Towards higher industrial efficiency in future waste-to-energy plants with high temperature latent heat storage-based thermal buffering technology

Xu, Haoxin

2019

Xu, H. (2019). Towards higher industrial efficiency in future waste-to-energy plants with high temperature latent heat storage-based thermal buffering technology. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/142057>

<https://doi.org/10.32657/10356/142057>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 07:37:50 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**TOWARDS HIGHER INDUSTRIAL EFFICIENCY IN
FUTURE WASTE-TO-ENERGY PLANTS WITH HIGH
TEMPERATURE LATENT HEAT STORAGE-BASED
THERMAL BUFFERING TECHNOLOGY**

HAOXIN XU

**School of Mechanical and Aerospace Engineering
Nanyang Technological University**

2019

**TOWARDS HIGHER INDUSTRIAL EFFICIENCY IN
FUTURE WASTE-TO-ENERGY PLANTS WITH HIGH
TEMPERATURE LATENT HEAT STORAGE-BASED
THERMAL BUFFERING TECHNOLOGY**

HAOXIN XU

SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

A thesis submitted to the Nanyang Technological University in
partial fulfilment of the requirement for the degree of Doctor of
Philosophy

2019

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

Aug 7th 2019

.....

Date

A handwritten signature in black ink, appearing to read 'Haoxin Xu', is shown on a light blue rectangular background.

.....

Haoxin Xu

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

Aug 7th 2019

.....

Date

.....

Alessandro Romagnoli

Authorship Attribution Statement

This thesis contains material from 4 papers published in the following peer-reviewed journals and 2 conference papers where I was the first or the second author.

Chapter 2 has its first section published as Xu H, Lin WY, Romagnoli A. Technological review on enhancing the energy efficiency of MSW incineration plant. *2018 Asian Conf. Energy, Power Transp. Electrification*, 2018, p. 1–7. doi:10.1109/ACEPT.2018.8610756.

The contributions of the co-authors are as follows:

- I gathered literature information and prepared the manuscript drafts apart from the introduction part in the manuscript. The introduction part was prepared by Dr Lin.
- Asst.Prof. Romagnoli helped to revise the manuscript drafts.

Chapter 3 is published as Xu H, Romagnoli A, Sze JY, Py X. Application of material assessment methodology in latent heat thermal energy storage for waste heat recovery. *Appl Energy* 2017;187:281–90. doi:10.1016/j.apenergy.2016.11.070.

The contributions of the co-authors are as follows:

- I provided the initial idea, carried out the methodology design, and prepared the manuscript.
- Asst.Prof.Romagnoli provided guidance to formulate the methodology.
- Dr.Sze revised the manuscript and helped to polish the language.
- Prof. Py revised the manuscript.

Chapter 4 is published as Xu H, Dal Magro F, Sadiki N, Mancaux J-M, Py X, Romagnoli A. Compatibility study between aluminium alloys and alternative recycled

ceramics for thermal energy storage applications. *Appl Energy* 2018;220:94–105. doi:10.1016/j.apenergy.2018.03.021.

The contributions of the co-authors are as follows:

- I designed the study method, conducted the study, and prepared the manuscript.
- Dr. Dal Magro provided the original idea.
- Dr. Sadiki assisted in the collection and interpretation of X-ray diffractometer testing data.
- Mr. Mancaux helped me prepare the laboratory equipment and purchase/sourcing of materials.
- Prof. Py and Asst. Prof. Romagnoli provided the initial project direction and revised the manuscript.

Chapter 5 has its second section published in the last result section in Dal Magro F, Xu H, Nardin G, Romagnoli A. Application of high temperature phase change materials for improved efficiency in waste-to-energy plants. *Waste Manag* 2018;73:322–31. doi:10.1016/j.wasman.2017.06.031.

The contributions of the co-authors are as follows:

- Dr. Dal Magro performed the material/mechanical analysis and wrote the manuscript apart from the last result section.
- I wrote the last result section of the manuscript regarding computational fluid dynamics simulation (This is the only part from this paper I included in *Chapter 5*).
- Asst. Prof. Romagnoli provided the initial project direction and revised the paper.

Also, the third section of *Chapter 5* and second section of *Chapter 6* were published in Xu H, Lin WY, Dal Magro F, Li T, Py X, Romagnoli A. Towards higher energy efficiency in future waste-to-energy plants with novel latent heat storage-based thermal buffer system. *Renew Sustain Energy Rev* 2019;112:324–37. doi:10.1016/j.rser.2019.05.009.

The contributions of the co-authors are as follows:

- I formulated the numerical model, carried out the simulation, participated in the experimental design and tests, and prepared the manuscript.

- Dr. Lin led the purchase and installation of experimental setup, and was involved in the experimental tests. She also provided comments on the manuscript revision.
- Dr. Dal Magro provided the original idea.
- Asst.Prof. Romagnoli provided the initial project direction and revised the paper.

Chapter 7 is published as Xu H, Wei C, Yvonne W, Romagnoli A. Techno-economic evaluation of a novel phase change materials-based thermal buffering technology for improving energy efficiency of waste-to-energy plants. *32nd Int. Conf. Effic. Cost, Optim. Simul. Environ. impact Energy Syst. (ECOS 2019)*, Wroclaw, Poland: 2019.

- I formulated study methodology, carried out in the simulation, and prepared the manuscript.
- Mr. Wei assisted in the simulation and calculation.
- Dr. Lin contributed to the formulation of the methodology, and revised the manuscript. .
- Asst.Prof. Romagnoli revised the paper.

Aug 7th, 2019

.....
Date

.....
Haoxin Xu

Acknowledgement

The author would like to express gratitude for the valuable guidance and supervision to her thesis advisor Asst. Prof. Alessandro Romagnoli from School of Mechanical and Aerospace Engineering in NTU and co-advisor Prof. Xavier Py from University of Perpignan. I would like to also acknowledge the fruitful discussions and collaborations with Dr. Yvonne Lin, Dr. Jiayin Sze and Dr. Fabio Dal Magro. This thesis would not be possible without their support.

Also, the author is thankful to her Thesis Committee Members Prof. Charles Yang Chun, Dr. Jonathan Hey Heng Kiat for their appreciated feedbacks on her progress.

Moreover, the author wishes to thank National Research Foundation and National Energy Agency, Singapore, for providing financial support to conduct part of her Ph.D. research.

Lastly, I would like to acknowledge my dear mother Mrs. Yang Shang Rong and Mr. Zydrunas Salcius for their unconditional support and encouragement throughout the hard times during my thesis. Their love and support will always be remembered and cherished.

Abstract

Modern Waste-to-Energy plants have the increasing potential to solve the urban waste accumulation issue faced around the world. However, their plant efficiencies are constrained by the temperature fluctuation of the steam and the high temperature corrosion on the ferrous surfaces. With the purpose of solving both issues, this PhD thesis proposes a latent heat based thermal buffering technology to replace the traditional refractory bricks on the waterwall. Using Aluminium Alloy based phase change materials as buffering media, this technology aims at reducing the temperature fluctuation of the steam, avoiding the corrosion in traditional superheater, and as well superheating the steam directly on the waterwall. In order to achieve this design outcome, this thesis adopts a comprehensive design procedure, including the material selection by a novel assessment methodology, compatibility study of the encapsulation and core materials, numerical investigation with computational fluid dynamic and Modelica tools, experimental study with a laboratory scale setup, and techno-economic study to quantify the energy savings and potential paybacks. At the end of the study, a laboratory scale brick prototype is developed. The results of experimental studies show that this prototype is able to buffer the thermal fluctuation from the furnace side and reduce the steam fluctuation from 10-20 °C to 2-4 °C, and at the mean time upgrade the steam output to an extra 20 °C. The numerical model, validated by the experimental results with a relative standard deviation less than 2%, showcases the technology integration scheme of this technology into the modern Waste-to-Energy plants, and concludes that a high steam output temperature of 600 °C could be achieved with multiple stages of buffering refractory bricks installed. With the technology specifications, the new plant would generate an extra power output of 10.1 MW and

requires a payback time of 7.5-8,5 years if the bricks could serve 5 years and more without major replenishment. While being highly prospective, this thermal buffering technology requires further research on the manufacturing method and flue gas corrosion issues, to increase its technology availability and market potential in the future.

Lay Summary

This PhD thesis tries to solve two major issues encountered in the modern Waste-to-Energy plants that limit the plants' energy efficiency: the temperature fluctuation of the steam, and the high temperature corrosion that hinders the lifetime of equipment. The solution proposed is a thermal buffering refractory brick to be installed on the waterwall instead of traditional refractory linings. This novel brick, featuring phase change materials, could absorb and release the heat while maintaining at the same temperature. In order to achieve a satisfactory prototype design, a comprehensive design procedure is carried out, including material study, configuration study, and experimental study to demonstrate the buffering effect. The results show that this final prototype is able to reduce the steam temperature fluctuation from 10-20 °C to 2-4 °C, and also increase the steam temperature 20 °C. Compared with the current plant, the future Waste-to-Energy plant based on this new technology will be able to achieve over 10% increase in the energy efficiency, meaning an annual saving of 7.6 kiloton of oil equivalent. In general, this technology could be a potential concept that transforms the future waste incineration plant design and brings enormous energy savings and carbon reductions to the world.

Table of Contents

Authorship Attribution Statement.....	iii
Acknowledgement	vi
Abstract.....	vii
Lay Summary.....	ix
Table of Contents.....	x
Table Captions	xv
Figure Captions.....	xvii
Abbreviations.....	xxii
Nomenclature.....	xxiv
Chapter 1. Introduction.....	1
1.1 Problem Statement.....	2
1.1.1 Waste-to-Energy plants in circular economy.....	2
1.1.2 Challenges to increase the Waste-to-Energy plant efficiency	4
1.2 Objectives of Research	6
1.3 Overview of Dissertation	7
1.4 Findings and Outcomes.....	10
Chapter 2. Literature Review.....	11
2.1 Existing Technologies to overcome efficiency limitations of Waste-to-Energy plants.....	12

2.1.1	Inconel alloy 625 cladding.....	13
2.1.2	HVOF and thermal sprayed coatings.....	14
2.1.3	Monolithic SiC concrete	16
2.1.4	Superheater with rear-ventilated tiles	17
2.1.5	Prism-shaped body in the first boiler pass	18
2.1.6	Comparison of existing technologies.....	20
2.2	Phase Change Material Thermal Energy Storage	21
2.2.1	Phase Change mechanism and material classification.....	21
2.2.2	Phase Change Materials in Thermal Energy Storage	25
2.2.3	Storage design and configuration.....	26
2.3	Summary of research gaps and interests.....	36
Chapter 3. Material Assessment Methodology For Latent Heat Thermal Energy Storage Applications.....		39
3.1	Introduction.....	40
3.2	Proposed Material Assessment Methodology.....	42
3.2.1	Pre-screening.....	44
3.2.2	Material ranking based on Multi-Attribute Decision Making	45
3.2.3	Examining performance objectives with Multi-Objective Decision Making	46
3.3	Case Study - Validation of Methodology	48
3.4	Case Study - LHTES in Co-generation Plant	51
3.5	Case Study - Encapsulated Ceramics for PCM-based Buffering Technology ...	54
3.6	Conclusions.....	57
Chapter 4. Compatibility of Molten Aluminium Alloys and Potential Encapsulation Ceramics		59
4.1	Introduction.....	59
4.2	Materials Used in the Study	61

4.2.1	Aluminium alloys.....	61
4.2.2	Alumina 99%	62
4.2.3	Recycled ceramics	63
4.3	Methods.....	65
4.3.1	Corrosion test	65
4.3.2	Post-corrosion characterization with Environmental Scanning Electron Microscopy, Energy Dispersive Spectrometry and X-ray diffractometer	67
4.4	Results and Discussions.....	68
4.4.1	Interaction of Alumina with aluminium alloys.....	68
4.4.2	Interaction of Cofalit with aluminium alloys.....	70
4.4.3	Interaction of blast furnace slag with aluminium alloys.....	74
4.4.4	Interaction of coal Fly Ashes (CFA) sintered ceramics with aluminium alloys	78
4.5	Conclusions.....	83
Chapter 5. Configuration Design of the PCMs-based Buffering Technology Based on Numerical Studies.....		86
5.1	Introduction.....	87
5.2	Numerical Investigation of the Preliminary Design with Finite Volume Method	90
5.2.1	The first geometry design	90
5.2.2	Numerical methods and boundary conditions.....	91
5.2.3	Results and implications	94
5.3	Numerical Investigation of the Second Geometry with One Dimensional Heat Transfer Analysis.....	97
5.3.1	Geometry refinement and rethinking the simulation strategy.....	97
5.3.2	Numerical methods and boundary conditions.....	98
5.3.3	Results and discussion	107
5.4	Conclusions.....	114

Chapter 6. System Design of the PCMs-based buffering Technology Based on Experimental Study.....	117
6.1 Introduction.....	118
6.2 Methods.....	119
6.2.1 Characterisation of feedstocks	119
6.2.2 Fabrication of refractory bricks	120
6.2.3 Experimental setup.....	123
6.2.4 Numerical model for the system level study.....	126
6.2.5 Protocol of investigation	128
6.2.6 Materials and boundary conditions	129
6.2.7 Post data processing and uncertainty analysis	130
6.3 Results and Discussion	132
6.3.1 Upgrading the steam output temperature by PCMs-bricks.....	132
6.3.2 Capturing the phase change inside the bricks	133
6.3.3 Demonstrating the fluctuation damping by PCM-bricks	135
6.4 Conclusions.....	138
Chapter 7. Techno-economic Study on the Waste-to-Energy Plants with PCMs-based buffering Technology	140
7.1 Introduction.....	141
7.2 Methods.....	142
7.2.1 The baseline WtE plant.....	142
7.2.2 The WtE plant with PCM-based refractory lining.....	143
7.2.3 Building the key performance indicators.....	144
7.3 Results and Discussion	147
7.3.1 Energy savings analysis	147
7.3.2 Economic analysis of newly built WtE with PCM-bricks	149
7.4 Conclusions.....	152

Chapter 8. Conclusions and Future Work	154
8.1 Conclusions.....	154
8.2 Summary of Contributions.....	157
8.3 Limitations and Future work.....	158
APPENDIX A. Analytical Hierarchy Process Method.....	163
APPENDIX B. Techniques for Order Preference by Similarity to Ideal Solutions Method.....	167
APPENDIX C. User-defined functions of the radiation boundary condition in ANSYS Fluent simulation	169
APPENDIX D. Pressure and Massflow Investigation for Reduced Steam Parameter in the Experimental Setup	171
REFERENCES	173

Table Captions

Table 2-1 Composition of Inconel Alloy 625	14
Table 2-2 Comparison of existing technologies	20
Table 2-3 Some major investigators and their field of interest in PCMs studies	25
Table 2-4 Selection of most suitable storage configuration [42,61–63]	28
Table 2-5 Summary of heat transfer enhancement techniques in melting and solidification processes	34
Table 3-1 Desirable PCMs properties	40
Table 3-2 Comparison between MADM and MODM [23,25]	43
Table 3-3 MADM performance matrix [100]	45
Table 3-4 List of eleven PCMs after pre-screening, their thermo-physical properties, simulation results and MADM rankings	49
Table 3-5 Relative weights of four thermo-physical properties	50
Table 3-6 List of PCMs after pre-screening, their thermo-physical properties and rankings	52
Table 3-7-3-8 List of ceramic candidates and their MADM ranking	55
Table 3-9-3-10 Relative and final weights of four mechanical and thermal properties	56
Table 4-1 Composition of the studied aluminium alloys (weight %)	62
Table 4-2 Thermo-physical properties of the studied aluminium alloys (weight %)	62
Table 4-3 Material names, origin of recycled ceramics, and their average values of properties from room temperature to 1000 °C	63
Table 4-4 Chemical compositions of tested Alumina in normalized weight percentage	69
Table 4-5 Element compositions of tested Cofalit in normalized weight percentage	71
Table 4-6 Observed phases in all samples from XRD analysis	74

Table 4-7 Element composition of tested slag samples in normalized weight percentage	76
Table 4-8 Chemical composition of tested CFA sample surfaces in normalized weight percentage	80
Table 5-1 Materials and boundary conditions for Baseline case and PCM case	93
Table 5-2 Material properties and design parameters of waterwall system.....	105
Table 5-3 Different wall thickness considered in the parametric study.....	108
Table 5-4 Type of PCM-based bricks to be applied in the WtE plant and the corresponding designed steam superheating temperature	112
Table 6-1 Melting point and latent heat of the PCMs.....	120
Table 6-2 Thermal debinding for the fabrication of the ceramic green part.....	122
Table 6-3 The optimum sintering profile, as determined by SIMTech	123
Table 6-5 Type of PCM-based bricks used in the numerical study of the waterwall system	130
Table 6-6 Uncertainties of the appliances used in the lab test.....	131
Table 6-7 Melting and solidification point temperatures of the PCMs	135
Table 7-1 Tuas South WtE plant design data [149,150]	142
Table 7-2 PCM-based refractory brick composition and material properties.....	143
Table 7-3 Retrofitted Tuas South WtE plant design parameter [149]	143
Table 7-4 Additional assumptions to the combustion process.....	148
Table A-0-1 Scale of relative importance level	163
Table D-0-1 Relationship between mass flow rate and heat transfer coefficient at a fixed pressure	171
Table D-0-2 Relationship between pressure and heat transfer coefficient at a fixed mass flow	172

Figure Captions

Figure 1-1 Number of WtE plants in the major participating countries/regions in year 2012-2015 (Produced based on data source [5–7]).....	3
Figure 1-2 Global WtE market revenue by thermal incineration from 2014-2024 [13] (Requested for reproduction)	4
Figure 1-3 Corrosion diagram of steel surface [14] (Permitted for reproduction)	5
Figure 1-4 Fluctuation of temperature inside of combustion chamber at 2s after secondary air injection in a typical WtE plant in Southern Italy [15] (Permitted for reproduction)	6
Figure 1-5 Scope and workflow of thesis research.....	8
Figure 2-1 The main components in the steam water loop of a typical Waste-to-Energy plant based on moving grate technology	12
Figure 2-2 Superheater tubes protected by SiC layer (Reproduced with the permission from original authors [29]).....	16
Figure 2-3 Superheater bundles used in WtE plant in Naples Italy (Photo borrowed with the permission of the original author [22])	17
Figure 2-4 Wall superheater with rear-ventilated tiles (Photo borrowed with the permission of the original author [29])	17
Figure 2-5 Rosenheim WtE plant configuration with radiant superheater (Photo borrowed with the permission of the original author [29])	18
Figure 2-6 Prism shaped tubular structure in the first boiler pass (Photo borrowed with the permission of the original author [32])	19
Figure 2-7 Comparison of latent heat and sensible heat with the same temperature range	22
Figure 2-8 Classification of PCMs based on family groups	23

Figure 2-9 PCM families in the enthalpy-temperature map (Reproduced with permission from the authors [42])	24
Figure 2-10 Shell and tube heat exchanger with PCMs filled	27
Figure 2-11 Configuration of LHTES packed-bed	30
Figure 2-12 Schematic design of building roof with PCM panel	31
Figure 3-1 Flowchart of material assessment methodology	43
Figure 3-2 Performance assessment using objective functions of PCMs in a HVAC case study.....	51
Figure 3-3 Performance assessment using objective functions of PCMs in cogeneration application.....	53
Figure 3-4 Sensitivity study of distances to varying weights	54
Figure 3-5 Performance objective examination based on MODM procedure.....	56
Figure 4-1 (a) recycled ceramic samples (20×20×10mm); (b) crucible setup.....	65
Figure 4-2 (a) schematic representation of furnace setup; (b) furnace used in thermal treatment	66
Figure 4-3 Post-treatment steps before characterisation with ESEM, EDS and XRD	67
Figure 4-4 Surface topology of Alumina samples (a) reference; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact.....	69
Figure 4-5 Surface topology of Cofalit samples (a) reference; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact	71
Figure 4-6 Cross-section topology of Cofalit samples: (a) reference; (b) Al99% post-contact ;) AlSi5% post-contact; (d) AlSi12% post-contact	71
Figure 4-7 X-ray diffraction patterns of the Cofalit group (Au: Augite; D: Diopside; C; Clynopyroxene).....	73
Figure 4-8 Surface topology of slag (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact	75
Figure 4-9 Cross-section view of slag sample (a) reference in chemical contrast; (b) AlSi12% post-contact in chemical contrast	76
Figure 4-10 X-ray diffraction patterns of the slag group (Me: Melilite; W: Wollastonite)	77
Figure 4-11 Surface topology of CFA sintered ceramic (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact	79
Figure 4-12 Cross-section topology of CFA sintered ceramic sample (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact	79

Figure 4-13 X-ray diffraction patterns of the CFA/alloys group (M : Mullite ; An : Anorthite ; Fe : Iron oxide ; A : Aluminum oxide).....	82
Figure 5-1 Integration between PCM-based technology and heat recovery boiler based on steam generation in a WtE plant	88
Figure 5-2 First geometry proposal of the PCM-buffering refractory brick.....	90
Figure 5-3 Schematic design of the PCM-integrated WtE plant	91
Figure 5-4 Baseline case geometry and materials (left) top view and (right) side view .	92
Figure 5-5 PCM case geometry and materials (left) top view and (right) side view.....	92
Figure 5-6 Temperature fluctuation of 8 rows of PCM pipes with time (Row No.1 is the closest to the radiation wall, and row No.8 is the closest to the steam pipe.).....	95
Figure 5-7 Temperature distributions in the refractory bricks of two cases	95
Figure 5-8 Fluctuation of area-averaged total surface heat flux on steam pipe wall of Baseline case	96
Figure 5-9 Fluctuation of area-averaged total surface heat flux on steam pipe wall of PCM case.....	96
Figure 5-10 Methodology of developing PCM-based superheater wall system.....	99
Figure 5-11 Physical model (left) and resistance/capacitance (right) model of (a) traditional water-wall, and (b) PCM-based water-wall.....	100
Figure 5-12 First boundary condition which considers gas temperature fluctuation.....	106
Figure 5-13 Second boundary condition which considers both the start-up ramp and the fluctuation of gas temperature	107
Figure 5-14 Average temperature of PCM bricks	109
Figure 5-15 Gas to wall heat flow and steam convection heat flow for different cases	109
Figure 5-16 Different steam temperature and corresponding PCMs temperature at different conditions of gas emissivity	110
Figure 5-17 Outer wall and inner wall temperature at the traditional and PCM bricks.	111
Figure 5-18 Gas to wall heat flow and steam convection heat flow for traditional and PCM-based cases	111
Figure 5-19 Outer wall and inner wall temperature at different bricks	113
Figure 5-20 Gas to wall heat flow and steam convection heat flow for three different PCM-bricks.....	113
Figure 5-21 Technology integration of PCM-based superheater wall in the furnace of WtE plant.....	114

Figure 6-1 Specific heat capacity of (a) alumina ceramic; and the PCM alloys (b) Al99; (c) AlSi12; (d) AlSi5	119
Figure 6-2 The brick fabrication process	121
Figure 6-3 (a) ceramic sample fabricated for mechanical strength test, with major cracks observed; (b) initial brick sample with major cracks at the bottom; (c) slightly improved brick sample with minor cracks at the bottom; (d) final prototype with refined appearance	122
Figure 6-4 Schematic diagram of the lab setup of the high temperature steam loop for brick testing, located in the Thermal Energy System Lab of Nanyang Technological University.....	124
Figure 6-5 Photos of the equipment used in the lab test	125
Figure 6-6 Schematic diagram of heat exchanger with refractory bricks covered and thermal couples installed at steam inlet, outlet and top bricks	126
Figure 6-7 Dynamic thermal network model of the waterwall.....	127
Figure 6-8 The protocol of investigation in flowchart.....	128
Figure 6-9 Comparison of Baseline and PCM cases at non-design condition, with lab test result of Baseline fitted with simulation result	132
Figure 6-10 Capturing the phase change of PCM1, 2 and 3 during our lab test on Feb 20 th , 2019.....	133
Figure 6-11 Lab test vs. simulation results for PCM case on Jun 19 th 2019	136
Figure 7-1 Waste generation and recycling amount in Singapore from 2006 to 2015 [4]	141
Figure 7-2 Comparison of energy savings for baseline and new plants	148
Figure 7-3 Net value of incineration plant versus the plant operation time at different brick service time from half year to 30 years at the highest brick cost scenario (6x).....	150
Figure 7-4 Net value of WtE plant versus the plant operation time at different combination of brick costs and brick service time (0.5 year and 5 years).....	151
Figure 7-5 Net present value of incineration plant versus brick service time with different brick cost.....	152
Figure D-0-1 comparison of effects of mass flow and pressure on heat transfer	172

Abbreviations

AHP	Analytical Hierarchy Process
AI	Annual Intake
AIN	Annual Income
CAPEX	Capital Expenditure
CSP	Concentrated Solar Power
CFA	Coal Fly Ashes
CFD	Computational Fluid Dynamic
CTE	Coefficient of Thermal Expansion
CV	Coefficient of Variance
DT	Disposal Tariff
DTN	Dynamic Thermal Network
EDS	Energy Dispersive X-ray Spectroscopy
ET	Electric Tariff
FOM	Figure Of Merit
HTF	Heat Transfer Fluid
HVAC	heating, Ventilation And Air-conditioning
IR	interest rate
LHTES	Latent Heat Thermal Energy Storage
MADM	Multi-Attribute Decision Making
MCDM	Multi-criteria Decision Making
MODM	Multi-Objective Decision Making
MSW	Municipal Solid Waste
NPV	Net Present Value

OECD	Organisation for Economic Co-operation and Development
OPEX	Operational Expenditure
ORC	Organic Rankine Cycle
PBT	Payback Time
PCMs	Phase Change Materials
PV	Present Value
SEM	Scanning Electron Microscopy
SD	Standard Deviation
SDGs	Sustainable Development Goals
STES	Sensible Thermal Energy Storage
TNM	Thermal Network Method
TOPSIS	Techniques for Order Preference by Similarity to Ideal Solutions
TSIP	Tuas South Incineration Plant
WHR	Waste Heat Recovery
WtE	Waste to Energy
XRD	X-ray Diffraction

Nomenclature

Roman symbols

A	Area
C	<i>Cost (USD)</i>
C''	Heat capacitance (J/K·m ²)
C_p	Heat capacity (kJ/kg·K)
c	<i>unit cost</i>
D	distance of material to Utopia point in objective plot
E	<i>Electricity output (kWh or MWh)</i>
f	Function
h	Heat transfer coefficient (W/m ² ·K)
$\dot{H}$	Unit mass enthalpy (kJ/kg)
k	Thermal conductivity (W/m·K)
L	latent heat of fusion (kJ/kg)
l	<i>Length/thickness (m)</i>
m	Mass (kg)
$\dot{m}$	Mass flow rate (kg/s)
Q	Heat flow (W)
T_{mp}	Melting point Temperature (°C)
T	Time (s or min)
R	Thermal resistance (m ² ·K/W)
W	Weight
v	Velocity (m ² /s)
X_{ij}	the value of property “j” possessed by material alternative “i”

ΔT temperature interval of charge/discharge (°C)

Greek symbols

α Thermal diffusivity ([m²/s](#))
 ε Emissivity
 η Efficiency (%)
 μ Dynamic viscosity (N s/m²)
 ρ Density (kg/m³)
 σ Boltzmann constant (m²·kg·s⁻²·K⁻¹)

Subscripts

b Brick
 c Convection heat transfer
 g Flue gas
 i Sections i on the waterwall
 liq Liquidus
 n Total number of sections on the waterwall
 P Pareto point
 p Steel pipe
 pcm PCM-based brick
 r Radiation heat transfer
 s Steam
 sol Solidus
 $trad$ traditional brick
 w Wall
 wi Inner wall (next to steel pipe)
 wo Outer wall (next to flue gas)
 x Direction in cartesian coordinate
 y Direction in cartesian coordinate
 z Direction in cartesian coordinate

Chapter 1.

Introduction

This chapter introduces the main field of interest, Waste-to-Energy plants, including their important role in the circular economy and the technical challenges that limit the efficiency, based on which the main objectives of this thesis are presented. In the last sections of this chapter, there is a brief overview of the thesis structure. At last, the main findings are concluded for a quick understanding of the thesis contribution.

1.1 Problem Statement

1.1.1 Waste-to-Energy plants in circular economy

In 2015, the United Nations Member States adopted a shared blueprint for the future world, and published “The 2030 Agenda for Sustainable Development”, where 17 Sustainable Development Goals (SDGs) were specified [1]. These 17 SDGs, including the 7th SDG (to ensure access to affordable, reliable, sustainable and modern energy to all), and 12th SDG (to ensure sustainable consumption and production patterns), are constantly challenged by the rapid global urbanization which has led to an excessive usage of energy and material resources and a growing concern over huge amount of waste generation. According to the World Bank [2], the Municipal Solid Waste (MSW) generation worldwide is expected to double from 1.3 billion tons in 2010 to approximately 2.2 billion tons in 2025. While presently the OECD countries are responsible for producing nearly half of the world’s waste, the lower-middle income countries are projected to experience a more momentous growing of waste generation due to their accelerating economic development [2].

With respect to the UN Sustainable Development Goals and the rising waste generation issues, the European Commission has initiated a flagship program aiming at transforming Europe into a resource efficient economy [3]. A clear pathway to increase resource production efficiency and to decouple economic growth from resource consumption and environmental impact is established. The concept of a “Circular economy” is identified to be the driving strategy to close the loop of material lifecycle and to keep energy, material and economic value of resources within the economy for as long as it can be. Waste management, comprises a hierarchy of implementation strategies from material recycle to landfill, plays a pivotal role in building towards the circular economy. In this hierarchy, waste recycling is defined as the priority over other options such as Waste-to-Energy (WtE) or landfill. As compared with landfill which requires huge space to dispatch, waste incineration is capable of reducing the solid waste volume up to 90%, making the next step of landfilling much less space consuming. Additionally, being capable of recovering the embedded energy in the waste helps to keep the energy value within the economy as far as possible [4]. A good

example of waste incineration is the WtE plants which recover the energy in the form of power and provide electricity supply to the grid as a primary energy carrier.

Figure 1-1 Number of WtE plants in the major participating countries/regions in year 2012-2015 (Produced based on data source [5–7])

WtE incineration plants have come on the stage since the middle of 20th century. The first batch was introduced primarily for the purpose of reducing the rising waste volume. It was later discovered the huge potential of energy recovery, which fostered the more advanced incinerator designs. It is estimated that 500 kWh/ton of energy from waste can be harvested with an average calorific value of 10 MJ/kg from the MSW [8]. Identified as a renewable energy source, WtE can be used as a primary energy source to offset fossil fuels and achieve carbon mitigation goals [9]. Up till now, there are more than two thousands WtE plants installed in the global scale [6,7,10], which are mostly situated in East Asia, Europe and the US (as shown in Figure 1-1). Despite their least participation in WtE market, Latin America, Africa and other non-OECD countries have the potential to contribute to a five-folds increase of the WtE primary energy share worldwide by 2050, as projected by the World Bank [11,12]. Figure 1-2 illustrates another forecast by Grandview Research Consultancy, which estimated a 34 million USD of the global WtE incineration market revenue in 2024 compared with 20 million USD in 2014, with a prospective 70% increase [12].

Figure 1-2 Global WtE market revenue by thermal incineration from 2014-2024 [13]

(Requested for reproduction)

1.1.2 Challenges to increase the Waste-to-Energy plant efficiency

The promising market outlook has driven WtE incineration industry to continuously investigate necessary measures to increase the plant electrical efficiency, such as adopting advanced combustion control, increasing steam temperature and pressure, and reducing the condenser temperature [4]. Increasing the steam temperature and pressure allows more energy to be recovered in the turbine, thus resulting in a higher electrical efficiency. However, this approach is hindered by two major difficulties in the plant operation, the high temperature corrosion on the ferrous tubes, and the fluctuation of combustion gas.

High temperature corrosion occurs when the heat exchanger metal surfaces are exposed to the high temperature flue gas with a significant concentration of acidic chlorides and sulphates. In MSW, the chlorides come from the gaseous products of the combustion of polyvinyl chloride plastic and food residues, and sulphates are derived from paper products and plastics. Instead of direct corrosion attack from the flue gas, the high temperature corrosion is mostly attributed to the aggressive species (chlorides of alkali metals and heavy metals) deposited on the ferrous surfaces, which triggers a series of chemical reactions and corrodes the surfaces. The degree of corrosion depends on the flue gas composition, the flue gas temperature and the steam temperature. In order to

operate the heat exchangers in a safe condition and avoid the corrosion, the steam temperature and gas temperature are both regulated within certain levels. One common practice is to limit the gas temperature around 350~550 °C and the steam temperature at 250~400 °C in the superheaters (see Figure 1-3(a)). Subsequently, the steam turbine works with limited steam parameters which will constrain the net power efficiency of whole plant.

Figure 1-3 Corrosion diagram of steel surface [14] (Permitted for reproduction)

Another limitation faced by the WtE plants is the temperature fluctuation of the combustion gas. The waste feedstock is characterized with an extensive variation of proximate composition and the energy content. Even with most advanced mixing at the refuse storage bunker before combustion, there still exists the fluctuation in heating characteristics and uneven boiler firing in the combustion chamber [12]. Figure 1-3(b) presents a typical temperature profile of the combustion chamber, extracted from operational data from a WtE plant in Vittore, Italy [15]. The temperature of combustion gas may vary over 70 °C in a span of 10 min. The challenge comes when the fluctuation from the gas side is transferred to the steam generation, which gives undesirable fluctuation in the steam temperature. This will induce complication to the energy recovery system and lead to inefficient operation of steam turbine. The temperature fluctuation of the flue gas is also associated with the corrosion rate of the metal surfaces, which may aggregate by several folds [16,17].

Figure 1-4 Fluctuation of temperature inside of combustion chamber at 2s after secondary air injection in a typical WtE plant in Southern Italy [15] (Permitted for reproduction)

1.2 Objectives of Research

In general, most of the technologies available in the market or in the pilot plant scale are primarily concerned with combating the corrosion issue. The fluctuation arising from the varying waste composition still exists. There still awaits the technology innovation which is able to address both the corrosion and the fluctuation issues simultaneously, and as well enhance the heat transfer of the boiler so as to push the steam parameters to even higher level.

