UNIVERSIDAD POLITÉCNICA DE MADRID

**ESCUELA TÉCNICA SUPERIOR DE INGENIERÍA Y DISEÑO
INDUSTRIAL**

**ANALYSIS OF REDOX REACTIONS IN A
FLUIDIZED/FIXED BED REACTOR FOR
THERMOCHEMICAL ENERGY STORAGE IN SOLAR
THERMAL POWER PLANTS**

TESIS DOCTORAL

Sandra Álvarez de Miguel

Ingeniera Química

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Autora: Sandra Álvarez de Miguel

Ingeniera Química

Directores: Dr. José González Aguilar

Dr. Juan Mario García de María

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LECTURA DE TESIS

El acto de lectura y defensa de la Tesis Doctoral se realizó el día ____ de _____ de _____, en la Escuela Técnica Superior de Ingeniería y Diseño Industrial de la Universidad Politécnica de Madrid, ante el tribunal aprobado por la Comisión de Doctorado de la UPM el ____ de _____ de _____ y formado por los siguientes doctores:

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*A mi abuela,
a mi hermana,
y a mi hijo,
con todo mi amor.*

*En la vida,
unas veces se gana,
y otras se aprende.*

Desconocido

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NOMENCLATURE

Symbol	Subscript	Meaning	Units
Ar		Archimedes number	-
A		Pre-exponential factor	-
g		Gravity acceleration	m/s ²
α		Thermal diffusivity	m ² /s
α		Fractional conversion	-
λ		Thermal conductivity	W/m·K
ρ		Density	kg/m ³
	s	Solid particle	
	f	Fluidizing gas	
cp		Specific heat capacity	J/kg·K
ΔP		Pressure drop	mbar
ΔT		Temperature step	°C
U		Velocity	m/s
	mf	Minimum fluidization	
	t	Terminal	
	max	Maximum	
L		Height of the test bed	m
n		order of the reaction	-
ϵ		Void fraction	-
μ		Dynamic viscosity	kg/m·s
	g	Related to gaseous phase	
	s	Related to solid phase	
d		Diameter	m
	p	Related to the particles or pellets	
ϕ		Sphericity	-
r(t) or r(s)		Desired value or setpoint	°C
y(t) or y(s)		System output signal	°C
e(t) or e(s)		Error signal	°C
u(t) or u(s)		Controller output signal	°C
	p	Proportional action	
	i	Integral action	
	d	Derivative action	
G _c (s)		Controller transfer function	°C
G(s)		Plant transfer function	°C
k		Gain	°C
	c	Static	
	c	Proportional	
	d	Derivative	
k		Reaction rate coefficient	mg/s
τ		Time	s

Symbol	Subscript	Meaning	Units
	,1,2	Constant	s
	i	Integral	s
	d	Derivative	s
θ		Time delay	s
θ		Phase angle	°
d		Numerical constant	-
E		Activation energy	kJ/mol
ξ		Damping factor	s ⁻¹
f(α)		Kinetic mechanism	-
m		Sample mass	mg
	i	Initial state	mg
	f	Final state	mg
P		Power	W
Qv		Volumetric air flow rate	m ³ /h
φ		Resistivity	$\Omega \cdot \text{mm}^2/\text{m}$
R		Electrical resistance	Ω
Re		Reynolds number	-
S		Cross-section area	mm ²
L		Length	m
V		Voltage	V
I		Electric current	A

ABBREVIATIONS

A	Pre-exponential factor
AC	Alternating current
ANN(s)	Artificial neural network(s)
CFD	Computational fluid dynamics
CSIC	Centro Superior de Investigaciones Científicas
CSP	Concentrated solar power
DC	Direct current
DLR	German Aerospace Center
DTA	Differential temperature analysis
E	Activation energy
F1	First-order model
FIFO	First-in first-out
FLC	Fuzzy logic control
FOPTD	First order plus time-delay
FPGA	Field programmable gate array
GA(s)	Genetic algorithm(s)
GS	Gain schedule

HMI	Human-machine interface
HTF	Heat transfer fluid
I/O	In and out
KCE	Kinetic compensation effect
MISO	Multiple input single output
MOS	Maximum overshoot
NFC	Neuro fuzzy control
NI	National Instruments
OS	Operating system
P	Proportional
PC	Personal computer
PCM	Phase change material
PI	Proportional-integral
PID	Proportional-integral-derivative
R3	Contracting volume model
RLF	Fluidized bed reactor from Spanish "reactor de lecho fluidizado"
RT	Real time
SISO	Single input single output
SOPTD	Second order plus time-delay
ST	Settling time
TES	Thermal energy storage
TGA	Thermogravimetric analysis
TOPTD	Third order plus time-delay
UML	Unified modelling language
USD	United States dollar
ZN	Ziegler-Nichols

ABSTRACT

The population is increasingly aware of the need to reduce the overall energy consumption as well as to increase the renewable share in the consumed electricity. Solar energy has the potential to supply enough electricity to match the energy consumption, its biggest challenge lies in overcoming its great dependence on the weather. To avoid these supply problems, the incorporation of an energy storage system that allows the production of electricity, independently of the availability of the solar resource, is being studied from different fronts.

Thermochemical energy storage, compared to sensible or latent heat storage systems, has several advantages. Its higher energy density could allow significant cost reduction. In addition, the energy can be stored for an indefinite period, including the possibility of transporting the chemical substances for the production of energy in a different place. Finally, the discharge process produces high quality thermal energy under isothermal conditions which would allow the use of highly efficient turbines for the production of electricity from this heat source.

In order to develop a thermochemical storage system of application in solar thermal power plants, it is necessary to identify chemical reactions that work in the appropriate temperature range and demonstrate their feasibility.

For central receiver solar power plants using air as heat transfer fluid, this work analyses the use of manganese oxide as a chemical material for thermal energy storage. Thus, an important effort has been made in the characterization of the manganese oxide in powder form: the kinetics of the reaction are analysed, but also other properties as conductivity, reactivity analysis or morphology are studied.

Considering that for heat storage application the material needs to be shaped to form pellets, a completely new methodology has been created to measure the evolution of the pelletized material in terms of hardness, density, porosity, volume, morphology and reactivity, with the different thermal cycles applied. Not only has the reactivity and suitability of pure manganese oxide been evaluated, but also a doped material consisting of manganese oxide with five percent iron oxide in its composition has been tested. Through this exhaustive analysis, a base line of the material characteristics is gathered. The compiled information will be used as reference in order to evaluate the effect of the thermochemical storage cycle on the material when using a fixed/fluidized bed reactor.

An experimental facility, able to provide the experimental conditions for assessing metal oxides pellets as suitable materials for thermochemical heat storage, has been designed, built and commissioned. The selection of the control variables, alerts, control parameters and the development of the data acquisition system is also developed. The control of the workbench is optimized through simulation and intermediate results. The facility is composed of a reactor where the material would be tested and, a workbench which reproduces the different working conditions which can change from very little air flow rates up to $60 \text{ Nm}^3/\text{h}$ and from room temperature up to 1100°C .

Firstly, the reactor is characterized by using inert materials consisting in alumina pellets. Secondly, pure and doped manganese oxides are tested in fixed and fluidized bed conditions. To conclude, the effect of the assays in the material is analysed and measured in comparison to the base material investigation performed

The conclusion of this study indicates that pure manganese oxide, while meeting the mechanical requirements for service in a solar plant, does not in itself have the chemical characteristics required to withstand loading and unloading cycles during several years of service. However, the doped material presents a great improvement of the chemical characteristics, being its reactivity more stable. The stick to this improvement lies in the reduction of the mechanical strength necessary to withstand the abrasion to which it would be subjected in the working conditions of the solar power plant.

The information obtained in the development of this Thesis leads to the conclusion that although manganese oxide may be the base substance for thermochemical storage in concentrated solar power plants, a combination with other metallic oxides is necessary to obtain a compromise solution between the mechanical requirements of the substance and its reactivity

RESUMEN

Cada día somos más conscientes de la necesaria reducción de los consumos eléctricos así como de la necesidad de aumentar la cantidad de electricidad de origen renovable. La energía solar tiene el potencial de producir la energía eléctrica requerida para el consumo de la población, pero para ello es necesario implantar un sistema de almacenamiento de energía que permita producir electricidad independientemente de la disponibilidad de luz solar.

