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D1.2 - Report on characterisation of the environments

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Main authors/contributors:	Towseef Ishmum Ahmad, M A Hye Chowdhury, Mohammad Ashadul Hoque, M A Rahman, T Khan, Fahim Chowdhury	
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Abstract		

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[*] Dissemination level security:

PU – Public (e.g. on website, for publication etc.) / **PP** – Restricted to other programme participants (incl. Commission services) /

RE – Restricted to a group specified by the consortium (incl. Commission services) / **CO** – confidential, only for members of the consortium (incl. Commission services)

CONTENTS

Summary

This report has examined and characterised four performance targets proposed in the FORGE project. The performance targets have been defined as follow:

- PT1: Corrosion in CO_2 environment for Carbon Capture and Storage (CCS) systems,
- PT2: H_2 embrittlement,
- PT3: Wear resistance
- PT4: Thermal stability.

Based on literature research and information from the industrial partners in the consortium, the overall environments for testing compositionally complex coating materials have been defined.

The results of this report will be used in later stages of the FORGE project to establish the simulated testing environments for the compositionally complex alloys and compositionally complex ceramic coating materials.

Objectives Met

The deliverable contributed towards the work package objective:

- To set up the simulated laboratory environment for material and coating performance testing.

1. INTRODUCTION

This report will focus on the characterisation of damage environments and how each of the four performance targets are critical to the goals of the FORGE Project.

Section 2 will cover the performance targets selected in the proposal of the FORGE project. This section will briefly discuss the basics of the degradation processes and based on literature data and information from deliverable report D1.1 and D1.3 proposed testing environments for compositionally complex materials for later stages of the project. Section 3 will summarise the key points for each performance target. Finally, section 4 will conclude the findings of this report.

2. DAMAGE ENVIRONMENT DESCRIPTIONS FOR FOUR PERFORMANCE TARGETS

In the FORGE project proposal and in deliverable report D1.1, four critical areas of damages were identified as the main factors that contribute to component damage for aluminium, cement, ceramic, and steel industries. This section will explain why each performance target is important and why this project has identified each of the following as a critical challenge to overcome.

The selected performance targets (PT) are:

- PT1: Corrosion in CO_2 environment for Carbon Capture and Storage (CCS) systems,
- PT2: H_2 embrittlement
- PT3: Wear resistance
- PT4: Thermal stability

2.1 Corrosion in CO_2 environment for Carbon Capture and Storage (CCS) systems (PT1)

Energy intensive industries, including the four within the FORGE consortium, emit significant amount of CO_2 in the atmosphere. Carbon capture and storage (CCS) technologies have become critical to reducing the impact of increasing levels of CO_2 in the atmosphere for these industries. However, the application of such technology to industrial streams is often met with significant component degradation. This is because, together with high concentrations of CO_2, other corrosion mechanisms are active [1]. The key factors determining corrosion in CCS systems are:

- Partial pressure of corrosive gases CO_2, H_2S, NOx, SOx and oxygen
- Concentration of corrosive impurities such as chlorides
- Water content and presence/absence of a free water phase
- Fluid temperature and velocity

As the development of a novel compositionally complex alloys (CCA) coating material is an aim of the FORGE project, this coating material would need to demonstrate superior degradation resistance compared to commercial alloys in such environments..

Several research studies have attempted to tackle the harsh conditions found in these systems. For instance, Xiao *et al.* conducted various experiments in an autoclave to determine the effects of corrosion on 13Cr steel in a CO_2, high temperature and steam environment.[2] The results of their experiments showed that greater the temperature, greater the adsorption of water on the surface of the steel. The layer of water acted as a medium for carbonic acid formation, and this in turn caused a chain reaction resulting in the degradation of the 13Cr Steel. Additionally, increasing the chloride concentrations also resulted in an increase in corrosion again due to higher concentrations, which removed iron from the surface of the steel, significantly weakening the material. Dugstad *et al.* also conducted experiments in an autoclave to determine the effects of various impurities along with CO_2 to see how the corrosion rates of samples of ferritic-pearlitic X65 pipeline steel changes in the presence of different impurities.[3] CO_2 has been transported through pipes for many years, though the effects of contaminants in CO_2 gases e.g., in flue gases (such as oxides of sulphur (SO_x) and nitrogen (NO_x), Oxygen (O_2), Carbon monoxide (CO), and water and Hydrogen sulphide (H_2S)) have yet to be fully understood. A more in-depth description of corrosion-related issues in CCS systems has been reported within deliverable D1.3 of this project.