This study seeks to develop and validate a thermal energy storage – based buffering technology to combat the fluctuation and corrosion issues encountered in the Waste-to-Energy plants in order to enhance the plant overall electrical efficiency. The detailed design objectives are summarized as below:

1. This study aims to realize a design prototype of a Phase Change Materials based refractory brick for waterwalls in combustion chamber, including material selection, geometry design, and laboratory scale fabrication of prototype.
2. This prototype shall demonstrate technical advantage of buffering heat fluctuation received from furnace and delivering a smoothed heat flux to the steam flow.
3. This prototype is also expected to deliver a higher heat flux to the steam flow,

providing a higher steam temperature compared with traditional case.

4. The prototype shall fulfill a preliminary goal of safety in operation, meaning that during the cyclic tests involved in the experimental study, it shall withstand the thermal-mechanical stress imposed without major physical defect.

1.3 Overview of Dissertation

With the purpose of realizing this design prototype, the research is carried out encompassing a wide range of topics. The workflow of this thesis study is presented in Figure 1-5. Following the workflow, the workload is broken down into a number of tasks:

- Task 1 is the material study, including assessment and selection of the suitable material candidates, and compatibility test between the candidates.
- Task 2 is the geometry design and modelling/computational analysis of the design with specific focus on the heat transfer process.
- Task 3 is the design and development of the experimental setup for laboratory tests; we shall first fabricate a PCM-heat exchanger of limited size to be tested in a lab-environment.
- Task 4 is the experimental testing of the fabricated sample prototype. The experimental results will be used to validate/correct the numerical model, based on which a second round of geometry optimization is done if necessary.
- Task 6 is the techno-economic study of the PCM technology in WtE applications.

Figure 1-5 Scope and workflow of thesis research

This dissertation is organized as such that each of the chapters focus on one aspect of the prototype development process.

Chapter 1 provides a rationale for the research by introducing the background of Waste-to-Energy plant and discussing the limitation of efficiencies. Then the goals and scope of this research are outlined.

Chapter 2 reviews the literature concerning current technologies available in the Waste-to-Energy market or in pilot stage for overcoming the limitations of plant efficiency. Following the review, this chapter continues to present a comprehensive overview of the phase change materials storage, including their storage mechanism, high temperature materials development, and configuration design. At the end of Chapter 2, a summary is provided to highlight the research gap and the research methodology.

Chapter 3 presents a material assessment methodology developed for the evaluation and selection of the phase change materials and their encapsulation materials. The

detailed algorithm of this methodology is explained with examples demonstrating its validity. In the end, the competent materials used for this thesis are presented as a result of the material assessment.

Chapter 4 introduces a compatibility study performed in the *Laboratory of Processes, Materials and Solar Energy (PROMES)* in Perpignan, France as part of the thesis collaboration. The study involves experimental tests to investigate the thermal-chemical compatibility of the selected materials at high temperature before being used in the real prototype design and fabrication.

Chapter 5 discusses the numerical studies carried out in this research. The first numerical study, using computational fluid dynamics tool, investigates the thermal performance of the initial geometry. With regards to the result, an optimization of the configuration is performed, producing the second geometry. Then, a one-dimensional analysis is used to assess the thermodynamic performance of the optimized geometry.

Chapter 6 introduced the experimental study in detail. First, the laboratory setup of a steam cycle is presented to provide a simulated environment to the test. Second, the design of experiment is provided with different testing scenarios explained. Last, the experimental testing results are elaborated in comparison with the results from numerical study, based on which further improvement on the numerical model and the prototype design is suggested.

Chapter 7 presents a techno-economic evaluation of the new Waste-to-Energy plant with this phase change material-based buffering technology installed. A sensitivity study is performed to assess the payback time and net present value of the plant with two sensitivity parameters, the brick lifetime and the brick cost, in comparison with the traditional brick.

.

Chapter 8 draws together all the results from each chapter and concludes the thesis with an extended discussion on how future work could be performed to further develop this prototype into commercialization.

1.4 Findings and Outcomes

This research leads to several novel outcomes by:

1. Conceptualizing a prototype of using PCMs-based refractory lining on the waterwall of thermal power plants to buffer the heat fluctuation from the furnace combustion, which is the first case in the realm of Waste-to-Energy domain.
2. Developing a comprehensive and systematic material assessment methodology which is applicable to several material selection scenarios, benefitting the scientific and engineering community.
3. Revealing the thermal-chemical corrosion compatibility of aluminium alloys with alumina and three types of recycled ceramics at high temperature, shedding lights on the compatibility considerations of using alumina or recycled ceramics in contact with molten aluminum alloys at high temperature in various applications.

Chapter 2.

Literature Review

This chapter provides the in-depth knowledge and methods related to the thesis work by the literature review. First, as a continuation of Chapter 1 in the discussion of the Waste-to-Energy efficiency limitations, the first section of this chapter reviews the existing technologies in the market trying to overcome the limitations followed by a comparison of all the technologies. The research gap arises in the midst of comparison, thus giving birth to a new concept which could use Phase Change Materials. The second section of this chapter reviews the Phase Change mechanism, the materials in use and the storage designs available. In the end of this chapter, a summary of research gap is presented to bring out the research interests which will be elaborated in detail in the following chapters.

---

*This section published substantial fraction in [18] .

2.1 Existing Technologies to overcome efficiency limitations of Waste-to-Energy plants

Figure 2-1 depicts the layout of the main sections of a typical WtE plant based on the state-of-the art moving grate technology, applied in power plant industry worldwide. The process shown in the figure includes the grate and furnace, the boiler passes and major heat exchangers, steam turbine and generator, cooling unit and main pump.

Figure 2-1 The main components in the steam water loop of a typical Waste-to-Energy plant based on moving grate technology

The waste is fed into the furnace and is combusted while being moved towards the end of the grate. The lower half of the furnace is protected by the refractory lining. The flue gas generated from combustion goes through the first and second boiler passes, the evaporators, superheater(s) and economizer while passing the heat to the water/steam loop. The flue gas is cleaned in the flue gas treatment unit to ensure safe discharge through the stack within the emission limit by local environmental law. The water is evaporated in the evaporators and waterwall heat exchanger (if included in the design) before being superheated to drive steam turbine for electricity generation. After the

turbine section, the condensate will be cooled and cleaned before being sent back to the water/steam loop.

Following the discussion in *Chapter 1* about the corrosion and fluctuation issues faced by the Waste-to-Energy plants, this section reviews the current technologies, from the materials to system layout point of view, used to minimize and protect the ferrous tubes from corrosion attack, so as to further improve the electrical energy efficiency of the incineration plant.

2.1.1 Inconel alloy 625 cladding

In the most corrosion prone area, such as part of the waterwall which is not covered by refractory protection and the superheater area, Inconel alloy 625 cladding on metal surfaces has been suggested as an effective method in preventing corrosion in flue gas [17,19,20]. The main composition of Inconel alloy 625 is 21Cr-9Mo-3.5Nb-Ni base (see Table 2). Overlaying the Inconel alloy cladding will protect the waterwall and superheaters from high corrosion risks. Therefore it allows the installation of a superheater to work at a higher temperature, even in the first gas pass.

The advantages include higher thermal conductivity (around 15 W/m•K at 400 °C [21]) than common refractory material [9], therefore it can be installed in the first gas pass to allow adequate heat transfer while being protective. To replace refractory material with Inconel alloy 625 cladding can reduce the gas temperature, thus protecting the downstream heat exchangers. The main disadvantage of Inconel alloy 625 cladding is the unpredictable lifetime, which is associated with the working temperature of the metal surface on top of which Inconel alloy 625 is overlaid. Some literature has reported that the lifetime of Inconel cladding will be reduced when the sub-layer metal surface works above 420 °C. As a result, it might not be recommended to be used for heat temperature superheater surfaces above 420 °C. Another limitation of Inconel 625 cladding is the cost. The initial cost of Inconel 625 is much higher than the cost of refractory lining. The maintenance cost of Inconel 625 clad superheater bundle unit can increase 40 % compared with a bare superheater bundle unit. Therefore, it is important to make sure the heat exchanger does not work beyond the allowable

temperature level to reduce the possible maintenance cost and to avoid low plant availability caused by maintenance.

Table 2-1 Composition of Inconel Alloy 625

Composition	Percentage
Nickel	58.0 min
Chromium	20.0-23.0
Iron	5.0 max
Molybdenum	8.0-10.0
Niobium (plus Tantalum)	3.15-4.15
Carbon	0.10 max
Manganese	0.50 max
Silicon	0.50 max
Phosphorus	0.015 max
Sulfur	0.015 max
Aluminum	0.40 max
Titanium	0.40 max
Cobalt	1.0 max

The Inconel alloy 625 cladding technology is quite well developed and has been applied in many WtE plants. In 2006, a WtE plant in Hameln, Germany replaced the old stoker/boiler unit from 1977 with a new one, which has Inconel 625 cladding protecting the membrane walls in the first boiler pass above the refractory lining. No significant corrosion has ever been observed in the furnace and the radiation boiler passes since the re-commission of this plant until a case was reported in 2010 [22]. In 2007, a new WtE unit in Amsterdam started commissioning, featuring Inconel alloy 625 cladding on the membrane walls in the furnace. The rate of corrosion was reported as an average of 0.1 mm/year. This allows a lifetime of over 10 years [23]. Another study reported a wastage rate of Inconel 625 to be 1.75 mm/year at metal temperature of 540 °C [24].

2.1.2 HVOF and thermal sprayed coatings

Apart from Inconel 625, many alloys have been developed for corrosion protection at high temperature in harsh boiler conditions, such as Nickel-Chromium Alloys (NiCr) and Nickel Chromium Tungsten Molybdenum Superalloy (Diamalloy 4006). Technologies such as Thermal spray coatings have been used to apply those aforementioned coating materials onto the metal surfaces. Thermal spray coatings include flame, arc, plasma, detonation, high velocity air-fuel (HVOF), high velocity oxy-fuel (HVOF) and cold spray. They are able to produce thick and dense coatings,

and lower the porosity of the metal surface for long term protection against corrosion attack [17].

Fantozzi et al.[25] Investigated the chlorine-induced high temperature corrosion of Inconel 625 coatings applied by different thermal spray techniques, including HVOF, HVAF, arc and cold spray. The coated surfaces were exposed in KCl salt for 168 hours at 550 °C. Results showed that HVOF and arc spray coating samples only underwent superficial corrosion degradation, and that Cold spray and HVAF coatings were subjected to different grades of internal degradation. Another study by Uusitalo et al.[26] did a series of erosion-corrosion tests on different thermal spray coatings. A superheater section of a circulating fluidized bed combustor is used as the test rig at specimen temperature of 550 °C. The test revealed that the nickel-based HVOF coatings performed well, but the carbide containing HVOF coatings and diffusion coatings wore away. Oksa et al.[27] conducted 168 hours of corrosion tests on various kinds of coating materials prepared by two different HVOF techniques at 575 °C and 625 °C. The metal alloys used as the coating materials include Inconel 625, NiCr, Diamalloy 4006 and SHS9172. Two spray methods were tested, carbide jet spray and hybrid diamond jet spray. Results showed that Diamalloy 4006 sprayed with diamond jet and SHS9172 sprayed with carbide jet spray had the best high temperature corrosion properties against molten salt attack. Nickel-based HVOP coatings and Inconel 625 plasma coatings have been used in real plant waterwalls, as well as TiO₂-Al₂O₃/Inconel 625 cement HVOF coatings applied on superheater tubes. Protection for over three years was reported by Lee et al.[17].

Thermal spray coatings have a wide range of applicability due to the fact that they are applicable to various coating and substrate materials. They also offer the damaged substrate another life by applying coating materials, instead of completely replacing it. The cost of thermal spray coatings depends on the methods and the cost of coating materials. Some may require very expensive apparatus, which can result in a high initial set up cost.

2.1.3 Monolithic SiC concrete

Another widely applied method employs monolithic SiC ceramic to protect the furnace walls and superheater pipes. In the Hameln WtE plant in Germany, the new stoker and boiler unit replaced in 2006 used SiC plates to protect the furnace membrane walls and the after burning zone [22]. Cases in which superheaters were protected with SiC concrete were reported in the Naples WtE plant in Italy (see Fig. 4) and the WtE plant in Stuttgart in Germany. With the protection on, the superheaters were able to operate at steam temperature of 500 °C for ten years of lifetime. However, regular inspection and direct repair of cracks on SiC layer should be conducted before the tubes showed signs of corrosion.

Munro and Dapkunas published a comprehensive review of the corrosion characteristics of SiC and concluded that the silica layer formed at the surface of SiC prevented the direct corrosion attack of the substrates by different species [28]. However, the silica layer itself might dissolve in the species, therefore it need replenishment on some occasions.

Figure 2-2 Superheater tubes protected by SiC layer (Reproduced with the permission from original authors [29])

Another investigation by Brossard et al.[30] reported three main failure mechanisms of SiC in WtE plants, including molten salt/slag attack, salt condensation and SiC oxidation. Cracks on tiles were observed after 8000 hours of service. The authors also suggested that reducing the open porosity and modifying the pore size distribution in the material could limit the salt condensation, and thus the failures that might follow.

Figure 2-3 Superheater bundles used in WtE plant in Naples Italy (Photo borrowed with the permission of the original author [22])

2.1.4 Superheater with rear-ventilated tiles

In recent practices to increase the steam parameters, corrosion protected superheaters with rear-ventilated tiles were proposed [29]. As shown in Fig. 5, the wall superheater with rear-ventilated tiles was installed in the WtE plant in Schwandorf in Germany. Another prototype appears in WtE plant in Rosenheim in Germany (see Fig. 6), where a radiant superheater with rear-ventilated tiles was installed in the upper furnace area of the first boiler pass. The tubes are protected against corrosion by the rear-ventilated tiles purged by sealing air and thus having a much longer lifetime. The steam parameters achieved in the Rosenheim WtE plant were 50 bar, 440 to 480 °C.

Figure 2-4 Wall superheater with rear-ventilated tiles (Photo borrowed with the permission of the original author [29])

However, in this technology, the upgraded steam parameter is compensated by increased plant complexity. Additional plant design, process control and operation are required to achieve safe operation of the superheaters.

In particular, since the superheater is placed at the upper furnace area of the first boiler pass, it might face severe working conditions such as varying flue gas temperature due to inhomogeneous composition of the waste in addition to high corrosion risk. Therefore, it is increasingly difficult to regulate the superheater output temperature and ensure the safe operation of superheater [31].

Figure 2-5 Rosenheim WtE plant configuration with radiant superheater (Photo borrowed with the permission of the original author [29])

2.1.5 Prism-shaped body in the first boiler pass

Another solution to the corrosion problem is the Keppel Seghers Boiler Prism [32]. As shown in Fig. 7, it is a prism-shaped component integrated at the exit of the combustion chamber. It contains two internal collectors with nozzles for the injection of secondary combustion air. As such, it ensures an optimised injection of secondary air, resulting in a highly uniform distribution of the flue gas flow in terms of velocity, temperature and oxygen content [33].

Figure 2-6 Prism shaped tubular structure in the first boiler pass (Photo borrowed with the permission of the original author [32])

It has been successfully retrofitted into an existing WtE plant in Netherlands. Adams et al.[34] presented the retrofitted prism design in the WtE plant (400 °C, 100 bar) and analyzed its effectiveness to combat the corrosion phenomenon and improvement of the combustion quality. According to the authors, it was a proven primary measure against high-temperature boiler corrosion, and it leads to higher throughput and higher availability of the waste-to-energy plant, and increased operation time between manual boiler cleanings.

However, the installation of such prism-shaped structure requires a long period of shutdown of the plant, thus resulting in a lower economic benefit which depends upon the total service lifetime.

2.1.6 Comparison of existing technologies

Six technologies were introduced in this section, which aim at dealing with the aforementioned limitations. As concluded in

Table 2-2, one of these technologies directly copes with the corrosion phenomenon by placing a prism-shaped body in the secondary combustion chamber to distribute the air injection. Other technologies such as Inconel alloy cladding, thermal spray coatings and SiC concrete are secondary measures which provide materials solutions to extend the lifespan of ferrous tubes and to reduce the corrosion attack. Other technologies feature retrofitting the plant configuration, such as placing radiant superheater in the first boiler pass with rear-ventilated tiles to employ the radiation heat transfer and enhance the steam parameters.

Table 2-2 Comparison of existing technologies

Technology	Issues to overcome	Superheated steam parameter	Current status of development
Inconel alloy 625 cladding	Corrosion-secondary measure	<420 °C	Commercialized
HVOF and thermal spray coatings	Corrosion-secondary measure	Depends on methods, coating materials and substrates	Commercialized
Monolithic SiC concrete	Corrosion-secondary measure	500 °C 90 bar	Commercialized
Superheater with rear-ventilated tiles	Corrosion secondary measure	440-480 °C 50 bar	Piloted in a few plants
Prism-shaped body in first boiler pass	Corrosion-primary measure	400 °C 100 bar	Piloted in a few plants
PCM-based waterwall	Temperature fluctuation; Corrosion-secondary measure	600 °C 90 bar	Laboratory test

In general, most of the technologies discussed above are primarily concerned with combating the corrosion issue. Even though the prism design to some extent decreases the temperature fluctuation of flue gas, the fluctuation still exists due to the inhomogeneous nature of feedstock. Unlike the corrosion issue which has been addressed by researcher, there is much less improvement in the design to deal with the fluctuation issue. It is commonly addressed by means of advanced mixing of feedstock, proportional–integral–derivative (PID) control or regulating the combustion process. Nonetheless, the fluctuation in steam production cannot be fully avoided even with the

best control system installed [20]. There still awaits the technology innovation which is able to address both the corrosion and the fluctuation issues simultaneously, and as well enhance the heat transfer of the boiler so as to push the steam parameters to even higher levels.

2.2 Phase Change Material Thermal Energy Storage

Latent Heat Thermal Energy Storage (LHTES) systems employ Phase Change Materials (PCMs) to store and release heat by reversible liquid/solid phase transformation [35]. LHTES is believed to be one of the most promising energy storage methods, owing to its high energy storage density and its ability to provide constant temperature output [36,37]. Since 1970s, LHTES has been applied frequently in the metal process industry (high grade waste heat) [38] and food industry (low grade waste heat) [39]. A typical LHTES coupled industrial refrigeration system [40] can charge with excess waste heat from industrial processes, store energy overnight, and discharge it during peak electrical tariff period or for backup application. In the case of middle and low-grade industrial waste heat (boiler exhaust, refrigeration condensates, waste steam, air compressors, bearings and lubricants in industrial processes), very limited applications of LHTES have been observed. This section reviews the phase change phenomenon and materials used for storage purpose and then introduces different types of storage designs and configurations, which provides important background knowledge to guide our design in this thesis.

2.2.1 Phase Change mechanism and material classification

Phase Change Materials (PCMs) are defined as materials which undergo phase transformation when they absorb or release heat while remaining at nearly constant temperature [41]. The heat absorbed increases the vibrant rates of the constituent molecular or atoms of the materials. When the materials lose energy, the molecular or atomic bonds loosen, and the materials transform from solid to liquid or from liquid to gas. The phase transformation cycle is commonly known as the melting-solidification cycle for liquid-solid phase change.

The heat absorbed or released during phase change cycles is called latent heat, which means the heat absorption or releasing does not happen during drastic temperature change, as compared with sensible heat. Figure 2-7 shows the comparison of sensible heat and latent heat during temperature change of materials. Apparently, the latent heat happened during phase change is much greater in capacity than the sensible heat happened during single phases, which makes latent heat an ideal option for Thermal Energy Storage.

Figure 2-7 Comparison of latent heat and sensible heat with the same temperature range

The equation governing sensible heat during temperature change is given as:

$$Q = \int_{T_i}^{T_e} mC_p dT = mC_p(T_e - T_i) \quad \text{Eq 2-1}$$

The equation governing latent heat during same temperature change is given as:

$$\begin{aligned} Q &= \int_{T_i}^{T_m} mC_{p,l} dT + mL + \int_{T_m}^{T_e} mC_{p,s} dT \\ &= m\{C_{p,l}(T_m - T_i) + L + C_{p,s}(T_e - T_m)\} \end{aligned} \quad \text{Eq 2-2}$$

As the value of latent heat is much greater than the sensible heat capacity, latent heat is the dominant parameter to determine the heat absorbed or released in total. Since the

latent heat of PCMs might be utilized for the benefit of heat regulation and management, the PCMs have been studied extensively in the past few decades.

Phase Change Materials can be categorized either by their family groups, or their melting temperature range. As described in Figure 2-8, based on their family groups, PCMs are classified into organic, inorganic, and eutectics. Organic PCMs include paraffin based and non-paraffin PCMs such as fatty acids, sugar alcohol, while inorganic PCMs include salts, salt hydrates and metals. Eutectics are divided into organic-organic, inorganic-inorganic, organic-inorganic combinations, and salt-water solutions. In terms of phase change temperatures as shown in Figure 2-9, salt-water solutions are found to have sub-zero phase change temperatures, while paraffins, fatty acids and salt hydrates have low phase change temperatures (0 to 100 °C) and sugar alcohols, salts and metals have higher phase change temperatures (> 100 °C) [7,13]. In the high temperature range (> 400 °C) appear metals (e.g. aluminium with melting temperature around 660 °C), chlorides (e.g. sodium chloride with the melting temperature of 800 °C [43]), and carbonates and fluorides.

Figure 2-8 Classification of PCMs based on family groups

Figure 2-9 PCM families in the enthalpy-temperature map (Reproduced with permission from the authors [42])

In terms of thermophysical properties, from Figure 2-9, there is a general trend that higher the melting temperature is, higher the latent heat of fusion is [42]. Most organics except for sugar alcohols have comparatively lower latent heat of fusion ($< 200 \text{ kJ/kg}$) than those of inorganics. Most of the time, their densities are less than 1000 kg/m^3 , thermal conductivity lower than $0.4 \text{ W/m}\cdot\text{K}$, but they show good thermal and chemical stability, non-toxicity with little sub-cooling. In contrast, inorganic PCMs exhibit higher latent heat of fusion, density and thermal conductivity. For instance, aluminium-silicon alloy with 88% of aluminium has a high latent heat of fusion around 560 kJ/kg [43]. Some present potential unstable cyclic behaviour such as segregation for salt hydrates, and sometimes high toxicity or chemical instability [42]. Salt hydrates also tend to cause corrosion to metal envelopes [44].

2.2.2 Phase Change Materials in Thermal Energy Storage

PCMs have been discovered and made use of by humans since ancient times, for example, ice storage in ancient Persia for the purpose of space cooling [45]. Modern application of PCMs began with NASA's introduction of PCMs as thermal capacitors to its space projects [46]. Since then, PCMs have been gradually studied and applied as a medium for TES in different occasions. In terms of absorbing thermal fluctuations, the Phase Change Materials (PCMs) undoubtedly offers a good solution, since they are able to absorb and release a large amount of latent heat during the phase change process while remaining at a nearly constant temperature [47]. This attractive characteristic has allowed PCMs to be applied in a wide range of temperature fluctuation scenarios, such as building thermal comfort management [48], temperature regulating for solar photovoltaic [49] and solar thermal panels [50], and electronic thermal management [41,51].

Table 2-3 lists some major researchers who has completed review work with impacts. As can be seen, the history of PCMs study also started from low to high temperature. It was not until recently that high temperatures PCMs have drawn attention to the research community. In the high temperature PCMs range, molten salts in the form of packed-bed or shell and tube storage tanks are quite commercially available solutions to Concentrating Solar Power (CSP) plants [52]. Recently, metal alloys have been drawing researchers' attention because of their competitive storage capacity, high density, and appealing thermal conductivity.

Table 2-3 Some major investigators and their field of interest in PCMs studies

Period	Investigators	PCMs melting temperature range	Purpose of study
1977-2003	NASA [46], Hale [46], Zalba [53]	< 100 °C	Material selection and heat transfer analysis
2004-2010	Sharma [54], Agyenim[55], Haillot [56]	100 ~ 200 °C	Material selection and heat transfer enhancement
2008-now	Kenisarin [57], Nomura [52], Gil [58]	120 ~ 1000 °C	Mid to high temperature materials and applications

To be applied as storage materials, good PCMs candidates should possess desirable thermal, physical, chemical and economical properties, as mentioned in almost every review article. Among those, a few critical properties stand out as the most influential ones. Firstly, the phase change temperature of this material should be within operating temperature range of the system. Secondly, the material should possess high latent heat of fusion and large specific heat, to ensure high storage density of system. Thirdly, the material might also be required to have high thermal conductivity, in order to achieve fast system charge/discharge powers. Lastly, material with large density is favored when the volume reduction is considered during the system design. Besides the above-mentioned merits, the material will be favored if it is at low cost with a high availability. Since none of the PCMs has a perfect property profile, and each application has unique thermal boundaries and operation goals, the good variety of PCMs makes it difficult to select one to match the thermal conditions and requirements in LHTES design.

2.2.3 Storage design and configuration

LHTES systems can be classified into four types according to design configuration [42]:

i) Heat exchanger type, which usually consists of storage tank filled with PCM and internal heat exchanger where the Heat Transfer Fluid (HTF) flows; ii) Direct contact type, in which the HTF is in direct contact with the PCM to eliminating the thermal resistance of the heat exchanger wall (both HTF and PCM are immiscible); iii) Modular type, in which the PCM is macro-encapsulated and located inside of the modules; iv) Slurry type, in which the PCM is microencapsulated and then mixed with HTF to consist of one fluid, thus both transferring and storing the heat.

Table 2-4 describes the pros and cons of different types of storage systems, based on which the configurations are applied in different scenarios.

Among all four types of configurations, the heat exchanger type is one of the most commonly practiced configurations found in LHTES applications. Several heat exchanger designs, including spiral, coil, double pipe, plate, compact and shell and tube heat exchangers, have been proposed and used according to literature [59]. It is also found in literature that shell and tube/concentric double pipe heat exchangers have the highest efficiency with a minimum volume, which means it is the most prominent type of configuration as a LHTES system [60]. A shell and tube heat exchanger is often used in PCM applications, usually with the PCM on the shell side and HTF on the tube side [41].

Figure 2-10 Shell and tube heat exchanger with PCMs filled

Another popular modular geometry LHTES is the packed-bed design. It is widely used in both large scale and domestic scale solar thermal systems. Macro-encapsulated PCMs are closely packed within the tank, where the heat transfer fluid passes through, charging or discharging the heat. The advantages of packed bed design include large heat exchange contact area, and significant cost reduction compared with two-tank design [41].

Table 2-4 Selection of most suitable storage configuration [42,61–63]

Configuration	Illustration	Advantages	Disadvantage	Major applications
Heat exchanger type: Very high power at initial stage due to the fluid filling the heat exchanger which is already at the PCM temperature; High to medium power at later stage depending on the design of the heat exchanger.		Shell and tube/concentric double pipe heat exchangers have the highest efficiency with a minimum volume; High storage density of PCM (up to 95% by volume).		Industrial plants, vehicles and others
Modular type: Very high power at the initial stage due to the fluid filling the heat exchanger, which is already at the PCM temperature. Medium to low power at the later stage depending on the design of the modular system.		Large heat exchange contact area; Volume change and material compatibility can be solved; Easy to scale up and to be customized to the tank size; Can be easily transported and handled.	Highest possible package density is lower than that for the heat exchanger type (about 74% in volume for spherical encapsulation).	Industrial and residential purpose

Slurry type:

High power due to reduced thermal resistance

high power due to more heat being transported per volume of HTF; improved heat transfer; reduced sub-cooling problem of the PCM with the use of proper nucleating agent.

increased storage density compared to pure HTF but less than the other types Space cooling

Direct contact type:

High to medium power

Low thermal resistance; High storage density of PCM (up to 90% by volume); surface area influential to the performance to a great extent.

HTF must be immiscible and of different density from PCMs; An extra pump and heat exchanger are required for the separation of the heat transfer fluid in the storage Solar and residential purpose

Figure 2-11 Configuration of LHTES packed-bed

Literature revealed that the latent heat and specific heat of the PCMs had a higher impact on the charge and discharge power of the system than flowrate of heat transfer fluid (HTF) [64]. Lee et al. [65] found out that the melting process was slowed down by inclusion of convection and conduction through the capsule wall, and that PCM material choice was the primary factor to influence the thermal response of system, followed by capsule material and convection rate. It was found that the inclusion of highly conductive macroscale particles in to the capsules can significantly enhance the solidification rate during discharging. Moreover, the particle fraction plays a more significant role in influencing the solidification rate than the conductivity of particles [66].

In 1978, General Electric proposed a novel design called the rolling cylinder system. The cylinder was filled with sodium sulphate decahydrate. The rotation of the cylinder, which was 3 rpm around its longitudinal axis, was designed to provide just enough stirring to keep the salt in uniform temperature. In order to enhance the solidification process of the material, the engineers inserted a nucleator through one end of the cylinder, which contained the crystals as the nucleation agents. The engineers believed that this rolling cylinder design was able to undermine the sub-cooling of the PCM and enhance the solidification rate [67–69].

In terms of storage design which delivers fast response to buffer instant heat fluctuation, the usual practice is to use a layer of PCMs in between the hot and cold sources. This

design strategy has been commonly adopted in the electronic thermal management and building/space temperature management scenarios. For example, in a review article on the PCMs storage technologies for the building applications [70]. The authors introduced a common building rooftop design with PCM panel layered in between the rooftop slab and concrete slab as shown in Figure 2-12. The PCMs used were chosen based on suitable phase change temperature, 6-7 °C above the ambient air temperature. It was reported that the PCM layered roof was able to substantially reduce the temperature variation of the tested building in Chennai, India by shifting the peak load demand and thus saving much energy on a year-round operational strategy. Using similar concept, Josh and Kim proposed a simple sandwich configuration for thermal management of periodic power dissipation device, which has the PCMs stacked in between the SiC and copper layers. Metallic PCMs with melting temperature in between of 150 to 250 °C were considered. The study also explored different heat transfer enhancement methods. The result showed that the PCM filled diamond channels could reduce the peak temperature by 25 °C at peak heat flux of 18000 W/cm².

Figure 2-12 Schematic design of building roof with PCM panel

Regarding the high temperature PCM based storage above 400 °C, early stage research has been carried out to conceptualize heat exchanger storage designs using aluminium-silicon series alloys as PCMs. Dal Magro et al. [71] has suggested a temperature smoothing device based on Aluminium as PCMs to enhance the energy recovery in the Electric Arc Furnace steelmaking process. Another study used Al-Si12% as a PCM [72] to smoothen the fluctuation from a billet reheating furnace and allows the downstream Organic Rankine Cycle system to operate at a higher capacity factor. A research group

in Australia led by Professor Erich Kisi has recently patented a technology called MGA, miscibility gap alloy, for high temperature thermal storage. One of MGA compound materials is graphite matrix holding aluminium based alloys inside. This graphite-aluminium structure has been investigated in direct-steam and fluid-mediate CSP systems, which offers potential advantage of higher maximum temperature in a short term thermal cycling [73,74]. Several other combinations of MGAs (Cu-Fe, Sn-Al) were previously proposed by the same research group [75,76]. The main concern with this technology is if it is possible to withstand the high corrosive environment inside the combustion chamber, if not safely encapsulated inside the heat exchanger but exposed to the flue gas directly. Otherwise, this concept proves to be a highly novel and interesting reference for our high temperature latent storage design.

The main design concern, or design objective, is thermal performance enhancement, which means reducing the thermal resistance between the heat transfer fluid and PCM, in order to deliver a fast melting rate and solidification rate [41]. Regarding heat transfer enhancement techniques, three general approaches have been proposed in the literature. One approach focuses on material improvements – microencapsulation of PCMs, or the inclusion of micro and/or nanoscale high conductivity material within PCM composites to modify PCM conductivity, for instance, carbon matrix or copper fibre [41][77]. Another approach is enhancement techniques involving system side improvement, including finned heat-sink embedded design, multi-tube design, with the fundamental idea of increasing the convective heat transfer area [59]. An extensive summary of fin configurations can be found in

Table 2-5, based on literature review. The optimal spacing and geometry of fins is usually a trade-off between enhancement of heat transfer rate and the energy storage amount, so customized optimisation of each design case by experimental and numerical studies is necessary. The third approach is employment of multiple PCMs in the storage unit, with PCMs arranged in the decreasing order of their melting points. Literature shows it has been numerically demonstrated that the system has a higher charging power when employing multiple PCMs instead of one [59].

Table 2-5 Summary of heat transfer enhancement techniques in melting and solidification processes

Enhancement objectives	Heat enhancement techniques	Key analysis/results	Observation and recommendations
Melting of noctadecane	Carbon fibre and brushes	Estimation of effective thermal conductivities using the semi-empirical equation from Fukai et al [78]	Heat brush/PCM composite was found to be inferior to the fibre-chip/PCM composite in terms of heat transfer rate of the bulk but the former was found superior to the latter in terms of overall heat transfer rate [78].
Melting of PCM	Straight fins on plate HE	Influence of fin placement; fin numbers and thickness for straight walls on heat transfer rate.	Horizontal fins with vertical heated walls could deliver twice of the heat transfer rate as compared with vertical fins and horizontal heated walls [79]. An optimisation should be performed to obtain the best combination of fin numbers and fin thickness [80] .
Melting of PCM	Spiral twisted fins attached to the inner tube	Influence of fin width on thermal performance	Fins with small width could result in better enhancement of thermal performance [81].
Melting of PCM	Annular fin	Influence of fin number, height, HTF inlet temperature and flow rate on heat transfer rate, energy stored and liquid fraction	Presence of fins did increase heat conduction and heat storage considerably for all ranges of mass flow rate and inlet temperature of HTF. Increasing of fin numbers would increase the heat transfer rate and energy stored at all conditions. However, the maximum enhancement will appear with moderate flow rates and low inlet temperature. Study on similar configuration revealed that increasing the fin height would result in the increasing of the liquid fraction of the PCM at any time during melting [82].
Melting of PCM with HTF of low conductivity	Internal longitudinal fins on HTF side	Influence of finned and unfinned system on melting rate; fin performance at different Reynolds numbers, fin thickness and heights	Finned system increases the melting rate compared with unfinned system, and that fins perform more efficiently at low Reynolds number ($Re=10^4$). Moreover, the melting rate can be increased with increasing thickness, height and thickness of fins [83].