El almacenamiento termoquímico de energía térmica, comparado con sistemas de almacenamiento sensible o latente, presenta mayor densidad energética lo que se podría traducir en menores costes del sistema de almacenamiento. Además, almacenar la energía en forma de enlaces químicos, permite su conservación durante un tiempo indeterminado, incluso el transporte de las sustancias químicas para la producción de energía en otro lugar. Por último, el proceso de descarga produce energía térmica de gran calidad en condiciones isotermas lo que permitiría el uso de turbinas de gran eficiencia para la producción de electricidad.

Para desarrollar los sistemas de almacenamiento termoquímico en centrales solares termoeléctricas es necesario seleccionar las reacciones químicas que se dan en ese rango de temperaturas y demostrar su correcto desempeño. Existen numerosas centrales solares con un amplio abanico de condiciones de trabajo, centrándose en una posible futura aplicación de centrales solares de receptor central, la investigación llevada a cabo propone el uso de óxido de manganeso como reactivo básico del sistema de almacenamiento.

En la presente Tesis se ha realizado un concienzudo análisis del uso de óxidos de manganeso como material para almacenamiento termoquímico. Con el óxido de manganeso en polvo, se ha estudiado su cinética, su conductividad térmica, reactividad y morfología. No obstante, considerando que para la aplicación de almacenamiento el material debe ser peletizado, se han desarrollado nuevas metodologías que permiten evaluar las variaciones en la dureza, densidad, porosidad, volumen, morfología y reactividad de los pellets tras la aplicación de diversos tratamientos térmicos. Se ha realizado un estudio pormenorizado del óxido de manganeso puro y también de un óxido de manganeso dopado con un cinco por ciento con hierro. La información obtenida de estos estudios crea la línea base para comparar los cambios sufridos por el material de estudio cuando es sometido a varios ciclos de carga y descarga en un reactor de lecho fijo y/o fluidizado.

En general, las condiciones experimentales que el material tendría en una planta solar, se ha diseñado, construido y puesto a punto una instalación experimental. Esta instalación ubicada en el IMDEA Energía de Móstoles, consta de un reactor y sus sistemas auxiliares capaces de producir caudales de aire hasta 60 Nm³/h desde temperatura ambiente hasta 1100 °C. Además se han definido todas las variables y parámetros de control, así como las alarmas pertinentes y se ha desarrollado un sistema de adquisición de datos.

Inicialmente el reactor se caracteriza empleando un material inerte, a continuación se realizan ensayos con óxido de manganeso puro y dopado tanto en condiciones de lecho fijo como en lecho fluidizado. El efecto que estos ensayos tienen en el material se evalúa y compara con la información previamente obtenida del material.

Si bien el óxido de manganeso puro mantiene unas buenas propiedades mecánicas, pierde la reactividad en un número muy limitado de ciclos térmicos, lo que hace inviable su aplicación. No

obstante, la mezcla del óxido de manganeso con hierro conlleva una gran mejora de las características químicas alcanzándose una estabilidad química, no así de las propiedades mecánicas que no serían suficientes para aguantar la abrasión que sufriría el material en una central solar.

La principal conclusión alcanzada en esta Tesis es que el óxido de manganeso puede servir de sustancia básica principal para el almacenamiento termoquímico de energía térmica, pero se requiere su combinación con otros óxidos metálicos que permitan llegar a un compromiso entre la estabilidad química del material y sus propiedades mecánicas.

CHAPTER I

1. INTRODUCTION

Scaling-up renewable energy and energy efficiency is currently considered as a key action to achieve the target fixed at the United Nations Convention on Climate Change's 21st Conference of the Parties in Paris in December 2015 [1]. The "research on, and promotion, development and increased use role of renewables" was already cited in the Kyoto Protocol, an international agreement linked to the United Nations Framework Convention on Climate Change, which commits its Parties by setting internationally binding emission reduction targets [2].

In this context, solar energy is surely one of the most promising alternatives being the cleanest and most abundant renewable energy source; 165000 terawatts of energy strikes the Earth on a continuous basis from the Sun, while the World energy consumptions in 2012 was 15 terawatts [3]. Indeed, numerous solar processes, more or less sophisticated, have been analysed and developed at commercial scale such as electricity generation using photovoltaic and solar thermal power plants, polygeneration by combination of photovoltaic and thermal systems, solar industrial process heat and cooling, building heating, solar water heating, etc.

Main shortcoming concern in the power sector regarding the use of solar and wind energy is their dispatchability, since electricity generation is highly dependent on solar or wind natural resource availability. In contrast to photovoltaic or wind power, concentrating solar power (CSP) has the potential to provide dispatchable power on a defined capacity level by integrating large-scale thermal energy storage (TES) [4]. Storing solar thermal energy allows for electricity generation during off-sun periods or when production does not cover the demand; improving the solar systems efficiency, making them more reliable and raising the potential market of CSP technology [5].

1.1. Concentrating solar thermal energy in the current energy scenario

The strategies to further improve CSP technologies are aiming at developing new concepts capable to handle higher solar concentration factors resulting in higher operation temperature and, consequently, higher overall conversion efficiency [6], [7].

CSP market remains less established than most other renewable energy markets. Nonetheless, up to 2014 the sector continued nearly a decade of strong growth. During the course of that year, four new projects totalling over 0.9 GW increased total global capacity by 27 % to nearly 4.4 GW. In the five years from end-2009 to end-2014, global operating capacity rose by an annual average of 46 % [4]. However, in 2015 only one project was commissioned adding 0.1 GW capacity. Up to February 2016, two more projects have been completed adding a total capacity of 0.2 GW. Figure 1.1 shows the evolution of the concentrating solar thermal power global capacity from year 2005 up to year 2015.

Solar thermal technologies are normally classified depending on the optical system for concentrating sunlight in linear-focused concentrators, such as parabolic trough, and point-focused technologies, such as central receiver solar tower, beam-down and parabolic dishes. Due to the fact that point-focused concentrators are able to achieve higher concentration factors [8], the foregoing classification also corresponds to medium and high temperature technologies [9].

Figure 1.1. Concentrating Solar Thermal Power Global Capacity, by Country/Region, 2005-2015 [1].

From the four existing technologies, parabolic trough collector is the most mature one. It is constructed as a long parabolic mirror with a lineal absorber running its length at the focal point. The solar concentration ratio is between 30 and 80 *suns*, being one “sun” the local value of direct beam insolation. The trough is usually aligned on a north-south axis, and it rotates to track the sun as it moves across the sky [10].

Parabolic trough plants represent the bulk of existing capacity with over 3.5 GW. Nevertheless, 2014 was a notable year in terms of the diversification of the CSP technology landscape. Capacities of newly deployed parabolic trough and tower plants drew closer, with 46 % of added capacity based on parabolic trough technology, and 41 % based on tower technology. The increase in tower capacity was due to commissioning in the United States of the Ivanpah plant; with a nominal generating capacity of 377 MW is the largest CSP plant in the world [4].

Central solar tower technology consists of a field of heliostats that concentrate their reflected sun light onto a receiver located on top of a tower. There is a modification of this technology that using a beam down reflects the solar energy to a receiver located on the ground [11]. The concentration factor in this technology reaches from 200 to 1000 *suns*. Early designs used the focused rays to heat water, and the resulting steam to power a turbine. A second generation of this technology includes the use of molten salts as working fluid [12], volumetric air receivers [13] or chemical reactors [14].

Also in 2014, the World’s largest linear Fresnel plant, with 125 MW, came on line in India. Linear Fresnel reflector is based on solar collector rows or loops, as parabolic trough is. However, in this case, the parabolic shape is achieved by almost flat linear facets. The radiation is reflected and concentrated onto fixed linear receivers mounted over the mirrors, combined or not with secondary concentrators. One of the advantages of this technology is its simplicity and the possibility to use low cost components. When a secondary reflector receiver is implemented Fresnel technology can achieve higher concentration factors than parabolic trough [15].

In 2015, the worldwide added capacity of 0.1 GW was based on parabolic trough collector technology used in the KaXu Solar One plant, located in South Africa. Up to February 2016, Moroccan

Noor 1 plant based in parabolic trough and South African Khi Solar plant based in solar tower have come on line with 160 MW and 50 MW respectively.

Spain remains the global leader in CSP cumulative capacity with over 2.25 GW, despite the fact that it added no new relevant capacity since 2013 [4],[16]. The paralysis of the Spanish market follows policy changes implemented in recent years, including a 2012 moratorium on feed-in tariffs for new plants and the severe curtailment in 2014 of tariff rates for plants already in operation.