2.1.1 Proposed testing environments for PT1

Recommendations in terms of amount of impurities in a CO_2 stream have been provided by some studies. The most referred to are from the DYNAMIC project [4], although others have also been published.In general, as reported by Dugstad et al., [3], a large variation in the reported impurities concentration is found, due to differences in fuel type, energy conversion process (i.e. post-combustion, pre-combustion or oxyfuel) and the capture process. A summary of available recommendations is reported in **Table 1.**

Table 1: Impurity concentrations (ppmv) reported in existing pipelines and tested at IFE by Dugstad et al., (from [3]). In blue, the minimum target concenytrations selected for the FORGE project, basedon the DYNAMIS[4] recommendations.

	Impurity levels in existing pipelines				**Published CO_2 recommendations**				
	Canyon Reef Carriers	**Central Basin Pipeline**	**Cortez Pipeline**	**Weyburn**	**DYNA MIS**	**NETL**	**Literature review**	**Tested at IFE**	**FORGE**
H_2O	122	630	630	20	500	730/500	20-650	300	>500
H_2S	<260	<26	20	9000	200	100	20-13000	100	0^{Δ}
CO	-	-	-	1000	2000	35	10-5000	-	>2000*
O_2	-		-	<70	<40000	40000/10	100-40000	350	>40000
NOx	-	-	-	-	100	100	20-2500	100	>100*
SOx	-	-	-	-	100	100	10-50000	100	>100*

Δ H_2S is commonly found in Oil&Gas streams but not in emissions from energy intensive industries.

* These chemicals require special H&S consideration in their handling, thus actual final values may vary.

Since the aim of the FORGE project is to develop a material resistant to a variety of conditions found in CCUS production, extremely harsh conditions are targeted. The exact concentrations used in the testing within the project will be defined by the testing hardware capability and health and safety considerations. However, target minimum concentrations have been selected as being the recommended quality target in the DYNAMIS project. This is reported in the last column in Table 1. Notice that the pressure of CO_2 is not reported in the table. Due to limitations in the maximum pressure allowed in the testing equipment in the project, the maximum pressure of CO_2 will be set to 10barg and the temperature will be in the range 50-150°C.

2.2 H_2 Embrittlement (PT2)

In the deliverable D1.1, the use of fossil fuels, and reducing agents, was reported as one of the main sources of CO_2 emissions for the steel industry. Although other energy intensive industries in the project also make use of fossil fuels and could thus benefit from using H2 instead from an environmental standpoint, it was decided in this project to focus the attention only to the steel industry. The use of hydrogen (produced via renewable energy) as a fuel would eliminate all CO_2 emissions as the combustion of H_2 results in only water. Although this is a clean source of energy, the storage and transport of H_2 proposes many challenges, one of which is a degradation mechanism known as H_2 embrittlement, a process in which H_2 found in metals penetrate the further into metals and cause cracking/fractures/loss of strength and ductility.[5] This is most common in metals such as steels. The steel industry is currently looking to manufacture pressure vessels which can withstand pressures which previously proved to be a limitation when considering H_2 storage and transport. So, the FORGE project is aiming to design coating materials which will be resistant to effects of H_2 embrittlement and withstand pressures higher than currently used materials.

