with the addition of a variable moisture and fouling rate.

The progress of the unit was developed for ceramic kilns and the potential of HPHE with extremely moist and particulate laden flows. The system operates as a cross flow configuration recovering waste heat from the exhaust of a ceramic kiln to a water heat sink in the condenser as shown in Fig.1a. The unit exists as a novel vertical unit, with the heat pipes being constructed from carbon steel. The unit operational properties are highlighted in Tab.2.

	Inlet Temperature	Outlet Temperature	Temperature Difference
Exhaust	258°C	150°C	108°C
Water	20°C	80°C	60°C
HPHE Effectiveness		45%	

TABLE 2: SMARTREC Ceramic Operational Conditions

The manufactured unit is shown in Fig.1b. The unit is currently being applied for the deployment and validation of the Smartrec loop, in the pilot plant of the "Instituto de Tecnología Cerámica", a research partner of Smartrec project, located in Castellón (Spain).



FIGURE 1: Smartrec HPHE Unit for the Ceramic Industry (a); Manufactured (b) and Installed (c) HPHE Unit.

Aluminium recycling

The development of the second Smartrec unit was developed for the implementation within the aluminium recycling industry. The primary aim of the HPHE is to recover waste heat from the exhaust of a kiln to a molten salt heat sink. Both streams are extremely corrosive allowing for the development of a novel unit for the Smartrec System.

HPHE Design and Manufacture

From the thermal model discussed previously and identification of the chemical properties of both exhaust and heat sink streams. The unit was constructed from stainless steel 306, due to the mutual corrosion resistance of chemicals identified in both exhaust and molten salt streams. The unit features a cross flow operation to maximise the effectiveness of the unit. Tab.3 highlights the operating conditions of the unit.

	Inlet Temperature	Outlet Temperature	Temperature Difference
Exhaust	600°C	300°C	300°C
Molten Salt	200°C	300°C	100°C
HPHE Effectiveness		75%	

TABLE 3: Smartrec Ceramic Industry HPHE

DMT MODELLING AND DESIGN

Storing waste heat allows transforming a batch process into a continuous process. When the process is on, the heat in excess is stored in a thermal energy system (TES), and when it is off, the heat is released at a controlled rate in the process. There are three different ways to store heat, sensible, latent or chemical storage [12]. Sensible storage is already industrial at large scale, such as water storage for district heating networks, two-tanks of molten salt on solar concentrated power plants or ceramic regenerators on glass manufactures whereas the 2 other methods are less mature. Sensible storage is also more versatile in terms of range of temperatures because it has not to be designed for a specific melting temperature (latent storage) or tuning temperature (chemical reaction). Moreover the storage density expressed in kWh/m³ can be correct if the difference of temperature between the hot charging and the cold discharging temperatures is high.

DMT materials selection

The criteria for the HTF and solid selection are many and include:

- Physical properties: the materials must have a high volumetric storage density. They must be stable on the range of operation temperatures, this last criterion is very selective.
- Mechanical properties (for the solid): the solid filler should have a low porosity and a high mechanical strength to sustain the bed load and thermomechanical stresses.
- Chemical properties. The chemical interactions between the HTF and solid material or HTF and tank material should be minimal on the whole range of temperature.
- Safety: No hazardous products if possible, no self-inflammation, no oxidizer, no toxic, no carcinogen, no mutagen. Apart from the hazards themselves, hazardous products will increase the costs.
- Economic: Waste heat is not a product with a high added value, all materials should thus_be as cheap as possible. The solid cost should be 3 to 10 times cheaper than the fluid it substitutes. The tank itself should be at atmospheric pressure, apart from very specific cases.