The United States has increased its operating CSP capacity up to 1.8 GW; thanks to the abovementioned Ivanpah tower plant (377 MW), the Mojave plant (250 MW) and the second (125 MW) phase of the Genesis plant (total 250 MW), both using parabolic trough technology. In October 2015, Crescent Dunes solar tower plant came in operation; it is based on molten salt receiver technology with thermal storage and has 110 MW maximum capacity.

Some other CSP plants are scheduled to start operation in the next months and the up-coming years. Nevertheless, the uncertainties in the CSP market made some commercial initiatives unsuccessful, as it has been the case in the dish technology. Dish concentrators use a reflective, parabolic dish which focuses the sunlight onto a single point above the dish, where a receiver, typically a Stirling engine, sometimes a steam engine, captures the heat and transforms it into electricity.

Stirling dishes show the highest efficiency, up to 32 %, compared to the other CSP technologies, solar tower or parabolic through, with 15 -16 %. This system has the potential to achieve higher temperatures due to the higher concentration of light, of about 1000 to 4000 suns [6]. Higher temperatures lead to better efficiency in the conversion to electricity and the dish system is very efficient on this point. Despite this potential, and the modular characteristic of these type of systems, there is no big scale plant in production. The high maintenance cost and the rigid frame and strong tracking system due to the fixed location of the engine on top of the structure are to be considered [17], [18]. But, the biggest withdrawn of the technology is that storage system cannot be implemented, and so, the electricity produced is not dispatchable.

Comparing the capacity of these technologies, it is observed that the parabolic trough technology has a single unit capacity of 30-80 MW per plant, while central solar power tower can reach up to 200 MW per plant. Dish design technology has a capacity from 5 to 25 kW per dish [19].

All these technologies imply the need for high temperature thermal storage technologies. Its employment would help to bridge the gap between peak solar and peak demand hours, improving plant efficiency and its economic viability.

The lack of storage, is the reason why Stirling dish technology could not compete against the falling costs of solar photovoltaics. In September 2011, Stirling Energy Systems of Scottsdale, Arizona, a system manufacturer of dish-engine solar plants, filed for bankruptcy and the Arizona project was decommissioned. Also, Infinia, leader in Stirling dish technology claim bankruptcy in September 2013.

The main advantage that CSP technologies, except dish Stirling, have over the photovoltaic systems is the thermal storage that can be integrated at low cost. Even so, the CSP industry is experiencing some difficulties. In 2013, Siemens closed its CSP business. Moreover, the Swiss company ABB exited the CSP market with the sale of its shares in Novotec Solar, but its French counterpart, Alstom,

became increasingly involved in the sector during 2014. Later that year, French linear Fresnel specialist AREVA closed its CSP business, after experiencing significant losses. Also in the same year, Schott Solar announce a stop in production of receiver manufacturing at its Mitterteich plant in Germany due to low demand. In the recent months, Spanish firm Abengoa Solar, the company with the world's largest portfolio of plants in operation or under construction, is experience severe financial problems.

There are still top companies involved in either one or a combination of CSP activities including project development, construction, ownership, operations and maintenance, and manufacturing: in Spain, there is Acciona, ACS Cobra, Elecnor, Sener/Torresol Energy and FCC; Brightsource and Solar Reserve in United States; and ACWA Power International in Saudi Arabia.

The strategies to further improve CSP technologies are aiming at plant concepts with higher solar concentration factors resulting in higher operation temperature and consequent higher overall conversion efficiency [19]. Given the role that CSP with TES can play in grid reliability, these technologies imply the need for high temperature thermal energy storage that can easily be integrated into the CSP plant at low cost. Thus, CSP research continued to focus heavily on the improvement of TES systems, and on the evaluation of alternative heat transfer media.

1.2. Thermal energy storage systems: sensible, latent and thermochemical heat storages

The thermal performance of a heat storage system depends on the thermodynamic properties of the material used. Heat storage materials can be judged in terms of the required store volume and long storage efficiency, in addition to important conditions as costs, toxicity and reliability [20].

The different routes investigated in TES, in descending maturity order, are classified into sensible, latent and thermochemical heat storage. Nevertheless, attending to the characteristic storage energy density, the order of these technologies is the opposite [21].

1.2.1. *Sensible heat storage*

Sensible heat storage materials undergo no phase change within the temperature range required for the application [22].

Sensible heat water storages are the most common systems because water has an extremely high thermal capacity per unit volume, is cheap and non-toxic. But nowadays water is not as widely available as we may wish. Apart from that, the technology has significant heat losses what makes small water storages inefficient for seasonal storage. Liquid water thermal storage capacity is also limited due to the temperature range of unpressurised water (0-100 °C) although higher temperatures can be achieved in pressurized steam storage.

A selection of materials with potential to be sensible heat storage resources is included in [23]. Among natural available materials, there can be used rocks, sand, soil, or technical materials like concrete, iron, etc. But it has to be considered that sensible heat is most effective when the heat is stored in a transportable medium as mineral oil [24].

For medium-high temperature storage in concentrating solar power plants, molten salts, mainly nitrate salt have been used [25]. Molten salts can rise the working temperature of the storage system up to 550 °C, but they solidify at 250 °C. If this would occur, pipes, pumps, and other equipment would be blocked [26]. So, a safety heating net must be included in salt installations

which rise up the cost of the plant. Nevertheless, several CSP plants started their operation with salt storage systems in the last few years in Spain and United States [5].

1.2.2. Latent heat storage, phase change material (PCM)

A considerable amount of energy can be stored in the phase transition of materials: solid to liquid and liquid to vapour transitions are normally considered [27]. As the medium freezes or condenses, it releases latent heat at a constant temperature [28].

The solid - liquid latent heat storage is for example used in ice storage for commercial cooling applications. The enthalpy change between the liquid and vapour phase is in general much larger than the enthalpy change associated with the solid - liquid transition. In some industrial cases, the water storage capacity is enlarged by pressurization; up to 50 bar and 264 °C in so-called steam accumulators. Although they take up too much space, they are widely used in cogeneration plants and they were integrated in the PS10 plant (Sanlúcar la Mayor, Spain), the first commercial solar tower plant, providing 20 minutes of extra power at full capacity.

No material yet studied has all the optimum characteristics required for a PCM, and the selection of a PCM for a given application requires careful consideration of the properties of the various substances and/or mixtures [29]. Most of the research effort nowadays relies in the encapsulation of the materials in order to make them easy to handle and to make it possible to work with fluidized bed and transporting heat exchanges [30], [31]. In order to improve the TES some researchers have also proposed a combination of PCM materials in a cascade device [32].

1.2.3. Thermochemical storage

Thermochemical heat storage is based on transforming thermal into chemical energy using reversible chemical reactions. Heat storing process takes place during the endothermic reaction, whilst thermal energy is released during the inverse (exothermic) reaction, generally at a different temperature level.

Thermochemical heat storage has various advantages compared to sensible and latent heat. Firstly, specific and volumetric energy densities are usually higher, which allows building smaller storage tanks. Secondly, it allows long-term thermal storage at room temperature, since energy is stored into chemical bonds. Thirdly, the reactants can be transported to release the heat in another location. Finally, high-grade heat can be produced due to the high temperatures at which the forward and reverse reactions take place [33].

There are many theoretically viable thermochemical cycles, each of them operates at a particular temperature covering a wide range of values. For low temperatures and residential applications, it is possible, for example, to use solid-gas sorption of bromide strontium as the reactant and water as the refrigerant fluid, which combined with a flat plate solar collector, can provide direct floor heating and cooling [34].

For medium temperature thermochemical storage application, between 400 °C and 500 °C, Australian National University studies the ammonia synthesis and dissociation reaction. The necessity of storage systems is so important that factors like ammonia toxicity are undertaken [35]. At the Institute of Engineering Thermodynamics (German Aerospace Center - DLR) they are working on the $\text{Ca(OH)}_2 - \text{CaO}$ reaction system [36], increasing a little the upper temperature limit, up to 650 °C.

High temperature thermochemical storage is the most challenging and promising system in order to achieve high efficiency energy conversion rates. The high temperature characteristic of some of the reactions made them perfect candidates for CSP energy storage: they make it possible to operate heat engines at high efficiency, as in electricity generation [37], and this high temperature heat is generated at essentially isothermal conditions.