Some studies have aimed at tackling these issues. Hafsi *et al.* examined the H_2 embrittlement of steel pipes originally designed for natural gas transport.[6] They modelled H_2 diffusion through 3 different metals API X52 steel (non-treated and nitrided) and API X80 steel as these are commercially used for pipelines. They found that the nitrided X52 and X80 steel pipelines were more resistant to hydrogen diffusion/embrittlement after supercharging with H_2 whereas the non-treated X52 steel was not. Ustolin *et al.* studied the loss of integrity of H_2 equipment.[7] They focused on H_2 embrittlement and the material selection for H_2 services. In the storage sector the most common method used are compressed H_2 tanks Where H_2 can be stored at up to 700 bar pressure. There are many other forms of storage methods, but compressed H_2 was noted to have the greatest pressure quantity. In the transport sector pipelines can carry H_2 between 0.5-550 km in pressures ranging from 1-100 bar. When considering safety of materials, especially when considering loss of integrity, H_2 embrittlement is a degradation mechanism that can cause fractures or cracking in materials. This affects materials which have low H_2 solubility such as metals with close packed hexagon or body centred cubic lattice structures. Barrera *et al.* studied the effects of H_2 embrittlement on metals with a focus on steels. They also examined mitigation strategies used for designing steels more resistant to H_2 embrittlement.[8] They found that diffusible H_2 (H_2 that could move inside the metallic lattice) was responsible for embrittlement. Murakami *et al.* studied the effects of supersaturating austenitic stainless steels (304 and 316L) with H_2. Rather than resulting in accelerated cracking or fatigue, this greatly improved the fatigue crack growth resistance.[9] Tzimis *et al.* reviewed the economic and technical status of technologies for hydrogen storage. [10] They found that even though gaseous storage was the most mature technology, there could be improvements in wight/volume efficiency and the optimisation of safe tank designs.

2.2.1 Proposed testing environments for PT2

Metal pressure vessels have been the most widely used materials for H_2 storage, and those made of steel can be vulnerable to the phenomenon of H_2 embrittlement. For H_2 pressure vessels, high strength carbon steels are more vulnerable to embrittlement at pressures of 7000-10000 bar. High strength steels are also ideal for using in transport of pure H_2 gas. To be able to effectively use high strength steels in such scenarios these would have to withstand pressures over 400 bar. Therefore, when designing new CCA coating materials, these alloys should be tested in the range of **400-10000 bar**. Figure 1 shows an image of a failed part in the steel industry due to damages caused by H_2 embrittlement.

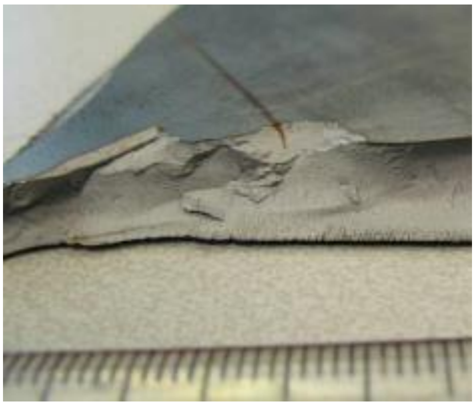

Figure 1: Image of a fractured surface of a failed part (due to H_2 embrittlement) in the steel industry [Courtesy of Arcelor-Mittal].

2.3 Wear resistance (PT3)

Mechanical damage occurs in almost all production processes in industries and the most frequently occurring damages were due to either wear or erosion of industrial components. Coating materials are in use in some industries, although the rate of wear and erosion are not sufficient to prevent degradation and this results in the contamination of processed raw materials or even final manufactured products. This section will study the causes and environments in which wear, and erosion was observed in the processes of cement, steel, ceramic and aluminium industries.

Erosion occurs throughout the manufacturing process of the **cement industry** mainly in waste heat recovery and raw mill components. In the WHR system clinker dust is the source of abrasive material. The system operates in the temperature range of 300-500 ℃ and is made of St37-2 steel. Currently an abrasion resistant coating is used to minimise wear and erosion. Despite the use of the current coating material, damage still occurs at the duct surfaces and this causes openings to occur. These openings then cause several issues such as false air intake and drops in temperature. The false intake causes high fan speeds, and this results in high energy consumption. Whilst the temperature drops lower steam production, and this significantly lowers energy production.

Erosion occurs throughout the various manufacturing process in the **steel industry**. This happens mainly due to abrasive particles eroding protective coatings or the vessels used throughout the steel making process. One example includes the pulverising mill in which coal particles of approximately 40 mm impacting on the flaps results in damaged components.

In the **ceramics industry** contamination of ceramic tiles occur due to erosion throughout the manufacturing processes. This happens mainly due to abrasive particles eroding currently used protective coating and then these contaminate the tiles.

The steel extrusion dies used in **aluminium industry** undergoes wear/erosion due to the presence of high silicon content in the aluminium extrusion alloys. Two different profile dies, Solid Profile Dies (SPD) and Open Profile Dies (OPD), are used. SPD are made of 2367 Unimax hot working steel (HWS) and are operated in temperatures of 450 ℃ and pressures of 0-285 bar. OPD are made of DIEVAR HWS and are operated in temperatures of 450 ℃ and pressures of 0-325 bar.