Freezing of 0.36 kg weight $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ [84]	Circular fins	Unfinned tube system: $\frac{q}{Q_{\max}} = 2.39 \times 10^{-2} Fo^{0.765} Ste^{0.528} Re^{0.195}, \quad Re \leq 7000;$ Finned tube system: $\frac{q}{Q_{\max}} = 2.23 \times 10^{-3} Fo^{0.781} Ste^{0.616} Re^{0.503}, \quad Re \geq 7000; [84]$	Radial temperature gradient in the finned tube system is uniformly larger than the unfinned tube system. The axial temperature difference for the finned tube was smaller than for the unfinned tube in the liquid phase.
Solidification of PCM	Longitudinal fins	Parabolic approximation and exponential approximation of temperature profile with fins [85]	Ten fins would be sufficient of PCM with $T_{\text{mp}} = 60^\circ\text{C}$ in an imposed freezing time of 180 min.
Solidification of Paraffin RT 60 and RT 58	fins, rings and bubble agitation	Recommended internal longitudinal fins and testing ring for solidification enhancement and the use of an evacuated tube for melting when using paraffin [86]	Thermal conductivity by employing paraffin with Lessing rings was ten times greater than the thermal conductivity of paraffin.
Solidification of PCM	Aluminium foil attached to the inside of shell and tube HE	The influence of fin numbers, thickness on the solidification rate	The solidification rate was 30 times faster than the speed of the system without fins, and the rate was almost linearly increasing with the increasing of the number of fins. However, even if increasing the fin thickness could increase the rate, further increasing of the thickness beyond a critical value did not bring significant change to the rate increasing [87].
Solidification of PCM	Straight fins on plate HE	The influence of placement of fins (vertical or horizontal) on the heat flux	Higher heat flux was harnessed by system with horizontal fins than by system with vertical fins [79].

2.3 Summary of research gaps and interests

Modern Waste-to-Energy plants face the technical limitations of high temperature corrosion on the metal tubes in heat exchangers, and the temperature fluctuation happening inside the combustion chamber. A combination of these two factors will result in a decreased steam parameter to the turbine and thus a lower overall electrical efficiency. A comprehensive literature review on the existing technologies adopted in the current Waste-to-Energy plants has been performed. Even though great effort has been made in combating the corrosion issues on metal surface, there is limited technology available that could address both the corrosion issues and fluctuation issue at the same time.

The past design using phase change material based thermal energy storage has shed light on resolving the fluctuation issue. Phase Change Materials have the unique advantage of huge latent heat compared with sensible storage materials, which could be made use of to absorb and release heat at a nearly constant temperature. This great benefit has drawn attention among researchers to investigate possibilities to use Latent Heat Thermal Energy Storage, to answer the question of time mismatch between heat source and sink.

The design of LHTES concepts encompasses a wide range of aspects, including material investigations, configuration design of the storage system/device, and system level investigation in terms of storage behaviour in the thermal process. The research gaps for each of these aspects are summarized below.

At the material level, further research shall be dedicated to expand the knowledge in the aspects below.

- A systematic material assessment strategy for PCMs with given boundary conditions and design objectives to choose the best PCM and encapsulation materials.
- Encapsulation and compatibility study of the chosen high temperature PCM with the encapsulation materials.

At the component design level, the focus will be:

- Optimisation of the storage configuration concerning storage density, the charging/discharging power, and cycle stability.

At the system level, the main concern will be:

- Successful laboratory demonstration and scaling up to be applied to different high temperature scenarios.
- Techno-economic evaluation of storage applications.

Being aware of the research trend, the thesis focuses on those aforementioned research gaps with the purpose of using PCMs based storage to increase the electrical efficiency in Waste to Energy plants.

Chapter 3.

Material Assessment Methodology

This chapter proposes a comprehensive and systematic methodology of Phase Change Material assessment for Latent Heat Thermal Energy Storage design, which comprises pre-screening, ranking and performance objective examination based on Multi-Criteria Decision Making tools. A good agreement observed between assessment results and a building thermal comfort simulation result from literature validated the proposed methodology. For the first time, performance assessment of Phase Change Materials with the methodology is carried out in the initial design phase of a Latent Heat Thermal Energy Storage system for a Waste Heat Recovery application in a cogeneration plant. Lastly, a material selection is performed to select the best candidate encapsulation material for the PCM-buffer technology in the Waste-to-Energy application.

---

*This section published substantially as [88].

3.1 Introduction

As introduced in *Chapter 2*, the selection of suitable PCMs and encapsulation materials stand out as the most important step for an optimal performance LHTES. Although PCM has been applied to several cases of solar air conditioning systems, the choice of PCMs has been based upon the melting temperature and latent heat of fusion. There is no systematic and thorough selection study that assesses the performance of existing and alternative materials for solar air conditioning systems. Furthermore, engineers often need to consider a wide set of criteria. Firstly, the phase change temperature of this material should satisfy the operating temperature range of LHTES. Secondly, the PCM should possess high latent heat of fusion and large specific heat, to ensure a high storage density system. Thirdly, the material is required to have high thermal conductivity, in order to achieve high discharge power. Lastly, a material with a large density is favoured when volume reduction is considered in the system design. Besides the above-mentioned merits, the material is favored if it has low cost with a high availability. Since none of the PCMs has a perfect property profile, and each application has unique thermal boundaries and operation goals, the good variety of PCMs makes it difficult to select one to match the thermal conditions and requirements in LHTES design.

Table 3-1 Desirable PCMs properties

Category	Properties	Type
Thermo-physical	Phase change temperature within operating temperature range	Boolean
	High latent heat of fusion	Quantitative
	Large specific heat	Quantitative
	High thermal conductivity	Quantitative
	Congruent melting behavior	Boolean
Kinetic	High nucleation rate	Quantitative/ranking
	Low supercooling	Ranking
	High crystallization rate	Quantitative/ranking
Chemical	Chemical stability	Boolean/ranking
	Complete reversible phase change cycle	Boolean
	Non-corrosive towards containers	Boolean
	Non-toxic and non-hazardous	Boolean
Economical	Cheap price or high availability	Quantitative/ranking

Materials assessment for industrial processes has always been a complicated issue requiring a systematic approach. Ashby et al. [89] proposed selection strategies for

materials and processes in a general point of view, which suggested four steps in the strategy:

- Interpret design requirements into specifications for material and process
- Screen out candidates unable to satisfy the specifications
- Rank the remaining materials and processes and identify their potentials
- Search for supporting information about the top-ranked candidates

Besides the general procedure, it is clearly indicated in literature that software algorithms and codes are demanded to assess PCM choices [42], and examine the match between material properties and application thermal requirements. Ashby's general strategy was adapted into Sensible Thermal Energy Storage (STES) material assessment which employed Multi-Objective Decision Making (MODM) to reach a compromise between conflicting objectives, such as minimizing cost and maximizing storage density [90]. This method was further practiced to examine the candidacy of recycled materials in STES [91], and to choose STES material for low-energy buildings [92].

However, for PCMs in LHTES, a comprehensive assessment strategy is still missing. Rathod and Kanzaria [93] adopted two Multi-Attribute Decision Making methods (MADM): Techniques for Order Preference by Similarity to Ideal Solutions (TOPSIS) and Analytical Hierarchy Process (AHP) to evaluate PCMs in solar hot water application, without clear evidence of validation. Similarly, another MADM tool multi-criteria optimization and compromise solution (VIKOR, acronym from the original Serbian: ViseKriterijumskaOptimizacija I KompromisnoResenje) was applied to rank low temperature PCMs [94], which also lacked further justification. In a Heating, Ventilation and Air-Conditioning (HVAC) application by Rastogi et al. [95], Ashby's approach was combined with the MADM method, by ranking objective functions instead of material properties. The author compared the ranking results with the results obtained from building simulations, and received positive compliance. Contrary to two other studies [93,94], this approach reflected the goals of the system by incorporating objective functions. However, in most real design situations, where the expertise and judgement of the engineers are crucial, subjective weights should be included [96], which Rastogi et al. did not address. If a property of the material chosen can be

enhanced later in the system design process by including additives, the engineer might want to level down the weight of one property over others in the early material selection step. Therefore, a more thorough and practical methodology should be brought out to overcome the shortcomings discussed above.

In this chapter, a comprehensive assessment methodology is proposed to prescreen, rank and evaluate PCMs for LHTES applications, which employs the MADM method in conjunction with the MODM method. It does not only allow for engineer's preference, but also reflects the system design objectives in an explicit manner. The assessment methodology is validated against the experimental results from HVAC case. Then, a detailed demonstration of how this methodology can be applied to a heat recovery process in cogeneration plant is performed, followed by sensitivity analysis to discuss the robustness of the choices. At last, with the purpose of developing a storage-based buffer refractory technology for Waste-to-energy plants, a material screening is performed to choose the best ceramic encapsulation material for Aluminium alloys based on this novel method.

3.2 Proposed Material Assessment Methodology

Figure 3-1 outlines the flowchart of the proposed assessment methodology. First of all, the TES system's requirements and goals are specified during the design process, which determines the assessment goals. Then the goals will be translated into pre-screening constraints which define the most important boundaries of the screening, such as the melting temperature range. The pre-screening step will eliminate the materials from the PCMs database which cannot meet the constraints, producing a list of pre-screened PCMs.

Figure 3-1 Flowchart of material assessment methodology

Multi-Criteria Decision Making (MCDM) is one of the common tools adopted in the search of the best candidate from the available candidate pool [20]. It is a preferable and popular approach as it deals with different and usually conflicting criteria presented in the decision making process. MCDM has been classified into Multi-Attribute Decision Making (MADM) and Multiple Objective Decision Making (MODM). The former approach uses algorithms to rank the material candidates with a matrix made of discrete numbers of attributes. The latter solves a functional relationship comprised of continuous properties by defining system's objectives and thus, reveals the favorable state of the system [97]. The differences between MADM and MODM are listed in Table 3-2.

Table 3-2 Comparison between MADM and MODM [23,25]

An example of a column heading	MADM	MODM
Criteria defined by:	Attributes	Objectives
Objective defined:	Implicitly	Explicitly
Attribute defined:	Explicitly	Implicitly
Constraints defined:	Implicitly	Explicitly
Alternatives defined:	Explicitly	Implicitly
Number of alternatives	Finite (Small)	Infinite (Large)
Decision maker's control	Limited	Significant
Relevant to:	Evaluation/choice	Design/search

There are three aspects that affect the choice of PCMs in the design of a TES system, which are (a) engineer's preferences, (b) material alternatives and attributes, and (c) system's objectives. MADM is employed to analyze the design space with discrete information of attributes and provides a means for engineer to assign subjective weights. It produces a straightforward ranking list. However, the third aspect in the design of a TES system, which is to meet the system's objectives, may not necessarily be achieved simply by using MADM. Thus, MODM uses the second and third aspects to form the objective space and clearly illustrates the performance of the alternatives. However, it does not allow the engineer's preference to be reflected. In order to allow for both the engineer's preferences of attributes and the *performance objectives*, where both the design space and the objective space demand explicit illustration, this section proposes a combined method of both MADM and MODM to run the main assessment step. The subsections below will present the reasoning and supporting computation behind of the proposed methodology in details. The execution of the methodology can be based on any computing tools capable of dealing with matrices, for instance, Microsoft Excel, C language or Python. In this study, Matlab 2013a is employed to run the algorithms step by step.

3.2.1 Pre-screening

Key material properties can be categorized into three types according to Ashby's approach: quantitative, Boolean properties, and rankings. Quantitative properties are described numerically, such as the latent heat of fusion and density. Boolean properties are answered with "Yes" (1) or "No" (0). For example, if the phase change temperature is within the operation temperature range, then the property is revealed as a "YES", or "1". Rankings as an expression of levels appear when no exact numerical numbers are available to describe this property. For example, the rate of sub-cooling can be comparatively indicated as high/medium/low as there is a large variation of published sub-cooling degrees due to their dependence on cooling rates and samples' volumes.

The pre-screening step is performed with qualitative properties, namely, Boolean and rankings. After the selection objectives become clear, key qualitative properties ought to meet certain boundaries. For instance, melting temperature has to fall within a

particular range, and the materials have to provide good congruent melting behavior. In this case, the materials with the melting temperatures not within this range (Boolean description of melting temperature returns a “0”), and materials with incongruent melting behavior (Ranking description of congruency is “low” and “medium”) will be screened out subsequently. The screening conditions follow the most fundamental selection objectives, which might also include particular families of materials, or latent heat of fusion below a certain limit. If different literature resources report different phase change temperatures or latent heat of fusions, the average value shall be taken as a rule of thumb.

3.2.2 Material ranking based on Multi-Attribute Decision Making

In the second step, a detailed assessment procedure is proposed based on Multi-Criteria Decision-Making tools to evaluate the pre-screened material candidates and narrow down the list of choices. Table 3-3 presents the typical MADM performance matrix composed of all alternatives and each attribute, as well as the weights for every attribute. In the context of material selection, alternatives denote material candidates, while attributes refer to the quantitative properties, such as latent heat of fusion, thermal conductivity, and so on. So X_{ij} from the matrix describes the value of property “ j ” possessed by material alternative “ i ”. The weights determine the importance of each attribute relatively to each other, which are assigned by the engineer by a certain technique. Having the matrix available, engineers can thus run through a MADM algorithm to sort out the ranking. In conclusion, it is crucial to apply both proficient weighting technique and ranking technique to achieve valid ranking result.

Table 3-3 MADM performance matrix [100]

	Attribute 1	Attribute 2	...	Attribute n
Material alternative 1	X_{11}	X_{12}	...	X_{1n}
Material alternative 2	X_{21}	X_{22}	...	X_{2n}
...	...	...	...	...
Material alternative m	X_{m1}	X_{m2}	...	X_{mn}
Attribute weights	W_1	W_2	...	W_n

Weights are determined either subjectively or objectively. The representative method belonging to the subjective category is the AHP method. Shannon’s entropy concept,

as an objective method, has been applied in various situations. The comparative study of AHP and Shannon's entropy methods revealed that AHP has better concordance than Shannon's entropy method when applied with the same ranking technique [99]. Moreover, in the context of selection of materials, engineer's preferences should be taken into consideration in most real situations. For example, one or more material properties could be enhanced in a later design stage, indicating that in the selection procedure, the weights for those properties shall be reduced accordingly. Therefore, AHP in subjective weighting is preferable in this study.

Regarding ranking techniques, there are quite a number of well-established MADM methods available. The TOPSIS (Technique for Order Performance by Similarity to Ideal Solution) has been adapted and used for ranking problems for over thirty years, since it was initially brought out by Hwang and Yoon [101]. TOPSIS ranks alternatives based on their distances to the positive and negative ideal solution. The best alternative solution can be determined by presenting the closest distance to the positive ideal solution and the farthest distance to the negative ideal solution [102]. Literatures reveal that TOPSIS has a good agreement with practical observations [103,104], and that the combination of TOPSIS and AHP is able to provide the closer results to real decisions made, compared with other MADM methods [99]. Therefore, this study adopts AHP and TOPSIS for weighting and ranking procedures respectively. The main steps of AHP and TOPSIS methods are summarized in the Appendices.

3.2.3 Examining performance objectives with Multi-Objective Decision Making

In the MADM procedure the candidates are ranked according to their overall performance of each independent property. Nonetheless, whether the collective effect of all properties necessarily produces good output in the system is not explicitly illustrated in the MADM procedure. Thus, the objective functions of Ashby's approach are considered to examine whether the *performance objectives* are in good agreement with the ranking goal.

Examples of *performance objectives* of thermal storage include minimizing the cost, maximizing the energy density, decreasing the storage volume, and decreasing thermal inertia. In order to address these *performance objectives*, three objective functions are

built. The first function, denoting the thermal energy stored per unit cost, can be expressed as:

$$f_1 = (L + C_p \cdot \Delta T)/c \quad \text{Eq 3-1}$$

where L (kJ/kg), is the latent heat of fusion, C_p (kJ/(kg·K)) its specific heat capacity, ΔT the temperature interval of charge/discharge, and c the cost per unit kg of material. The thermal energy stored per unit of volume, as the second function, is composed in the same manner:

$$f_2 = (L + C_p \cdot \Delta T) \cdot \rho \quad \text{Eq 3-2}$$

where ρ (kg/m³) is the material density. Furthermore, some applications require the material having low thermal inertia, meaning a good ability to conduct heat within the material, given a certain amount of energy absorbed. Then, the PCM is capable of fast response to thermal fluctuations and providing stabilized thermal output for downstream application. Thermal inertia is generally represented by the material thermal diffusivity, $k/(\rho \cdot C_p)$, where k (W/(m·K)) is the thermal conductivity. However, the denominator of the thermal diffusivity only considers the sensible heat absorbed. By replacing sensible heat capacity C_p with the overall heat capacity of a PCM $(L + C_p \cdot \Delta T)/\Delta T$, the third objective function can be obtained, the phase change material's equivalent thermal diffusivity:

$$f_3 = k \cdot \Delta T / (L + C_p \cdot \Delta T) \cdot \rho \quad \text{Eq 3-3}$$

The optimal result is to find the material with highest performance amongst all necessary objective functions. However, objective functions genuinely aim for different goals, indicating their underlying conflicting nature. Hence the relative performance of material in objective functions can be analysed by plotting the results of two conflicting objective functions in one chart. As both functions are intended to be maximized, the materials with material index lying within the Pareto front of the chart are typically preferred. This MODM procedure with Pareto optimization will be further demonstrated in the following case study.

An initial outcome of this first part of the analysis is that design engineers are able to assess if the material is performing well enough to keep it on the list. If the ranking result aligns with the *performance objectives*, the top ranked materials will be chosen for system design. If they differ from each other, design engineer should check the system goals, repeat the process again from the pre-screening list, while be careful deciding the relative weights of different properties. The loop will continue until a good alignment is confirmed from both the ranking and the performance objective examination. After the main selection process, the top selected materials will be subject to system level assessment. Final choice will be made based on the judgements from all above procedures.

3.3 Case Study - Validation of Methodology

In this section, we apply our methodology to a building HVAC application by Rastogi et al. [95] to validate the methodology with their simulation results. The HVAC system requires the PCM to respond quickly to temperature fluctuation and accommodate a large amount of heat. According to the requirements of the HVAC system, it can be concluded that the goals are selecting materials with high volume energy density and high thermal diffusivity for simulation. Based on these two system requirements, two objective functions were brought out respectively by Rastogi et al., which were called *Figure of Merits*¹ (FOMs). These two FOMs were plotted against each other, and then ranked by TOPSIS with equal weights. Referring to the simulation results provided by Rastogi et al. with PCM Express revealed that the use of PCMs can extend the duration of indoor thermal comfort to a certain extent (% of indoor thermal comfort hours), as shown in the second last column of Table 3-4. In Rastogi's work, only top ranked materials were selected for building simulations. Therefore, four materials on our pre-screened list have simulation results.

Applying our proposed methodology to the case study, pre-screening is first performed based on the list of 35 available materials by setting the thermal conductivity to be at least 0.45 W/m·K and higher. A list of eleven pre-screened materials is selected as shown in Table 3-4. Secondly, relative weights provided in the AHP method (between

---

$$\rho \cdot L \quad k/(\rho \cdot C_p)$$

1 and 9) are fixed and shown in Table 3-5. The final weight is calculated as follows: 0.161, 0.332, 0.091, and 0.417 corresponding to ρ , L , C_p , and k , respectively. With weights obtained, a TOPSIS ranking is thus generated and shown in the last column of Table 3-4.

Table 3-4 List of eleven PCMs after pre-screening, their thermo-physical properties, simulation results and MADM rankings

PCMs	T_{mp} (°C)	ρ (kg/m ³)	L (kJ/kg)	C_p (kJ/kg·K)	k (W/m·K)	Extension of indoor thermal comfort hours by use of PCMs (%)[95]	Ranking by MADM procedure
KF·4H ₂ O	18.5	1455	246	1.62	0.5	-	1
RUBITHERM SP 24 E	24-35	1500	190	2	0.6	18.4	2
RUBITHERM SP 26 E	25-27	1500	190	2	0.6	17.0	3
RUBITHERM SP 25 E2	24-26	1500	180	2	0.6	15.3	4
RUBITHERM SP 21 E	21-23	1500	160	2	0.6	12.4	5
PlusICE PCM S25	25	1530	180	2.2	0.54	-	6
LebastLehmplatte PCM 23(generisch)	22-23	1300	170	1.6	0.45	-	9
PlusICE PCMS23	23	1530	175	2.2	0.54	-	8
savENRG PCM- HS24P	24	1820	185	2.26	0.5	-	10
PlusICE PCMS21	21	1530	170	2.2	0.54	-	11
savENRG PCM- HS22P	23	1540	185	3.05	0.5	-	7

The materials' performance is shown in the objective space with objective functions f_2 and f_3 plotted in Figure 3. Pareto solutions and a *Utopia point* are additional tools used to quantitatively compare the PCMs and thus be able to provide a performance assessment of the PCMs based on their attributes. In Pareto solutions, dominated and non-dominated solutions are differentiated. PCMs ranked No. 6, 8, 9, 11 have both objectives' values worse than some PCMs and thus are referred to as dominated solutions. A Pareto front is then generated with extreme performers No.1 and 5, and non-dominated PCMs No. 2, 3, 4, 7 and 10. Top ranked materials from MADM results

appeared in the Pareto set which indicates a good alignment between MADM and MODM methods.

Table 3-5 Relative weights of four thermo-physical properties

	ρ	L	Cp	k
ρ	1	3	0.5	3
L	0.3333	1	0.333	1
Cp	2	3	1	5
k	0.3333	1	0.2	1

It was observed that PCMs No. 7 and 10 lie on the Pareto front but did not rank highly using the MADM method. In order to quantitatively assess the performance within the Pareto set, a *Utopia point* is set up and its value in the x-axis and y-axis (f_{2u} and f_{3u}) comes from the highest f_2 and f_3 values of all materials considered. Equation 4 is used to calculate the distances of all Pareto optimum materials to the *Utopia point*. Preferences of *performance objectives* are considered in the equation by employing two weights W_{f2} and W_{f3} , based on engineers' choices. In this case study, equal weights are assigned to both objectives. In Figure 3, the distance is indicated by the arrow pointing from a specific material to the Utopia point, with the calculated values displayed beside of the corresponding materials. As shown, material No.2 and 3 have the shortest distance to the Utopia point, followed by PCMs No.4 and 5. PCMs No. 7 and 10 has high and undesirable D_p values which aligns well to their poor ranking by MADM procedure.

$$D_p = W_{f2} \cdot f_{2u}/f_{2p} + W_{f3} \cdot f_{3u}/f_{3p} \quad \text{Eq 3-4}$$

(p = non-dominated material ranking numbers)

Figure 3-2 Performance assessment using objective functions of PCMs in a HVAC case study

Material ranking No.2 (RUBITHERM SP 24 E) is the top performing material in our performance assessment and had demonstrated the best performance by having 18.4% longer indoor thermal comfort duration than the conventional system without PCMs, followed by material No. 3 and 4 [95]. The performance assessment obtained by our proposed methodology is thus comparable to the simulation results and this is a validation of the methodology. This comprehensive methodology conducted at an early selection stage enables an accurate performance assessment of selected PCMs, thus reducing the need of computational resource in numerical simulation.

3.4 Case Study - LHTES in Co-generation Plant

The proposed methodology was next applied to a case study of using LHTES system in WHR applications for cogeneration plant. This case study considers a typical peaking arrangement in a cogeneration power plant using a LHTES system to solve time mismatch between supply of waste heat and demand for electricity produced by an Organic Rankine Cycle (ORC). The storage system charges during off-peak hours with excess flue gas from engine/turbine, and discharges during peak hours to drive the ORC and thus, achieving peak shaving in the power plant [105].[105].

In this case study, PCMs with phase change temperatures between 200 and 350°C are considered, assuming the downstream ORC operates between 100 and 200°C. As the storage system is expected to have daily cyclic frequency, it is regarded as short to mid-

term storage. During periods of sharp peaking power profiles, the PCM in the storage system is expected to have fast response and low thermal inertia to attain high discharge power to run the ORC. Economic considerations necessitate that the installation of a WHR system should have reasonable pay back periods so high energy storage density at low cost is an attractive aspect. Thus, two objective functions, which have been previously described in section 2.3, are adopted in this case study and they are thermal energy stored per unit cost (f_1), and materials' equivalent thermal diffusivity (f_3). A list of commercial materials from PCM Products Ltd. has been pre-screened, with the criterion of a phase change between 200 and 350 °C. Table 6 shows the pre-screened materials, their key attributes and their unit cost per kg. The last column in the same table presents the ranking result calculated by the MADM procedure from highest to lowest rank.

Table 3-6 List of PCMs after pre-screening, their thermo-physical properties and rankings

PCMs	T_{mp} (°C)	ρ (kg/m ³)	L (kJ/kg)	C_p (kJ/kg·K)	k (W/m·K)	C_m (USD/kg)	Ranking by MADM procedure
PlusICE-H280	282	2250	160	1.535	0.527	0.68	1
PlusICE-H290	292	2200	150	1.545	0.533	0.82	2
PlusICE-H300	302	1900	130	1.55	0.537	0.89	3
PlusICE-H285	285	2200	85	1.54	0.53	1.10	4
PlusICE-H305	305	1570	150	1.555	0.541	4.11	5
PlusICE-H335	334	2110	80	1.51	0.553	1.71	6
PlusICE-H325	327	2110	80	1.505	0.549	1.78	7
PlusICE-H320	320	2100	70	1.5	0.545	1.78	8
PlusICE-H230	227	1553	105	1.52	0.518	6.30	9
PlusICE-H250	250	2380	280	1.525	0.521	12.33	10
PlusICE-H255	254	2380	270	1.53	0.524	12.33	11

Figure 3-3 plots the objective functions of the above materials to quantitatively assess the performance of the materials. After identifying the non-dominated materials (PCM No. 6, 8, 9, 10 and 11), the Pareto front is generated with materials ranked No.1, 2, 3, 4, 5, and 7. The top ranked materials reside on the Pareto optimum, which reveals a good alignment with the MADM ranking. Following the methodology, the *Utopia point* is defined and the distances from the Pareto front to the *Utopia point* is calculated for each PCM and is shown on the right of the Pareto front next to the corresponding material. As shown in Figure 4(a), given that same weight has been assigned to both

objectives ($W_{f1} = W_{f3} = 0.5$), material No.3 lies closest to the *Utopia point*, followed closely by No.1 and 2.

Figure 3-3 Performance assessment using objective functions of PCMs in cogeneration application

The weights of objective functions can be varied and as a result, a broad range of probable values of D_p for each PCMs will affect their performance assessment and ranking by the MODM procedure. A sensitivity analysis by applying varied weights to objective functions was conducted. Based on five varied sets of weights ($W_{f1} = \{0.1, 0.3, 0.5, 0.7, 0.9\}$ and $W_{f3} = \{0.9, 0.7, 0.5, 0.3, 0.1\}$), the distance of PCMs from the *Utopia point* is calculated and shown in Figure 3-4. From this sensitivity analysis, additional observations of the performance of PCMs can be inferred. When a heavier weight has been applied to f_1 , material No.1 obtained the best performance judged by lowest D_p that can be possibly achieved. By applying a high weight of 0.9 to f_3 , PCMs No. 4, 5 and 7 can outperform PCM No.3. PCM No.3 appears to remain quite stable in this sensitivity analysis because its proximity to an equal balance between f_1 and f_3 . With a thorough methodology, the performance assessment provides good confidence to recommend PCM No.3 PlusICE-H300 for further simulation study, assuming a preference for equal weights assigned to f_1 and f_3 .

Figure 3-4 Sensitivity study of distances to varying weights

In most cases, assessment of PCMs is based on raw materials instead of encapsulated ones, thus in the case study, raw materials without encapsulation are considered. However, if engineers have the full properties of encapsulated PCMs available, the methodology can also be applied accordingly.

3.5 Case Study - Encapsulated Ceramics for PCM-based Buffering Technology

The selection of supporting ceramic material for PCMs is one of the most important aspects in the design. Ceramic material encapsulating the PCM, is subjected to temperature fluctuation, certain degree of corrosion and thermal stress. Therefore, to reduce thermal resistance the material is expected to conduct the heat promptly. In order to better assess the options without using complicated laboratory tests, the material selection methodology, comprising of ranking and performance objective examination procedures, is applied to assist the selection process.

Ten commercial ceramic materials were selected and four important parameters were ranked with the result listed in Table 3-73-8. The four parameters are critical performance indicators of material service to the system. Young's Modulus measures

the ceramic's elasticity. Thermal expansion rate explains the material's ability to expand under thermal stresses. Thermal conductivity tells how fast the material is capable of passing the heat through, and flexural strength indicates how much stress is needed to cause flexure of the material. In our case, since the ceramic is expected to be able to withstand the temperature fluctuation in the flue gas, as well as the physical expansion that will be caused by the phase change, the ceramic should have low Young's modulus, and high values for the other parameters. Thermal expansion rate of the ceramic material should be as high as possible to match the expansion rate of the PCM alloy to avoid high thermal stress between them.

With the purpose of deciding the weights between these four parameters, a survey was conducted to reflect their relevant weight, based on which the final absolute weight is computed. As shown in Table 3-93-10, Thermal expansion rate is given the highest weight, followed by Young's modulus. Flexure strength and thermal conductivity are perceived as less critical in this case. Since flexure is quite difficult to trigger even under extreme conditions, and the PCM will be the main conduction contributor while the role of the ceramic is reduced.

Table 3-73-8 List of ceramic candidates and their MADM ranking

Ceramics	Young's modulus E (GPa)	Thermal expansion rate CTE ($10^{-6}/^{\circ}\text{C}$)	Thermal conductivity k (W/m·K)	Flexural strength MOR (MPa)	Ranking by MADM procedure
96% Alumina	300	8.2	25	345	1
94% Alumina	300	8.1	18	330	2
99.5% Alumina	375	8.4	35	379	3
Mullite	151	5.4	6	180	4
Aluminium Nitride	330	4.5	160	320	5
Hot Pressed Silicon Nitride	310	3.3	30	830	6
Sintered Reaction Bonded Silicon Nitride	310	3.3	29	689	7
Boron Nitride BO Grade	73.8	3.1	33	113	8
Sialon	288	3	17.5	760	9
Boron Nitride Grade CA	75	0.87	31	60	10

Table 3-93-10 Relative and final weights of four mechanical and thermal properties

	E	CTE	K	MOR
E	1	3	0.5	3
CTE	0.3333	1	0.333	1
K	2	3	1	5
MOR	0.3333	1	0.2	1
Weights	22.57%	56.55%	4.72%	16.16%

The last column of Table 3-73-8 indicates the ranking number of all ten ceramics. Not surprisingly, the alumina family occupies the first three, owing to their high expansion rate, followed by mullite, which has both a favourable Young's modulus and thermal expansion rate. Following the methodology two objective functions need to be defined to reflect the system preferences. In this case it is required that the material has high elasticity (low Young's modulus), and a high thermal expansion rate to accommodate the high thermal stress that might incur. Therefore, we plot the performance of all material candidates on the map of Young's modulus and thermal expansion rate. As can be seen from Figure 3-5, material No.1, 2, 3, 4 and 8 forms the Pareto front line. The Utopia point lies in the up-left corner of the map. Clearly, material No. 4, Mullite, has the shortest distance to Utopia point, given both same amount of credits to Young's modulus and thermal expansion rate. However, in this case, we still value thermal expansion rate more than Young's modulus, therefore material No.1, 96% Alumina will be the final choice.

Figure 3-5 Performance objective examination based on MODM procedure

3.6 Conclusions

This chapter has overcome the shortcoming of existing selection methods by proposing a comprehensive and systematic methodology that includes prescreening of PCMs, ranking by AHP and TOPSIS and followed lastly by a quantitative evaluation of the performance objectives. This comprehensive assessment methodology defines *performance objectives* and pre-screening criteria, and integrates successive complementary Multi-Attribute Decision Making with Multi-Objective Decision Making to ensure the explicit alignment of *performance objectives* with ranking. This study proposes three objective functions, namely f_1 , f_2 and f_3 , in MODM step to interpret the real situations in design process.

In the first case study, we apply our methodology to a building HVAC application from literature to validate our performance assessment methodology against their simulation results. The use of objective functions f_2 and f_3 has been demonstrated in this case study. Results obtained by proposed methodology reveals good agreement with their simulation result, which shows that the top ranking PCMs demonstrates the best performances to prolong indoor thermal comfort hours in a building.

After validation, the methodology is applied to a case study of a Latent Heat Thermal Energy Storage system for Waste Heat Recovery application in a cogeneration plant. The use of objective functions f_1 and f_3 has been demonstrated in this case study. The results from the performance assessment provide good confidence to recommend PCM No.3 PlusICE-H300 for further simulation study.

In order to find the best ceramic encapsulation material for our PCM-based buffering refractory in Waste-to-Energy furnaces, the last case study utilizes this developed methodology to screen and rank 10 commercial ceramics candidates. Four material properties are used as the ranking attributes, which are the thermal expansion rate, Young's modulus, Flexural strength and thermal conductivity. Alumina out-performs all other material in both the ranking and the objective function examination and is our final choice for the design.

In conclusion, this study has proven that the assessment methodology is a thorough and competent tool to effectively evaluate PCMs for various WHR applications. This assessment methodology allows the engineers to evaluate the performances of selected PCMs with minimal computational resources. The results from these case studies can be beneficial to future research required to address the application of LHTES systems in various fields. A further study can be considered on the coupling effect between of materials and system configuration to achieve a state-of-art TES system design procedure.

Chapter 4.

Compatibility of Molten Aluminium Alloys and Potential Encapsulation Ceramics

This chapter investigates the compatibility of these ceramics with three kinds of aluminium-based alloys at high temperature. The ceramics explored include Alumina, Cofalit, blast furnace slags, and coal fly ashes sintered ceramics. The study consists of a steady state thermal treatment of ceramic samples in contact with the three different alloys at 1000°C for 100 hours, and a post instrumental characterization of ceramic samples. Results demonstrate that Alumina has quite excellent compatibility with all three alloys. Cofalit shows chemical stability with Al99% but instability with AlSi5% and AlSi12%. Blast furnace slag presents quite good thermochemical stability towards molten AlSi5% and AlSi12%. Coal fly ashes sintered ceramics are highly interactive towards all three aluminium alloys.

---

*This section published substantially as [106].