1.3. Materials for thermochemical heat storage for CSP applications

Considering the high temperatures required in CSP applications, thermochemical reactions are very interesting. Inorganic hydroxide, carbonate compounds and, metal oxide based systems have all been proposed as potential thermochemical energy storage candidates [33]. Equation (1) shows the basic reaction for inorganic hydroxide systems; where M is mainly substituted by calcium or magnesium. Equation (2) shows the general principle of carbonate compound thermal decomposition; where M normally represents calcium, magnesium, lead or potassium. Equation (3) indicates the reduction oxidation reaction for metal oxides.

Among the before mentioned possibilities, multivalent solid oxides based systems have an advantage because air is used as both heat transfer fluid and reactant, which eliminates the requirements to store CO_2 or to evaporate water, needed in the other cases, and allows the possibility of open-loop operation.

Considering reaction temperature between 750 °C and 1050 °C, CO_3O_4 , BaO, Mn_2O_3 , and CuO, were found to have the redox behaviour required for thermal heat storage. The most favourable re-oxidation kinetics is shown for cobalt oxide. Nevertheless, it has been proved that the use of a secondary oxide, mechanically mixed in and annealed, increases the re-oxidation ratio [38].

Considering material and process cost, only BaO and Mn_3O_4 , are abundant and cheap enough to have the potential to meet the United States Department of Energy cost target [39] which corresponds to a cost per kilowatt-hour of 0.06 USD [40]. Comparing the storage density of both chemical species, the Mn_3O_4 is pointed out as very interesting material for thermochemical storage.

The temperature range of the Mn_3O_4 redox reaction makes of it an attractive alternative to be implemented in future CSP plants with volumetric air receivers or supercritical CO_2 fluid, which will work at high enough temperature intervals as to enhance their efficiency.

Using manganese oxides in the storing process would consist of three steps: charge, storing and discharge. During the charge, part of the heat produced by the solar radiation is used to reduce the Mn_2O_3 into Mn_3O_4 . By this endothermic reaction, solar energy is being stored in chemical bonds without any heat loss. Later, when heat is required during the off-sun periods to produce electricity in the power block, the discharge process is performed by releasing energy through the exothermic oxidation of Mn_3O_4 to form Mn_2O_3 .

1.4. Motivation of the thesis' topic

Dispatchable electricity production is the key factor to determine the successful integration of the commercial CSP plants in the grid. In order to reach so, the development of energy storage systems able to cover the gap between energy production and consumption times, is mandatory.

In recent years, chemical heat storage for solar thermal applications has aroused widespread pieces of research. Thermochemical storage (TCS) is a comprehensive technology involving multiple disciplines, so that when designing a superior system, there are many factors that need to be taken into account, among them [41], [42]:

- Chemical kinetics: reaction selection, reversibility and possible side reaction control and reaction rates, and effective catalyst development.
- Chemical engineering and chemical machinery: the internal conversion rules of material flow and energy flow, reactor and heat exchanger design, mass transfer in the reaction process, the realization of ideal condition, and the optimal cycle efficiency.
- Thermodynamics and heat transfer: exergy flow structure of an energy storage system, internal field influence on the reaction process, the dynamic characteristics of a reaction bed, thermal conductivity of the reaction medium, and thermal analysis in the endothermic/exothermic reactor.
- Materials: corrosion, compatibility, impurity effects, and other non-expensive material consumption.
- System analysis and control: system design, operation and control, decision variables and constraints, thermal economic analysis, and control of energy storage/release.

However, because of complex technology, high cost or/and unsatisfied material performance, the solar thermal power generation using TCS systems is still in the experimental stage, and large-scale thermal power stations have not yet been built, but the unparalleled advantages provided by the TCS still make it promising in the high-temperature thermal storage applications.

There is an international interest in overcoming the intermittence problems of solar energy the led to the creation of the Thermochemical Energy Storage for Concentrated Solar Power Plants (TCSPower) consortium supported under the grant agreement number 282889, with EU funding of 4.253 million euros. This consortium gathers together universities, research centres and industry: German Aerospace Center, (DLR) (leading partner), Erachem Comilog (Belgium), Siemens AG (Germany), Paul Scherrer Institute (Switzerland), Bühler (Switzerland), Universität Siegen (Germany) and IMDEA Energy Institute (Spain).

The TCSPower project started in November 2011 and finished in July 2015. Its goal was to achieve a *“new efficient, reliable and economic thermochemical energy storage for concentrated solar power plants, with the capacity to contribute significantly to further cost reduction of regenerative electricity production and to widen its applicability towards intermediate-load and even base load power supply”* [43].

During the course of the project two different low cost materials were tested, one for medium temperatures based on dehydration/hydration reactions of Ca(OH)_2 , and the other for high temperatures based on reduction-oxidation of Mn-based oxides ($\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$).

It is in this scientific-technological context where the Thesis work is framed, trying to provide an in-depth study of the viability of manganese oxides for thermochemical storage in CSP.

1.5. Objectives of the thesis

The present work addresses the analysis of thermochemical heat storage using 1-step gas-solid redox reactions based on metal oxides and various reactor concepts for concentrating solar power plants. Specifically, the analysis is focused on the redox reaction $\text{Mn}_2\text{O}_3 \leftrightarrow \text{Mn}_3\text{O}_4$, which requires temperatures between 500 °C and 1100 °C, and fixed and fluidised bed reactors.

The objectives to fulfil within this thesis work are:

1. Improve the knowledge on materials based in metal oxides for their use in thermochemical storage.
2. Demonstrate the feasibility of the gas-solid redox reaction of manganese oxide in fixed and fluidized bed reactors with a view to its application in thermochemical heat storage systems.
3. Design, built and commissioning of an experimental facility able to provide the experimental conditions for assessing metal oxides pellets as suitable materials for thermochemical heat storage.

1.6. Thesis structure

In order to achieve the aforementioned objectives, a comprehensive research work has been carried out, new methodologies has been developed together with a great deal of effort put in design and engineering work. In addition to the present Introduction, the results have been organized in the next five chapters:

Chapter II deals with the state of the art of the main research issues addressed in this work; (i) the reactors used for thermochemical energy storage and an overview of the possible system to be considered; (ii) the control mechanisms for air heating devices of application for the workbench development; and, (iii) a review of all available information about manganese oxide related to thermochemical heat storage.

Chapter III presents the experimental facility located at the IMDEA Energy Institute, in Mostoles, Madrid, where the experimental work of this thesis has been carried out. Its objective is to reproduce different CSP plants working conditions to test various metal oxides in order to evaluate their behaviour as thermochemical storage material. The working conditions can change from very little air flow rates up to 60 Nm³/h and from room temperature up to 1100 °C. This device is made up of a reactor where the material would be tested and, a workbench which will reproduce the different working conditions required by each metal oxide. The whole device is designed, built and tuned-up ex-novo for this application. The selection of the control variables, alerts, control parameters and the development of the data acquisition system is also developed. The control of the workbench is optimized through simulation and intermediate results.

Chapter IV focuses on the material characterization of the manganese oxide in powder form and in pellets: the kinetics of the reaction are analysed, but also other properties as conductivity, reactivity analysis or morphology of the powder material are studied. Considering that for heat storage application the material needs to be shaped to form pellets, a completely new methodology has been created to measure the evolution of the pelletized material in terms of hardness, density, porosity, volume, morphology and reactivity, with the different thermal cycles applied. Through this

exhaustive analysis, a base line of the material characteristics is gathered. The compiled information will be used as reference in order to evaluate the effect of the thermochemical storage cycle on the material when using a fixed/fluidized bed reactor.

Chapter V presents the results gathered from the tests performed in the reactor. Firstly, the reactor is characterized by using inert materials consisting in alumina pellets. Secondly, pure and doped manganese oxides are tested in fixed and fluidized bed conditions. To conclude, the effect of the assays in the material is analysed and measured in comparison to the base investigation performed in CHAPTER IV.

Chapter VI gathers the main conclusions reached in the development of the present thesis. It also addresses further work to be performed in order to attain a dispatchable heat storage base in the manganese oxide redox reaction.

Finally, several annexes have been included for clarifying purposes. They compile the extra information that has been referenced but not presented in the body of the text together with further detailed experimental data.

CHAPTER II

2. STATE OF THE ART

This chapter summarizes the main research issues addressed in this work: (i) the reactors used for thermochemical energy storage and an overview of the possible system to be considered; (ii) the control mechanisms for air heating devices of application for the workbench development; and, (iii) a literature review on manganese oxide related to thermochemical heat storage.