2.3.1 Proposed testing environments for PT3

The main causes of wear and erosion were found to be abrasive raw materials or compounds used in the manufacturing processes of the cement and aluminium industries. The environmental conditions such as pressure and temperature will be dependent on the conditions the industrial components are used in. The novel coatings of the FORGE project will have to be resistant to wear and erosion from abrasive particles (such as those present in Cement manfacturin) or to pressures of 0 – 350 bar and temperatures of 300-500 ℃ (such as those acting on the dies in Aluminum extrusion**)**, hence if a new coating can be designed for such purposes then it can be used in all forms of industries in which such degradation occurs. Figures 2 and 3 shows components from the cement and aluminium industries in new and damaged conditions due to wear and erosion.

Figure 2: Inner sections of a damaged section of a WHR system due to wear and erosion in the Cement industry a) overall image and b) a more detailed image of damages [Courtesy of Cimsa Cimento].

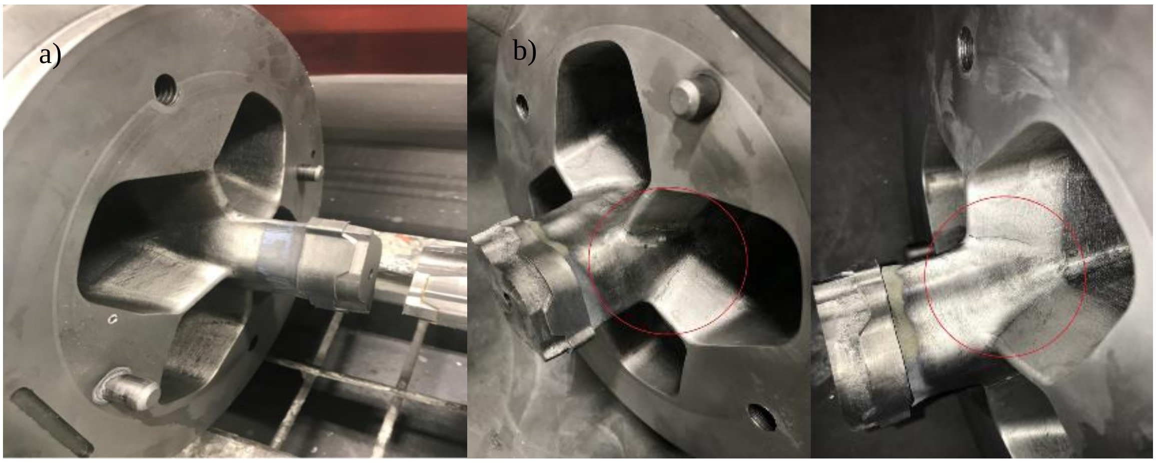

Figure 3: Solid profile dies used in the aluminium industry a) in new condition and b) in damaged condition due to wear and erosion [Courtesy of ASAȘ].

2.4 Temperature stability (PT4)

High temperatures or heat can radically modify degradation mechanisms. In most cases this increases degradations such as corrosion, embrittlement and erosion as examined in sections 2.1, 2.2, and 2.3, respectively. This phenomenon is seen in the **ceramic industry**, where conditions can exceed 1,000 ℃ in the ceramic firing kilns. This leads to an increase in corrosion of the fire bricks due to the acidic elements penetrating and eroding the bricks from within. This also occurs in other industries alongside other degradation processes. In section 2.3 the working conditions of the **cement** and **aluminium** industries are in the range of 300-500 ℃, in these conditions wear and erosion occur at high temperatures and this results in the damage of components. The development of novel coating materials that can resist frequently occurring degradation processes is a critical goal of the FORGE project. The creation of coating materials, such as CCA and CCC that can retain degradation resistance even in extreme temperatures will increase the longevity of industrial components. This in turn will mean less raw materials will be consumed to replace or repair industrial components, which will increase manufacturing efficiency and sustainability of industrial processes.