The main families for the DMT HTF are water (pressurized or not), thermal oils such as Therminol VP1 or Therminol 66, molten salts such as Hitec, Solar salt or other pure salts or eutectic binary to quaternary mixtures, and gases (pressurized or not) such as air or supercritical CO₂. Exotic expensive fluids or very corrosive fluids should be banished as they are not convenient for very massive storage systems containing hundreds of tons of fluid. Solid materials are classified in four families, polymers and elastomers, metals and alloys, ceramics and glasses (including concrete and bricks), and hybrids and composite (including natural rocks and industrial wastes). The discriminant criteria are their stability under temperature or in contact with a specific HTF and their cost. Polymers do not sustain high temperature. Metals are too expensive. The 2 last families are more complex. Some fire bricks and concretes could suit up to 500°C [13]. Some natural rocks such as quartzite or basalt could suit up to 550°C in contact with some molten salts [14][15][16]. And some industrial waste such as vitrified asbestos or steel slag could be stable up to 550°C in air or molten salts even if the results highlight strong discrepancies for this last group of materials, probably because their properties vary a lot.

For the module itself, there are several alternatives such as water pools (long-term water storage), underground volume with concrete walls [17], above ground volumes with metallic walls or concrete walls.

A more common solution for high temperature modules is the use of metallic walls. Plain carbon steel is used satisfactory for water, thermal oils or molten salts up to 450°C. More resistant alloys, steel ASTM A273 and A274, alloy steel with 15-16% chromium iron or stainless steels type 304, 304L or 316, are recommended for higher operating temperatures. More expensive alloys are not competitive for large scale storage systems.

DMT design and manufacture

Many thermal models can be found in the literature, they show that a 1D approach is generally sufficient to model a DMT module [18]. For the Smartrec design needs, a 1D multi-phase model of the DMT was developed under Matlab [19] and was used to design the module in operating conditions. This model takes into account 4 phases, the solid filler, the HTF, the metallic walls, and eventually a second small size filler that can be used to close the bed porosity, this last phase is in thermal equilibrium with the HTF. Thermal exchanges are mainly convective, bed conduction can have an effect during slow charges or stand-by periods and radiation can have an effect for high temperature and gaseous HTFs. The heat losses to the ambient are also modelled. For the design the following parameters must be provided:

- Nominal charging Temperature (or hot temperature)
- Nominal discharging Temperature (or cold temperature)
- Nominal stored energy
- Nominal stored power during charge or nominal charge duration or nominal HTF flowrate, these three information are similar. The values can be given for the discharge if preferred.
- The fraction of the thermocline gradient that is allowed to go out of the module at the end of charge or discharge, this parameter depends on the process flexibility and not on the storage module itself.

For the Smartree application on the secondary aluminium industry, the design parameters are summarized in Tab.4. The levels of temperature and the heat power are issued from the design of the Heat-Pipe Heat-Exchanger (HPHE) described previously. The charge duration and the fraction of thermal gradient were selected according the process. From the level of temperatures, it was either possible to select a thermal oil or a molten salt but, as one of the objectives in the future is to increase the level of stored temperature, Hitec was selected in the end.

Design parameters						Smartrec configuration			
Hot T (°C)	Cold T (°C)	Energy (kWh)	Heat power (kW)	% of thermocline gradient out	HTF	Solid	Walls		
300	200	400	200	20%	Hitec, 40%vol	Quartz pebbles, 60%vol, nominal diameter 40 mm. No sand	SS304		

TABLE 4: Design parameters of the Smartrec DMT and final configuration

The model allowed calculating the volume of the DMT bed, 7.6 m³. The bed diameter and height were a compromise between a high storage efficiency (the higher bed the larger efficiency) and the ease for the solid filling operation (a diameter larger than 1.5 m is needed to have a worker inside the tank), a diameter of 1.8 m and a height of 3 m were selected.

The DMT tank was designed for a pressure of two bars relative and a temperature of 400°C as fluctuations up to 350°C can occur at the outlet of the HPHE. The tank is a pressure vessel, was designed, and manufactured according the CODAP2015 construction code and DESP 2014/68 /UE norm. It includes a cylindrical shell with some tight taps for instrumentation, two domed ends and an upper flange allowing the solid filling operation. The packed bed lies on a bottom grid. The whole tank holds on a skirt bolded on the concrete basement (Fig.2). The tank weights approximatively 4.7 tons, the bed of pebbles 12 tons and the Hitec salt 9.8 tons. Electric heaters with a total power of 17 kW were designed for the DMT and will serve for preheating the packed bed and walls prior to filling the Hitec salt and for compensating the heat losses during long stand-by periods when in operation. The DMT and the electric tracers were manufactured in France, transported on the demonstration site in February 2019 and will be installed soon.