4.1 Introduction

In order to facilitate the application of metal alloys as high temperature PCMs, it is crucial to find an encapsulation material that meets the requirements of adequate thermal properties and mechanical strength, availability with low price, and compatibility with metal alloys at operational temperature. Literature has indicated that ceramics could serve as good candidates for encapsulating molten aluminium alloys. A study by R. Fukahori et al. [107] investigated the corrosion behaviour between Al-Si alloys and commercial ceramics. The alloys and ceramics were placed in a tube furnace and underwent thermal treatment at 1000 °C for 100 hours. Then microstructural analysis of the sample surfaces was performed by means of Scanning Electron Microscopy and Energy-Dispersive Spectrometry. The results concluded that Al_2O_3 , AlN and Si_3N_4 showed high corrosion resistance to $\text{AlSi25\%}$ and $\text{Al99.7\%}$. Another study by Yan and Fan [108] reviewed the durability of ceramic materials in molten aluminium alloys. They concluded that besides the aforementioned ceramics, graphite, sialons and aluminosilicate refractories were also characterized as inert in molten aluminium. However, the manufacturing process of commercial high purity ceramics are highly energy intensive and produces a large quantity of waste since it involves multiple stages in which the product is subject to high temperature treatment [109]. The alumina refineries, according to the International Aluminium Institute, have an average total energy consumption of 11.2 GJ/ton [110].

Unlike the high purity ceramics from commercial sources, ceramics recycled from industrial waste contribute to a more sustainable environmental pathway if used as refractory materials. These recycled ceramics are made from industrial wastes such as asbestos containing wastes, steel slags or coal-fired power plant fly ash. Due to the nature of the recycled ceramics, they are usually available in most industrialized areas with much lower cost. Besides being inexpensive, available in large quantity with potential environmental benefit such as low greenhouse gas emission and low embodied energy, the recycled ceramics also present quite good thermo-physical properties and mechanical strength [91,111]. Gutierrez et al. [112] reviewed several industrial wastes from different sources and reported the origin, properties and the current related research work. It is noteworthy that the thermal properties of some recycled ceramics are even comparable with the commercial high purity ones. For instance, recycled ceramics made from asbestos containing wastes, Cofalit, has a density of around 3120 kg/m^3 and heat capacity of 0.8-1.03 $\text{kJ/kg}\cdot\text{K}$. The Fly ash coming from municipal

wastes has a density of around 2900 kg/m^3 and heat capacity ranging from 0.9 to 1.1 kJ/kg·K. The mechanical strength of Cofalit is reported as very stable even after severe thermal cycling operating conditions.

In summary, recycled ceramics demonstrate great advantages of low environmental cost, low capital cost, and reasonably good thermo-mechanical properties as encapsulation materials for high temperature LHTES systems. A number of corrosion studies have been carried out [47,111,113] to examine the compatibility between molten salts and inorganic industrial waste ceramics, for their application in solar thermal storage systems. However, few studies have reported the compatibility behaviour between liquid metal alloys and the inorganic industrial waste ceramics. This research gap limits the application of recycled ceramics as the encapsulation material for high temperature LHTES in which metal alloys serve as phase change materials.

With the purpose of further justifying the feasibility of using alumina and recycled ceramics as shell material for aluminium based alloys, this section investigates the compatibility of three kinds of Al-Si alloys with alumina99% and three different recycled ceramics (Cofalit from asbestos containing waste, blast furnace slag and Coal fly ashes sintered ceramic) regarding their corrosion behaviour under high temperature thermal treatment for a long duration. The study will engage Environmental Scanning Electron Microscopy (ESEM), Energy Dispersive Spectrometry (EDS), and X-ray diffraction (XRD) for post thermal treatment analysis.

4.2 Materials Used in the Study

4.2.1 Aluminium alloys

Metals and metal alloys have greater potential as high temperature PCMs than molten salts since they have higher thermal conductivity, larger latent heat per volume and smaller volume expansion [57]. In particular, aluminium-silicon alloys have been considered as one of the most promising choices for PCM in the high temperature range [114,115] due to their suitable melting temperature, high latent heat of fusion and high thermal conductivity [116]. In this study, the reactivity of three commercial aluminium

alloys with different silicon contents (0-12 wt%) have been investigated; Table 4-1 reports the composition of the examined alloys. Table 4-2 reports the main thermo-physical properties of the aluminium alloys considered. A recent study investigated the thermal reliability of AlSi12.2 eutectic alloy and reported that the melting point, latent heat and thermal conductivity of the alloy sample showed outstanding stability even after 1000 thermal cycles [117], which supports its suitability as a phase change material for TES applications.

Table 4-1 Composition of the studied aluminium alloys (weight %)

Name	Standard Code ER	Al	Si	Fe	Cu	Mn	Mg	Zn	Ti	Others
Al99	1050	Balance	≤ 0.25	≤ 0.4	≤ 0.05	≤ 0.03	≤ 0.03	≤ 0.07	≤ 0.03	≤ 0.25
AlSi5	4043	Balance	4.5-6	≤ 0.8	≤ 0.3	≤ 0.05	≤ 0.05	≤ 0.1	≤ 0.2	≤ 0.15
AlSi12	4047	Balance	11-13	≤ 0.8	≤ 0.3	≤ 0.15	≤ 0.1	≤ 0.2	≤ 0.2	≤ 0.15

Table 4-2 Thermo-physical properties of the studied aluminium alloys (weight %)

Name	Standard Code ER	Melting point (°C)	Latent heat (kJ/kg)	Thermal conductivity (W/m·K)
Al99	1050	657	390	227
AlSi5	4043	573-632	412	163
AlSi12	4047	557	498	160

While being competent in thermos-physical properties, their limited compatibility with encapsulation materials has posed great challenges to their application as high temperature PCMs. In this thesis, this is one of the focuses of investigation.

4.2.2 Alumina 99%

Several past studies showed that alumina has quite high corrosion resistance to aluminium alloys such as Al99.7% and AlSi25% [107,108]. Thus, it is expected to be inert in molten AlSi5% and AlSi12%. In order to confirm its corrosion resistance, this study included an additional group of alumina, which will undergo same thermal treatment as the recycled ceramic samples. If the alumina group confirms the inert behaviour, its conservation of both surface aspect and element composition will serve as a reference for the results obtained from recycled ceramics. The alumina sample used here is standard 99% Alumina purchased from Latech Scientific Supply Pte.Ltd [118].

4.2.3 Recycled ceramics

This study focuses on three kinds of recycled ceramics, namely Asbestos containing waste (Cofalit), blast furnace slags and coal sintered fly ash ceramics. Table 4-3 shows their origins and thermo-mechanical properties.

Table 4-3 Material names, origin of recycled ceramics, and their average values of properties from room temperature to 1000 °C

Material	Sources	ρ (kg/m ³)	C_p (kJ/kg·K)	k (W/m·K)	CTE (10 ⁻⁶ /°C)	Cost (euros/ton)	Ref.
Cofalit	Asbestos containing waste	3120	0.8-1.034	2.1-2.4	8.8	8-10	[119,120]
Blast furnace slags	Metallurgic furnaces	2800	0.7	1-1.5	-	19	[121,122]
Coal fly ashes sintered ceramics	Coal fired power plant	2000	0.735-1.3	1.3-2.1	-	10-1200	[120,123, 124]

Cofalit is a low-cost recycled ceramic industrially produced by a high temperature plasma treatment or microwave heating of asbestos-containing waste, and then moulded and cooled down at a controlled cooling rate. The specific cooling conditions lead to the formation in the ceramic of fine isotropic micro size crystals, which offers high thermochemical properties. The sample used in this compatibility test originates from INERTAM [125]. The composition of Cofalit is mainly calcium magnesium iron alumino-silicate with impurities like Ti, Na etc. Lab testing of the Cofalit obtained proves that this ceramic demonstrates very stable refractory behaviour under thermal cycling between room temperature and 1000 °C [126]. The annual production of Asbestos containing waste in France is around 250,000 ton, of which 2.4% is industrially inertised while the rest goes to landfill [112]. This results in the low cost of Cofalit, around 8-10 euros/ton as reported by Kere [120].

Steel slags are the high temperature by-products of steelmaking. Molten steel slags are removed from the liquid steel by density difference. Then, the molten slags are solidified into recycled ceramics at a controlled cooling rate. Slags are mainly a mixture of metal oxides, with potentially metal sulphides and heavy metals. The European slag

association summarised the main treatment processes for ferrous slags to give rise to difference type of steel slags such as Electrical arc furnace slag, blast furnace slag, and Basic oxygen furnace slag [127]. The slag samples used in this study were blast furnace slags received from Arcelor Mittal [128]. These slags were re-melted and cooled down into plate shape before being prepared and used in the compatibility test. The global production of steel slag annually is about 250 million tonnes, out of which 24% goes to landfill or is stored in steel-making plants [112]. It is suggested that dumping of steel slags requires long term planning due to its nature of being potentially environmental hazardous [112]. The recycling of steel slags as refractory materials can be an alternative solution to dumping, landfill or construction materials for dam, road or other infrastructure. According to a report released by the U.S. Geological Survey the estimated price of steel slag in 2009 was equivalent to 19 euros/ton [122].

Coal fly ash (CFA) come from the gaseous effluents of coal combustion and are collected by electrostatic filters. Their main compounds include SiO_2 , Al_2O_3 , CaO , which make the major contribution to the measured properties of coal fly ashes. CFA ceramic used in this study was obtained from Eco-Tech-Ceram® [124]. They produced the ceramic samples by lab sintering of CFA powders received from the EDF company [129]. The main component of the product ceramic is a well-known refractory material, mullite. There is an average porosity of 20% in the samples. The high production of CFA globally, 750 Mton per year, presents a huge potential for the production of CFA ceramics. However, the price of CFA sintered ceramic depends highly on the local production and sintering methods. It is noteworthy that all recycled ceramics discussed here in this study present quite stable mechanical properties until the melting point around 1100 °C [130].

Utilization of recycled ceramics contributes to a circular and restorative economy because of:

- Less depletion of natural resources;
- Lower cost and thus higher plant economy compared with commercial high purity ceramics;
- Recycled ceramic can be shaped into a particular geometry of optimized heat exchanger, which offers additional value to the materials and a better system

efficiency due to less interface area for transfer if compared with separated heat exchanger and storage material;

- More energy can be saved extracting slag-based ceramics at the outlet of furnaces when slags are still molten; this contributes to fast payback time especially for high temperature applications.

4.3 Methods

The compatibility study follows the methodology of sample preparation, corrosion testing in the tube furnace, and post-corrosion characterization by Environmental Scanning Electron Microscopy, Energy Dispersive Spectrometry and X-ray diffractometer.

4.3.1 Corrosion test

Figure 4-1 shows the materials and testing rig employed in the thermal treatment. The ceramic materials were cut into small rectangular shaped samples with the dimensions $20 \times 20 \times 10$ mm. Then the contact surfaces were polished to ensure flatness. The aluminium alloys were initially available in the shape of bars. In order to increase the contact area with ceramic samples, the bars were compressed into thin plates by hydraulic press. After cleaning by an ultrasonic device, the samples were held in alumina crucibles with aluminium alloy plates placed on top of their upper surface.

Figure 4-1 (a) recycled ceramic samples ($20 \times 20 \times 10$ mm); (b) crucible setup

The corrosion test involves thermal treatment of ceramic samples in contact with different aluminium alloys of thickness from 1 to 2 mm, at 1000°C for 100 hours in an

argon environment. The Nabertherm tube furnace in Figure 4-2(a) provides thermal treatment and an argon environment for the crucibles during the treatment. In order to reduce the thermal gradient in the longitudinal direction, its two sides exposed outside the furnace were covered with high temperature insulation material Superwool 607. The corrosion test was performed in PROMES laboratory in Perpignan France. The ramping and cooling rate of the thermal treatment was strictly controlled as 5°C/second to prevent any thermal shock that could happen inside of the furnace. Since the thermal treatment itself might possibly result in a change of sample properties besides their contacts with alloys, for each of the three recycled ceramics, there is a control sample, which underwent the same thermal treatment without being in contact with the alloys. This is to better analyse the corrosion effect while excluding the influence of thermal treatment.

The post treatment was:

- fine-polishing-off (grain size $\leq 0.1\mu\text{m}$) of the entire aluminium surface to expose the interactive surface topology of the ceramics. The end result of the polishing was similar to one when cutting, but precisely at the level of interaction.
- cutting a cross-section of samples using diamond blade for characterization of deep penetration.

Figure 4-2 (a) schematic representation of furnace setup; (b) furnace used in thermal

Figure 4-3 Post-treatment steps before characterisation with ESEM, EDS and XRD

4.3.2 Post-corrosion characterization with Environmental Scanning Electron Microscopy, Energy Dispersive Spectrometry and X-ray diffractometer

After the thermal treatment, it was quite important to adopt the appropriate post-corrosion characterization method for analysis. Since it was forbidden to open the furnace at high temperature due to safety reasons, the samples could not be separated from the alloy until they were cooled down. However, at room temperature, it was hardly possible to separate the ceramic samples from the alloy without tearing each part due to the high wettability of the alloys on the ceramic sample surfaces. Therefore, the corrosion rate method could not be executed. Eventually, the post-corrosion characterization was determined following the procedure of fine polishing of ceramic samples' surfaces, and cutting cross-sections, Environmental Scanning Electron Microscopy for surface inspection, X-ray energy-dispersive spectrometry to examine element composition of sample surfaces, and X-ray diffractometer to analyse the structural modification.

The Environmental Scanning Electron Microscopy SEM Hitachi 5-4500 was used to examine the surface topology of the upper surfaces of the samples and their cross-section images. For complicated topologies, chemical contrast images were also

examined. The SEM apparatus operates at 15 kV in low vacuum mode. A Noran XEDS (X-ray energy-dispersive spectrometry) detector was also adopted to study the composition of the samples, both globally across the surface and locally to analyse the composition of some specific points. The EDS characterization employs an accelerating voltage of 10kV and a fixed penetration depth of 2 μm for this study. The measurement provides an accuracy of close to 2%.

The X-ray diffractometer analysis was performed at room temperature using a PANalyticalXpert Pro diffractometer ($\text{CuK}\alpha$ radiation, $\lambda = 0.15418 \text{ nm}$). X-ray diffraction measurements of 2θ symmetrical scans were made over an angular range of 10 to 80° . The step size and the time per step were fixed at 0.01° and 20 s, respectively. The X-ray diffraction spectra were recorded and studied using the PANalytical software. The instrumental function was determined using a reference material (SRM 660, lanthanum hexaboride, LaB_6 polycrystalline sample) and could be expressed by a polynomial function. The crystalline phases were identified by comparison of the obtained diffraction patterns with available models of standard references in database provided by the International Centre for Diffraction Data [131].

4.4 Results and Discussions

4.4.1 Interaction of Alumina with aluminium alloys

Previous investigations have reported the inert behaviour of alumina with aluminium alloys such as aluminium and Aluminium-Si25%. However, it is the first time in literature to report alumina's interaction with AlSi5% and AlSi12%. The first visual observation indicates a high wettability of all three alloys on Alumina sample surfaces. Thus, it was necessary to expose the sample surfaces by fine-polishing them before the examination under microscopy. The SEM result, shown in Figure 4-4, demonstrates very minimum surface disturbance on post-contact surfaces. Compared with reference surface, almost all post-contact surfaces remain visually intact and preserve surface aspect such as texture, porosity and colour. Table 4-4 presents the elemental composition of all sample surfaces within a depth of 2 μm . The dominating elements are oxygen and aluminium, corresponding to the content of high purity aluminium

oxide. The composition varies slightly within the uncertainty range of EDS (2%), thus there is no significant deviation of elements' composition between four sample surfaces. The existence of heavy metal Au on sample surfaces of alumina/AlSi5% and alumina/AlSi12% is due to the necessary pre-conditioning metallization of the sample surface prior to the scan to increase the conductivity of the samples. Since alumina presents obvious corrosion resistance to all alloys, the XRD analysis does not report the alumina group.

Table 4-4 Chemical compositions of tested Alumina in normalized weight percentage

	Reference alumina	Alumina/Al99%	Alumina/AlSi5%	Alumina/AlSi12%
O	31.86	31.42	32.58	32.05
Al	68.14	68.58	65.99	66.19
Ca	0	0	0	0.53
Fe	0	0	0.74	0
Au	0	0	0.69	1.24

Figure 4-4 Surface topology of Alumina samples (a) reference; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

4.4.2 Interaction of Cofalit with aluminium alloys

The first general visual inspection of sample surfaces after corrosion test reports that all three alloys have very low wettability of the Cofalit surfaces. Figure 4-5 shows the topology view of Cofalit samples under the microscope. Compared with the reference sample, there are surface disturbances observed in all three post-contact samples. Figure 4-5 (b) illustrates very minor changes on Cofalit/Al99% compared with reference Cofalit, while Figure 4-5 (c) and (d) display that there is a significant increase of surface heterogeneity for Cofalit/AlSi5% and Cofalit/AlSi12%. A number of light grey spots are observed on sample Cofalit/AlSi5%, corresponding to locations with high iron concentrations, confirmed by point EDS analysis. Major surface depressions, holes and micro cracks also appear in samples Cofalit/AlSi5% and Cofalit/AlSi12% which were not present before the test. Cross-section view in Figure 4-6 illustrates the same trend. The element composition of all tested Cofalit samples from the EDS results are concluded in Table 4-5. To increase the statistical reliability of data, each composition is a global average of several local measurements. It can be inferred from the results that Cofalit samples contain large amount of silicon and calcium oxides, and other oxides such as aluminium and magnesium oxides. The weight percentage of two main elements, Silicon and Calcium, decreased significantly on Cofalit/AlSi5% and Cofalit/AlSi12%. On the contrary, there is a major increase of iron content in these two groups, corresponding to the light grey spots in the SEM images in Figure 4-5 (refer to Table 4-5). This phenomenon indicates possible surface interaction. If compared with the alumina group, the result given by the Cofalit/Al99% shows quite decent performance in terms of conservation of both surface aspect and elemental composition, while Cofalit/AlSi5% and Cofalit/AlSi12% do not.

Figure 4-5 Surface topology of Cofalit samples (a) reference; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Figure 4-6 Cross-section topology of Cofalit samples: (a) reference; (b) Al99% post-contact ; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Table 4-5 Element compositions of tested Cofalit in normalized weight percentage

Atomic elements	Reference Cofalit	Cofalit/Al99%	Cofalit/AlSi5%	Cofalit/AlSi12%
C	2.05	4.17	0	0
O	25.03	25.81	23.31	17.37
Na	0.75	0.60	3.78	7.21
Mg	2.55	2.43	0	0
Al	4.28	3.79	4.05	3.35

Atomic elements	Reference Cofalit	Cofalit/Al99%	Cofalit/AlSi5%	Cofalit/AlSi12%
Si	21.96	18.74	13.28	10.3
Cl	0	0.25	2.31	3.28
K	0.6	0.51	1.42	0.65
Ca	25.00	23.52	16.83	12.69
Ti	0.38	0.65	1.19	0.83
Fe	17.40	19.52	33.84	44.33

In order to further study the change of micro-structure, the X-ray diffraction patterns for Cofalit group are obtained and presented in Figure 4-7. The results indicate the augite as the main phase, diopside ferroan and clynopyroxene as the other phases. All phases belong to the same family of pyroxene. All signal peaks representing the main phases are similar between samples, except for minor differences in the strength of the peaks. The heights of peaks indicate different phase composition, which is summarised in Table 4-6. In comparison with raw Cofalit, the three post-contact samples have degradations in the diopside phase, resulting a progressively increasing of augite phase. This trend is not obvious for Cofalit/Al99%, but particularly noteworthy for Cofalit/AlSi5% and Cofalit/AlSi12%. A new phase Clynopyroxene appeared in Cofalit/AlSi5%. All the evidence indicates interactions of Al-Si alloys with the sample surface but without modifying the structure.

Figure 4-7 X-ray diffraction patterns of the Cofalit group (Au: Augite; D: Diopside; C; Clynopyroxene)

Table 4-6 Observed phases in all samples from XRD analysis

Sample	Observed phases
Cofalit reference	Augite aluminium (59%) $\text{Ca}(\text{Mg,Al,Fe})\text{Si}_2\text{O}_6$ Diopside ferroan (41%) $\text{Ca}(\text{Mg}_{0.82}\text{Fe}_{0.18})\text{Si}_2\text{O}_6$
Cofalit/Al99%	Augite (58%) $(\text{Mg,Fe,Al,Ti})(\text{Ca,Fe,Na,Mn})(\text{Si,Al})_2\text{O}_6$ Diopside 42% $(\text{Mg}_{0.6}\text{Fe}_{0.2}\text{Al}_{0.2})\text{Ca}(\text{Si}_{1.5}\text{Al}_{0.5})\text{O}_6$
Cofalit/AlSi5%	Augite (86%), clynopyroxene (or calcium iron silicate) (14%)
Cofalit/AlSi12%	Augite (72%) diopside (28%)
Slag reference	Melilite (53%) $(\text{Ca,Na})_2(\text{Mg,Fe,Al})[(\text{Al,Si})\text{SiO}_7]$ wollastonite 1A (47%) CaSiO_3
Slag/Al99%	Melilite (70%) , wollastonite 1A (30%)
Slag/AlSi5%	Melilite (57%) , wollastonite 1A (43%)
Slag/AlSi12%	Melilite (48%) , wollastonite 1A (52%)
CFA reference	Mullite $\text{Al}_{4.52}\text{Si}_{1.48}\text{O}_{9.74}$
CFA/Al99%	Mullite (38%), anorthite(19%) $\alpha\text{-Al}_2\text{O}_3$ (43%)
CFA/AlSi5%	Anorthite (89%) $(\text{Ca}_{0.89}\text{Na}_{0.11})(\text{Al}_{1.89}\text{Si}_{0.11})\text{Si}_2\text{O}_8$, iron oxide (11%) $\text{Fe}_{2.133}\text{O}_{3.2}$
CFA/AlSi12%	Mullite(16.8%), $\alpha\text{-Al}_2\text{O}_3$ (40.6%), anorthite($\text{Ca}_{0.8}\text{Na}_{0.2}\text{AlSi}_{2.23}\text{O}_8$) (42.6%)

Taking into consideration the change of surface aspect, element composition, and the evolution of chemical species, it is safe to conclude that Cofalit underwent insignificant interaction with AlSi99% and thus could be recommended to be used with molten AlSi99% at high temperature. However, there are major interactions of Cofalit with AlSi5% and AlSi12%, and as a result they are not recommended to be the potential encapsulation material for these two alloys. This study only concludes the interaction of materials under the laboratory conditions. Further mechanical testing need to be performed to investigate how much material properties (such as mechanical strength) of Cofalit have changed due to interaction.

4.4.3 Interaction of blast furnace slag with aluminium alloys

First, visual inspection reveals that the alloys have medium wettability of slag sample surfaces. Figure 4-8 presents the surface topology of four slag samples under SEM. As we can see, there is no significant difference between the surface topology of slag/Al99% or slag/AlSi5% compared with the reference sample. However, the sample which had contact with AlSi12% shows more heterogeneity on the surface. In order to check if there was a corroded layer formed at the interface, cross section of slag/AlSi12% is put under examination with results shown in Figure 4-9, in chemical contrast. Compared with the reference sample, the slag which had contact with AlSi12% does not reveal any significant difference at the cross-section. There is no corrosion layer visible. The

white spots observed in Figure 8(d) could be due to attached alloy residue. Table 4-7 displays the element composition of all slag samples from EDS analysis. The main elements detected are oxygen, silicon and calcium, indicating a large amount of silicon and calcium oxides. There are also small amounts of aluminium and iron oxides presented. There are slight deviations in elements composition between post-contact samples and the reference sample. However, the deviations are not statistically significant in the presence of the EDS uncertainty. This result is similar to the result obtained for the alumina group. In both groups, the surfaces did not present noteworthy changes and the elemental compositions are preserved.

Figure 4-8 Surface topography of slag (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Figure 4-9 Cross-section view of slag sample (a) reference in chemical contrast; (b) AlSi12% post-contact in chemical contrast

Table 4-7 Element composition of tested slag samples in normalized weight percentage

Atomic elements	Reference slag	Slag/Al99%	Slag/AlSi5%	Slag/AlSi12%
O	28.85	29.34	27.77	29.16
Mg	5	4.96	3.54	4.26
Al	4.5	5.73	3	5.45
Si	23.76	24.11	26.55	23.79
Ca	32.77	31.37	35.44	33.62
Ti	0.9	0.95	0.79	0.51
Fe	4.23	3.53	2.91	3.22

From the XRD results, two phases are identified in the slag samples: melilite $(\text{Ca,Na})_2(\text{Mg,Fe,Al})[(\text{Al,Si})\text{SiO}_7]$ which crystallizes in the tetragonal system (space group P-421m) and wollastonite 1A- CaSiO_3 in the anortic system with a space group P-1. Figure 4-10 presents similar XRD patterns within the slag group, with minor differences in the peaks heights and areas. From Table 4-6, which concludes the phase composition of each sample identified in XRD, it is observed that there is a major degradation of the wollastonite phase in Slag/Al99% and a corresponding increase of melilite in the same sample, indicating an interaction without change of structure. Slag/AlSi5% and slag/AlSi12% present minor changes of composition compared with the reference sample. This diffusion seems to be related to the viscosity of the alloy, the roughness of the contact surface, the pore size and the wettability (contact angles) of the alloy on the contact surface.

Figure 4-10 X-ray diffraction patterns of the slag group (Me: Melilite; W: Wollastonite)

In general, blast furnace slag presents good thermochemical stability in contact with AlSi5% and AlSi12% due to conserved internal composition and the absence of corroded layer. However, it is not recommended to encapsulate Al99% since major change of phases was detected in the Slag/Al99% sample. Further investigations to be performed, before drawing final conclusions.

4.4.4 Interaction of coal Fly Ashes (CFA) sintered ceramics with aluminium alloys

The first visual inspection of the sample surfaces revealed that the alloys have very high wettability on CFA sintered ceramic. In fact, the alloys seem to have “melted” into the ceramics and form visible corroded layers in the samples. It is quite interesting to see from Figure 4-11 that on all three post-contacted surfaces, porosities were filled up with alloys during the interaction. Further inspection on the sample cross-sections (in Figure 4-12) reveals the substantial change of sample texture if comparing the corroded with non-corroded layers. The corroded layers have compact and dense texture while the non-corroded one has clearly similar porous and arbitrary texture as the reference sample. Further, the thickness of the corroded layers are measured as 0.8-4 mm for CFA/Al99%, 1-1.5 mm for CFA/AlSi5%, and 1.2 mm CFA/AlSi12%. The extreme surface modification shows the opposite result compared with the alumina group. EDS revealed the same phenomenon.

Figure 4-11 Surface topology of CFA sintered ceramic (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

Figure 4-12 Cross-section topology of CFA sintered ceramic sample (a) reference sample; (b) Al99% post-contact; (c) AlSi5% post-contact; (d) AlSi12% post-contact

The global EDS characterization determined the surface composition as presented in Table 4-8. The dominating elements are oxygen, aluminium and silicon, indicating the possible composition of aluminium and silicon oxides. In addition, there might be a small amount of iron and calcium oxides. Compared with the reference sample, there is a substantial increase of Al content, and on the contrary, a decrease of Si and Fe content in all post-contact samples. This can be explained by the infiltration of

aluminium alloy into the porous structure of the samples. However, it is unknown if any structural modification took place. Therefore, the XRD results are obtained to further understand the process.

Table 4-8 Chemical composition of tested CFA sample surfaces in normalized weight percentage

Atomic elements	Reference CFA	CFA/Al99%	CFA/AlSi5%	CFA/AlSi12%
O	32.93	21.78	24.05	25.46
Na	0.06	0	0	0
Mg	0.33	1.91	0	0
Al	15.34	57.55	57.88	62.66
Si	30.94	8.11	12.49	6.08
K	3.74	0	0	0
Ca	5.82	3.58	2.02	4.97
Ti	1.49	2.27	0	0
Fe	9.36	1.32	3.56	0.83

The XRD results show that the main phases in the CFA samples include mullite $\text{Al}_{4.52}\text{Si}_{1.48}\text{O}_{9.74}$, solid solution, which crystallizes in the orthorhombic space group (Pbam), anorthite ($\text{Ca}_{0.49}\text{Na}_{0.11}$) ($\text{Al}_{1.89}\text{Si}_{0.11}$) Si_2O_8 in anorthic (space group P-1) and iron oxide $\text{Fe}_{2.133}\text{O}_{3.2}$ which crystallizes in tetragonal (space group P43212). Mullite is a non-stoichiometric compound with the following formula [132]:

derived from the well-known sillimanite (Al_2SiO_5) structure obtained by substituting aluminium atoms by silicon in tetrahedral sites, creating oxygen vacancies to preserve the electro-neutrality.

The phase compositions of each sample identified in XRD are presented in Table 4-6. Compared with reference CFA sintered ceramic, CFA/Al99% and CFA/AlSi12% reveal the appearance of over 40% of α -alumina phase, with a corresponding decrease in the mullite phase. CFA/AlSi5% has no mullite phase identified, but a majority of anorthite and a small portion of iron oxide. The presence of the α -alumina phase arises from the oxidation of aluminium during cooling, which fills into the porosity of CFA ceramic samples. It was previously studied and reported in [133] the infiltration of

molten aluminium alloys into ceramic structures which results in the creation of a ceramic/aluminium composite. It shows that the infiltration depth is associated with the size of the porosity, the additional agents such as silicon in the molten alloys. The synthesized composite usually presents different mechanical and thermal properties. In our case, there was a structure discontinuity between the infiltrated part and the remaining part of the ceramic sample. The infiltrated part fell apart from the original sample block after the samples cooled down.

Figure 4-13 X-ray diffraction patterns of the CFA/alloys group (M : Mullite ; An : Anorthite ; Fe : Iron oxide ; A : Aluminum oxide)

From the above result, it is observed that apart from mullite and α -alumina phases, certain new phases were generated during the thermal treatment, including anorthite, and iron oxide. The lack of corrosion resistance of CFA ceramic samples is due to the presence of the mullite phase, which exhibits thermodynamic instability in presence of aluminium. The same behaviour was observed in a previous study about mullite in contact with Al–Si alloy [134]. All the evidences from SEM, EDS and XRD confirmed that CFA sintered ceramic is not thermochemically compatible with any of the tested alloys, and it is consequently not recommended for the encapsulation of aluminium alloys in PCM technology.

4.5 Conclusions

Prior to this work, numerous studies have been dedicated to the compatibility between liquid metals and commercial ceramics [107,108,133], and molten salts with inorganic industrial waste ceramics [111,135,136]. Nonetheless, little research has reported the compatibility behaviour between liquid metals and the inorganic industrial waste ceramics. With the purpose of examining the potential application for recycled ceramics as encapsulation materials for molten aluminium alloys, this chapter presents a compatibility study of molten aluminium alloys with recycled ceramics at high temperature. Three industrial waste ceramics, asbestos containing waste (Cofalit), blast furnace slag, and coal fly ashes sintered ceramics were placed in tube furnace in the argon environment for 100 hours at 1000 °C, while being in contact with three Al-based alloys, Al99%, AlSi5% and AlSi12%. A group of alumina samples underwent same treatment to confirm its corrosion resistance and to serve as a reference group for good encapsulation ceramics. The post-characterization with Scanning Electron Microscopy, Energy Dispersive Spectrometry and X-ray diffractometer revealed the following results:

- Alumina presents inert behaviour in contact with all three molten aluminium alloys.
- Cofalit shows a good conservation of the surface aspect and composition in molten Al99%, but undergoes substantial surface reaction with molten AlSi5%

and AlSi12%. Thus, it is recommended to be used in direct contact with molten Al99% but not AlSi5% and AlSi12%.

- Similar to alumina, blast furnace slag has good conservation of both surface aspect and chemical composition with molten AlSi5% and AlSi12%. So it is recommended to be used in direct contact with these two alloys at high temperature.
- Coal fly ash sintered ceramics had major chemical interactions with all three alloys. Therefore, they are not recommended for use in direct contact with these alloys at high temperature.

Judging from the results, Cofalit and blast furnace slag can serve as potential candidates for the encapsulation in PCM-brick technology mentioned in the introduction [14]. However, there exists certain limitations of the conclusions due to the constraint in time and resources in this experimental study, which shall be noted and subject to future investigations and improvement:

1. The post-treatment involved fine polishing of the interface layer to remove the solidified metal alloys and expose the interaction surface. This was performed with caution by the author, but there was still a possibility that the interaction layer was scratched by the fine polishing. So the ESEM scan result of surface topology was analysed as a complementary material to the EDS and XRD results rather than serving to conclude directly.
2. In the preparation of the cross-sections, the samples were cut into halves by diamond blade and put under the microscope directly without fine-polishing. This might have resulted in less profound cross-section presentations and imperfect right angle between top surface and cross-section of samples.
3. Without further mechanical testing, it is difficult to judge if the mechanical strength and other properties of the ceramics have been undermined or maybe even upgraded by the interactions. However, the interactions did indicate a certain portion of metal alloys being consumed during the experiment. Therefore, the author has recommended the suitable ceramics be used as the encapsulation material with a more conservative perspective. In order to fully understand the post-interaction ceramics, more mechanical testing on the strength, expansion rate, etc. shall be conducted to determine if the interacted ceramics are qualified as encapsulation materials or not.

Further from this study, a design-optimization approach could be completed to further justify its applicability as an encapsulation material. First, it is crucial to design the PCM-based refractory brick with encapsulation ceramic made of the proposed recycled ceramics, and conduct stress calculation to see if it is able to withstand the thermal stress due to a significant difference between the expansion rates of ceramics and alloys in the dynamic environment. Second, a design optimization based on the heat transfer analysis of the PCM-brick needs to be performed. Thirdly, it is important to conduct the laboratory testing/prototyping of the PCM brick to examine the long-time cyclic performance in terms of buffering effect, system stability and safety of operation.

Since both Cofalit and blast furnace slag are cheaply produced with low embodied energy, they exhibit great potential to be economically viable alternatives to the commercial ceramics. This work identified their excellent corrosion resistance to molten AlSi5% and AlSi12%, which could further help engineers to establish cheap alternative design solutions to their specific high temperature applications.

Chapter 5.