2.4.1 Proposed environments for PT4

Throughout this report, examples of thermal influence on degradation were prominent. In these cases, other degradation factors increase with temperatures e.g., abrasive particles causing friction or H_2 embrittlement or acids causing further corrosion on metal components. Hence the thermal environments for the simulated testing of the novel FORGE coating CCMs will be dependent on the conditions in which the effected components are utilised. This varies from industry to industry, for example in the aluminium extrusion, the temperature of the dies constantly changes during the process **(up to 450 ℃)**, whilst the pressure is between **0-325 bar** and in the ceramics industry the kilns are fired between **800-1,200 ℃** in the presence of other contaminants such as potassium, chloride, fluorine, sulphur and water vapour. The latter has been selected as target environment for this PT in the project, where the condition of high temperature, together with corrosive species, represent a major issue for the degradation of the refractory bricks in the kilns within the ceramic industry (Figure 4).

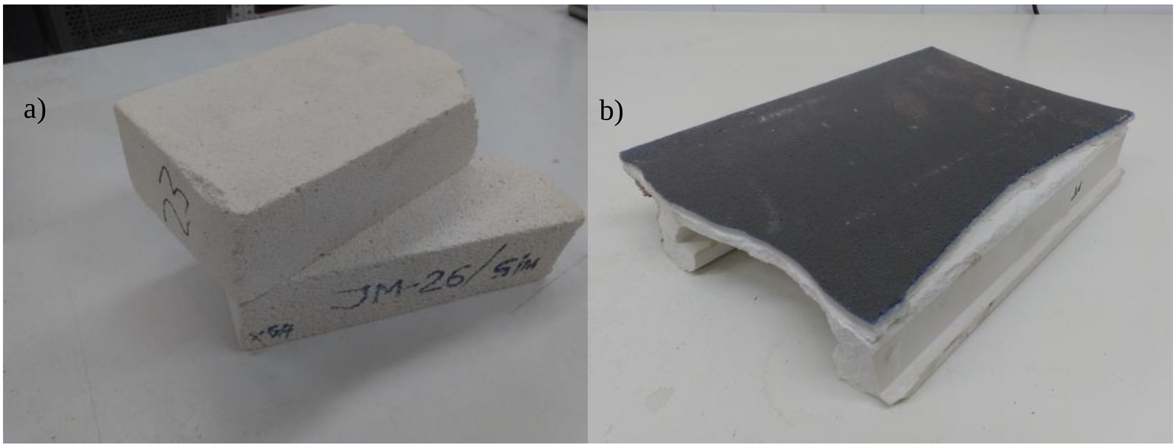

Figure 4: Fire bricks used in the ceramic industry a) in new condition and b) in damaged condition due to corrosion in high temperature environments.

3. SUMMARY OF PROPOSED TESTING ENVIRONMENTS

Table 2 summarises the various testing conditions that have been proposed in this report. For PT1 this table has provided the two extreme values for the gaseous acidic species based on literature values. As the testing environments will be simulated initially the upper most known conditions have been listed for the acidic species to test how much resistance newly developed coatings will achieve. For each performance target, of the four industry partners of the FORGE project, the most applicable industries have been listed alongside the respective degradation mechanism that greatly effects those industries.

Table 2: Overall summary of proposed testing target for novel FORGE coating materials in simulated environments.

ID	Performance target	Applicable Industries	CO_2 / barg	SO_X / ppm	NO_X / ppm	O_2 / ppm	CO / ppm	H_2O / ppm	H_2S / ppm	Wear type	Pressure / bar	Temperature / °C
PT1	Resistance to corrosion in CO_2-rich environment	Cement, Steel, Ceramic and Aluminium	<10	>100	>100	>40000	>2000	>500	0	-	<10	50-150
PT2	H_2 Embrittlement resistance	Steel	-	-	-	-	-	-	-	-	400-10000	-
PT3	Wear resistance	Cement Aluminium	-	-	-	-	-	-	-	Erosion Sliding	1 0-350	300-500 450
PT4	Temperature stability	Ceramic	K, F, S, H_2O species also found in the environment							-	1	800-1200