2.1. Thermochemical heat storage reactors for high temperature processes

There are three different reactor concepts for CSP plants attending to the way in which thermal energy is supplied to the reactions:

- Direct absorption reactor: solar radiation directly impinges on the surface of the reactants.
- Indirect absorption reactor: The solar radiation hits onto a material that contains the reactants and heat is transferred from that material to the reactants.
- Irradiation independent reactor: A heat transfer fluid (HTF), which has been previously heated using solar energy, heats up the reactants downstream in the process.

In central air receiver for high temperature CSP plants, the thermochemical storage systems considered are based in the “irradiation independent reactor” concept. Here the air is the heat transfer fluid that transports thermal energy from the receiver to the reactants, so the operation of the reactor where the heat is stored is independent of the solar irradiation captation system. Thus, the traditional classification for gaseous-solid reactors is maintained: Fixed bed, fluidized bed and moving bed reactors.

The characteristics of irradiation independent reactors are described in detail through this section, nevertheless a summary is shown in Table 2.1.

Table 2.1. Summary of reactor concepts [44].

Reactor concept	Modes	Types	Particle size (mm)	Residence time	Volume changes	Permeability	Thermal conductivity	Disadvantages	Advantages
Fixed bed		Direct or indirect contact	1 - 10		Difficult to handle. Big impact in reaction kinetic and process control	(Direct contact) Particle sizes should be at the upper limit.	(Indirect contact) It has to be improved by chemical modification of TCS material and by reactor design	Reaction kinetics is critical for loading and unloading power with particle sizes in the upper range.	Abrasion is acceptable.
Fluidized bed		Circulating fluidized bed, pneumatic transport reactor, spouted, stage bed	0.5 – 5	min to 1 h.	Not beneficial	Permeability of the bulky system can be low. Typically 20 – 70 mbar for fluidized systems over the bed.	It can be low due to given particle sizes.	Solid back mixing. Impact of particle attrition. Recovery of fines.	Temperature uniformity Good heat transfer Ability to continuously remove particles.
Moving bed	Axial, Radial, overflow	Gravity assisted (vertical column, slit type, roof type), agitation assisted (rotary kiln, screw)	0.5 – 5	min - h	Difficult to handle.	It can be low.	It can be low due to given particle sizes		Soft impact of particle attrition

2.1.1. Fixed bed reactor

Known as well as packed bed reactor, it is widely used in the chemical industry for high tonnage chemicals production because of its simplicity. In this system there are normally two different gas flows: one for heat transporting and a second one as reactive gas.

Fixed bed reactors are sub-classified into direct or indirect contact reactors. In the direct contact units, reaction gas and transporting gas are mixed and feed together to the reactor, see Figure 2.1 (a), while in the indirect contact units, reaction gas and transporting gas would never be mixed, see Figure 2.1 (b).

Figure 2.1. Schematic direct (a) and indirect (b) fixed bed reactors.

In the design of indirect contact reactors, it is especially important to take into account the conductivity of the constructing materials because it could limit the heat transfer rate. Once the construction materials are fixed, a possible way to increase heat transfer rate is to add some highly conductive material but addition dopants may affect the chemical reaction. To decrease heat transfer problems without changing the composition of solids a direct contact system should be chosen, but this is only possible when there is no danger in mixing the heat transporting fluid and the reactive gases. It has to be considered that process control of the direct contact reactor is more difficult as two gases have to be mixed.

Attending to the physical form of the solids and to their arrangement, there is also a secondary classification: the solid material can be used in packed or unpacked particles or pellets form, as well as in a monolith form. In this case, volume changes during the reaction should be regarded as a difficulty because of the unmoved definition of the reactor.

The physical form and size of solids is closely related to the pressure drop observed in the reactor. Normal particle size is in the range of 1 - 10 mm. The lower limit is related to an acceptable pressure drop in the reactor, while the upper limit is related to the internal diffusion restrictions in the particles.

Also the physical form of solids has an effect on the pressure drop through the reactor; it would be affected by varying the particle size or changing the porosity of the material. A porous material will also lead to higher reaction kinetics. Another possibility to decrease pressure drop and to increase reaction kinetics is to limit soil height by a multi floor or chamber reactor (regenerator). The sketch of this type of reactor is shown in Figure 2.2. A

drawback of this arrangement is the more complex control unit and pipe configuration as well as the danger to mix the gas.

Figure 2.2. Regenerator reactor concept.

Volume changes in the solids are difficult to handle as space is limited and volume changes will have a big impact in reaction kinetic and process control. Nevertheless abrasion is acceptable as materials are not moving. Reaction kinetics is critical for loading and unloading power with particle sizes in the upper range.

2.1.2. Fluidized bed reactor

The behaviour of a fluidized bed reactor depends in essence on the particle characteristics and on the gas velocity. Particle size handle in this devices are in the range of 0.5 to 5 mm and their velocities are in the range of 0.01 – 6 m/s, therefore particle stability is critical. The residence time of the solids may vary between 1 and 60 minutes. Volume changes of the solids may not be beneficial, but they can be handled.

Fluidized bed reactors can be classified regarding their flow regimes (see Figure 2.3). With constant particle sizes, regimes are changing with increasing gas velocity from a fixed, to a homogenous fluidized bed, to a bubbling, slugging spouted bed. At the end, a turbulent flow regime is present. Figure 2.3 also includes circulating fluidized beds and the pneumatic transport.

Figure 2.3. Different flow regimes observed in fluidized beds [45].

The homogenous regimen is best characterized by a pressure drop - ΔP - versus gas velocity - U - plot. Measurements performed at increasing and decreasing flow rates lead to the hysteresis observed in Figure 2.4, due to lower interparticle forces for defluidization conditions. For this reason, essential information of the characteristics of the bed is obtained in practice from decreasing gas flow rate data.

Figure 2.4. Pressure drop vs. gas velocity plot for the determination of U_{mf} [44].

Below a characteristic gas velocity known as the minimum fluidization velocity, U_{mf} , a packed bed of solids particles remain fixed and pressure drop is proportional to gas velocity accordingly to Ergun equation (4).

$$\frac{\Delta P}{L} = 150 \cdot \frac{(1 - \varepsilon)^2}{\varepsilon^3} \cdot \frac{\mu_g \cdot U}{(\phi \cdot d_p)^2} + 1.75 \cdot \frac{1 - \varepsilon}{\varepsilon^3} \cdot \frac{\rho_g \cdot U^2}{(\phi \cdot d_p)^2} \quad (4)$$

Where L is the height of the particle bed, ε is the void fraction, μ_g is the dynamic viscosity of the gas, ρ_g is the density of the gas, d_p is the diameter of the particles in the bed and ϕ their sphericity.

U_{mf} is calculated from experimental curves (see Figure 2.4) as the intersection point between the straight line corresponding to the fixed bed and the plateau observed during fluidization.

At U_{mf} the particles are essentially supported by the gas stream and bed expansion occurs. For gas velocities higher than U_{mf} , the drag force on an individual particle exceeds the force exerted by gravity, thus leading to fluidization regime, there pressure drop equals the weight of particles per unit area, and the solid particles behave similar to liquids.

Theoretically, for spherical particles, U_{mf} can be estimated from equation (6), where the minimum fluidization Reynolds number, Re_{mf} , is calculated with equation (5), obtained by algebraic operations on expression (4).

$$Re_{mf} = 42.9 \cdot (1 - \varepsilon) \cdot \left(\sqrt{1 + \frac{\varepsilon^3}{(1 - \varepsilon)^2} \cdot \frac{Ar}{3214}} - 1 \right) \quad (5)$$

$$U_{mf} = Re_{mf} \cdot \frac{\mu_g}{d_p \cdot \rho_g} \quad (6)$$

Ar is the Archimedes number calculated according to equation (7):

$$Ar = d_p^3 \cdot \rho_g \cdot (\rho_s - \rho_g) \frac{g}{\mu_g} \quad (7)$$

where ρ_g is the density of the particles and g is the acceleration of gravity.

Further increases in gas velocities will usually not cause increases in pressure drop up to another characteristic gas velocity value, call terminal velocity of fluidization - U_t -. For gas velocities higher than U_t , the pressure drop decreases due to powder entrainment and pneumatic transport.