Configuration Design of the PCMs-based Buffering Technology Based on Numerical Studies

This chapter presents the numerical investigations on different configurations of the PCM-based refractory technology. First, an initial geometry is examined with Computational Fluid Dynamic tools. Since this geometry fails to demonstrate thermal buffering effect, a second geometry is proposed and examined with the Dynamic Thermal Network method. A one-dimensional transient model is constructed with all material compositions represented as thermal resistances and capacitances. Real plant data are extracted from a Waste-to-Energy plant in Southern Italy as the boundary conditions. A 10% of higher energy conversion rate is realized by the new brick technology. Lastly, the study proposes a plant scheme to integrate three types of PCM-based brick into the waterwall. As such, continuous superheating of the steam from 400 °C to 600 °C can be achieved.

---

* A small fraction of this section was published in [137], and substantially in [138].

5.1 Introduction

As previously introduced in *Chapter 1* and *2*, this thesis aims at fulfil a prototype design of a thermal buffer technology which has the potential of increasing the net energy efficiency of Waste to Energy Plants beyond 30%. This will be achieved by a novel approach to store and release the thermal energy generated by the combustion of municipal waste. This novel technology will be able to solve two main technical limitations affecting net electrical efficiency in WtE plants: the limits on steam temperature and steam production fluctuation. The proposed technology is based on Phase Change Materials (PCMs) instead of the usual refractory wall. The proposed technology shall enable the thermal energy from the combustion process to be stored and controlled thus enabling to achieve net electrical efficiencies above 30%, while still maintaining low maintenance costs and high plant availability. Moreover, this technology shall be integrated into the best available plant configurations and combustion control systems [139].

Ideally, this novel PCM-technology would store a variable heat flux coming from a high temperature heat source (i.e. incineration chamber) and release it on demand as a steady heat flux. Therefore, introducing an extra degree of freedom in the heat recovery/management which did not exist before in combustion processes. In fact, the steady heat flux will be used to avoid steam production fluctuation and to increase temperature of superheated steam over current corrosion limits (450 °C) without using coated superheaters.

Figure 5-1 shows an example of how the PCM-based technology can be integrated with a traditional heat recovery boiler in order to avoid steam production fluctuation and to increase steam parameters. This integration includes two heat exchange components: PCM-Evaporator and PCM-Superheater. The PCM-walls store a part of the fluctuating thermal power generated by the waste combustion process. The stored thermal energy is then steadily transferred to the PCM-Superheater for steam temperature increase and to the PCM-evaporator for steam production control. Steam generation into the PCM-evaporator can be easily managed by varying the mass flow rate of the steam control

pump which connects the steam drum to the PCM-evaporator; the generated steam is then used to completely avoid fluctuation in steam production.

Figure 5-1 Integration between PCM-based technology and heat recovery boiler based on steam generation in a WtE plant

The proposed PCM-technology exploits the working principle of thermal energy storage based on latent heat. This kind of heat storage system stores or releases latent heat when a phase change material (PCM) undergoes a phase transition from solid to liquid, or vice versa. The storage and release of heat occurs at the phase transition temperature of the PCM which can be considered to be constant. This technique for heat storage allows designing thermal energy storage systems with a high energy density capable to store heat at high temperature ($>300^{\circ}\text{C}$). There are some major benefits associated with this concept:

- Making use of the significant high latent heat and thermal conductivities of aluminium-alloys, this technology is expected to buffer heat fluctuation from the flue gas and produces a higher and steadier heat flux to the steam than traditional refractory.
- While enhancing the heat transfer, this design allows superheat of the steam flow directly in the secondary combustion chamber.
- Since the superheating will be achieved in the combustion chamber, it will reduce the risks of overheated steam in the traditional superheater unit, thus avoiding the typical corrosion issues.

The PCM-based technology that this project intends to develop is based on aluminium and its eutectic alloys (inorganic) because they offer good thermal properties amongst high temperature PCM [57]:

- High thermal conductivity (solid state > 200 W/mK – liquid state > 90 W/mK);
- High latent heat of fusion ($280 \sim 560$ KJ/kg)
- High melting temperature ($470 \sim 660$ °C)

Section 4.2.1 has a detailed description of the thermal and mechanical properties of the three PCMs chosen. In particular, aluminium99% is the most suitable PCM for steam superheating because it has the highest melting temperature (660°C). The use of aluminium99% as high temperature PCM allows heating the superheated steam up to $550\text{-}600^{\circ}\text{C}$, thus leading to very high efficiency of the WtE plant. On the other hand, for the steam production control, the eutectic alloy Al-12Si is more suitable because of its higher latent heat of fusion (560 KJ/kg) and lower melting point (576 °C).

Apart from suitable thermal properties of the PCMs, selection of encapsulation and their compatibility with the aluminium alloys poses a great challenge to the design process. From the research presented in *Chapter 3* and *4*, high purity alumina has been selected as a potential encapsulation material, and its compatibility with all three aluminium alloys at high temperature has been confirmed experimentally. With the purpose of justifying the thermal buffering concept at this first design stage, this project adopts alumina 99% as the encapsulation material for the PCMs.

In this chapter, the research activity will focus on the geometrical design and a thermal performance study based on two numerical methods. The first numerical method adopted is the computational fluid dynamics (CFD) with Finite Volume Method (FVM). This method was used to study the first proposed geometry in two-dimensional form. Then with the conclusion and implications drawn from that study, the second geometry was proposed and studied using Modelica modelling in one-dimensional form. The heat transfer and thermal buffering effect is examined with different geometrical parameters in a sensitivity study. The numerical studies and their output lay the foundation for the lab prototype and testing that will be explicitly described in the next chapter.

5.2 Numerical Investigation of the Preliminary Design with Finite Volume Method

5.2.1 The first geometry design

The first geometry design is proposed on the basis of the traditional refractory design used to cover the waterwall pipes in the combustion chamber. As shown in Figure 5-2, the new refractory brick design features PCMs encapsulated in the small circular holes inside the ceramic bricks. The new refractory brick is installed on the surface of waterwall, on top of a SiC mortar that is used to further protect the waterwall pipes. The geometrical consideration includes the number of PCM rows and the spacing of PCM holes. A preliminary thermal-mechanical assessment of this geometry is reported by Dal Magro et al.[137], which proposes eight rows of PCM holes with 9mm of center-to-center distance. The detailed geometrical parameters are presented in section 5.2.2.

Figure 5-2 First geometry proposal of the PCM-buffering refractory brick

Figure 5-3 Schematic design of the PCM-integrated WtE plant

Figure 5-3 illustrates the schematic design of the new WtE plants with retrofitted PCM refractory bricks. As shown, the waterwall system in the combustion chamber has been divided into two sections. In the upper section, the waterwall is covered with PCM-evaporator refractory bricks which feature PCMs with phase change temperature around 200-300 °C. In the lower section where the Secondary Combustion Chamber is located, the waterwall is covered with PCM-superheater refractory bricks which feature the aluminium alloys as PCMs for the purpose of superheating the steam further after the traditional superheater (the red block in the post combustion boiler pass). The superheated steam after passing the lower section is directed into the turbine for electrical output.

5.2.2 Numerical methods and boundary conditions

This part of work aims at demonstrating the feasibility of the design in the Finite Element Method (FEM) and Computational Fluid Dynamic (CFD) simulation environment, before the concept is tested in the laboratory setup. Thanks to the Computer Aided Engineering (CAE) laboratory in NTU MAE, the author was able to

get access to a number of numerical software and high-speed computing facilities. The geometry model was constructed in the *Solidworks* modelling complex, and was thereafter simulated in the ANSYS workbench by a specific module of *Transient Thermal* and *Fluent*.

Two different cases, one baseline case featuring the original water wall design and another PCM case featuring the innovative refractory brick technology, are examined and compared under the same boundary conditions. The geometry, materials and boundary conditions are consolidated in the figure and table below. In order to better reflect the fluctuating nature of flue gas temperature, a *user-defined function* (udf) is implemented on the radiation wall in *Fluent* (please refer to Appendix C. for the script).

Figure 5-4 Baseline case geometry and materials (left) top view and (right) side view

Figure 5-5 PCM case geometry and materials (left) top view and (right) side view

Since the entire domain of the *PCM case* includes turbulent flow, heat transfer, and phase change, in the 2D FLUENT simulation, k-epsilon ($k-\epsilon$) turbulence model, heat

transfer model and solidification & melting model are employed for better accuracy. The mesh statistics are shown in Table 5-1 below. To facilitate the turbulent heat transfer process, all pipes including steam pipes and PCM pipes were constructed with a boundary layer mesh.

Table 5-1 Materials and boundary conditions for Baseline case and PCM case

		Baseline case	PCM case
Materials	Refractory bricks	Alumina 90%	Alumina 96%
	PCM	--	Aluminium
	Mortar	Silicon Carbide	
	Steam pipe	Carbon Steel	
Boundary conditions	Steam inlet temperature (°C)	450	
	Steam pressure (bar)	40	
	Steam inlet speed (m/s)	15	
	Flue gas radiation temperature	Fluctuating profile around 950 °C	
Mesh statistics	Element amount	1796	5711
	Average orthogonal value	0.953	0.978

The numerical models used in the simulation are as follows:

Heat conduction dominates the solid region, thus the governing equation for the refractory region, SiC mortar and steam pipe is:

$$\frac{\partial T}{\partial t} = \alpha_i \left(\frac{\partial^2 T}{\partial^2 x} + \frac{\partial^2 T}{\partial^2 y} + \frac{\partial^2 T}{\partial^2 z} \right) \quad \text{Eq 5-1}$$

i denotes the different regions. For the PCM region, even though the viscosity of aluminium is quite high, contributing to a fairly low flow, convection is still considered in the governing equation:

$$\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} = \alpha_{AL,j} \left(\frac{\partial^2 T}{\partial^2 x} + \frac{\partial^2 T}{\partial^2 y} + \frac{\partial^2 T}{\partial^2 z} \right) \quad \text{Eq 5-2}$$

j stands for either liquid or solid phase. At the solid-liquid interface, an energy balance occurs:

$$k_s \frac{\partial T_s}{\partial r} - k_l \frac{\partial T_l}{\partial r} = \rho_{Al,j} L \frac{\partial x_i}{\partial t} \quad \text{Eq 5-3}$$

For the melting process, $\rho_{Al,l}$ is used in the above equation, while for solidification process, $\rho_{Al,s}$ is used. Here it is assumed that phase change only occurs towards the x direction, which is the direction from the flue gas to the steam pipe. The interface moves until the domain reaches single phase, then continues temperature change with Eq 5-2.

For the steam flow temperature, since there is only axial flow (z direction), the governing equation is:

$$\frac{\partial T}{\partial t} + v_z \frac{\partial T}{\partial z} = \alpha_{vapor} \left(\frac{\partial^2 T}{\partial^2 x} + \frac{\partial^2 T}{\partial^2 y} + \frac{\partial^2 T}{\partial^2 z} \right) \quad \text{Eq 5-4}$$

The corresponding governing equation for steam flow and continuity are:

$$\rho \frac{\partial v_z}{\partial t} = -\frac{\partial P}{\partial z} + \mu \left(\frac{\partial^2 v_z}{\partial^2 x} + \frac{\partial^2 v_z}{\partial^2 y} \right) \quad \text{Eq 5-5}$$

$$\frac{\partial v_z}{\partial z} = 0 \quad \text{Eq 5-6}$$

5.2.3 Results and implications

The CFD and FEM simulation demonstrate high feasibility of this technology in terms of buffering heat flow, reducing thermal gradient within ceramics, and delivering much higher heat flux to the steam flow. Figure 5-6 shows the temperature fluctuation of 8 rows of PCM pipes in the direction from radiation wall to the steam pipe (reversed x direction). The melting point temperature of aluminium is also illustrated with the dashed line. As can be seen, all of the rows of PCM pipes successfully experience phase change during the temperature fluctuation. The closer the PCM pipes to the steam pipe, the less fluctuation of temperature they experience.

Figure 5-6 Temperature fluctuation of 8 rows of PCM pipes with time (Row No.1 is the closest to the radiation wall, and row No.8 is the closest to the steam pipe.)

Figure 5-7 Temperature distributions in the refractory bricks of two cases

Figure 5-7 reports the temperature difference across the refractory bricks along the direction from the steam pipe to the radiation wall. Contrary to the baseline case, which experiences over 200 °C of temperature difference across the refractory material, the PCM case reveals a much lower temperature difference of less than 50 °C. The result indicates that the innovative design helps to reduce the thermal gradient to a great extent,

thus mitigating the thermal stress to which the highly brittle refractory materials are exposed.

Figure 5-8 Fluctuation of area-averaged total surface heat flux on steam pipe wall of Baseline case

Figure 5-9 Fluctuation of area-averaged total surface heat flux on steam pipe wall of PCM case

Figure 5-8 and Figure 5-9 illustrate the total surface flux on the steam pipe wall of two cases. The time-averaged value of total surface flux for the PCM case is 22139 W/m², which is almost twice the value of that of Baseline case. It can be concluded that a significant increase of total surface flux is observed by using the innovative technology instead of the baseline design.

Even though the results have shown that the PCM case is able to provide higher thermal output to the steam and lower temperature gradient within the brick, the results reveal that the design is constrained to deliver a thermal buffering effect. In fact, in Figure 5-6, there is quite a big magnitude of temperature fluctuation of rows 1 to 3. Moreover, after 450s, almost all the PCMs are operating above the melting temperature, implying that the latent heat is not being utilized after 450s.

In order to simplify this design-optimization issue and demonstrate the thermal buffering effect, a new geometry with less geometrical parameters shall be considered. Also, another type of simulation method should be adopted to facilitate a more efficient parametric study on the second geometry. The next section will discuss this approach in detail.

5.3 Numerical Investigation of the Second Geometry with One Dimensional Heat Transfer Analysis

5.3.1 Geometry refinement and rethinking the simulation strategy

Even though the PCM-refractory brick is a very promising concept, the proposed geometry in section 5.2 has several limitations which need to be further justified. The small holes in the encapsulating ceramic brick will present a challenge during the manufacturing process, especially when the holes are to be filled up with molten aluminium alloy. Judging from the result of the thermo-fluid dynamic analysis, the first few rows of PCM which are close to the gas side do not operate around the PCM melting temperature and face overheating problems, which means these PCM were not working under the design conditions. Moreover, in the thermo-fluid dynamic analysis, only the temperature distribution within the brick itself was reported. It is not clear whether the PCM-brick will be able to fully buffer the fluctuation from the gas side and deliver a more constant and steadier output to the steam side.

With the purpose of further justifying the feasibility and applicability of the technology, this chapter adopts a parametric study to find the designed operational points of PCM-based refractory bricks. Then, the study focuses on the transient response of PCM-based

refractory brick compared with traditional brick, and analyses the dynamic performance of the two different water-walls when receiving fluctuating boundary conditions. In the end, this chapter proposes a technology integration of three different PCM bricks in the waterwall of the combustion chamber to realise the continuous superheating of steam flow at various temperature stages.

As discussed previously, the geometry used in the previous section ought to be refined both in the geometry design, and designed operational points. Geometry refinement can be achieved by techniques such as computational fluid dynamic (CFD) simulation. In fact, before going into CFD, it is essential to study the concept with a simpler and more universal geometry to prove the feasibility of technology. Therefore, to simplify the issue, this study adopts the one-dimensional analysis, which only considers the thickness of the brick compositions along the direction of the heat flow as the sole geometry parameters. Since the new geometry is under patent application along with this technology, this study only presents the simplified model to illustrate the 1D study.

5.3.2 Numerical methods and boundary conditions

Figure 5-10 illustrates the workflow of this study. First of all, a one dimensional mathematical model is built to describe the thermodynamic process from the gas inside of combustion chamber to the steam flow. The second step is to conduct a parametric study which explores how variables could affect the performance of PCM-bricks, and whether the PCM-brick is operating under the design points or not. Design points are defined as the operational conditions when PCMs inside the brick is undergoing phase change. This is quite a crucial step since if PCM bricks are not operating around the design points, the PCM-bricks show no advantages over traditional bricks other than being better conductive materials, since they cannot make use of their high latent heat to absorb or release heat.

Figure 5-10 Methodology of developing PCM-based superheater wall system

The third step comprises a comparative case study which aims at demonstrating the different performances of traditional waterwall and the proposed PCM waterwall. This chapter suggests three objectives for the novel PCM-based waterwall to achieve:

- When it is operating at the design points, the PCM brick integrated waterwall shall rectify the fluctuation of heat flux received from the gas side in both frequency and magnitude, and produces a smoothed heat flux to the steam.
- The PCM brick integrated waterwall shall provide higher average heat flux in order to superheat the steam.
- The temperature gradient within the PCM brick shall be low to avoid high thermal stress.

The last step of this methodology involves a thorough parametric study by which it proposes three different PCM-based refractory bricks to retrofit into different sections of the waterwall to superheat the steam at different temperature stages. Then the energy saving is calculated to highlight the benefit of the PCM-based refractory brick and the noval waterwall technology.

a. One-dimensional thermodynamic model by Dynamic thermal Network

The thermal Network Method (TNM) is a modelling technique of the heat transfer process analogous to electrical networks. The physical objects in the thermal network are represented as thermal resistors and conductors. Driven by the “voltage”, the temperature

difference, the “current” of the thermal network, the heat flow, travels through the resistances and conductance [140]. TNM is widely used in the analysis of steady-state heat conduction processes to calculate the heat flux and the temperature gradient. This study adopts the Dynamic Thermal Network (DTN) method to analyse the transient response of the waterwall heat transfer process. The DTN is an extension of TNM, which describes boundary temperature and heat flux by time-varying thermal resistances and capacitances. It is capable of dealing with dynamic boundary conditions, making it a good fit for the one-dimensional thermodynamic modelling.

Figure 5-11 Physical model (left) and resistance/capacitance (right) model of (a) traditional water-wall, and (b) PCM-based water-wall

Figure 5-11 presents the physical models (on the left) and the DTN models (on the right) of traditional waterwalls and PCM-based waterwalls. Each of the resistances and capacitances are associated with a physical object, such as the gas, the brick and the pipe. The nodes represent the surface connections between two physical objects. For example, in the model of traditional waterwall, the node b,p represents the surface connection between brick and steel pipe. For each of the nodes, a thermal equilibrium equation can be established. Then with all the resistance and capacitances well-defined, the model is solved numerically using computational tools.

For all the objects in these two waterwalls, the one dimensional transient heat transfer process is governed by:

$$\frac{C''}{l} \cdot \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left(k \cdot \frac{\partial T}{\partial x} \right) \quad \text{Eq 5-7}$$

C'' , l , and k are respectively the thermal capacitance, thickness and thermal conductivity for the object modelled. Thermal resistance is introduced to describe Fourier's law:

$$-kA \cdot \frac{\partial T}{\partial x} \Big|_x = A \cdot \frac{\Delta T}{R} \quad \text{Eq 5-8}$$

where ΔT is the temperature difference between the upstream and downstream nodes of one object. It is calculated continuously at the boundary condition described in section 2.2 and the values of the previous time step. The capacitance and resistance model for each object is introduced below.

Traditional waterwall Heat flow travels from the gas side to the steam side, passing through the gas resistor, the brick resistor, the pipe resistor and the steam convection resistor which generate heat losses and temperature gradient. While passing by the brick and the pipe capacitors, heat is absorbed or released depending on the local temperature level. The thermal equilibrium equations below are established consecutively for node (g,h), node (b,p) and node (p,s):

$$A \cdot \frac{(T_g - T_{g.b})}{R_g} = A \cdot \frac{(T_{g.b} - T_{b.p})}{R_b} \quad \text{Eq 5-9}$$

$$A \cdot \frac{(T_{b.p} - T_{p.s})}{R_p} = A \cdot \frac{(T_{g.b} - T_{b.p})}{R_b} - AC_b'' \cdot \frac{\partial T}{\partial t} \quad \text{Eq 5-10}$$

$$A \cdot \frac{(T_{p.s} - T_s)}{R_s} = A \cdot \frac{(T_{b.p} - T_{p.s})}{R_p} - AC_p'' \cdot \frac{\partial T}{\partial t} \quad \text{Eq 5-11}$$

For the gas to wall heat transfer, both the radiation and convection are considered for better model accuracy. Thus the heat flow from gas to the wall is calculated as:

$$Q_g = Q_{g,r} + Q_{g,c} \quad \text{Eq 5-12}$$

where $Q_{g,r}$ is the radiation heat flow. Here the enclosure grey body radiation model is used. The corresponding thermal resistance is expressed as:

$$R_{g,r} = \left(\sigma \cdot \epsilon_g \cdot \frac{T_g^4 - T_b^4}{T_g - T_b} \right)^{-1} \quad \text{Eq 5-13}$$

And the convective resistance is:

$$R_{g,c} = h_g^{-1} \quad \text{Eq 5-14}$$

So the total thermal resistance R_g can be expressed as:

$$\frac{1}{R_g} = \frac{1}{R_{g,r}} + \frac{1}{R_{g,c}} \quad \text{Eq 5-15}$$

The resistances for the brick, the pipe and the steam respectively are:

$$R_b = \frac{l_b}{k_b} \quad \text{Eq 5-16}$$

$$R_p = \frac{l_p}{k_p} \quad \text{Eq 5-17}$$

$$R_s = h_s^{-1} \quad \text{Eq 5-18}$$

The capacitances for brick and the pipe are:

$$C_b'' = \rho_b \cdot C_{p,b} \cdot l_b \quad \text{Eq 5-19}$$

$$C_p'' = \rho_p \cdot C_{p,p} \cdot l_p \quad \text{Eq 5-20}$$

PCM-based waterwall The thermal equilibrium equations for node (g,wo), (wo, pcm), (pcm, wi), (wi,p), (p,s) are respectively:

$$A \cdot \frac{(T_g - T_{g.wo})}{R_g} = A \cdot \frac{(T_{g.wo} - T_{wo.pcm})}{R_{wo}} \quad \text{Eq 5-21}$$

$$\begin{aligned} A \cdot \frac{(T_{wo.pcm} - T_{pcm.wi})}{R_{pcm}} \\ = A \cdot \frac{(T_{g.wo} - T_{wo.pcm})}{R_{wo}} - AC_{wo}'' \cdot \frac{\partial T}{\partial t} \end{aligned} \quad \text{Eq 5-22}$$

$$\begin{aligned} A \cdot \frac{(T_{pcm.wi} - T_{b,p})}{R_{wi}} \\ = A \cdot \frac{(T_{wo.pcm} - T_{pcm.wi})}{R_{pcm}} - AC_{pcm}'' \cdot \frac{\partial T}{\partial t} \end{aligned} \quad \text{Eq 5-23}$$

$$A \cdot \frac{(T_{b,p} - T_{p.s})}{R_p} = A \cdot \frac{(T_{pcm.wi} - T_{b,p})}{R_{wi}} - AC_{wi}'' \cdot \frac{\partial T}{\partial t} \quad \text{Eq 5-24}$$

$$\begin{aligned} A \cdot \frac{(T_{p.s} - T_s)}{R_s} = A \cdot \frac{(T_{b,p} - T_{p.s})}{R_p} - AC_p'' \\ \cdot \frac{\partial T}{\partial t} \end{aligned} \quad \text{Eq 5-25}$$

In the PCM-based waterwall, the resistances of the gas, the pipe and the steam are the same as in the traditional waterwall. So equations 5, 6, 7 and 9, 10 are used to represent the resistance models. Apart from those, the resistance models for the outerwall of the PCM-based brick, the PCM layer, and the inner wall of the PCM-based brick are:

$$R_{wo} = \frac{l_{wo}}{k_{wo}} \quad \text{Eq 5-26}$$

$$R_{pcm} = \begin{cases} \frac{l_{pcm}}{k_{sol}} & \text{if } T_{pcm} \leq T_{sol} \\ l_{pcm} \cdot \left(k_{sol} + \frac{(T_{pcm} - T_{sol}) \cdot (k_{liq} - k_{sol})}{T_{liq} - T_{sol}} \right)^{-1} & \text{if } T_{sol} < T_{pcm} < T_{liq} \\ \frac{l_{pcm}}{k_{liq}} & \text{if } T_{pcm} \geq T_{liq} \end{cases} \quad \text{Eq 5-27}$$

$$R_{wi} = \frac{l_{wi}}{k_{wi}} \quad \text{Eq 5-28}$$

Respectively, the capacitance of the pipe is the same in the traditional waterwall and the PCM-based waterwall, thus equation 5-12 is also used in the PCM-based waterwall model. The capacitances of outer wall, PCM layer and the inner wall are expressed as:

$$C''_{wo} = \rho_w \cdot C_{p,w} \cdot l_{wo} \quad \text{Eq 5-29}$$

$$C''_{pcm} = \begin{cases} \rho_{pcm} \cdot C_{p,sol} \cdot l_{pcm} & \text{if } T_{pcm} \leq T_{sol} \\ \rho_{pcm} \cdot \frac{L}{T_{liq} - T_{sol}} \cdot l_{pcm} & \text{if } T_{sol} < T_{pcm} < T_{liq} \\ \rho_{pcm} \cdot C_{p,liq} \cdot l_{pcm} & \text{if } T_{pcm} \geq T_{liq} \end{cases} \quad \text{Eq 5-30}$$

$$C''_{wi} = \rho_w \cdot C_{p,w} \cdot l_{wi} \quad \text{Eq 5-31}$$

b. Material properties and boundary conditions

The thermodynamic model is realized with the Modelica language in the Dymola [141] environment. To execute the simulation, the boundary conditions shall be specified. Table 2 shows the material properties and initial values of the design parameters used in the simulation. Design parameters used in the modelling are collected from real cases or reasonably speculated based on literature results.

Table 5-2 Material properties and design parameters of waterwall system

	Parameter	Value	Ref.
Universal	Area depth of 1D study (m)	1	
	temperature at 2s after second air injection ($^{\circ}\text{C}$)	960	[142]
Furnace gas	Gas emissivity (-)	0.3 (0.1-0.5)	
	Gas flow speed (m/s)	1	[15]
	Flue gas pressure (Bar)	1	
Traditional brick	Traditional brick	high alumina 90%	
	Refractory thickness(m)	0.06	[143]
	Refractory conductivity($\text{W/m}\cdot\text{K}$)	16.7	[144]
	Refractory heat capacity(J/kg)	920	[144]
	Refractory density(kg/m^3)	3600	[144]
PCM-based brick outer/inner wall	Wall material	Alumina 99%	[145]
	Thickness (m)	0.005	
	Thermal Conductivity ($\text{W/m}\cdot\text{K}$)	35	[145]
	Specific Heat Capacity ($\text{J/kg}\cdot\text{K}$)	880	[145]
	Density (kg/m^3)	3890	[145]
PCMs	Thickness (m)	0.005	
Steam pipe	Pipe material	Carbon steel	[15]
	Pipe dimension	2 inch (schedule 40)	[146]
	Pipe conductivity ($\text{W/m}\cdot\text{K}$)	59	[146]
	Pipe heat capacity (J/kg)	490	[146]
	Pipe density (kg/m^3)	7690	[146]
Steam	Superheated steam temperature ($^{\circ}\text{C}$)	400	[142]
	Superheated steam pressure (Bar)	42	[142]
	HT transfer coeff. ($\text{W/m}^2\cdot\text{K}$)	250	[9]

A universal area depth of 1 m^2 is adopted in this one dimensional study. The average temperature of combustion gas is around $960 \text{ }^{\circ}\text{C}$ according to the study done by Costa et al. [15] in 2012. The gas emissivity is an unknown property, which is a variable depending on the fuel type and combustion process of the WtE plant. In general, it varies from 0.1 to 0.5. High alumina 90% is a common material choice for the refractory brick material in the incineration process [9], and thus it is assumed to be the traditional refractory brick material. The PCM-based brick uses high alumina 99% to encapsulate the PCM layer. To accommodate the thermal expansion that might cause high thermal stress in the inner and outer wall of PCM brick, the same thickness is proposed for both the inner and outer walls. This design consideration also applies to the parametric study.

The superheated steam temperature and pressure are extracted from the Southern Italy WtE case [15]. An average convective heat transfer coefficient of $250 \text{ W/m}^2\text{K}$ is used for the steam convection in the simulation.

Table 5-2 introduces the material properties of three aluminium based PCMs. Since AlSi12 has the lowest melting temperature range, it is used for the parametric study to find the design points of the first PCM-based brick to buffer the fluctuation of steam flow superheated at temperature 450°C . Then in the following section, the other two PCMs are studied and are proposed to buffer superheated steam at higher temperature.

Figure 5-12 First boundary condition which considers gas temperature fluctuation

There are two types of boundary conditions applied in the study. Figure 5-12 illustrates the fluctuating furnace gas temperature during normal operation. The two-hour long data profile of the fluctuating gas temperature was extracted from furnace monitoring system of a WtE plant in Southern Italy (see Figure 1-4). This boundary condition is used in the parametric study to find the design points for the PCM brick. Figure 5-13 shows another boundary applied to the waterwall, including the start-up temperature ramp and the fluctuation of gas temperature. The second boundary condition is used in the comparative study to examine the different performance of the PCM brick and the traditional brick.

Figure 5-13 Second boundary condition which considers both the start-up ramp and the fluctuation of gas temperature

5.3.3 Results and discussion

a. Parametric study to find the design points

The most important design criterion of the PCM-based brick is to allow the PCM to operate at their melting temperature. Therefore, the parametric study is dedicated to finding the design points of the PCM-brick. Three parameters are examined in the parametric study, including the thickness of the PCM layer and wall layer, the steam temperature, and the emissivity of the combustion gas. Table 5-3 presents five different cases of PCM and encapsulating wall thickness. The thickness ranges from 5 mm to 15 mm. With the consideration of high thermal stress that could happen within the PCM brick due to the high expansion rate of metal, the encapsulation wall thickness is kept no less than the PCM thickness to support the thermal stress. Case A, B and C have the same PCM thickness, while the wall thickness increases. Case C, D and E have the same wall thickness, while the PCM thickness increases. The first boundary condition shown in Figure 5(a) is applied at the gas side.

Table 5-3 Different wall thickness considered in the parametric study

Case	Thickness (mm)	
	PCM	inner and outer wall
A	5	5
B	5	10
C	5	15
D	10	15
E	15	15

Figure 5-14 presents the average temperature of PCM bricks for different cases, while Figure 5-15 illustrates the gas-to-wall heat flow and the steam-convection heat flow in each case. Since different wall thickness will result in different thermal resistance of PCM bricks, it influences the PCM working temperature and the heat delivered to the steam. Ideally the PCM shall work within the melting temperature range (shaded in yellow colour in Figure 6(a)). Case A and E fulfil the requirement. Consequently, the steam-convection heat flow is smoothed. In case B, C and D, the temperature of PCM exceeds the melting range and fluctuates. This leads to fluctuation in heat flow to steam.

Comparing Case A, B and C, it is evident that the thicker the encapsulation wall is, the more likely the PCM will not be at the melting temperature range, since the thicker walls “pushed” the temperature of PCMs off the melting range. For Case C, D and E, when increasing the PCM thickness, it goes back to operate in the melting range and produces smoothed heat flow to the steam. Case C produces the highest and longest fluctuation from 4000s to 8000s, while case D has only a small jump-up around 8000s. PCMs in case A and E operate at the design point, but case E delivers much lower heat to the steam side. This is due to higher thermal resistance with thicker PCM bricks. Based on the principle of reducing the material cost as much as possible, this study adopts case A as the standard design point for the following studies.

Figure 5-14 Average temperature of PCM bricks

Figure 5-15 Gas to wall heat flow and steam convection heat flow for different cases

Besides the thickness of the PCM bricks, other parameters that could lead to the change of operating temperature of the PCM include the emissivity of gas and the steam temperature. A parametric study is performed to correlate the PCM operating temperature with these two parameters. The gas emissivity from 0.1 to 0.4 are considered. As presented in Figure 5-16, the result shows that the higher the gas emissivity is, the higher the PCM temperature is; for the same gas emissivity, the higher the steam temperature is, the higher the PCM temperature is. The yellow shaded area highlights the design points which allow

PCMs to operate at melting temperature range. The points are ($T_s=410$ °C, $\epsilon_g=0.4$), ($T_s=450$ °C, $\epsilon_g=0.3$), ($T_s=490$ °C, $\epsilon_g=0.2$), ($T_s=530$ °C, $\epsilon_g=0.1$).

Figure 5-16 Different steam temperature and corresponding PCMs temperature at different conditions of gas emissivity

b. Comparative case study of traditional waterwall and PCM-based water-wall

The comparative study applies the temperature profiles in the second boundary condition to the gas and steam sides, and compares the transient thermal performance of the traditional and PCM-based brick. Figure 5-17 demonstrates the temperature on the outer and inner wall of traditional brick and PCM-based brick. It is obvious from the result that after 250 min at fluctuating phase, there is a huge difference between the outer and inner wall of the traditional brick, which is about 70 °C. Contrary to the traditional case, the PCM-based brick has a much lower temperature difference between the outer and inner walls, which signifies a much smaller thermal resistance compared with traditional brick. Also the temperature profiles of the PCM brick are much steadier than those of the traditional brick.

Figure 5-17 Outer wall and inner wall temperature at the traditional and PCM bricks

Figure 5-18 Gas to wall heat flow and steam convection heat flow for traditional and PCM-based cases

Figure 5-18 illustrates the corresponding gas-to-wall heat flow and steam-convection heat flow. As can be seen, during the startup phase (0-240 min), the difference in performance between traditional brick and PCM-based brick is very small. After 300 min, during the fluctuation phase, the PCM-based brick delivers a much higher and smoother heat to the steam. The average heat flow to the steam by the PCM-based brick is around 30.7 kW,

while the average heat flow by the traditional brick is 27.8 kW. The PCM case allows a 10% upgrade of energy harvesting on the waterwall.

c. Technology integration with different types of PCM-based brick in furnace waterwall

By the parametric study and the comparative study, it is shown that when working at the proposed design points, the PCM-based brick is capable of smoothing the fluctuation of heat flow, providing higher energy output to the steam while maintaining a low temperature gradient within the brick itself. To provide superheated steam with higher parameters to the inlet of steam turbine, it is necessary to appropriately integrate the PCM-based bricks into the waterwall to achieve continuous superheating of steam from 400 °C to higher parameters. Table 5-4 proposes three different PCM-based bricks to superheat the steam at three temperature levels (450 °C, 500 °C and 545 °C). Each brick contains one type of aluminium alloy from Table 3 which melts at different temperature range. Parametric study has been performed for each of the brick to find its design points. Figure 5-19 and Figure 5-20 show the temperature of outer and inner walls of the three PCM-based bricks, and their heat buffering performance. As shown, all of them are able to buffer the heat flow from the gas side and provide much smoother heat flow to the steam side.