4. CONCLUSIONS

This report has examined the performance targets emerged from the SoA and FMEA analysis and proposed in the FORGE project. Materials employed in CCS systems (PT1) degrade mainly due to the presence of CO_2, SO_X, NO_X and O_2 gases, together with presence of water and chlorides. Targets for these species have therefore been set according to guidelines commonly employed in the field. H_2 embrittlement environment (PT2) is an area in which safety is especially important. Though there are already materials in use for the storage and transport of H_2 to date, these materials are limited by the pressure levels beyond which it's not safe to store due H_2 to the compromise in structural integrity because of the embrittlement phenomenon. This project will aim to address this by creating novel coating materials which are resistant to embrittlement damage mechanism, being this a transversal interest for all Energy Intensive Industries willing to adopt H2 technologies, as fuel or reducing agent. Mechanical damage (PT3) was observed to be the most occurring damaging mechanism across all four of the participating industries. In most cases the damaging species were abrasive particles or raw materials. Although there are coating materials in use in industries today, these materials are not effective enough to prevent erosion from causing degradation and the contamination of products. The cement and aluminium industry have been selected as case studies within the project due to diversified and extreme severity of the conditions encountered. For Thermal stability (PT4) it was found that in high temperature conditions the likelihood of other damage mechanisms increases and, in most cases, high temperatures accelerated degradation mechanisms. Overall, the working temperature in which new FORGE coatings will be applied for this PT are between 800-1200 ℃ and presence of other contaminants, as found within the ceramic industry.

The proposed environments summarised in section 3 of the various environments of PT 1-4 will be used as the basis for simulation conditions in later parts of the FORGE project. These conditions will be detailed in the project within deliverable D1.4 considering literature values, analysis of the available testing equipment and observations made through industry partners for all of the stages.

REFERENCES

1. M.A. Billingham, C.-H. Lee, L. Smith, M. Haines, S.R. James, B.K.W. Goh, K. Dvorak, L. Robinson, C.J. Davis, and D. Peralta-Solorio, Corrosion and materials selection issues in carbon capture plants, Energy Procedia, 4, (2011) 2020-2027
2. G. Xiao, S. Tan, Z. Yu, B. Dong, Y. Yi, G. Tian, H. Yu, and S. Shi, CO2 corrosion behaviors of 13Cr steel in the high-temperature steam environment, Petroleum, 6(1), (2020), 106-113
3. A. Dugstad, M. Halseid, and B. Morland, Testing of CO2 Specifications With Respect to Corrosion and Bulk Phase Reactions, Energy Procedia, 63 (2014) 2547-2556
4. E. de Visser, C. Hendriks, G. de Koeijer, S. Liljemark, M. Barrio, A. Austegard, and A. Brown, DYNAMIS CO2 quality recommendations, D3.1.3 report, (2007)
5. A. Pradhan, M. Vishwakarma, and S. K. Dwivedi, A review: The impact of hydrogen embrittlement on the fatigue strength of high strength steel, Materials Today: Proceedings, 26, Part 2, (2020) 3015-3019
6. Z. Hafsi, M. Mishra, and S. Elaoud, Hydrogen embrittlement of steel pipelines during transients, Procedia Structural Integrity, 13, (2018) 210-217
7. F. Ustolin, N. Paltrinieri, and F. Berto, Loss of integrity of hydrogen technologies: A critical review, International Journal of Hydrogen Energy, 45, Issue 43, (2020) 23809-23840
8. O. Barrera, D. Bombac, Y. Chen, T. D. Daff, E. Galindo-Nava, P. Gong, D. Haley, R. Horton, I. katzarov, J. R. Kermode, C. Liverani, M. Stopher and F. Sweeney, Understanding and mitigating hydrogen embrittlement of steels: a review of experimental, modelling and design progress from atomistic to continuum. J Mater Sci, 53, (2018) 6251–6290
9. Y. Murakami, T. Kanezaki, and Y. Mine, Hydrogen Effect against Hydrogen Embrittlement. Metall Mater Trans A 41, (2010) 2548–2562
10. E. Tzimas, C. Filiou, S. D. Peteves and J.-B. Veyret, HYDROGEN STORAGE: STATE-OF-THE-ART AND FUTURE PERSPECTIVE (2003)
11. B. Delpech, M. Milani, L. Montorsi, D. Boscardin, A. Chauhan, S. Almahmoud, B. Axcell, and H. Jouhara, Energy efficiency enhancement and waste heat recovery in industrial processes by means of the heat pipe technology: Case of the ceramic industry, Energy, 158, (2018) 656-665
12. B. Egilegor, H. Jouhara, J. Zuazua, F. Al-Mansour, K. Plesnik, L. Montorsi, and L Manzini, ETEKINA: Analysis of the potential for waste heat recovery in three sectors: Aluminium low pressure die casting, steel sector and ceramic tiles manufacturing sector, International Journal of Thermofluids, 1–2, (2020) 100002