In order to estimate the terminal velocity, equation (6) is used substituting the minimum fluidization Reynolds number with the Reynolds number calculated for heterogeneous fluidized bed condition, Re_{t_hetero} , calculated by Reh's formula [46] shown in equation (8).

$$Re_{t_hetero} = \sqrt{\frac{4}{3} \cdot Ar} \quad (8)$$

For the fluidized or spouted bed different bed layouts are imaginable, for example a laterally or vertically staged bed to influence the permeability and reaction kinetic is possible (see Figure 2.5).

Figure 2.5. (a) Vertically – (b) Laterally staged bed .

When reaction times are of the order of seconds or very few minutes, a circulating fluidized bed or a pneumatic transport reactor can be used (see Figure 2.6).

In these devices, gas velocities are in the range of four to ten times U_{mf} . Therefore heat transfer, gas /solid mixture, kinetics in general as well as abrasion is high and particle integrity difficult to maintain. If lower attrition is necessary, a fluidized bed should be chosen.

Volume changes of the solids during reaction are possible but complicate the process control due to a wider conversion time distribution. Very fine particles (fines) produced during the reaction are separated and sucked off, but have to be reintegrated into the process to avoid high losses.

Figure 2.6. (a) Circulating fluidized bed and (b) pneumatic transport reactor.

The situation described above holds for ideally fluidizable particles. However, the behaviour of a fluidization system is closely dependent on the properties of the solid particles, such as size, density, cohesiveness or the amount of fines they often contain. Consequently, data obtained for one powder cannot be used for others with different properties.

To limit the need for systematic experimental investigations, Geldart classified powders into four different groups characterized by mean diameters and the density difference between solid particles and fluidizing gas [47]. This classification is schematically presented in Figure 2.7, focused on conditions prevailing for fluidization with a gas rather than with a liquid.

Figure 2.7. Geldart's powder classification [45].

The powders easiest to fluidize belong to groups A and B. Group A gathers particles with small mean size (20–150 μm) and/or low particle volume mass (less than about 2 g/cm^3). Group B contains most powders composed of particles whose mean size and density range are between 40 and 500 μm , and 1–4 g/cm^3 , respectively, sand is the most typical material of this group. Group D corresponds to particles which are large, i.e. whose diameter exceeds 800 μm , and/or very dense. Finally, group C contains powders which are in anyway cohesive, due to (i) very small particles size (typically less than 20 μm , but this limit is rapidly shifted to larger particles size with decreasing density difference between the particles and the fluidizing gas), (ii) strong electrostatic charges or (iii) the presence in the bed of very wet or sticky materials [47].

It is worth noting that, in Geldart's classification, groups C and A, and groups A and B are separated by transitional regions rather than by sharp boundaries. The presence of these transitional zones, especially between groups C and A, makes it difficult to classify a priori such particles and, as different rules govern fluidization of the two groups, to control their evolution. Hence, it is often necessary to experimentally determine the fluidization behaviour for each of these particular cases.

2.1.3. Moving bed reactor

Apart from fluidized beds, there are other technical solutions that have been used to induce relative particles movement, they are known as moving bed reactors. Particle sizes handled in these devices are in the range of 0.5 to 5 mm, and their velocities are in the range of 0.02 to 0.4 m/s. These systems have a wide retention time range going from several minutes to hours.

Attending to the gas flow mode, moving bed reactors are classified in radial, axial and overflow. Attending to the force involved in producing the movement, there are agitated and gravity assisted reactors.

Agitated assisted reactors

Agitated assisted reactors use moving parts to improve the mixture of gas and solids. In the rotary kiln, see Figure 2.8 (a), the particles are moved by a rotating drum. Its main advantage is that volume and particle size changes have no big influence on the process. The restricting factor is the bad reaction control (heat transfer and particle guiding).

To improve the reaction control, instead of a bulky material, a moving monolith like in a rotating wheel can be used, see Figure 2.8 (b). For this kind of reactor the material should be stable without big volume changes and in a porous form. This type of reactor has been successfully used for example in hydrogen production processes by catalytic dehydrogenation of propane.

Another possible reactor type is the screw heat exchanger (Figure 2.8 (c)). Due to the mixing, a good heat transfer can be attained in these systems. Volume changes of the material are possible if the screws are not fully filled. Detrimental here is the high abrasion due to the rotating screws heading to unstable particles which complicate the process.

Figure 2.8. Agitated assisted reactors: (a) rotary kiln, (b) monolith rotating wheel and, (c) screw heat exchanger.

Gravity assisted reactors

Gravity assisted bulk flow reactors have the advantage that no moving heat sensitive parts are necessary in the reactor. They are driven in counter current mode up to gas velocities of 0.6

times the minimal fluidization velocity. The possible reactor types, shown in Figure 2.9, are vertical column heat exchanger, slit type heat exchanger and roof type heat exchanger.

The vertical column as well as the slit type heat exchanger can consist of several smaller columns which are arranged beside each other. Difference between these reactors is the flow type; gas is streaming vertically in the first case and horizontally in the second case. The vertical column has disadvantages compared to the slit type heat exchanger, the pressure drop is higher, and the kinetics and heat transfer are lower. That is the reason why material permeability and conductivity in this case should be higher.

These disadvantages of the vertical column heat exchanger could be reduced with the roof type heat exchanger. Here bulk density is lower and a better heat exchange with a gentler solid handling is possible without changing material properties. Another difference is that surface area with material contact is higher.

Figure 2.9. Gravity assisted reactors: (a) Vertical column, (b) slit type and, (c) roof type heat exchanger.

2.1.4. Experimental reactor developments

For solar thermal energy storage in chemical bonds, there are two possibilities: Direct use of solar radiation where the chemical compounds directly absorb the energy in a receiver-reactor system or indirect use, coupling the energy source to the thermochemical process by using a HTF. Although the work in simulations has been very productive the number of experimentally developed reactors in the last few years for thermochemical energy storage is much smaller.

Among those based on the direct application of solar radiation, rotary kind receivers have been quite popular. They combine a good heat transfer between the gas and the solid phase, allow high mass flow rates and by particles motion, sintering problems are improved.

Neises et al. [14] developed a rotary kiln to test the cobalt oxide redox reaction. The heating rate and the temperature of the reactor were controlled by adjusting the solar flux entering in the reactor. Samples of one or two hundred grams of pure cobalt oxide or cobalt oxide mixed with alumina oxide were tested for several cycle experiments with air flow rates between 4 and 8 L/min. Although the reactor is equipped with a quartz window, some material was lost during the experiment due to entrainment problems. The authors had some difficulties in calculating conversions over the thermal cycles but observed up to 50 % conversion in average.

The test material behaviour was to form a cohesive layer in the kiln wall instead of forming a dust cloud which protected the quartz windows, one of the most sensible part in these devices. They observed a material transformation in morphology indicating that there had been sintering and agglomeration of the material. They could not identify influence of the rotational speed in the reaction, apparently the maximum allowed speed of 6 rpm is too small to appreciate variations in the reaction.

Alonso et al. [48] develop a lab-scale reactor in which direct solar radiation (produced by a solar simulator) would drive the metal oxide thermal reduction arranged in a packed bed. This reactor was not developed in order to store energy but to analyse the kinetic properties of different metal oxides.

Alonso et al. [49] also developed a rotary kiln to test copper oxide redox reaction. They place 10 g of CuO into the reaction chamber, closed by a quartz window and set the gaseous flow rate at 10 L/min at a rotation speed of 4 rpm. They performed several campaigns of three cycle experiments concluding that copper oxide is suitable for thermochemical energy storage, obtaining conversions of the reduction reaction up to 80 % in argon atmosphere.

Among the experimental reactors using indirectly the Sun radiation, research on calcium hydroxide seems promising. In a first stage, a 10 kW reactor has been developed at Deutsches Zentrum für Luft und Raumfahrt (DLR) in Germany. This reactor is based in a plate heat exchanger, filled with 20 kg of material, where up to ten cycles at temperatures above 410 °C and pressures above 0.1 bar were verified [50].

It is known that large fixed bed present high pressure drops and heat and mass transfer barriers. In order to avoid those effects, Pardo et al. [51] propose a fluidized bed for calcium hydroxide reaction. A mixture in weight of 70 % Al_2O_3 and 30 % Ca(OH)_2 was used to obtain good enough fluidization material characteristics. The amount of 1.93 kg mixture was charge in the fluidized bed reactor and 50 cycles were demonstrated with an average conversion of 80 %.