FIGURE 2: Internal and external drawings of the Smartrec DMT.

LIFE CYCLE ASSESSMENT AND COST MODELLING OF SMARTREC SYSTEMS

The environmental and economic impacts of the Smartrec system are investigated through the life cycle assessment (LCA) and cost modelling analyses, respectively.

We have considered a Smartrec system consisting of a 200 kW HPHE and a 400 kWh DMT subassemblies along with instrumentation & control system, piping system, end user heat exchanger (HX). For LCA study of the Smartrec system, life cycle inventory (LCI) data were collected from primary [20] [21] and secondary sources. All the collected data were normalised to the functional unit 1 MWh of the Smartrec system and then imported into SimaPro 8.5.2.0 LCA tool [22]. The LCA results of three damage categories of environmental impacts of 1 MWh Smartrec system are given in Tab.5.

Impact category	Units	Total	Use phase	HPHE	DMT	End-of-life
Human health	DALY	-4.6x10 ⁻⁵	6.2x10 ⁻⁶	-5.7x10 ⁻⁵	5.2x10 ⁻⁶	2.5x10 ⁻⁷
Ecosystem quality	PDF*m ² *yr	-8.5	1.9	-12.6	1.8	0.32
Resources	MJ primary	-1844	54	-2066	140	28
TABLE 5. Eminant and the set you be a few antice meters for functional unit of 1 MWh						

TABI	LE 5:	Environmental	impact resu	lts oj	Smartrec	system j	for f	unctional	unit	of	ΙΛ	1И	'n
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The environmental impacts of 1 MWh Smartrec system in all damage impact categories are positive, where resources damage category contributes the most and human health affects the least. A Smartrec system with capacity of 200 kW will recover 788.4 MWh of useful thermal energy annually from the intermittent waste flue gas source of secondary aluminium industry. This could replace 946.08 MWh of fossil fuel (such as natural gas, coal or oil etc.) and 788.4 MWh of electrical energy that are used to generate hot water by conventional boiler (assuming 80% and 100% boiler efficiency for fossil and electric based system respectively). The emission factors of natural gas, coal (averaged for different grades), diesel and electricity (EU average energy mix) are 0.240 t CO₂-eq /MWh 0.368 t CO₂-eq /MWh (23], 0.566 t CO₂-eq /MWh [24]. Therefore, a 200 kW capacity of Smartrec system will save significant amount of primary and secondary fuel as well as associated emissions.

The cost modelling of the Smartrec system comprising the CAPEX (CApital EXpenditures) and OPEX (Operational expenditures) of the Smartrec system. The total costs of the Smartrec system is the sum of costs of HPHE, DMT, molten salt tank pump, pipes, instrumentation & control system and heat exchanger, and these are calculated and estimated based on the primary and secondary data for the demonstrational and commercial scenarios.

For demonstrational purposes, we need many ancillary instruments to monitor the pressure, temperature, Hitec mass flow rates at different locations of the Smartrec loop (e.g. 3 mass flow rate transmitter analogue output probes). For commercial manufacturing of the Smartrec system, a smaller number of ancillary instruments will be needed e.g. single mass flow rate transmitter analogue output probe, 20 temperature transmitter analogue output probes etc. The results of the cost analysis of the Smartrec system for demonstrational and commercial purposes are presented in Tab.6.

Items	Costs of components of the Smartrec systems (€)				
	Demonstrational	Commercial			
200 kW HPHE	23,484	17613			
400 kWh DMT system installed and filled	116,771	87578			
Molten salt tank pump	8008	6006			
Pipes	2,631	1973			
Instrumentation and control	207,284	45530			
Heat exchanger, 100 kW	12,672	9505			
Total costs of the Smartrec system	370,850	168,205			
Installation cost	7,417	16,821			
Capex of Smartrec system	378,267	185,026			

TABLE 6: Costs of various components of the Smartrec systems

It is seen from the Tab.6 that the total costs of the commercial Smartrec system is about half of the cost of the demonstrational Smartrec system. In addition to installation cost of DMT system, the total integration and installation cost of the commercial Smartrec system is assumed to be 10% of the total costs of the Smartrec system.