Table 5-4 Type of PCM-based bricks to be applied in the WtE plant and the corresponding designed steam superheating temperature

PCM Brick	PCMs applied	Thickness of PCM layer (mm)	Thickness of wall layers (mm)	Temperature of steam received for further superheating (°C)
1	AlSi12	5	5	450
2	AlSi5	15	15	500
3	Al99	10	10	545

Figure 5-19 Outer wall and inner wall temperature at different bricks

Figure 5-20 Gas to wall heat flow and steam convection heat flow for three different PCM-bricks

Figure 5-21 presents how the PCM-based bricks shall be retrofitted into the WtE plant. As shown, the waterwall of the combustion chamber is divided into two parts. Upper part features lower chamber temperature so that it is used to evaporate water to saturated steam. After the steam is superheated in the convectional superheater, it reaches 400 °C. Then it

goes through the PCM-based superheater on the lower part of the waterwall to be superheated from 400 °C to higher parameters. Three types of PCM-based bricks are installed consecutively from top to the bottom to superheat the steam at 400 °C, 500 °C and 545 °C. An overall steam output of 600 °C is expected to be achieved for the turbine inlet. As such, the WtE plant is upgraded to deliver a much higher electrical efficiency without too much alteration of its original configuration.

Figure 5-21 Technology integration of PCM-based superheater wall in the furnace of WtE plant

5.4 Conclusions

This chapter presents a detailed numerical study of the novel concept of a combustion chamber waterwall featuring Phase Change Materials-based refractory brick to upgrade the thermodynamic efficiency of the energy conversion in the waterwall. The first geometry, which takes the shape from traditional refractory design and adds PCMs filled holes, is examined with Computational Fluid Dynamic tools. Results show that the PCM-based bricks, , allow a higher thermal output and lower temperature gradient within the brick itself compared with baseline refractory. However, this geometry fails to demonstrate a thermal buffering effect due to the reason that most of the PCM bricks are not operating around their melting temperature.

In order to capture the thermal buffering effect of the PCM, a simpler one-dimensional geometry is proposed. The dynamic Thermal Network method is employed to construct a one-dimensional transient model with all material compositions represented as thermal resistances and capacitances. Real plant data are extracted from a Waste-to-Energy plant in Southern Italy as the boundary conditions. This study performed parametric studies to locate the design points where the PCM-based bricks are able to operate around their melting temperature range. Then the study compared the thermal performance of a traditional waterwall and the PCM-based waterwall, and found that the PCM-based waterwall delivers a much higher and smoother heat flux to the steam side, while maintaining a low temperature gradient across the brick itself. A 10% of higher energy conversion rate is realized by the new brick technology. Lastly, the study proposes a plant scheme to integrate three types of PCM-based brick into the waterwall. As such, continuous superheating of the steam from 400 °C to 600 °C can be achieved, while the majority of the original plant configuration is retained. This integration plan sheds light on the system level study with experimental setup which will be discussed in the next chapter.

Chapter 6.

System Design of the PCMs-based Buffering Technology Based on Experimental Study

This chapter describes the experimental study of the PCMs-based technology to further validate the buffering concept in the lab scale. A process of powder injection moulding and inert furnace melting is carried out to fabricate the ceramic encapsulation and PCMs-bricks. Then a lab scale high temperature steam heat exchanging system is built up to replicate the waterwall for the testing of the prototype bricks. Results show that the PCMs –bricks are able to deliver higher heat flux to the steam resulting in higher steam outlet temperature compared with traditional bricks, and when operating under design conditions, PCMs-bricks could reduce the steam temperature fluctuation from a magnitude of 12°C to 2-4°C, enhancing the stability of the steam input to the turbine and reduce the metal corrosion that is aggregated by the fluctuations.

---

*This section published a small fraction in [138].

6.1 Introduction

As a continuation of the PCM-based refractory design for the efficiency enhancement of WtE plants, in previous chapters, the material selection and assessment, compatibilities of the major components of the brick, and numerical performance of the bricks with two rounds of geometry design were investigated. Up till now, all effort has been paid to develop the refractory bricks. There awaits a study that puts all the theories into practice in a physical system and examines how the refractory bricks could help to achieve the design goals in the system level. Therefore, an open-loop steam cycle is realized in the Thermal Energy System Lab of Nanyang Technological University to facilitate this process.

This steamloop is built to provide actual steam in the laboratory for the designed waterwall superheating unit. As a continuation from *Chapter 5*, three different PCM-based refractory bricks were proposed to retrofit into different sections of the waterwall to superheat the steam at different temperature stages. Then, a waterwall heat exchange system was realized inside an electrical furnace that holds steam passing through and the refractory bricks are installed on the steam pipes. This furnace is the key component that will be manipulated to provide fluctuating boundary conditions. The response of the steam temperature at the exit of this heat exchange system is recorded as a result of traditional or PCM-based refractory bricks. The laboratory unit created opportunities for the exploration of the interaction between bricks and the steam cycle, and helped to understand the limitations of the design. There are three objectives of this experimental study:

- To validate the numerical model
- To compare the traditional refractory bricks and the PCM-based refractory bricks in terms of providing higher heat flux, and buffering the thermal fluctuation
- To gather performance feedback from the designed brick prototype that could be used for further optimization

6.2 Methods

6.2.1 Characterisation of feedstocks

Due to the limited temperature range of the DSC measurement available in NTU, the materials were sent to a commercial laboratory to analyse the heat capacity (C_p) up to 1000°C. The various PCMs (Al99, AlSi12 and AlSi5) were concurrently tested. Figure 6-1 shows the heat capacity of the sintered alumina ceramic and PCMs as a function of temperature.

Figure 6-1 Specific heat capacity of (a) alumina ceramic; and the PCM alloys (b) Al99; (c) AlSi12; (d) AlSi5

Previously, it was reported that the measured C_p of the alumina ceramic was found to increase with temperature up to 500°C. Further analysis shows that the C_p of alumina decreased slightly after 600°C. The decrease is not significant and should not affect the

functionality at high temperature. The PCM latent heat and melting point measurements obtained by the laboratory DSC test are shown in Table 6-1 below. It is noted that these results differ from standard, possibly due to variable material composition in the feedstock.

Table 6-1 Melting point and latent heat of the PCMs

PCM alloy	Melting point (°C)	Latent heat (J/g)
Al99	686.9	307.7
AlSi12	604.5	394.2
AlSi5	592.5	328.2

6.2.2 Fabrication of refractory bricks

The fabrication of refractory bricks, illustrated in Figure 6-2, was carried out in collaboration with New Universe and SimTech. New Universe responsible for the supply of the alumina powder feedstock, mold making, and injection molding, whereas SimTech was in charge of the water debinding, thermal debinding and sintering process. After each batch of bricks was fabricated, there was a visual inspection to decide if the brick quality is acceptable and if the recipe needs further modification. Empty bricks without major or mirco cracks were used as a replacement of traditional bricks in the lab test. Then they were disassembled, and sent to be filled with PCM pellets followed up melting of PCMs inside the bricks under inert furnace heating. The brick and mould design and all lab tests were performed in NTU.

Figure 6-2 The brick fabrication process

At the beginning of some trials, major and minor cracks appeared quite often within the samples. After further improvement of the fabrication process of the ceramic bricks, the microcracks were significantly reduced. Firstly, the mould used for the injection of the green parts was slightly modified to reduce the weld lines. Secondly, the water and thermal debinding, followed by sintering stages was refined to achieve a better final prototype with fewer micro cracks.

Figure 6-3 (a) ceramic sample fabricated for mechanical strength test, with major cracks observed; (b) initial brick sample with major cracks at the bottom; (c) slightly improved brick sample with minor cracks at the bottom; (d) final prototype with refined appearance

For the water debinding step, the green parts were soaked in tap water gently stirring up for 3 days. The water was changed twice a day. After which, the green parts underwent thermal debinding. The thermal profile is shown in Table 6-2 below. Finally, the green parts were sintered, according to the temperature profile in Table 6-3.

Table 6-2 Thermal debinding for the fabrication of the ceramic green part

Step	Temperature profile (°C)	Time (min)
1	Room temperature → 80	60
2	Hold at 80	240
3	80 → 145	300
4	Hold at 145	60
5	145 → 155	300
6	155 → 160	300
7	Hold at 160	300
8	160 → 170	450
9	Hold at 170	120
10	170 → 200	360
11	Hold at 200	120
12	200 → 250	300
13	250 → 320	210
14	Hold at 320	180
15	320 → 200	120
16	200 → Room temperature	90

Table 6-3 The optimum sintering profile, as determined by SIMTech

Temperature (°C)	30	600	1100	1500	1630	1500	1200	30
Ramp rate (°C/min)	--	5	5	4	2	3	4	5
Holding time (min)	0	30	60	60	180	0	0	0

6.2.3 Experimental setup

A laboratory scale setup is built to reproduce the waterwall performance, whereby the steam is re-directed to the secondary combustion chamber after being superheated in the traditional superheater.

Figure 6-4 is a schematic diagram of the lab setup. The main components include the steam boiler, superheater, the electric furnace which further superheats the steam, and the condenser. The feed water passes through the water softener and charges the water tank, where the pump draws water from and supplies water to the electric boiler. The steam boiler works in a nearly automated mode and provides continuous saturated steam at a mass flow rate of 40 to 50 kg/h. Then the superheater heats up the saturated steam further to 400 °C which is directed into the simulated waterwall inside the furnace.

There in the furnace, the refractory bricks are installed on the surface of the steam pipes, facing the electric heating elements which provide the radiating heating power. There are four steam pipes inside of the furnace, and each pipe has 13 bricks installed, which contributes to a small-scale waterwall system comprising a total number of 52 bricks. The furnace is customized to produce different temperature ramping profiles with simple programming. The pressure is set to 3 bars due to the pressure limit by the laboratory regulation, and the tradeoff between maintaining steam mass flow rate and high pressure. Investigation on the pressure and mass flow influence on the heat transfer indicates that the pressure has much less influence than the mass flow rate (see Appendix. D for details). So, it was decided to decrease the pressure to 3 bar to keep the mass flow rate at a reasonable high level. After passing through the electric furnace, the superheated steam of 500-600 °C is directed into one air cooled and one water cooled heat exchangers to be cooled below 80 °C for a safe discharge into the ambient. The other detailed material and boundary conditions used in this lab test are described in the following section.

Figure 6-4 Schematic diagram of the lab setup of the high temperature steam loop for brick testing, located in the Thermal Energy System Lab of Nanyang Technological University

Figure 6-5 contains photos of some key equipment used in the laboratory setup. The 36-kW electrical steam generator in 3 phase 400 VAC, is able to provide 50 kg/hour of steam flow up to 250 °C. The 20-kW electrical superheater is capable of superheating the steam up to 600 °C. The furnace is equipped with an external programmer for user-defined ramping profiles. It can withstand up to 1100 °C of temperature inside. A programmable logic controller (PLC) is adopted to integrate all control functions of the major equipment. A touch screen is featured as the user-interface.

Figure 6-5 Photos of the equipment used in the lab test

All the major equipment has internal thermocouples (TC) installed at various locations for temperature regulation. Additional TCs are installed inside the furnace to track the thermal performance of the experimental bricks. Figure 6-6 presents a schematic diagram of how the heat exchanger was covered with refractory bricks and where the TCs were installed. There are three TCs installed recording the temperature levels of steam inlet, outlet and middle in-between the second and the third pipes. Four TCs were installed on the first top bricks of each pipe, and one more in the middle of the furnace (about 10-20cm away from the heating coils and facing the refractory bricks) for temperature monitoring. All the TCs' parameters were logged in real-time by the National Instrument's data acquisition system with a LabVIEW interface.

Figure 6-6 Schematic diagram of heat exchanger with refractory bricks covered and thermal couples installed at steam inlet, outlet and top bricks

6.2.4 Numerical model for the system level study

In order to fully represent the heat exchange process of the waterwall system, the 1D heat transfer model formulated in section 5.3.2 was expanded into a thermal network system. This thermal network system not only takes into consideration the detailed heat transfer from gas to steam through each individual brick, but also allows us to study the continuous effect of PCM-based bricks superheating the steam in a simulated waterwall system. Moreover, this thermal network model can be easily compared with laboratory test results, to validate and showcase the PCM-superheating effect.

As illustrated in Figure 6-7, the left side presents the physical model of the waterwall system. The waterwall is divided into n sections, where each section represents one brick and one corresponding part of the steam pipe. Here the *BRICK* can be a traditional refractory brick or the PCM-based bricks. The heat transfer starts from the radiation between gas and brick, then heat conduction from brick to pipe, and lastly convection to the steam. At the same time, steam passes the entire n sections of bricks/pipe, while getting heated up continuously. The physical model is translated into the thermal

network model shown on the right side in Figure 6-7. The 1D heat transfer model described in Section 5.3.2 is used for each of the n sections. All sections share the same gas temperature. The heat transfer driven by the difference between T_g and $T_{s,i}$ is different for each of the sections. On the right side, the incoming steam flows through the pipe and passes by nodes $T_{s,1}, T_{s,2}, \dots$ and finally exits at temperature $T_{s,out}$. The dashed boxes represent the corresponding bricks installed, which could be either the traditional brick or the PCM-based bricks. The resistance and capacitance models for bricks inside the dashed boxes originate from the dashed boxes shown in Figure 5-11, as to their mathematical models.

Figure 6-7 Dynamic thermal network model of the waterwall

Each section i shares the same mathematical governing equations from equation 1-25. The sections are connected at nodes $T_{s,i}$ with:

$$\dot{m}_s \cdot \dot{H}_{s,i} = \dot{m}_s \cdot \dot{H}_{s,i-1} + Q_{s,i} \quad \text{Eq 6-1}$$

Where $\dot{m}_s$ denotes the steam flow rate. Whereas $\dot{H}_{s,i}$ and $\dot{H}_{s,i-1}$ are the steam enthalpy after and before the node $T_{s,i}$. $Q_{s,i}$ represents the heat flow from brick number i to the steam at node $T_{s,i}$. The total enthalpy gain for steam passing through the waterwall can be summarized as

$$\dot{m}_s \cdot H_{s,out} = \dot{m}_s \cdot H_{s,in} + \sum_{i=1}^n Q_{s,i} \quad \text{Eq 6-2}$$

Where $H_{s,out}$ and $H_{s,in}$ are the steam enthalpy at outlet and inlet of the waterwall heat exchange system. The steam temperature at the exit can be obtained from the known enthalpy value.

6.2.5 Protocol of investigation

Previously in section 6, the main objectives have been introduced, including validation of the numerical model, experimental demonstration of the capabilities of PCM-bricks to upgrade the heat transfer and also to buffer the heat fluctuation. So the protocol of study is designed to fulfil these objectives. Figure 6-8 compiles the protocol in the format of a flowchart. There were three batches of runs carried out during the experimental investigation. The first batch of preliminary runs with only bare pipe in the heat exchanger, was performed during the fabrication of alumina bricks. The preliminary runs allowed us to become familiar with the equipment and safety protocols of operation. In addition, it was used to obtain stable steam inlet conditions for the heat exchanger, in preparation for later runs.

Figure 6-8 The protocol of investigation in flowchart

The second batch were baseline runs with empty bricks. The empty bricks with air gaps in between the inner and outer walls were adopted to imitate the traditional type of

refractory bricks which are composed of less pure alumina (usually around 80-92%). It was possible to explore the steam outlet temperature profile as a result of different temperature levels of the furnace ramping profiles. The furnace ramping profiles were designed with two main considerations, the ramping rate, magnitude and the mean temperature level. According to the temperature fluctuation profiles reported by Costa et al. in [15], the usual furnace temperature inside WtE combustion chamber is within the magnitude of less than 100 °C with a duration of 10 min, meaning the maximum ramping rate is 10 °C/min. Thus, the temperature ramping programmed in our furnace follows this rule. With the DSC results presented in section 119, we were able to speculate possible furnace temperature levels for the phase change to take place. However, due to the unspecified system inertia, and the discrepancies between laboratory characterization and real phase change behaviour, the speculated levels might not work for the PCMs. What's more, there were constraints on the project time and resource to produce another batch of empty bricks to repeat the furnace temperature levels at which the PCMs melt for the sake of demonstration of two objectives in one comparison. In order to accommodate this issue, we proposed the validation procedure below to achieve the aforementioned objectives separately.

In the PCM runs, first of all, a long ramping profile was used (heating up/cooling down from 500 – 800 °C) at a rate of 10 °C/min to capture the phase change behaviour. Then the different temperature levels used in the Baseline runs were repeated for the PCM runs. The results were used to validate the baseline numerical model, and to compare the steam output temperature levels of the baseline and the PCM cases. If the repeated furnace temperature profiles cannot provide the phase change conditions, other furnace temperature levels with the same magnitude and rate of ramping would be imposed, until we could demonstrate the buffering effect due to the effect of the phase change. With the protocol of investigation established, it was possible to achieve the two main objectives with limited time and resources in the lab.

6.2.6 Materials and boundary conditions

Since this section involves laboratory testing to validate the system level model, materials and boundary conditions were specifically designed for the laboratory environment. Both numerical studies from section 5.3 and 6.2 share the same PCM

materials and fluctuation magnitude of the furnace gas temperature to ensure the consistency of the investigation. A few modifications based on the section 5.3 boundary conditions were carried out. Firstly, as introduced by section 6.2.3, the operational pressure of steam supply was downsized to 3 bar. Secondly, the steam pipe in the laboratory setup was built with Stainless Steel 316, different from section 5.3. Thirdly, a 17mm alumina 99% brick with a 5mm of air gap in the middle of the brick was used to represent the traditional brick in the lab test, instead of using the high alumina 90% as described in the literature. The numerical model was subsequently adapted to include this air gap effect. Furthermore, in the lab environment, the furnace was manually programmed to create significant temperature fluctuation (maximum 100 °C/10 min as indicated by literature) to test the waterwall and steam response. Eventually the temperature profile generated by the furnace was shown together with the results. In the numerical study, three PCM-based bricks were used on each of the four sections of the steam pipe (see Table 6-4). The thickness of PCMs and encapsulation wall layers are suggested with the method of finding brick design point introduced in section 5.3.

Table 6-4 Type of PCM-based bricks used in the numerical study of the waterwall system

PCM Brick	PCMs applied	Thickness of PCM layer (mm)	Thickness of wall layers (mm)	Number of bricks
1	AlSi12	5	6	26
2	AlSi5	5	6	13
3	Al99	5	6	13

6.2.7 Post data processing and uncertainty analysis

The post data processing and uncertainty analysis was performed in Matlab environment. The purpose of the uncertainty analysis was to understand how close the results of the numerical model and the experimental setup were, and if the numerical model was able to predict the experimental results with high precision. From the analysis, the future strategy of how to improve either the predictability of the numerical model or the experimental setup could be formulated.

Considering the experimental datasets y_i ($i = 1, 2, 3, \dots, n$) and the numerical model $f(x_i)$ ($i = 1, 2, 3, \dots, n$), for each data acquisition at point i , the numerical model is expected to give a close prediction, which means $f(x_i) \approx y_i$.

The Residual Sum of Squares (RSS) between these two datasets is:

$$RSS = \sum_{i=1}^n (y_i - f(x_i))^2 \quad \text{Eq 6-3}$$

The Standard Deviation between these two datasets can be expressed as:

$$SD = \sqrt{\frac{1}{n-1} \sum_{i=1}^n (y_i - f(x_i))^2} \quad \text{Eq 6-4}$$

Thus the Coefficient of Variation (CV) or Relative Standard Deviation (RSD) is calculated as:

$$CV = \frac{SD}{\bar{y}_i} \quad \text{Eq 6-5}$$

The CV is used to judge the percentage difference between the two. The uncertainty of the measuring devices are summarised below to give an overview of their possible contribution to the overall accuracy of the result.

Table 6-5 Uncertainties of the appliances used in the lab test

Appliance	Uncertainty
Furnace temperature controller	+/- 1 °C
Type K thermal couples	+/- 2.20 °C or +/- 0.75%
Flow meter	+/- 1~2.5%

6.3 Results and Discussion

6.3.1 Upgrading the steam output temperature by PCMs-bricks

Following the investigation protocol, we were able to repeat the same furnace heating profile (shown in Figure 6-9 as maroon and black dashed lines) in our lab tests on Jan 9th 2019 for baseline with empty bricks, and on Feb 13th 2019 for the PCM case. With this heating profile, the PCM bricks did not operate around the design conditions (around the melting/solidification temperatures). However, it is essential to compare the performance of the Baseline and PCM cases with the same heating profile to understand how the PCM bricks could help to enhance the heat transfer in general.

Figure 6-9 Comparison of Baseline and PCM cases at non-design condition, with lab test result of Baseline fitted with simulation result

As we can see from Figure 6-9, the green coloured solid line is the steam input temperature, which is kept around 400–420 °C across all the tests for both baseline runs and PCM case runs. The baseline case has a slightly higher heating profile than the PCM case, less than 10 °C. Nonetheless, the steam outlet temperature from the PCM case, illustrated by the blue dashed line in the figure, is overall 20 °C higher than the steam outlet temperature from the baseline case, shown by the cyan colored solid line.

The numerical model, used to fit with the baseline case, predicts the steam output temperature shown as the magenta colored dotted line in the figure. The coefficient of variation of the simulation and the lab test results is around 0.67%, indicating a quite satisfactory prediction of the baseline result.

6.3.2 Capturing the phase change inside the bricks

After a few test runs were performed with the PCM bricks, a new phenomenon appeared that the PCMs, of which the temperatures are monitored with the thermal couples, did not exhibit phase change behaviour at the designed heating profile. So, it is essential to locate the phase change temperatures of the PCMs before making use of the latent heat to achieve a buffering effect. With this purpose, a wide ramping profile illustrated in Figure 6-10 (maroon red solid line) with 200 °C peak-to-peak temperature gap was adopted in the lab test on Feb 20th, 2019. A slow ramping rate of 5 °C/min was also imposed to fully capture the visual phenomenon of the temperature plateaus, which are typically displayed in the temperature-time graph during phase change.

Figure 6-10 Capturing the phase change of PCM1, 2 and 3 during our lab test on Feb 20th, 2019

As shown in Figure 6-10, the lab run indeed successfully detected and recorded the phase change phenomenon of PCM1, 2 and 3. PCM4, with the highest phase change temperature 660 °C, was not captured.

A few observations can be made based on the test result. First, it was surprising that, the phase change temperatures were not exactly the same as reported by DSC (in section 6.2.1). The melting and solidification temperatures of the PCMs measured by the TCs are slightly shifting within 5 °C from test to test, but they are all quite far away from the DSC results (10-30 °C apart). This discrepancy could be due to several facts:

- a) The lab test conditions were quite far away from the DSC conditions. The DSC measured a small sample size up to a few grams in an inert condition at a quite low heating rate of 5 °C/min. Whereas in the real lab test, the sample size is around 20 grams. The cyclic condition is not inert but air. The heating rate is around 10 °C/min. All these differences could lead to different measurement accuracy and precision.
- b) The thermocouples were placed on top of the PCMs in the lab test. Only after the PCMs melted during the initial cycling of the lab test, could the TCs probes penetrate the oxidized alloy surface and sink inside the PCM. However, since the PCMs initially in the pellet form, and they are supposed to have been melted in the vacuum furnace, there could still exist some gaps inside the PCM domains which the TCs might end up probing. The TCs might also touch the encapsulation wall which cannot be judged from the outside. In a word, there could be some systematic bias caused by the placement of TCs.

Another important observation is that the PCM3, AlSi5%, has two phase change temperatures. This is revealed by the short plateaus happened around 60 min and 110 min, and two unusual slopes around 75min and 90min. The two short plateaus indicate the first melting/solidification point at around 579 °C. The two slopes with abrupt changes of the sloping rates indicate possible another latent heat embedded along the way. This happens around 620 °C.

The third observation is that: while the heating/cooling rates of the furnace temperature profile are the same, PCMs have different rates between heating and cooling, apart from PCM4 which only engages in sensible heating/cooling. This phenomenon of unsymmetrical heating/cooling of PCMs could be due to the differences in dT between heat source and PCM-bricks, which gives different heat fluxes to the PCMs. This dT could be attributed to the thermal inertia of the system. For example, it is common to see that the peaks of the PCMs temperature are a couple of minutes delayed than the furnace peak temperature.

A comparison of the DSC and the lab test results is summarised in Table 6-6. The melting/solidification temperatures recorded during the lab tests were used to guide our design of the heating profile to make use of the buffering effect which results are presented in the next section.

Table 6-6 Melting and solidification point temperatures of the PCMs

PCM alloy	Melting point (°C)		Solidification point (°C)
	By DSC	By lab test	By lab test
AlSi12	604.5	579-589	579-583
AlSi5	592.5	579	575-579, 618-622
Al99	686.9	-	662

6.3.3 Demonstrating the fluctuation damping by PCM-bricks

From May 2nd to Jun 19th 2019, several runs were carried out with PCM-bricks attached to the steam pipes. With the obtained phase change temperatures as described in the previous section, the fluctuating heating profile of furnace was adjusted to operate around the PCMs' melting and solidification points which are called the design conditions. Even though the temperature level of the heating profile has been changed to adapt to the new phase change conditions, the ramp range and rate were kept at 100 °C and 10 °C/min, the same as what would happen in the combustion furnaces of real WtE plants. Another unchanged boundary condition is the steam inlet temperature and pressure, which were maintained at 400-420 °C and 3 bars respectively.

Figure 6-11 presents the test results from the lab run on Jun 19th 2019 and the respective simulation predictions (dotted lines). As shown as the maroon colored line in the figure,

eleven fluctuations on the heating profile were imposed. The temperature of PCM1 closely follows the fluctuations but there is a clear sign of a phase change plateau in each of the small fluctuations, which is not reflected in the simulation result of PCM1. According to the simulation, if all the PCMs are participating, there shall be a higher inertia and more smoothed temperature profile of the PCMs (illustrated by the dotted magenta line in the graph).

Figure 6-11 Lab test vs. simulation results for PCM case on Jun 19th 2019

As we can see, the fluctuation of the steam outlet temperature (shown as an orange line) is quite stabilized and minimized to around 2-4 °C after 100 min. This demonstrates a quite satisfactory buffering effect compared with the magnitude of steam outlet temperature fluctuation in the Baseline, which is normally around 12 °C (shown in section 6.3.1).

The Steam Mid temperature, measured by the TC_{mid} illustrated on Figure 6-6, showcases the temperature of the steam after passing through two pipes. Here in Figure 6-11, it is represented in green solid line. Since this heating profile can only engage phase change of PCM1 and PCM2, so the steam mid temperature is used for the numerical fitting. The simulation predicted result of steam mid temperature, plotted in the dotted blue color, closely follows the fluctuations after 150 min. However, the

simulated steam mid temperature profile is slightly smoother as compared with the lab test result, indicating a better buffering performance in theory than in the real lab situation. The coefficient of variation is about 2.4% between the lab test and simulation results of the PCM1 temperature and 1.66% of the steam mid temperature.

The above comparisons of simulation results and the lab test results in different scenarios indicate a good prediction by the numerical model in the sensible heat process ($CV=0.67\%$), whereas in the latent heat process, the numerical model gives a more ideal result compared with the lab test result ($CV = 1.66\%$). This discrepancy between the lab test and numerical results could be explained by the combination of the following reasons:

- 1) PCMs-bricks: The filling of PCM alloys inside the encapsulation bricks is not perfect, which leaves too many air gaps and hollow spaces that might weaken the heat transfer and eventually impair the thermal buffering effect. This could be especially noticeable in the phase change process which is assumed as ideal in the simulation.
- 2) Numerical model: The numerical model assumes only one-dimensional heat transfer, which in reality is complicated by the furnace structure and imperfect heat insulation inside the furnace. Thus, the PCM or steam might receive heat from other directions other than the designated heat transfer direction.
- 3) Unknown system parameters: There are quite a number of system parameters that do not have the measured data, such as the real radiation source (the heating coils) temperature, and the copper coils inside the steam pipes. The radiation heat transfer and steam convection heat transfer in the numerical model are only a rough estimate of the experimental results.
- 4) Unconfirmed material properties: The conductivities of PCMs and alumina fed into the numerical models are not characterized in the lab. Rather, the literature values are used. The heat capacity of the alumina feedstock is available but not the heat capacity of the encapsulation sample fabricated after the injection molding process. The porosity of the ceramic sample, which mainly depends on the treatment methods applied, is a major influencer on the heat capacity and conductivity.

6.4 Conclusions

In order to test the buffering effect of the PCMs-bricks compared with traditional refractory bricks, a small-scale lab setup was built to replicate the waterwall heat exchanging conditions. Fifty two encapsulation ceramic bricks are fabricated in partnership with SIMTech. Those empty bricks are firstly installed in the waterwall heat exchanger unit to represent the traditional refractory bricks as Baseline case which are tested with different heating profiles. Then the bricks are dissembled and filled up with PCMs melted in an inert atmosphere furnace. The PCMs-bricks are installed to the heat exchanger tubes again to run the same heating profiles as in the Baseline cases. However, since the phase change temperatures are not as reported by DSC characterisation, a three-step protocol of investigation was established to be able to reach a conclusion.

First, the same heating profile as the Baseline is repeated in the PCM runs, of which the results are used to compare with the Baseline results. Second, a wide-range heating profile is designed to locate the phase change conditions of all PCMs. Last, the heating profile is adjusted to be able to employ the phase change behaviour of at least two pipes of PCMs installed. The buffering effect can be demonstrated in the comparison of the magnitude of steam temperature fluctuations of Baseline and PCM cases. The results demonstrate that:

- With the same heating profile from the furnace, even if the PCM-bricks are not operating at the design conditions, they are able to provide a higher heat flux to the steam, which leads to higher steam outlet temperature compared with the Baseline case.
- The PCMs show different phase change temperatures from the characterisation results obtained in DSC. This could be due to the different test conditions and accuracy of apparatus.
- When operating at the design conditions, two rows of PCMs bricks (26 in total) are able to smooth the steam temperature fluctuation at the outlet to a minimum of 2-4 °C, from an initial 12 °C found in the Baseline cases. This could enhance the

stability of the steam input to the turbine and reduce the metal corrosion that is caused by the fluctuations.

Both the numerical model and the lab test setup shall be improved in the following ways to increase the prediction capability of numerical simulation, which could be considered in the second phase of the project.

- 1) It is suggested to measure the thermal conductivities and heat capacity of all the tested samples in the setup, instead of the feedstocks, in order to have a good estimation of the real behaviour of the sample after the fabrication process.
- 2) An effort shall be made to increase the quality and transparency of material/dimensions used in the lab setup. There are many discrepancies found in the lab setup from the designed values which increase the uncertainty in the numerical prediction.
- 3) The numerical model shall be improved to consider the additional thermal impact by the thermocouples, or necessary heat insulation procedure shall be performed to eliminate additional heat transfer to the PCM from the heat conducted by the thermocouple metal wires when exposed to the furnace.

Chapter 7.

Techno-economic Study on the Waste-to-Energy Plants with PCMs-based Buffering Technology

This chapter aims to evaluate the PCMs-buffering design for Waste-to-Energy plants from the techno-economic perspective with the establishment of a cost-benefit analysis model. A real-life Waste-to-Energy plant, the Tuas South Incineration Plant, is used as the baseline from which the new plant is projected. The energy saving from this retrofitting is quantified, and from which the economic analysis takes place. The influence of refractory service time and cost on the payback time of both newly built plant is presented in a sensitivity analysis. Finally, the optimum service time and brick total cost is recommended as future research & development with the goal of achieving high market penetration rate for PCM-based refractory brick.

---

*This section published substantially as [147].

7.1 Introduction

According to the World Bank report (2018) [2], world cities generated about 2.01 billion tonnes of solid waste in 2016. By 2050, this is projected to increase to 3.40 billion tonnes. Figure 7-1 presents the waste generation and recycling situation in Singapore from 2006 to 2015. As can be seen, there were both a 50% increase of waste generation and waste recycling over 10 years. However, after taking into consideration reuse, recycling and other waste-to-energy methodologies like anaerobic digestion, there is still a significant amount of incinerable waste left. However, the initial high investment costs of building a waste incineration plant, in addition to high operating and maintenance costs, could make WtE plants a less attractive waste disposal option. Significantly improving the efficiency of harvesting energy from WtE plants through the use of improved technology, would reduce the payback period of a WtE plant from the revenue of generating higher electricity output.

Figure 7-1 Waste generation and recycling amount in Singapore from 2006 to 2015 [4]

In the context of further improving the energy recovery rate of WtE plant, a new technology, featuring Phase Change Materials (PCMs) based refractory brick to replace the existing refractory lining in the WtE plants, was proposed in this thesis. Though being technologically promising, this PCM-based refractory brick could bring an extra investment and operation cost to the WtE plant. First of all, the brick is composed of aluminium alloys and high purity alumina, which are much more expensive than traditional refractory brick. Secondly, the current way of manufacturing the brick is by

powder injection. This is a very expensive technology which could only provide low capacity of manufacturing. Thirdly, there is no long-term fatigue/failure test of the new brick technology under real plant situation yet. Though Xu etc.[106,148] reported the good compatibility between aluminium alloys and alumina99% under high temperature for 100 hours, it does not guarantee that in the real plant situation where acidic gas and repeated cycling prevail, there is no or comparatively less maintenances. Operational cost to service or to replace bricks might be necessary. In order to better quantify the economic benefit of which the new brick technology would provide the WtE plant, it is necessary to conduct a holistic techno-economic study taking into consideration the possible higher initial and operational cost before the commercialization of this technology. This chapter focuses on a local WtE plant in Singapore, the Tuas South WtE plant, as a baseline reference, to conceptualize the additional investment and operational cost, and provide the total payback time of this technology with a sensitivity study of different brick life.

7.2 Methods

7.2.1 The baseline WtE plant

In order to quantify the potential economic gain/loss of using the PCM-based refractory bricks, a real WtE plant, the Tuas South Incineration Plant (TSIP) situated in the southwest corner of Singapore, is used as a baseline for the comparison. The TSIP was built with state-of-the art technology and the initial investment of S\$890 million. As the fourth and the largest incineration plant in Singapore, it commenced commissioning in 2000, and is able to accommodate 3000 tonnes of incinerable waste per day. The TSIP has a power generation capacity of 80 MW, with an average electricity output from waste of 550 kWh/t [4]. Table 1 lists some of the design parameters of TSIP.