Although, for the best of our knowledge, it has not been constructed yet, it is remarkable the effort put in developing a thermochemical storage system base in honeycomb monolithic structure. There have been publications about material configuration in different porous ceramic structures and redox pair oxides chemistry [52], and extended work in simulating thermochemical storage system based in that material [53]–[56]. This research line carried out in DLR lead to think in a close future experimental set-up to test cobalt oxide redox behaviour in monolithic structure.

2.2. Control systems for air heating devices

Temperature control is a challenging issue in technological processes in many branches of industry, particularly in temperature control of air heating systems which are widely used in metallurgic, chemical or pharmaceutical industries [57]. In the Thesis framework an air heating device is design and constructed, also the control of this system is developed. Here the base knowledge of control used for the development and optimization of the air heating unit is included.

The proportional-integral-derivative (PID) structure is one of the most popular control algorithms and has been successfully applied in many processes for temperature control purposes because of its simplicity and robustness. Specialized controllers for many different applications are also based on PID control. The block diagram of a classical feedback PID controller is presented in Figure 2.10.

Figure 2.10. Block diagram of a feedback PID controller system.

Here:

- $r(t)$ is the desired value or setpoint (sp), the reference input of the system;
- $y(t)$ is the system output signal, the value measured in the plant or process variable (pv);
- $e(t)$ is the error signal, which is the difference between $r(t)$ and $y(t)$; and,
- $u(t)$ is the controller output signal.

The study of signals and systems can be carried out in terms of either a time domain or a transform domain formulation. Both approaches are often used together in order to maximize our ability to deal with analysis and design problems in control engineering.

By applying the Laplace transform, an equivalent representation to Figure 2.10, in terms of transform domain, is shown in Figure 2.11.

Figure 2.11. Block diagram of a feedback controller system.

Where $r(s)$, $e(s)$, $u(s)$ and $y(s)$ have equivalent meaning to $r(t)$, $e(t)$, $u(t)$ and $y(t)$. $G_C(s)$ is defined as the controller transfer function and $G(s)$ is the plant transfer function.

Classic PID schemes and controllers have been updated and enhanced over the years from the early controllers, based on relays and synchronous electric motors or pneumatic or hydraulic systems towards the current microprocessors. The most recent improvements in the field of PID tuning are the development of the set point overshoot method, in the closed-loop approach [58], and the direct synthesis method in the open-loop approach. The latest method has been evaluated in various unstable processes with time delay obtaining nominal and robust control performances, improving close-loop approach performances and reducing the

undesirable overshoot [59]. This progress have also been accompanied by software developments, such as the inclusion of gain scheduling of PID controllers which dynamically adjust the gains of the PID algorithm during the control process [60] and the real-time implementations in languages, such as Matlab [61] or LabVIEW [62].

Even so, electric furnaces operation, like those to be controlled in the present research work, are characterized by large inertia, time delay, non-linear and time-varying phenomena, which have been the motor for the development of more advanced control schemes. In [63], a temperature controller is developed based on the combination of fuzzy and PID controls. In [64], a fuzzy controller is designed through the application of an adaptive genetic algorithm for PID parameter's optimization. In [65], the fuzzy adaptive control is combined with a grey prediction control to develop a grey prediction fuzzy adaptive control. In these three studies, advanced controllers for furnaces without air heating flow production are simulated as well as the pertinent conventional PID control for comparison purposes. Although there is no a clear definition of the temperature application range, simulated results show no-quantified better performances of the advanced control schemes compared to the conventional PID controllers.

Ref. [66] presents the optimization of a fuzzy logic controller for an electric air heater system. Although authors do not provide the air flow rate used in the simulation, the controller performance is evaluated with a set point change from 30 °C to 120 °C. This work shows an insight of the complexity in the optimization of the fuzzy logic control (FLC) with the evaluation of five types of membership function with four different sizes of rule base. Although there is no comparison with a PID controller, the results show that fifteen out of the twenty controllers simulated have an average overshoot of 20 °C, four controllers do not reach the set point in 200 min, and only the fuzzy logic controller with combined trapezoid and triangular membership function and 3x3 rule achieves an overdamped temperature response in 178 min.

Four different control schemes are optimized and compared in an air heater in [67]. The study is based on the model obtained from an open-loop step response from 30 °C to 55 °C. This model is used to design a PID control strategy and subsequently the optimum PID controller design is used to develop a FLC scheme. The membership values are optimized using genetic algorithms (GAs) in conjunction with FLC. Scale mapping is performed using triangular membership function with the help of artificial neural networks (ANNs). The ANN models developed for fuzzification of input variables are used in a neuro-fuzzy control (NFC) scheme. The comparison of the closed-loop responses of the above mentioned controllers shows in terms of integral error criteria that NFC has the best performance followed by FLC-GA, PID and FLC. In terms of integral time absolute error the faster controller is NFL, followed by FLC-GA and FLC, being the PID the slowest controller.

Nevertheless, many modern controllers on the market are based in PID structure; according to a survey conducted in 2010, the ratio of application of PID control, conventional advanced control and model predictive control, is about 100:10:1 [68].

In order to get any control law in a given system, the first step is to perform a system identification defining the desired output response $y(s)$ to an arbitrary input $u(s)$ over a time interval [69]. The second step is to determine the parameters of the PID controller. There is

extensive literature about methods for tuning of PID controllers for different controller structures and from different approaches [70].

Sections 2.2.1 and 2.2.2 are included here as theoretical basis for the control work developed in the Thesis in sections 3.4.4 System identification and 3.4.5 Control tuning, respectively.

2.2.1. System identification

System identification consists in building mathematical models of a dynamic system based on measured data. Here the approach known as black-box model or input-output model is applied, since no attempt is made to describe the “internal” behaviour of the system and only the relation between input and outputs is modelled.

System identification basically comprises the following steps:

1. Design an experiment and collect input-output data from the process to be identified.
2. Perform a data treatment consisted in remove trends and outlying values and apply filtering to enhance important frequency ranges.
3. Choose a mathematical model.
4. Fit the parameters of the chosen model to minimize an estimation error function.
5. Validate the model by comparing the model output with experimental data.

Step-response analysis, also known as transient analysis, is applied to study the relation between signals in the system which is described in terms of curves or equations. Experimentally, it is based in recording how and in what time, a variation in inputs as a step or impulse affect to the measurable variables of the system. If we know the system’s response to an impulse, we will also know its response to any input.

The system response is typically fitted to one of the following simple mathematical models: first order plus time-delay (FOPTD), second order plus time-delay (SOPTD) or higher order plus time-delay [69].

If the model of the system expressed as higher-order plus time-delay model or frequency response data, then most PID tuning rules cannot be used. By this reason, it is recommended to reduce the system model to a FOPTD model [71].

The parameters of the PID controller should be tuned in terms of the process dynamics, so the process model should be identified prior to the control tuning.

FOPTD

The transfer function of a FOPTD process is shown in equation (9).

$$G(s) = \frac{k_c}{\tau s + 1} e^{-\theta s} \quad (9)$$

where k_c , τ and θ are the static gain, the time constant and the time delay respectively.

Equivalent to equation (9), the differential equation (10) describes the FOPTD process in the time domain.

$$\tau \frac{dy(t)}{dt} + dy(t) = k_c u(t)(t - \theta) \quad (10)$$

Solving differential equation (10) for the step input defined in (11), where d is a constant, leads to the step input response shown in equation (12):

$$u(t) = d \text{ for } t \geq 0 \text{ and } u(t) = 0 \text{ for } t < 0, y(t) = 0 \text{ for } t \leq 0 \quad (11)$$

$$y(t) = \left[1 - \exp\left(-\frac{t-\theta}{\tau}\right) \right] k_c d \text{ for } t \geq \theta, y(t) = 0 \text{ for } t < \theta \quad (12)$$

The following equations can be obtained from (12),

$$y(\infty) = \left[1 - \exp\left(-\frac{t-\theta}{\tau}\right) \right] k_c d \Big|_{t=\infty} = k_c d \quad (13)$$

$$y(t)|_{t=\theta+\tau} = \left[1 - \exp\left(-\frac{t-\theta}{\tau}\right) \right] k_c d \Big|_{t=\theta+\tau} = [1 - \exp(-1)]k_c d = 0.6321y(\infty) \quad (14)$$

$$\frac{dy(t)}{dt} \Big|_{t=\theta} = \exp\left(-\frac{t-\theta}{\tau}\right) \frac{k_c d}{\tau} \Big|_{t=\theta} = \frac{k_c d}{\tau} = \frac{y(\infty)}{\tau} \text{ for } \frac{dy(t)}{dt} = 0 \text{ for } t < \theta \quad (15)$$

The information contained in the equations above is shown graphically in Figure 2.12.