In a typical secondary aluminium industry, furnace operates for 4 hours and stops for 4 hours for emptying and filling procedures in an 8 hours cycle [25]. Based on the primary and secondary data, we calculated and estimated the operating costs and listed in Tab.7.

Breakdown of the OPEX	Costs (€)
Preheating energy costs of Hitec	220
Preheating energy costs of DMT Pipes	250
Electrical Energy costs of Pump	1,892
Labour costs during downtime	1,295
Cleaning costs of HPHE	835
Annual OPEX of the Smartrec system	4,492

TABLE 7: The annual OPEX of the Smartrec system

To evaluate the economic viability or cost competitiveness of Smartrec system, we have performed discounted cash flow analysis to determine the Levelised cost of heat energy (LCOH). The levelised cost of energy approach is one of the best tools to compare the cost competitiveness of energy production from different sources. The levelized cost of heat (LCOH) is the constant heat price needed during the lifetime of the waste heat recovery (WHR) project to reach break-even over the lifetime of the project. This means in fact that the Net Present Value is equal to zero, when the energy is sold @ LCOH. We can write the equation for LCOH as:

$$LCOH(\notin/MWh) = \frac{CAPEX(Smartrec system) + \sum_{t=1}^{n} \left[\frac{OPEX(t)}{(1+\alpha)^{t}}\right]}{\sum_{t=1}^{n} \left[\frac{E_{recovered}(\frac{MWh}{year})}{(1+\alpha)^{t}}\right]}$$

Here, " α " is the discount rate and "n" is the operating life. $E_{recovered}$ is the energy recovered by the SMARTREC system per year.

We have estimated the CAPEX of the demonstrational and commercial Smartrec systems (Tab.6) and calculated OPEX which is \notin 4,492 (Tab.7). For discount rate of 5% and 20 years of service life, the LCOH of the heat recovered by Smartrec systems is found to be \notin 24.53 per MWh.

According to the Eurostat, the EU-28 average price of natural gas and electricity for non-household consumers are $\in 0.031$ per kWh (Eurostat online data codes: nrg_pc_203) and $\in 0.1142$ per kWh (Eurostat online data codes: nrg_pc_205). Moreover, additional investment and operational cost will be required to install and maintain boiler to produce thermal energy based on these primary and secondary sources of energies. Therefore, in terms of cost competitiveness, energy recovered by Smartrec system is superior to traditional fossil fuel-based energy system.



FIGURE 3: Scale up cost of Smartrec system(a); LCOH of recovered energy at scale up (b).

Moreover, at scale up, the cost of Smartrec system will be reduced further. This is likely to happen due to the significant reduction of instrumentation and control system cost compare to TES and HPHE. As shown in Fig.3a, specific cost of 1600 kW Smartrec system compare to 200 kW system will be reduced to ϵ 729/kW from ϵ 925/kW. For a 1600 kW capacity Smartrec system, the LCOH will be of ϵ 19.74/MWh which will be 19.5% lower compare to base case (i.e., 200 kW capacity Smartrec system). At both lower and higher scale, Smartrec system can provide competitive solution to recover waste heat from intermittent waste heat source, allowing Smartrec to significantly contribute both in increasing energy efficiency and decarbonisation of energy system.

CONCLUSIONS

Energy efficiency plays a paramount role in the industrial sector. Therefore, Smartrec has been developed as a flexible solution for heat recovery in industrial processes. The main Smartrec objectives – high temperature and switch from batch to continuous heat recovery- have been reached by the application of latest technologies on Heat Transfer Fluid, Heat Storage and Heat Exchanger design and manufacturing. The environment and cost life cycle LCA and LCC showed a positive impact of the proposed Smartrec solution with potential upgrade when the heat recovery temperature increase and the manufacturing cost decrease for standardized solutions.

A profitable investment in the HR initiative for industrial applications has been demonstrated with high potential of future developments; the Smartrec system has a positive environmental impact and contributes to a significant CO_2 reduction.

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http://smartrec.eu/



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