Table 7-1 Tuas South WtE plant design data [149,150]

Parameters	Values
Incineration capacity	3000 tonnes/day
Steam generation per boiler	105 tonnes/boiler at 35 barG and 370 °C
Number of boilers	6
Condensing pressure	0.17 barA
Power generation capacity	2 turbine-generator sets, =<80 MW, 10.5 kV generator voltage

Parameters	Values
Plant availability	83-86%
Projected plant lifetime	30 years
Refractory brick lining cost	1800 SGD/m ²
Refractory brick service time	5 years

The TSIP was chosen as the baseline plant for this case study since it represents the state-of-art. The steam parameters achieved by this plant are also representative of the other plants in Singapore. Another reason for choosing TSIP is to investigate the commercial capability of this technology within the Singapore market before demonstrating in other markets, and TSIP offers a good example of retrofitting the design.

7.2.2 The WtE plant with PCM-based refractory lining

Figure 5 7.2 presents the schematic design of the WtE plants where the new refractory lining buffers the gas temperature fluctuation, enhances the heat transfer from gas to steam, and eventually heats up the steam from 400 to 600 °C. The brick compositions and the material properties are listed in Table 7-2 below.

Table 7-2 PCM-based refractory brick composition and material properties

PCM-based brick	Melting point (°C)	Latent heat (kJ/kg)	Thermal conductivity (W/m•K)	Density (kg/m ³)
Alumina 99% (encapsulation)	-	-	35	3890
Aluminium alloys (PCMs)	570-660	390-498	160-227	2650-2750

As can be seen, both the encapsulation material alumina 99% and alumina alloys present advantageous thermal conductivity. The melting point of the chosen aluminium alloys match well with the desired superheating temperature of steam. The latent heat of fusion possessed by the PCMs is also considerably large for being a good buffer material. The compatibility between alumina 99% and the chosen PCMs have been previously experimentally confirmed by [106] and in *Chapter 4*.

Table 7-3 Retrofitted Tuas South WtE plant design parameter [149]

Parameters	Values
Incineration capacity	3000 tonnes/day
Steam generation per boiler	105 tonnes/hour
Number of boilers	6
Steam from the traditional superheater	35 barG and 370 °C
Power generation capacity	2 turbine-generator sets, =<100 MW, 10.5 kV generator voltage

Parameters	Values
Steam from the PCM-wall superheater	35 barG and 600 °C
Condensing pressure	0.17 barA

Some of the key design parameters of the new WtE plant with PCM-bricks are shown in Table 7-3. The newly built plant will maintain the major plant configuration, including the refuse dealing capacity, numbers of boilers and turbines, and so on. The only changed parameter is the steam temperature before the turbine inlet, which will be around 600 °C compared with 370 °C in the original plant. Given the change to the steam parameters and therefore the increased installed capacity of the steam turbines, an extra capital cost of the steam turbine units shall be added to the new WtE plant. According to the Department of Energy of U.S., for steam turbines of capacity above 15 MW, the ratio of the capital cost to installed capacity is around \$666/kW [151]. This ratio is used as a reference figure to adjust the capital cost of the new WtE plant from the baseline plant.

7.2.3 Building the key performance indicators

The Key Performance Indicators (KPI) offers a good quantitative comparison of the plant output. They encompass a range of aspects, including the energy savings, economical savings, and payback time. The WtE plant availability is defined as:

$$\begin{aligned} & \text{Plant Availability (\%)} \\ &= \frac{\text{Annual plant operations hours}}{\text{Total available hours in a year}} \end{aligned} \quad \text{Eq 7-1}$$

So, the annual electricity output will be:

$$\begin{aligned} E_{\text{annual}} &= \text{energy capacity}_{\text{msw}} \\ &\cdot AI_{\text{msw}} \cdot \text{Plant Availability} \end{aligned} \quad \text{Eq 7-2}$$

The *energy capacity of MSW* is reported to be 550 kWh/t by [4]. The AI_{msw} is the annual intake of MSW by this plant. Thereby, the annual income by selling electricity can be obtained:

$$AIN_e = E_{annual} \cdot ET \quad \text{Eq 7-3}$$

The latest selling price of electric tariff ET can be retrieved from [152]. The other income from refuse disposal is:

$$AIN_{refuse} = AI_{msw} \cdot DT \quad \text{Eq 7-4}$$

The disposal tariff of refuse is available in [4]. The annual income from by-product sales is:

$$AIN_{metal} = AI_{msw} \cdot BPS \quad \text{Eq 7-5}$$

The price of by-product sales is available in [5]. The total annual income is then composed:

$$AIN_t = AIN_e + AIN_{refuse} + AIN_{metal} \quad \text{Eq 7-6}$$

$CAPEX$ denotes the initial investment of TSIP, where $CAPEX_{re}$ is the initial capital investment of the newly built plant including the additional brick cost. The operation and maintenance cost is calculated based on a ratio of the annual MSW throughput at 75.20 \$SGD/ton MSW, provided in [4].

$$OPEX = c_{o\&m/msw} \cdot AI_{msw} \quad \text{Eq 7-7}$$

Another expense during annual operation is the ash disposal cost which is also a ratio of the annual MSW throughput:

$$C_{ash} = c_{ash/msw} \cdot AI_{msw} \quad \text{Eq 7-8}$$

The net annual income is then calculated as:

$$AIN_{net} = AIN_t - OPEX - C_{ash} \quad \text{Eq 7-9}$$

In the end, the present value of annual net income and the net present value of income can be obtained:

$$PV = AIN_{net} \cdot \left[\frac{(1 + I.R)^n - 1}{I.R(1 + I.R)^n} \right] \quad \text{Eq 7-10}$$

$$NPV = PV - CAPEX \quad \text{Eq 7-11}$$

The payback time could be accounted:

$$PBT = CAPEX / AIN_{net} \quad \text{Eq 7-12}$$

This is a simplified equation to calculate the *PBT*. In fact, in the results, the *PBT* is obtained by using the graphical method, taking into consideration of the discounting effect. For the new WtE plant, the material quantity of PCMs for retrofitting the waterwall is calculated by estimating the collective latent heat needed to superheat the steam from inlet to outlet.

$$m_{pcm} L_{pcm} = m_s (\dot{H}_{s,o} - \dot{H}_{s,i}) \quad \text{Eq 7-13}$$

In the previous study [153], using same thickness of inner and outer encapsulation wall as the thickness of PCM layer is suggested to minimize the potential thermal-mechanical stress during heating up and cooling down process, so the amount of encapsulating alumina 99% used will be:

$$2 \cdot m_{pcm} / \rho_{pcm} = m_{encap} / \rho_{encap} \quad \text{Eq 7-14}$$

So, the material cost of PCM, encapsulation material, and the total bricks will be:

$$C_{pcm} = c_{pcm} * m_{pcm} \quad \text{Eq 7-15}$$

$$C_{encap} = c_{encap} * m_{encap} \quad \text{Eq 7-16}$$

$$C_{brick} = C_{pcm} + C_{encap} \quad \text{Eq 7-17}$$

the annual electricity output calculated assuming same MSW throughput of the new plant as that of the baseline plant.

$$E_{annual,*} = \eta_{e,*}/\eta_e \cdot E_{annual} \quad \text{Eq 7-18}$$

The annual electricity selling income and the total income are then calculated as:

$$AIN_{e,*} = E_{annual,*} \cdot ET \quad \text{Eq 7-19}$$

$$AIN_{t,*} = AIN_{e,*} + AIN_{refuse} + AIN_{metal} \quad \text{Eq 7-20}$$

As for the capital expense, it is defined as:

$$CAPEX_* = CAPEX + C_{brick} + \Delta C_{turbine} \quad \text{Eq 7-21}$$

The calculation for *OPEX*, ash disposal fee, and net income follow the same manner as from Eq.6-8. The net (present) value of the incineration plant as well as the payback time of the whole plant are projected using Eq.9-11. Before the results are obtained, some assumptions are made to simplify the problem:

- The initial investment is paid in full amount in the first year.
- All plants have the same service duration of 30 years.
- The discount rate used is 7% per year as the nominal case.

7.3 Results and Discussion

7.3.1 Energy savings analysis

With the available plant information provided in section 7.2, thermodynamic modelling was performed to quantify the approximate energy savings for both the baseline and the new cases. A few assumptions were made to achieve the direct comparison: (i) both the baseline and the new plants share the same condensation pressure; (ii) the isentropic expansion efficiency of the steam turbines is 90% for the baseline plant, and 80% for the new plant due to higher enthalpy drop; (iii) the mechanical efficiency of the steam

turbine is around 75%. (iv). A list of specifications related to the combustion process is summarised below.

Table 7-4 Additional assumptions to the combustion process

Parameters	Values
LHV of incoming waste	7.6 MJ/kg (7~10 MJ/kg in Singapore)
Brick thickness	As proposed in Chapter 6
Refractory coverage	2,200 m ² (private figure)
Furnace temperature	850 °C

The Tuas South Incineration Plant with 3,000 tpd of fuel input, 370°C and 35bar of steam parameters, produces about 65 MW of electricity output, accounting for 24.6% of gross efficiency with LCV base. With PCM-buffer technology, the plant would produce about 75.1 MW of electricity output, thus resulting gross efficiency of 28.5% with LCV base.

Figure 7-2 summarizes the energy output of both cases. Taking into consideration of the plant availability, the estimated annual energy output has been calculated. The baseline plant produces around 48.9 ktoe of energy, while the new plant will result in 56.6 ktoe, indicating 15.5% of extra energy saving per year. This energy saving could play a substantial role in enhancing Singapore's energy security since over 90% of its energy supply is imported [152].

Figure 7-2 Comparison of energy savings for baseline and new plants

7.3.2 Economic analysis of newly built WtE with PCM-bricks

In the economic analysis, two important sensitivity parameters were introduced, being the total PCM-brick cost and the brick service time. Since currently the available material cost of PCM-bricks are obtained through lab scale quotations, it does not provide credibility to be used in the economic analysis, three costs – one time, three times, or six times of the baseline refractory brick cost – is superimposed on the PCM-based bricks as a sensitivity factor. On the other hand, since the brick service time plays an important role in the economic saving of the newly built incineration plant, a series of brick service times from half a year to 30 years are imposed to obtain the net values for the incineration plant over the lifespan.

Figure 7-3 presents the WtE net values with respect to plant operation time at the different brick service time while the brick cost is at six times of the baseline brick cost. As we can see, only when the net value crosses the x axis, the plant starts to profit. The plant operation time from when the WtE starts to profit is the plant's break-even time, or payback time. The shorter the brick service time is, the longer is the payback time of the incineration plant. In the most extreme scenario when the brick service time is only half year, two full-replacements are to be carried out within one year, giving a long plant payback time of more than 30 years, making it an unviable business case. When the brick service time is equal to or more than 1 years, the payback time falls within 7-9 years. At this stage, further increase of brick service time does not result in a much shorter payback time, since the average brick cost from replacement is too diluted to be influential.

Figure 7-3 Net value of incineration plant versus the plant operation time at different brick service time from half year to 30 years at the highest brick cost scenario (6x)

Figure 7-4 illustrates the net value of the newly built IP along the plant operation timeline. 6 difference scenarios are provided with 2 different brick service time (the most extreme situation of half year, and the nominal situation of 5 years), and 3 different brick costs (1x, 3x and 6x of the baseline brick costs). As can be seen, the worst scenario of half year brick service time and 6x brick cost gives more than 30 years of payback, while the best scenario of 5 year brick service time and 1x brick cost gives 7.5 years of payback. The 5-year brick service time gives similar payback projection, which is about 7.5-8.5 years.. Hoever, for the scenarios of half year brick service time, payback time varies distinguishly depending on the brick costs. 1x and 3x of brick costs still make a possible business case but not 6x. This indicates that in order to avoid long payback time, it's crucial to extend the brick lifetime to more than half a year, unless the PCM-bricks cost the same as the baseline bricks. It is also advisable to decrease the brick cost through R&D effort, especially at the scenarios of short brick service time.

Figure 7-4 Net value of WtE plant versus the plant operation time at different combination of brick costs and brick service time (0.5 year and 5 years)

Figure 7-5 shows the net present value (NPV) of the incineration plant with different brick service time and different brick costs at an annual discount rate of 7%. As can be seen, when the brick service time is equal to or less than 1 year, the NPV of the WtE is negative no matter what brick cost is. The longer the service time is, the greater the NPV of the WtE is, and the less the NPV difference is among three brick cost scenarios. When the brick service time is more than 5 years, the NPV turns positive for 1x brick cost scenario, which is 10 years for 3x brick cost scenario. Only when the brick service time is 30 years that the NPV of the plant turns positive for 6x brick cost scenario.

This indicates that (i) both brick cost and brick service time play an important role in affecting the profitability of the business case. (ii) Reducing the brick cost through R&D work will help to increase the NPV of the WtE. (iii). If the brick cost can be kept equal to or below 3 times of baseline brick cost, the WtE could be made profitable.

Figure 7-5 Net present value of incineration plant versus brick service time with different brick cost

7.4 Conclusions

A PCM-based refractory brick was previously proposed to replace the existing refractory lining in the waterwall of Waste-to-Energy plant. The results of an energy analysis suggest that the new plant with PCM-bricks will produce an extra 10.2 MW due to the elevated superheated steam parameters, which will translate into an annual saving of 7.7 kilo ton of oil equivalent. The plant payback time decreases significantly with the increase of the brick service time when it is less than 1 years. When the brick service time is equal to or more than 5 years, the plant payback time remains at a less affected value of 7.5-8.5 years, even with the 6x of brick cost scenario. Another analysis on the plant net present value suggests that in order to remain profitable, the PCM-based bricks for the newly built plant shall be able to work more than 2 year with 1x brick cost. The scenario of 6x brick cost would make it not a profitable business case unless the brick could work without replacement for 30 years. Future R&D should focus on extending the brick service time or reducing the brick total cost to ensure a reasonable payback. In conclusion, this study presents an overview of the potential energy and economic benefits this PCM-based technology could offer, which could give an economic guidance on the configuration design and retrofitting to plant designers and investors. Suggested future work includes a techno-economic comparison with the high parameter WtE plants which have extra superheaters to push

the steam parameters up. This part of the work will further examine the market readiness of the PCM-brick retrofitted WtE plants. Also, further sensitivity analysis could be explored with different discount rate, investigating the robustness of the investment in different economic scenarios.

Chapter 8.

Conclusions and Future Work

8.1 Conclusions

In the context of seeking an advanced solution that could tackle both the temperature fluctuation and high temperature corrosion issues exhibit in modern WtE plants, this Ph.D. thesis aimed to develop a phase change material based latent storage brick concept, to be installed on the waterwall of the first boiler pass and secondary combustion chamber and replace the traditional refractory lining. By employing the high latent heat of the PCMs, the proposed PCMs-brick lining could mitigate and reduce heat fluctuation coming from the waste combustion and deliver a much smoother and possibly even higher heat flux to the water/steam that is evaporated inside the waterwall tubes. Furthermore, even superheating could possibly be achieved in the secondary combustion chamber with the right PCM-bricks designed and placed, thus leading to an upgrade of the steam parameter for the turbine inlet.

With the purpose of realising this concept and to demonstrate the buffering effect, the research was carried out in five main tasks. Each of the tasks is essential in the formulation of the complete research methodology. The main activities and key findings are summarized as follows.

In the material assessment, the proposed methodology is capable of comprehensively evaluating a large pool of material candidates based on their attributes and their

performance in the objective functions. This methodology is validated against the literature result and proves to be a very efficient and thorough tool for the engineers in material screening and selection. Being validated, the methodology aids our design of the PCMs-bricks by identifying the optimum encapsulation material, the high purity alumina which shows satisfactory performance both in the material ranking and the objective examination. With the Al-Si series alloys determined as the PCMs based on their matching phase change temperature with our intended steam superheating temperature the next task was commenced.

The compatibility study, conducted in collaboration with our French counterpart, PROMES laboratory of Processes, Materials, and Solar Energy, examined the chemical compatibility of Al99%, AlSi5% and AlSi12% with Alumina 99.5% and three recycled ceramics, Cofalit, Blast furnace slag, and Coal fired ashes sintered ceramic. The rationale behind engaging three recycled ceramics is that these materials are common waste materials from industrial processes, and if their compatibility with aluminium alloys can be confirmed, there is a huge economic interest of using them to replace the current practiced encapsulation choices, in the context of the circular economy. After being in contact with each other in the 1000 °C for 100 hours, these samples were examined by the Scanning Electron Microscope, Energy Dispersive Spectroscopy and the X-ray diffractometer. The results show that the alumina99.5% presents inert behaviour in all molten aluminium alloys; Cofalit has a good conservation of the surface aspect and composition in molten Al99%, but undergoes substantial surface reaction with molten AlSi5% and AlSi12%. Thus, it is recommended to be used in direct contact with molten Al99% but not AlSi5% and AlSi12%. Similar with alumina, blast furnace slag has a good conservation of both surface aspect and chemical composition with molten AlSi5% and AlSi12%. Thus, they are recommended to be used in direct contact with these two alloys at high temperature. Coal fly ash sintered ceramics had major chemical interactions with all three alloys. They are not recommended to be used in direct contact with these alloys at high temperature. With the compatibility confirmed, now we could proceed to the configuration design and numerical optimization tasks.

The configuration design and optimization was performed with two types of numerical tools, the computational fluid dynamics and the one-dimensional dynamic thermal simulation. The CFD is applied to examine the heat transfer performance of the first

geometry proposed, a brick with equally spaced vertical holes filled with PCMs. With the fluctuating temperature boundary condition applied to the gas radiation, the brick is able to reduce the thermal gradient and improve the heat transfer within the brick itself but not able to buffer the thermal fluctuation as compared with the performance of the traditional refractory brick. With the lessons learnt in the CFD study, a new geometry was proposed which is a simpler design that considers the thickness of encapsulation wall and the PCM layer along the heat transfer direction as the main parameters affecting the heat transfer performance of the brick. Based on Modelica language a one-directional dynamic thermal network model was constructed in the Dymola environment with each object (layer) represented as thermal capacitances and resistances. A parametric study with this numerical model shows that there are a few contributing factors that could affect the buffering effect: the thickness of each layer, the flue gas emissivity, and the steam temperature. With properly chosen parameters, the PCMs-bricks are able to smoothen the steam temperature and deliver 10% higher heat flux to the steam side as compared with the traditional case, when the real WtE plant fluctuation profile is applied to the gas side. At the end, a re-configuration plan of the WtE plant was proposed, to integrate the PCMs-bricks on the waterwall of the secondary combustion chamber to achieve a continuous superheating of the steam.

With the configuration obtained in the numerical study, sample bricks were fabricated in the collaboration with our partner SIMTech, and then installed in a laboratory-scale high temperature steam heat exchanger system with steam pipes going through an electric-heated furnace. Different levels of fluctuating heating profile were imposed in the furnace to create the similar fluctuation scenarios inside the combustion chamber of real plant. The temperature levels of steam flow and bricks were recorded. The results showed that compared with traditional bricks, represented as the empty ceramic bricks in this study, the PCMs-bricks are able to deliver a 20 °C higher of steam output temperature. When working in the design conditions, the PCMs-bricks are capable of minimizing steam fluctuations from an average magnitude of 12 °C captured in the traditional case to a small magnitude of 2-4 °C. The numerical model can predict the performance of the traditional case with a relative standard deviation of 0.67%, and the performance of PCMs case with a RSD of 1.66%. In general, the experimental study showcases the capability of this design to buffer a high magnitude of thermal fluctuation and the numerical study is proved to have a close prediction of the experimental results.

The last part of this research, was to conduct a techno-economic study to quantify the total energy savings and economic gains of this PCMs-buffering technology, if put into practice in a real WtE plant, such as the Tuas South Incineration Plant. The key performance indicators were formulated, and two sensitivity parameters are identified to potentially have big impact on the techno-economic performance, the brick lifetime and the brick total cost. It is concluded that, in the real plant scenario of Tuas South, the new technology would bring an extra power output of 10.1 MW in operation, and an annual energy saving of 7.6 kilo toe. The economic study revealed that the plant payback is more sensitive to the brick lifetime when the brick lifetime is less than 1 years, and not so much affected and remains to be around 7.5-8.5 years if the brick lifetime is more than 5 years. Another analysis on the plant net present value suggested that in order to remain profitable, the PCM-based bricks for the newly built plant shall be able to work at least 5 year without major replenishment

As a conclusion, this thesis has reached its initial design objective and proposed a prototype of PCMs-based brick configuration which is proved numerically and experimentally to be able to buffer the thermal fluctuation from the furnace and deliver a smoothed and higher thermal output to the steam, while being techno-economically feasible.

8.2 Summary of Contributions

The main contributions of the thesis may be summarized from the perspective of different levels. At the collective level, the thesis proposes a novel concept of using a latent heat storage device to achieve thermal buffering in the context of high temperature fluctuations, and successfully demonstrates the technological feasibility and economic viability of this PCM-brick technology to be used in the waterwall system of the combustion chambers and first boiler pass. This has led to the re-configuration of the WtE plant that could allow the continuous superheating of the steam inside the waterwall. This technology integration plan would result in a substantial increase in the steam temperature for the turbine inlet, and eventually a higher electrical output. This novel concept has been the first in literature, and could be applied to numerous other

scenarios of high temperature fluctuation such as high temperature solar thermal energy, and industrial waste heat recovery.

Besides this main contribution introduced, this thesis contributes to the knowledge pool in the field of energy and engineering in different ways. First, the material assessment method proposed in *Chapter 3* is the first methodology recorded in literature to consider both the Multi-attribute and Multi-objective tools and systematically evaluates material candidates with a high credibility. The ease of application and the potential of assessing a large amount of candidates make it an accessible instrument for the design engineers to rank, assess and select the optimum choices. Its application, in this thesis, is emphasized on latent heat storage materials. Nonetheless, this model could be applied to many other scenarios involving a large candidature pool with discrete information while being presented with multiple distinctive objectives.

Another contribution that deserves highlight is the result of the compatibility study described in *Chapter 4*. Prior to this work, the compatibility study of AlSi5%, AlSi12% with pure alumina has never been reported, not to mention the compatibility of the AlSi alloys with inorganic waste ceramics. This thesis not only confirms the excellent compatibility of Al99%, AlSi5% and AlSi12% with pure alumina, but also reports Cofalit and Blast furnace slag's corrosion resistance to AlSi alloys. Since these two alloys are cheaply produced with low embodied energy, they exhibit great potential to be economically viable alternatives to the commercial ceramics. With the rising awareness of waste utilization and circular economy, it is of critical importance to foster the recycle and reuse of these waste materials by providing this practical information to today's and future engineers.

8.3 Limitations and Future work

The PCMs-brick prototype developed in this research, currently classified as level 3-4 in the Technology Readiness Level (TRL), is subject to many limitations. This section tries to identify each major limitation and specify a counteracting solution to overcome the limitation in order to further push this technology development to higher TRL in the future.

First and foremost, in the design aspect, the current PCMs-brick prototype is a design based on lab scale requirement, which is used mainly for the demonstration of thermal buffering concept. It is far from the real refractory bricks used in the furnace of WtE plants. In the next step of R&D work, the lab scale prototype has to be re-scaled to the actual refractory brick or slab size. This re-scaled prototype shall be able to be installed directly in the plant environment for testing.

Another important issue regarding the design aspect is the manufacturing method. The current method of fabrication is powder injection molding of the encapsulation bricks, plus the direct melting of PCMs pellets inside the ceramic bricks in inert environment. Apparently, this method has left many critical issues. This current method is quite expensive, energy intensive, and it cannot be scaled up to mass production due to the limited throughput of most powder injection molding devices. New manufacturing methods shall be investigated with the requirement of being both economical and scalable. Reducing the manufacture cost would significantly reduce the total brick cost, thus reducing the payback time of new plant with this technology installed. Therefore, this shall be one of the main areas of R&D in the next phase. Another potential risk factor for the design and manufacturing process is the density difference between the solid and liquid phases of the PCMs. Additional space inside the encapsulation could be considered to accommodate the thereafter thermal expansion in the liquid phase, by for instance, inclusion of moving parts or non-reactive gas.

As for the material aspect, it is not yet known if the bricks could withstand the highly acidic environment inside the furnace, since typical WtE plants are notorious for creating the highly corrosive flue gas environment. It would be highly favorable if the re-scaled bricks/slabs could be put into the real plant environment and experience a number of cycles to quantify the corrosion rate. Only after this is performed, could the mitigation solution be explored, such as having another layer of coating, or changing the encapsulation to another type of materials. Again, the cost-benefit analysis would need to be repeated to understand the levelized impact on savings.

Another issue that could potentially affect the future material choice is the shifting of phase change temperatures observed in our experimental studies. This phenomenon

shall be fully explored and understood to make sure that it is not an effect from the repeated cycling of the PCMs, nor will it further develop if long term cyclic use is imposed.

In the choice of using recycled ceramic materials to encapsulate PCMs, future investigation on the mechanical strengths of the ceramics after corrosion test would help to better understand how the interaction actually changes the mechanical properties of the ceramic materials, and better identify potential encapsulation alternatives.

Regarding the experimental study, on one hand, the current lab setup lacks precision in many parameters, such as the temperature of the radiation source, and the real speed/dimension of the copper coils inside the steam pipes and etc. These unknowns have caused an increase in uncertainty and worse agreement of the numerical model with the test results. The current lab setup shall be globally upgraded and also adapted to as close to the real environment as possible. On the other hand, it is still recommended to conduct onsite testing of the re-scaled prototype, in order to understand the material response, as part of the experimental investigations.

The numerical model used is a one-dimensional dynamic thermal network model that lacks the capacity to consider multi-directional heat transfer such as observed in the furnace of the lab test. The numerical model should be expanded into 2D and/or 3D to include complex heat transfer processes that could allow better prediction of the experimental results and refractory performance. Furthermore, a plant level numerical model associated with a feedback control loop should be constructed to demonstrate the dynamics of the plant and how “zero” fluctuation could be achieved with the interaction between plant equipment and facilities after the reconfiguration. Additionally, for a more accurate heat transfer and thermodynamic analysis, all the temperature dependant properties shall be treated as functions of temperature, such as density, thermal capacities and thermal conductivities. These could lead to better description of the physical process and better matches to the experimental results.

There is still a long way to go before a real pilot scale prototype of this PCMs-buffering technology can be commercialized. Nevertheless, the aforementioned future work

points in a direction which will, hopefully, lead to the final success of this technology and to a more sustainable and energy/environmental-friendly society in the future.

APPENDIX A. Analytical Hierarchy Process Method

The geometry mean model of Analytical Hierarchy Process (AHP) method [154] is adopted and executed in the scope of this thesis. The geometry mean model of Analytical Hierarchy Process (AHP) method [154] is adopted and executed in the scope of this thesis.

Step one: Perform a pairwise comparison of relative importance (RI) between all attributes (Attribute 1, Attribute 2 ... Attribute n) based on Table A-1, producing a relative importance matrix $[A]$ as in Equation (A-1). For instance, if A_{ij} equals to 9, it means that Attribute i has absolute importance over Attribute j . The diagonal values are always 1 as a result of self-comparison of each attribute.

Table A-0-1 Scale of relative importance level

Importance description	Relative importance (RI)
Equal importance	1
Relative weak importance	3
Relative strong importance	5
Very strong importance	7
Absolute importance	9
Intermediate values	2, 4, 6, 8

$$A = \begin{bmatrix} 1 & A_{12} & \cdots & A_{1n} \\ A_{21} & 1 & \cdots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \cdots & 1 \end{bmatrix} \quad \text{Eq A-1}$$

Step two: Compute the geometric means of each row. Then obtain the relative normalized weights of each attribute by normalizing the geometric means.

$$GM_i = \left(\prod_{j=1}^n A_{ij} \right)^{1/n} \quad i, j = 1, 2, \dots, n \quad \text{Eq A-2}$$

$$W_i = \frac{GM_i}{\sum_{i=1}^n GM_i} \quad \text{Eq A-3}$$

After the weights are acquired, a consistency check is performed to ensure the consistency of the decision.

Step three: Multiply matrix A with column vector W , producing a new column vector B . Calculate the consistency values by element-wise division of B by W .

$$B = A * W = \begin{bmatrix} 1 & A_{12} & \cdots & A_{1n} \\ A_{21} & 1 & \cdots & A_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ A_{n1} & A_{n2} & \cdots & 1 \end{bmatrix} \begin{bmatrix} W_1 \\ W_2 \\ \vdots \\ W_n \end{bmatrix} \quad \text{Eq A-4}$$

$$= \begin{bmatrix} B_1 \\ B_2 \\ \vdots \\ B_n \end{bmatrix}$$

$$CV_i = \frac{B_i}{W_i} \quad \text{Eq A-5}$$

Step four: Calculate the average of the consistency values, which denotes the maximum eigenvalue λ_{max} . Then obtain the consistency index.

$$CI = \frac{(\lambda_{max} - n)}{(n - 1)} \quad \text{Eq A-6}$$

Step five: From Table A-2, find the corresponding random index to the number of attributes in the matrix. Here only up to ten numbers of attributes are shown due to lack of space. However, more random index can be found in literature.

Table A-2 Random index corresponding to the number of attributes in matrix

Number of attributes	3	4	5	6	7	8	9	10
Random index	0.52	0.89	1.11	1.25	1.35	1.4	1.45	1.49

Step six: Compute the consistency ratio CR , which should fall below the upper limit of 0.1. If CR appears to exceed 0.1, then the weights obtained beforehand will be

abandoned, while the AHP procedure will be iterated until the CR value is accepted.

$$CR = \frac{CI}{RI} \quad \text{Eq A-7}$$

APPENDIX B. Techniques for Order Preference by Similarity to Ideal Solutions Method

The Techniques for Order Preference by Similarity to Ideal Solutions (TOPSIS) method [102] seeks to find the best alternative which is the closest to the ideal (hypothetically best) solution and the farthest to the negative ideal (hypothetically worst) solution. The procedure of this method is as follows: The Techniques for Order Preference by Similarity to Ideal Solutions (TOPSIS) method [102] seeks to find the best alternative which is the closest to the ideal (hypothetically best) solution and the farthest to the negative ideal (hypothetically worst) solution. The procedure of this method is as follows:

Step one: Construct a performance matrix $[X]_{mn}$ which displays n numbers of attribute values for m numbers of alternatives. Each attribute stands for a property or other decision criteria of one alternative.

$$X = \begin{bmatrix} X_{11} & X_{12} & \cdots & X_{1n} \\ X_{21} & X_{22} & \cdots & X_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ X_{m1} & X_{m2} & \cdots & X_{mn} \end{bmatrix} \quad \text{Eq B-1}$$

Step two: Perform the column normalization of matrix $[X]_{mn}$, obtaining a new matrix $[N]_{mn}$. Then multiply the normalized matrix with weights designated for each attribute.

$$N_{ij} = \frac{X_{ij}}{\sqrt{\sum_{i=1}^m X_{ij}^2}} \quad i = 1, 2, \dots, m; j = 1, 2, \dots, n \quad \text{Eq B-2}$$

$$R_{ij} = N_{ij} * W_j \quad \text{Eq B-3}$$

Step three: Calculate the ideal solution and the negative ideal solution with the equations below.

$$R^+ = \left\{ \begin{matrix} \max & \min \\ (R_{ij}/J), & (R_{ij}/J')/i = 1, 2, \dots, m \end{matrix} \right\} \quad \text{Eq B-4}$$

$$= \{R_1^+, R_2^+, \dots, R_n^+\}$$

$$R^- = \left\{ \begin{matrix} \min & \max \\ (R_{ij}/J), & (R_{ij}/J')/i = 1, 2, \dots, m \end{matrix} \right\} \quad \text{Eq B-5}$$

$$= \{R_1^-, R_2^-, \dots, R_n^-\}$$

Where $J = (1, 2, \dots, n)/j$, associated with the beneficial attributes. While $J' = (1, 2, \dots, n)/j$, associated with the non-beneficial attributes.

Step four: Compute the separation distances of each alternative to the ideal and negative ideal solutions with the Euclidean distance equations.

$$D_i^+ = \left\{ \sum_{j=1}^n (R_{ij} - R_j^+)^2 \right\}^{0.5} \quad i = 1, 2, \dots, m \quad \text{Eq B-6}$$

$$D_i^- = \left\{ \sum_{j=1}^n (R_{ij} - R_j^-)^2 \right\}^{0.5} \quad i = 1, 2, \dots, m \quad \text{Eq B-7}$$

Step five: Obtain the relative closeness of all alternatives to the ideal solution. Then rank all the closeness in the descending order to find the ranking of the alternatives.

$$C_i = \frac{D_i^-}{D_i^+ + D_i^-} \quad \text{Eq B-8}$$

APPENDIX C. User-defined functions of the radiation boundary condition in ANSYS Fluent simulation

This User Defined Function is used to impose radiation boundary condition in the numerical study described in Chapter 5 section 5.2.

```
#include "udf.h"

DEFINE_PROFILE(Gas_temperature, thread, position)
{
    face_t f;

    begin_f_loop(f, thread)
    {
        real t = CURRENT_TIME;
        F_PROFILE(f, thread, position) = 1223 + 75*sin(2*3.14159*t/600);
    }
    end_f_loop(f, thread)
}
```


APPENDIX D. Pressure and Massflow Investigation for Reduced Steam Parameter in the Experimental Setup

When the experimental setup was being built, the steam parameters were subject to certain reduction due to necessary laboratory safety regulations. Therefore, a parametric investigation on the pressure and mass flow rate was performed to identify which parameter had a substantial influence on the heat transfer coefficient. The main objective was to reduce the steam parameter in the lab scale setup while maintaining the heat transfer from furnace to steam at a similar level to the real plant.

Table D-0-1 Relationship between mass flow rate and heat transfer coefficient at a fixed pressure

Pressure 35 bar	
Mass flow rate (kg/h)	Conv. Heat transfer coefficient (W/m ² K)
10	80
15	285
20	415
25	598
30	733
35	858
40	977
45	1091
50	1201

Table D-0-2 Relationship between pressure and heat transfer coefficient at a fixed mass flow

Mass flow rate 50 kg/h	
Pressure (bar)	Conv. Heat transfer coefficient (W/m ² K)
5	1146
10	1155
15	1164
20	1173
25	1182
30	1191
35	1201

The figure below shows that mass flow rate is the most sensitive parameter affecting heat transfer. Thus, in the lab setup, the mass flow rate was maintained at 50 kg/h, and the pressure was reduced from 35 bar to 3 bar without too much affect on heat transfer.

Figure D-0-1 comparison of effects of mass flow and pressure on heat transfer

REFERENCES

- [1] United Nations. Transforming our world: The 2030 agenda for sustainable development. United Nations: 2015. doi:10.1007/s13398-014-0173-7.2.
- [2] Hoornweg D, Bhada-Tata P. What a Waste: a Global Review of Solid Waste Management. 2012.
- [3] European Commission. A resource-efficient Europe - Flagship initiative under the Europe 2020 Strategy. Brussels: 2011.
- [4] Tong H, Yao Z, Lim JW, Mao L, Zhang J, Ge TS, et al. Harvest green energy through energy recovery from waste: A technology review and an assessment of Singapore. *Renew Sustain Energy Rev* 2018;98:163–78. doi:10.1016/j.rser.2018.09.009.
- [5] Zhang D, Huang G, Xu Y, Gong Q. Waste-to-energy in China: Key challenges and opportunities. *Energies* 2015;8:14182–96. doi:10.3390/en81212422.
- [6] Statista. Japan number of waste incineration facilities 2018. <https://www.statista.com/statistics/689599/japan-number-of-waste-incineration-facilities/>.
- [7] ISWA. Waste-to-Energy State-of-the-Art Report. 2012.
- [8] Porteous A. Why energy from waste incineration is an essential component of environmentally responsible waste management. *Waste Manag* 2005;25:451–9. doi:10.1016/j.wasman.2005.02.008.
- [9] Niessen WR. Combustion and Incineration Processes. 4th ed. Andover, Massachusetts, USA: Taylor & Francis; 2010.
- [10] Dorn T, Flamme S, Nelles M. A review of energy recovery from waste in China. *Waste Manag Res* 2012;30:432–41. doi:10.1177/0734242X11433530.
- [11] Hoornweg D, Bhada-Tata P. What a waste: A global review of solid waste management. 2012. doi:10.1111/febs.13058.
- [12] Makarichi L, Jutidamrongphan W, Techato K. The evolution of waste-to-energy

- incineration : A review 2018;91:812–21. doi:10.1016/j.rser.2018.04.088.
- [13] Makarichi L, Jutidamrongphan W, Techato K anan. The evolution of waste-to-energy incineration: A review. *Renew Sustain Energy Rev* 2018;91:812–21. doi:10.1016/j.rser.2018.04.088.
- [14] Dal Magro F, Xu H, Nardin G, Romagnoli A. Application of high temperature phase change materials for improved efficiency in waste-to-energy plants. *Waste Manag* 2017. doi:10.1016/j.wasman.2017.06.031.
- [15] Costa M, Dell'Isola M, Massarotti N. Temperature and residence time of the combustion products in a waste-to-energy plant. *Fuel* 2012;102:92–105. doi:10.1016/j.fuel.2012.06.043.
- [16] Dionel O. Albina, Karsten Millrath, N. J. Themelis. Effects of Feed Composition on Boiler Corrosion in Waste-to-Energy Plants. 12th North Am Waste To Energy Conf 2004:1–11. doi:10.1115/NAWTEC12-2215.
- [17] Lee SH, Themelis NJ, Castaldi MJ. High-temperature corrosion in waste-to-energy boilers. *J Therm Spray Technol* 2007;16:104–10. doi:10.1007/s11666-006-9005-4.
- [18] Xu H, Lin WY, Romagnoli A. Technological review on enhancing the energy efficiency of MSW incineration plant. 2018 Asian Conf. Energy, Power Transp. Electrifi., 2018, p. 1–7. doi:10.1109/ACEPT.2018.8610756.
- [19] Lombardi L, Carnevale E, Corti A. A review of technologies and performances of thermal treatment systems for energy recovery from waste. *Waste Manag* 2015;37:26–44. doi:10.1016/j.wasman.2014.11.010.
- [20] De Greef J, Villani K, Goethals J, Van Belle H, Van Caneghem J, Vandecasteele C. Optimising energy recovery and use of chemicals, resources and materials in modern waste-to-energy plants. *Waste Manag* 2013;33:2416–24. doi:10.1016/j.wasman.2013.05.026.
- [21] Composition LC, Smc- PN, Corporation SM. INCONEL alloy 625 n.d. <http://www.specialmetals.com/assets/smc/documents/alloys/inconel/inconel-alloy-625.pdf>.
- [22] Main A, Maghon T, Main, Armin Maghon T. Concepts and experiences for higher plant efficiency with modern advanced boiler and incineration technology. *Proc. 18th Annu. North Am. Waste-to-Energy Conf., Orlando, Florida, USA: 2010*, p. 1–8.
- [23] Murer MJ, Spliethoff H, De Waal CMWD, Wilpsaar S, Berkhout B, Van Berlo MAJ V, et al. High efficient waste-to-energy in Amsterdam: Getting ready for the next steps. *Waste Manag Res* 2011;29:20–9. doi:10.1177/0734242X11413334.

- [24] Wilson A, Forsberg U, Noble J. Experience of composite tubes in municipal waste incinerators. *Corrosion* 1997;97:153.
- [25] Fantozzi D, Matikainen V, Uusitalo M, Koivuluoto H, Vuoristo P. Chlorine-induced high temperature corrosion of Inconel 625 sprayed coatings deposited with different thermal spray techniques. *Surf Coatings Technol* 2017;318:233–43. doi:10.1016/j.surfcoat.2016.12.086.
- [26] Uusitalo MA, Vuoristo PMJ, Mäntylä TA. Elevated temperature erosion-corrosion of thermal sprayed coatings in chlorine containing environments. *Wear* 2002;252:586–94. doi:10.1016/S0043-1648(02)00014-5.
- [27] Oksa M, Tuurna S, Varis T. Increased lifetime for biomass and waste to energy power plant boilers with HVOF coatings: High temperature corrosion testing under chlorine-containing molten salt. *J Therm Spray Technol* 2013;22:783–96. doi:10.1007/s11666-013-9928-5.
- [28] Munro RG, Dapkunas SJ. Corrosion characteristics of silicon carbide and silicon nitride. *J Res Natl Inst Stand Technol Res Natl Inst Stand Technol* 1993;98:607–31. doi:10.6028/jres.098.040.
- [29] Martin JJE, Koralewska R, Wohlleben A. Advanced solutions in combustion-based WtE technologies. *Waste Manag* 2015;37:147–56. doi:10.1016/j.wasman.2014.08.026.
- [30] Brossard JM, Prigent P, Poirier J. High temperature corrosion of oxide bonded silicon carbide refractory lining in WtE facilities. *J Eur Ceram Soc* 2013;33:2065–72. doi:10.1016/j.jeurceramsoc.2013.02.015.
- [31] Mengarelli M, Magro FD, Py X, Romagnoli A. Environmental performance assessment of the application of high temperature phase change materials in waste-to-energy plants. *Energy Procedia* 2017;143:460–5. doi:10.1016/j.egypro.2017.12.711.
- [32] Keppel Seghers. Waste-to-Energy: Keppel Seghers Boiler Prism. Keppel Seghers 2006. <http://www.keppelseghers.com/en/>.
- [33] Hesseling WFM, Rademakers PLF. Efficiency Increase of Waste-to-Energy Plants-Evaluation of experience with boiler corrosion and corrosion reduction 2003. http://task36.ieabioenergy.com/wp-content/uploads/2016/06/Efficiency_Increase_of_Waste-to-Energy_Plants_Evaluation_of_Experience_with_Boiler_Corrosion_and_Corrosion_Reduction.pdf.
- [34] Adams B, Diederen HSW, Peeters K, Wijnhoven JPF, Eeraerts D. Seghers boiler prism: a proven primary measure against high temperature boiler corrosion. 12th Annu. North

- Am. Waste-to-Energy Conf., ASME; 2004, p. 229–40. doi:10.1115/NAWTEC12-2227.
- [35] Lei J, Yang J, Yang E-H. Energy performance of building envelopes integrated with phase change materials for cooling load reduction in tropical Singapore. *Appl Energy* 2016;162:207–17. doi:10.1016/j.apenergy.2015.10.031.
- [36] Kong LB, Li T, Hng HH, Boey F, Zhang T, Li S. Waste energy harvesting: mechanical and thermal energies. vol. 24. Springer; 2014. doi:10.1007/978-3-642-54634-1.
- [37] Pereira A, Caroff T, Lorin G, Baffie T, Romanjek K, Vesin S, et al. High temperature solar thermoelectric generator - Indoor characterization method and modeling. *Energy* 2015;84:485–92. doi:10.1016/j.energy.2015.03.053.
- [38] Katter LB, Randel L H. Application of thermal energy storage to process heat and waste heat recovery in the primary aluminum industry. 1979. doi:10.1017/CBO9781107415324.004.
- [39] Lundberg WL, Christenson JA. Application of thermal energy storage to waste heat recovery in the food processing industry. 2014. doi:10.1007/s13398-014-0173-7.2.
- [40] Cristopia Energy System. Thermal energy storage systems 2016. http://cristopia.co.in/wp-content/uploads/2012/03/Brochure_Thermal-Energy-Storage-Systems.pdf (accessed January 1, 2016).
- [41] Fleischer AS. Thermal Energy Storage using Phase Change Materials fundamentals and applications. Minneapolis, MN, USA: Springer briefs in applied science and technology thermal engineering and applied science; 2015.
- [42] Cabeza LF, Inés Fernández A, Barreneche C, Ushak S. PCM Storage. *Handb Clean Energy Syst* 2015;4:1–23. doi:10.1002/9781118991978.hces144.
- [43] Nomura T, Okinaka N, Akiyama T. Technology of latent heat storage for high temperature application: a review. *ISIJ Int* 2010;50:1229–39. doi:10.2355/isijinternational.50.1229.
- [44] Sharma SD, Sagara K. Latent heat storage materials and systems: A review. *Int J Green Energy* 2005;2:1–56. doi:10.1081/ge-200051299.
- [45] Wikipedia. Yakhchal. Wikipedia 2012. <https://en.wikipedia.org/wiki/Yakhchal>.
- [46] Hale BD V, Hoover MMJ, Lockheed N, Huntsville BD, September E, Cha P, et al. Phase Change Materials Handbook, NASA CR-61363 1971.
- [47] Guillot S, Faik A, Rakhmatullin A, Lambert J, Veron E, Echegut P, et al. Corrosion effects between molten salts and thermal storage material for concentrated solar power plants. *Appl Energy* 2012. doi:10.1016/j.apenergy.2011.12.057.
- [48] Farid MM, Khudhair AM, Razack SAK, Al-Hallaj S. A review on phase change energy

- storage: Materials and applications. *Energy Convers Manag* 2004;45:1597–615. doi:10.1016/j.enconman.2003.09.015.
- [49] Choubineh N, Jannesari H, Kasaeian A. Experimental study of the effect of using phase change materials on the performance of an air-cooled photovoltaic system. *Renew Sustain Energy Rev* 2019;101:103–11. doi:10.1016/j.rser.2018.11.001.
- [50] Haillot D, Nepveu F, Goetz V, Py X, Benabdelkarim M. High performance storage composite for the enhancement of solar domestic hot water systems. Part 2: Numerical system analysis. *Sol Energy* 2012;86:64–77. doi:10.1016/j.solener.2011.09.006.
- [51] Yoo D, Joshi YK. Energy efficient thermal management of electronic components using solid – liquid phase change materials. *IEEE Trans Device Mater Reliab* 2004;4:641–9.
- [52] Nomura T, Akiyama T. High-temperature latent heat storage technology to utilize exergy of solar heat and industrial exhaust heat. *Int J Energy Res* 2016. doi:10.1002/er.
- [53] Zalba B, Marín JM, Cabeza LF, Mehling H. Review on thermal energy storage with phase change: materials, heat transfer analysis and applications. *Appl Therm Eng* 2003. doi:10.1016/S1359-4311(02)00192-8.
- [54] Sharma A, Tyagi V V., Chen CR, Buddhi D. Review on thermal energy storage with phase change materials and applications. *Renew Sustain Energy Rev* 2009;13:318–45. doi:10.1016/j.rser.2007.10.005.
- [55] Agyenim F, Hewitt N, Eames P, Smyth M. A review of materials, heat transfer and phase change problem formulation for latent heat thermal energy storage systems (LHTESS). *Renew Sustain Energy Rev* 2010. doi:10.1016/j.rser.2009.10.015.
- [56] Haillot D, Bauer T, Kröner U, Tamme R. Thermal analysis of phase change materials in the temperature range 120–150°C. *Thermochim Acta* 2011;513:49–59. doi:10.1016/j.tca.2010.11.011.
- [57] Kenisarin MM. High-temperature phase change materials for thermal energy storage. *Renew Sustain Energy Rev* 2010;14:955–70. doi:10.1016/j.rser.2009.11.011.
- [58] Gil A, Medrano M, Martorell I, Lázaro A, Dolado P, Zalba B, et al. State of the art on high temperature thermal energy storage for power generation. Part 1-Concepts, materials and modellization. *Renew Sustain Energy Rev* 2010;14:31–55. doi:10.1016/j.rser.2009.07.035.
- [59] Al-Abidi A a., Bin Mat S, Sopian K, Sulaiman MY, Lim CH, Th A. Review of thermal energy storage for air conditioning systems. *Renew Sustain Energy Rev* 2012;16:5802–19. doi:10.1016/j.rser.2012.05.030.
- [60] Energy Canada Department of Mines and Resources. Waste heat recovery. *Energy*

- Manag Ser 1988;7–58.
- [61] Castell A, Soler C, Medrano M, Roca J, Cabeza LF, García D. Natural convection heat transfer coefficients in phase change material (PCM) modules with external vertical fins. *Appl Therm Eng* 2008;28:1676–86. doi:10.1016/j.applthermaleng.2007.11.004.
  - [62] Regin AF, Solanki SC, Saini JS. Heat transfer characteristics of thermal energy storage system using PCM capsules: A review. *Renew Sustain Energy Rev* 2008;12:2438–51. doi:10.1016/j.rser.2007.06.009.
  - [63] Jankowski NR, McCluskey FP. A review of phase change materials for vehicle component thermal buffering. *Appl Energy* 2014;113:1525–61. doi:10.1016/j.apenergy.2013.08.026.
  - [64] Arkar C, Medved S. Influence of accuracy of thermal property data of a phase change material on the result of a numerical model of a packed bed latent heat storage with spheres. *Thermochim Acta* 2005;438:192–201. doi:10.1016/j.tca.2005.08.032.
  - [65] Lee YT, Hong SW, Chung JD. Effects of capsule conduction and capsule outside convection on the thermal storage performance of encapsulated thermal storage tanks. *Sol Energy* 2014;110:56–63. doi:10.1016/j.solener.2014.08.034.
  - [66] Lakshmi Narasimhan N, Bharath R, Ramji SA, Tarun M, Arumugam AS. Numerical studies on the performance enhancement of an encapsulated thermal storage unit. *Int J Therm Sci* 2014;84:184–95. doi:10.1016/j.ijthermalsci.2014.05.003.
  - [67] Herrick CS, Zarnoch KP. Heat storage capability of a rolling cylinder using Glauber's salt. 1078. doi:10.1017/CBO9781107415324.004.
  - [68] Johnson SA. Heat storage apparatus and method 1980.
  - [69] Abhat A. Short term thermal energy storage. *Energy Build* 1981;3:49–76. doi:10.1016/0378-7788(81)90005-0.
  - [70] Parameshwaran R, Kalaiselvam S, Harikrishnan S, Elayaperumal A. Sustainable thermal energy storage technologies for buildings: A review. *Renew Sustain Energy Rev* 2012;16:2394–433. doi:10.1016/j.rser.2012.01.058.
  - [71] Dal Magro F, Meneghetti A, Nardin G, Savino S. Enhancing energy recovery in the steel industry: Matching continuous charge with off-gas variability smoothing. *Energy Convers Manag* 2015;104:78–89. doi:10.1016/j.enconman.2015.05.012.
  - [72] Dal Magro F, Jimenez-Arreola M, Romagnoli A. Improving energy recovery efficiency by retrofitting a PCM-based technology to an ORC system operating under thermal power fluctuations. *Appl Energy* 2017;208:972–85. doi:10.1016/j.apenergy.2017.09.054.

- [73] Reed S, Sugo H, Kisi E. High temperature thermal storage materials with high energy density and conductivity. *Sol Energy* 2018;163:307–14. doi:10.1016/j.solener.2018.02.005.
- [74] Reed S, Sugo H, Kisi E, Richardson P. Extended thermal cycling of miscibility gap alloy high temperature thermal storage materials. *Sol Energy* 2019;185:333–40. doi:10.1016/j.solener.2019.04.075.
- [75] Sugo H, Kisi E, Cuskelly D. Miscibility gap alloys with inverse microstructures and high thermal conductivity for high energy density thermal storage applications. *Appl Therm Eng* 2013;51:1345–50. doi:10.1016/j.applthermaleng.2012.11.029.
- [76] Rawson A, Kisi E, Sugo H, Fiedler T. International Journal of Heat and Mass Transfer Effective conductivity of Cu – Fe and Sn – Al miscibility gap alloys. *Int J Heat Mass Transf* 2014;77:395–405. doi:10.1016/j.ijheatmasstransfer.2014.05.024.
- [77] Agarwal A, Sarviya RM. Thermal conductivity enhancement of PCMs in annular tube heat storage : A review. *Int J Res Aplied Sci Eng Technol* 2014;2:69–73.
- [78] Hamada Y, Ohtsu W, Fukai J. Thermal response in thermal energy storage material around heat transfer tubes: Effect of additives on heat transfer rates. *Sol Energy* 2003;75:317–28. doi:10.1016/j.solener.2003.07.028.
- [79] Gharebaghi M, Sezai I. Enhancement of Heat Transfer in Latent Heat Storage Modules with Internal Fins. *Numer Heat Transf Part A Appl* 2007;53:749–65. doi:10.1080/10407780701715786.
- [80] Shatikian V, Ziskind G, Letan R. Numerical investigation of a PCM-based heat sink with internal fins: Constant heat flux. *Int J Heat Mass Transf* 2008;51:1488–93. doi:10.1016/j.ijheatmasstransfer.2007.11.036.
- [81] Liu Z, Sun X, Ma C. Experimental investigations on the characteristics of melting processes of stearic acid in an annulus and its thermal conductivity enhancement by fins. *Energy Convers Manag* 2005;46:959–69. doi:10.1016/j.enconman.2004.05.012.
- [82] Lacroix M. Study of the heat transfer behavior of a latent heat thermal energy storage unit with a finned tube. *Int J Heat Mass Transf* 1993;36:2083–92. doi:10.1016/S0017-9310(05)80139-5.
- [83] Zhang YW, Faghri A. Heat transfer enhancement in latent heat thermal energy storage system by using the internally finned tube. *Int J Heat Mass Transf* 1996;39:3165–73. doi:10.1016/0017-9310(95)00402-5.
- [84] Choi JC, Kim SD. Heat transfer in a latent heat-storage system using $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ at the melting point. *Energy* 1995;20:13–25. doi:10.1016/0360-5442(94)00051-4.

- [85] Horbaniuc B, Dumitrascu G, Popescu A. Mathematical models for the study of solidification within a longitudinally finned heat pipe latent heat thermal storage system. *Energy Convers Manag* 1999;40:1765–74. doi:10.1016/S0196-8904(99)00069-2.
- [86] Ismail KA., Alves CL., Modesto MS. Numerical and experimental study on the solidification of PCM around a vertical axially finned isothermal cylinder. *Appl Therm Eng* 2001;21:53–77. doi:10.1016/S1359-4311(00)00002-8.
- [87] Guo C, Zhang W. Numerical simulation and parametric study on new type of high temperature latent heat thermal energy storage system. *Energy Convers Manag* 2008;49:919–27. doi:10.1016/j.enconman.2007.10.025.
- [88] Xu H, Romagnoli A, Sze JY, Py X. Application of material assessment methodology in latent heat thermal energy storage for waste heat recovery. *Appl Energy* 2017;187:281–90. doi:10.1016/j.apenergy.2016.11.070.
- [89] Ashby MF, Bréchet YJM, Cebon D, Salvo L. Selection strategies for materials and processes. *Mater Des* 2004;25:51–67. doi:10.1016/S0261-3069(03)00159-6.
- [90] Fernandez AI, Martí M, Segarra M, Martorell I, Cabeza LF. Selection of materials with potential in sensible thermal energy storage. *Sol Energy Mater Sol Cells* 2010;94:1723–9. doi:10.1016/j.solmat.2010.05.035.
- [91] Navarro ME, Martinez M, Gil A, Fernandez AI, Cabeza LF, Olives R, et al. Selection and characterization of recycled materials for sensible thermal energy storage. *Sol Energy Mater Sol Cells* 2012;107:131–5.
- [92] Jeanjean A, Olives R, Py X. Selection criteria of thermal mass materials for low-energy building construction applied to conventional and alternative materials. *Energy Build* 2013;63:36–48. doi:10.1016/j.enbuild.2013.03.047.
- [93] Rathod MK, Kanzaria H V. A methodological concept for phase change material selection based on multiple criteria decision analysis with and without fuzzy environment. *Mater Des* 2011;32:3578–85. doi:10.1016/j.matdes.2011.02.040.
- [94] Wang Y, Zhang Y, Yang W, Ji H. Selection of low temperature phase change materials for thermal energy storage based on the VIKOR method. *Energy Technol* 2015;3:84–9. doi:10.1002/ente.201402098.
- [95] Rastogi M, Chauhan A, Vaish R, Kishan A. Selection and performance assessment of Phase Change Materials for heating, ventilation and air-conditioning applications. *Energy Convers Manag* 2015;89:260–9. doi:10.1016/j.enconman.2014.09.077.
- [96] Lotfi FH, Fallahnejad R. Imprecise Shannon's entropy and multi-attribute decision making. *Entropy* 2010;12:53–62. doi:10.3390/e12010053.

- [97] Rao RV. Decision making in the manufacturing environment using graph theory and fuzzy multiple attribute decision making methods. Springer; 2012.
- [98] Hwang CL, Paidy SR, Yoon K. Mathematical programming with multiple objectives A tutorial. *Comput Oper Res* 1980;7:5–31.
- [99] Karami A. Utilization and comparison of multi-attribute decision making techniques to rank Bayesian network options. University of Skövde, 2011.
- [100] Rao RV. Decision making in the manufacturing environment using graph theory and fuzzy multiple attribute decision making. London: Springer; 2007.
- [101] Hwang CL, Yoon K. Multiple attribute decision making: methods and applications. A state of the art survey. New York: Springer-Verlag; 1981. doi:10.1007/978-3-642-48318-9.
- [102] Zavadskas EK, Mardani A, Turskis Z, Jusoh A, Nor KMD. Development of TOPSIS Method to Solve Complicated Decision-Making Problems — An Overview on Developments from 2000 to 2015. *Int J Inf Technol Decis Mak* 2016;15:645–82. doi:10.1142/S0219622016300019.
- [103] Chauhan A, Vaish R. Magnetic material selection using multiple attribute decision making approach. *Mater Des* 2012;36:1–5. doi:10.1016/j.matdes.2011.11.021.
- [104] Chauhan A, Vaish R. Hard coating material selection using multi-criteria decision making. *Mater Des* 2013;44:240–5. doi:10.1016/j.matdes.2012.08.003.
- [105] Manfrida G, Secchi R, Stańczyk K. Modelling and simulation of phase change material latent heat storages applied to a solar-powered Organic Rankine Cycle. *Appl Energy* 2016;179:378–88. doi:10.1016/j.apenergy.2016.06.135.
- [106] Xu H, Dal Magro F, Sadiki N, Mancaux J-M, Py X, Romagnoli A. Compatibility study between aluminium alloys and alternative recycled ceramics for thermal energy storage applications. *Appl Energy* 2018;220:94–105. doi:10.1016/j.apenergy.2018.03.021.
- [107] Fukahori R, Nomura T, Zhu C, Sheng N, Okinaka N, Akiyama T. Thermal analysis of Al-Si alloys as high-temperature phase-change material and their corrosion properties with ceramic materials. *Appl Energy* 2016. doi:10.1016/j.apenergy.2015.10.164.
- [108] Yan M, Fan Z. Review durability of materials in molten aluminum alloys. *J Mater Sci* 2001:285–95. doi:10.1023/A:1004843621542.
- [109] Monfort E, Mezquita A, Granel R, Vaquer E, Escrig A, Miralles A, et al. Analysis of energy consumption and carbon dioxide emissions in ceramic tile manufacture. *Bol La Soc Esp Ceram Y Vidr* 2010;49:303–10.
- [110] Mach T. Energy Consumption in the Bayer Process 2012:375–8.

- [111] Motte F, Falcoz Q, Veron E, Py X. Compatibility tests between Solar Salt and thermal storage ceramics from inorganic industrial wastes. *Appl Energy* 2015;155:14–22. doi:10.1016/j.apenergy.2015.05.074.
- [112] Gutierrez A, Miró L, Gil A, Rodríguez-Aseguinolaza J, Barreneche C, Calvet N, et al. Advances in the valorization of waste and by-product materials as thermal energy storage (TES) materials. *Renew Sustain Energy Rev* 2016. doi:10.1016/j.rser.2015.12.071.
- [113] Calvet N, Gomez JC, Faik A, Roddatis V V., Meffre A, Glatzmaier GC, et al. Compatibility of a post-industrial ceramic with nitrate molten salts for use as filler material in a thermocline storage system. *Appl Energy* 2013;109:387–93. doi:10.1016/j.apenergy.2012.12.078.
- [114] Nomura T, Zhu C, Sheng N, Saito G, Akiyama T. Microencapsulation of metal-based phase change material for high-temperature thermal energy storage. *Sci Rep* 2015;5:9117. doi:10.1038/srep09117.
- [115] Wang Z, Wang H, Li X, Wang D, Zhang Q, Chen G, et al. Aluminum and silicon based phase change materials for high capacity thermal energy storage. *Appl Therm Eng* 2015;89:204–8. doi:10.1016/j.applthermaleng.2015.05.037.
- [116] Khare S, Dell’Amico M, Knight C, McGarry S. Selection of materials for high temperature latent heat energy storage. *Sol Energy Mater Sol Cells* 2012;107:20–7. doi:10.1016/j.solmat.2012.07.020.
- [117] Wang Z, Wang H, Yang M, Sun W, Yin G, Zhang Q, et al. Thermal reliability of Al-Si eutectic alloy for thermal energy storage. *Mater Res Bull* 2017;95:300–6. doi:10.1016/j.materresbull.2017.07.040.
- [118] Latech. Latech Scientific Supply 2017. <http://www.latech.com.sg>.
- [119] Liu M, Steven Tay NH, Bell S, Belusko M, Jacob R, Will G, et al. Review on concentrating solar power plants and new developments in high temperature thermal energy storage technologies. *Renew Sustain Energy Rev* 2016;53:1411–32. doi:10.1016/j.rser.2015.09.026.
- [120] Kéré A. Stockage d’électricité par compression adiabatique d’air 2014.
- [121] Duan W, Yu Q, Wang K, Qin Q, Hou L, Yao X, et al. ASPEN Plus simulation of coal integrated gasification combined blast furnace slag waste heat recovery system. *Energy Convers Manag* 2015;100:30–6. doi:10.1016/j.enconman.2015.04.066.
- [122] Salazar K, McNutt MK. Mineral Commodity Summaries 2010. *US Geol Surv* 2010:196. doi:<http://dx.doi.org/10.3133/70140094>.

- [123] Winnefeld F, Leemann A, Lucuk M, Svoboda P, Neuroth M. Assessment of phase formation in alkali activated low and high calcium fly ashes in building materials. *Constr Build Mater* 2010;24:1086–93. doi:10.1016/j.conbuildmat.2009.11.007.
- [124] Eco-Tech-Ceram. Eco-Tech-Ceram 2017. <https://www.ecotechceram.com/>.
- [125] INERTAM. INERTAM. INERTAM 2017. <http://www.inertam.com/>.
- [126] Py X, Calvet N, Olives R, Meffre A, Echegut P, Bessada C, et al. Recycled Material for Sensible Heat Based Thermal Energy Storage to be Used in Concentrated Solar Thermal Power Plants. *J Sol Energy Eng* 2011;133:031008. doi:10.1115/1.4004267.
- [127] Directive W. Position Paper on the Status of Ferrous Slag. *Regulation* 2012;32.
- [128] ArcelorMittal. ArcelorMittal n.d. <http://corporate.arcelormittal.com/>.
- [129] EDF Energy. EDF Energy 2017. <https://www.edfenergy.com/>.
- [130] Calvet N, Py X, Olivès R, Bédécarrats JP, Dumas JP, Jay F. Enhanced performances of macro-encapsulated phase change materials (PCMs) by intensification of the internal effective thermal conductivity. *Energy* 2013. doi:10.1016/j.energy.2013.03.078.
- [131] International Center for Diffraction Data. Database of International Center for Diffraction Data 2017. <http://www.icdd.com/products/pdf2.htm>.
- [132] Duval DJ, Risbud SH, Shackelford JF. Mullite. *Ceram. Glas. Mater. - Struct. Prop. Process.*, Springer; 2008, p. 27–38.
- [133] Han GW, Feng D, Yin M, Ye WJ. Ceramic/aluminum co-continuous composite synthesized by reaction accelerated melt infiltration. *Mater Sci Eng A* 1997;225:204–7. doi:10.1016/s0921-5093(96)10573-6.
- [134] Ortiz-Covarrubias KE, Almanza-Robles JM, Cortés-Hernández DA, Escobedo-Bocardo JC, Flores-Valdés A. Synthesis of Al₆Si₂O₁₃-BaAl₂Si₂O₈-ZrO₂-based composites and their wettability by molten Al and an Al-Si alloy. *Ceram Int* 2015;41:4360–73. doi:10.1016/j.ceramint.2014.11.126.
- [135] Ushak S, Marín P, Galazutdinova Y, Cabeza LF, Farid MM, Grágeda M. Compatibility of materials for macroencapsulation of inorganic phase change materials : Experimental corrosion study. *Appl Therm Eng* 2016;107:410–9. doi:10.1016/j.applthermaleng.2016.06.171.
- [136] Kere A, Sadiki N, Py X, Goetz V. Applicability of thermal energy storage recycled ceramics to high temperature and compressed air operating conditions. *Energy Convers Manag* 2014. doi:10.1016/j.enconman.2014.08.008.
- [137] Dal Magro F, Xu H, Nardin G, Romagnoli A. Application of high temperature phase change materials for improved efficiency in waste-to-energy plants. *Waste Manag*

- 2018;73:322–31. doi:10.1016/j.wasman.2017.06.031.
- [138] Xu H, Lin WY, Dal Magro F, Li T, Py X, Romagnoli A. Towards higher energy efficiency in future waste-to-energy plants with novel latent heat storage-based thermal buffer system. *Renew Sustain Energy Rev* 2019;112:324–37. doi:10.1016/j.rser.2019.05.009.
- [139] Dal Magro F, Romagnoli A, Xu H, Nardin G. Application of high temperature phase change materials for improved efficiency in waste-to-energy plants. *Proc 6th Int Symp Energy from Biomass Waste* 2016.
- [140] Rees SJ, Fan D. A numerical implementation of the Dynamic Thermal Network method for long time series simulation of conduction in multi-dimensional non-homogeneous solids. *Int J Heat Mass Transf* 2013;61:475–89. doi:10.1016/j.ijheatmasstransfer.2013.02.016.
- [141] Claytex Services Ltd. Demola n.d. <https://www.claytex.com/products/dymola/>.
- [142] Crescenzi R. Technical sheet of Vitorre incineration plant 2015. http://www.regione.lazio.it/binary/rl_main/tbl_documenti/RIF_DD_G00063_13_01_2016_Allegato1.pdf.
- [143] Costa M, Dell’Isola M, Massarotti N. Numerical analysis of the thermo-fluid-dynamic field in the combustion chamber of an incinerator plant. *Energy* 2009;34:2075–86. doi:10.1016/j.energy.2008.08.024.
- [144] Auerkari P. Mechanical and physical properties of engineering alumina ceramics. *Tech Res Cent Finl* 1996:26.
- [145] Accuratus Ceramic Corporation. 99.5% Alumina Material Properties. 2013.
- [146] Atlas Specialty Metals. Carbon steel pipe and fittings. 2008.
- [147] Xu H, Wei C, Yvonne W, Romagnoli A. Techno-economic evaluation of a novel phase change materials-based thermal buffering technology for improving energy efficiency of waste-to-energy plants. 32nd Int. Conf. Effic. Cost, Optim. Simul. Environ. impact Energy Syst. (ECOS 2019), Wroclaw, Poland: 2019.
- [148] Xu H, Sadiki N, Magro FD, Py X, Mancaux JM, Romagnoli A. Compatibility tests between molten Aluminium alloys and recycled ceramics from inorganic industrial wastes. *Energy Procedia* 2017;142:3689–96. doi:10.1016/j.egypro.2017.12.263.
- [149] National Environment Agency. Tuas South Incineration Plant. *Natl Environ Agency* 2013:2–3.
- [150] NEA. National Environment Agency of Singapore 2019.
- [151] U.S. Department of Energy. Combined heat and power technology fact sheet series -

- Steam Turbines. 2016.
- [152] Company EM. Wholesale electricity prices in Singapore 2019. <https://www.emcsg.com/marketdata/priceinformation>.
- [153] Dal F, Xu H, Nardin G, Romagnoli A. Application of high temperature phase change materials for improved efficiency in waste-to-energy plants. *Waste Manag* 2017. doi:10.1016/j.wasman.2017.06.031.
- [154] Hotman E. Base reference analytical hierarchy process for engineering process selection. In: Khosla R, Howlett RJ, Jain LC, editors. *Knowledge-Based Intell. Inf. Eng. Syst.* 9th Int. Conf. KES 2005, Melbourne, Aust. Sept. 14-16, 2005, Proceedings, Part I, Berlin, Heidelberg: Springer Berlin Heidelberg; 2005, p. 184–90. doi:10.1007/11552413_27.