Figure 2.12. Step response of a FOPTD process.

SOPTD

The transfer function of a SOPTD process is shown in equation (16).

$$G(s) = \frac{k_c}{\tau^2 s^2 + 2\tau\xi s + 1} e^{-\theta s} \quad (16)$$

where k_c , τ , ξ and θ are the static gain, the time constant, the damping factor and the time delay respectively.

Considering the possible roots of the denominator in equation (16), there are three types of step response for a SOPTD process:

- Overdamped process. The roots are distinct and real or equivalently, $\xi > 1$. Step response of these process is shown in equation (18). As seen in Figure 2.13, the response of an overdamped process does no show oscillation.
- Critically damped process. The denominator has a real double root or equivalently, $\xi = 1$. Step response of these process is shown in equation (19). As in overdamped process, the corresponding response has not oscillation.
- Underdamped process. The roots of the denominator are distinct and complex or equivalently, $\xi < 1$. Step response of these process is shown in equation (20). Graphically, see Figure 2.13, these responses show oscillation.

Figure 2.13. Step response of a SOPTD process as function of the damping factor.

Solving differential equation equivalent to equation (16), for the step input defined in(17), leads to the step input response:

$$u(t) = d \text{ for } t \geq 0 \text{ and } u(t) = 0 \text{ for } t < 0, y(t) = 0 \text{ for } t < 0 \quad (17)$$

For $\xi > 1$ (Overdamped process)

$$y(t) = k_c d \left\{ 1 - \frac{\tau_1 \exp \left[- (t - \theta) / \tau_1 \right] - \tau_2 \exp \left[- (t - \theta) / \tau_2 \right]}{\tau_1 - \tau_2} \right\} \quad (18)$$

For $\xi = 1$ (Critically damped process)

$$y(t) = k_c d \left\{ 1 - \left[1 + (t - \theta) / \tau \right] \exp \left[- (t - \theta) / \tau \right] \right\} \quad (19)$$

For $\xi < 1$ (Underdamped process)

$$y(t) = k_c d \left(1 - \exp \left[-\xi(t - \theta)/\tau \right] \left\{ \cos \left[\frac{\sqrt{1 - \xi^2}}{\tau} (t - \theta) \right] + \frac{\xi}{\sqrt{1 - \xi^2}} \sin \left[\frac{\sqrt{1 - \xi^2}}{\tau} (t - \theta) \right] \right\} \right) \quad (20)$$

where:

$$\tau_1 = \frac{\tau}{\xi - \sqrt{\xi^2 - 1}}, \tau_2 = \frac{\tau}{\xi + \sqrt{\xi^2 - 1}} \quad (21)$$

with condition (22) for the whole range of values of ξ .

$$y(t) = 0 \text{ for } t < \theta \quad (22)$$

2.2.2. PID Control and tuning

Control tuning is the process of determining the controller parameters that produce the desired output. In a PID controller, the control action is generated as a sum of three terms, as the algorithm given in equation (23) shows.

$$u(t) = u_p(t) + u_i(t) + u_d(t) \quad (23)$$

where $u_p(t)$, $u_i(t)$ and $u_d(t)$ are the proportional, integral and derivative contributions respectively.

The proportional part is a simple feedback, as shown in equation (24)

$$u_p(t) = k_p \cdot e(t) \quad (24)$$

where $e(t)$ is the control error and k_p is the controller gain. The control error, shown in equation (25), is defined as the difference between the setpoint and the process output.

$$e(t) = r(t) - y(t) \quad (25)$$

Proportional control normally gives a system that has a steady-state error, because the proportional controller cannot be a nonzero constant when the error is zero at steady state. Integral action is introduced to remove this offset. This is possible because the integral term can be a nonzero constant due to the accumulated error. Integral action is mathematically defined by equation (26).

$$u_i(t) = \frac{k_p}{\tau_i} \int e(t) dt = k_i \int e(t) dt \quad (26)$$

where τ_i is the integral time and k_i is the integral gain. Provided that the average of the control error has the same sign over a long period, control action is taken even if the error is very small. Thus, the offset introduced by the proportional control is compensated by the integral action, but a phase lag is added into the system.

Derivative control is used to provide anticipative action. It is defined by equation (27).

$$u_d(t) = k_p \tau_d \frac{de(t)}{dt} = k_d \frac{de(t)}{dt} \quad (27)$$

where τ_d is the derivative time and k_d is the derivative gain. Derivative control is used to decrease and eliminate overshoot of system response and introduce a phase lead action that removes the phase lag introduced by the integral action.

The detailed algorithm of the PID controller is given in equation (28).

$$u(t) = k_p \cdot e(t) + \frac{k_p}{\tau_i} \int e(t)dt + k_p \tau_d \frac{de(t)}{dt} \quad (28)$$

In terms of transfer functions, the analogous algorithm for a PID controller is shown in equation (29).

$$G_C(s) = k_p \cdot \left(1 + \frac{1}{\tau_i \cdot s} + \tau_d \cdot s \right) \quad (29)$$

Although PID controllers are widely used in industry, the tuning of these parameters can be very challenging. A poorly tuned controller results in low responses, oscillations and instability of the system. The tuning parameters should be set with in-depth consideration of the process dynamics; the basic requirements of the output are stability, desired rise time, peak time and overshoot. It is important to know in the practice the effect of the tuning parameters on the behaviour of the process output:

- The proportional gain k_p is too large when, for a step setpoint change, the process output shows a big oscillation centred on the setpoint.
- The proportional gain k_p is too small when, for a step setpoint change, the process output shows an overdamped response.
- The integral time is too small, which means that the integral action is too strong, when for a positive step setpoint change, the process output oscillates and stays above the setpoint longer than under it.
- The integral time τ_i is too large, which means that the integral action is too weak, when for a positive step setpoint change, the process output oscillates and stays under the setpoint longer than above it.
- The derivative time τ_d is too large, when for a step setpoint change the process output signal shows a high-frequency oscillation from the start to the steady state.

Among the extensive literature about methods for tuning of PID controller parameters, for concision purposes, only the Ziegler-Nichols (ZN) tuning rule for step response would be included.

In the ZN tuning method for step response of systems identified as FOPTD, the controller parameters are obtained by applying the equations shown in Table 2.2.

Table 2.2. ZN tuning parameters for step response.

Controller	k_p	τ_i	τ_d
P	$\tau/k_c\theta$	∞	0
PI	$0.9\tau/k_c\theta$	3.33θ	0
PID	$1.2\tau/k_c\theta$	2θ	$\theta/2$

The tuning parameters selected for the control system are crucial to effectively regulate the air flow and its temperature in the test bench designed to reproduce the working conditions of a CSP plant incorporating a thermochemical storage system with high-temperature fluid bed reactor.

2.3. Manganese oxide: synthesis methods, physical and chemical properties

The thermochemical energy storage of application for the present Thesis will be based on manganese oxide material. Next, the state of the art of this material characterization and reaction kinetics is included.

Manganese oxides have different commercial applications, among them: syngas production [72], Li/MnO₂ battery [73], hydrogen production by water splitting [74] and oxygen carrier in chemical combustion [75]. The manganese oxides knowledge, gathered from the investigation done for those applications, is used as a starting point to investigate their application as thermochemical heat storage material.

It is known that the common stable crystalline phases in the Mn-O system are MnO₂, Mn₂O₃, Mn₃O₄ and MnO. It is also known the existence of a metastable structure - Mn₅O₈ - that appears between the temperature formation of MnO₂ and Mn₂O₃ [76].

MnO₂ varies from grey colour to black, Mn₂O₃ has a colour between red and brown, Mn₃O₄ is black and, MnO is a grey-green or dark-green powder.

Under suitable conditions of temperature and oxygen partial pressures, MnO₂ decomposes into a number of lower manganese oxides, MnO_x, with x value between 1 and 1.6 [77]: at about 650 °C the first thermal reduction, shown in (30), from MnO₂ to Mn₅O₈ takes place. In the range of 820 – 830 °C, Mn₅O₈ is no longer present because it is transformed to Mn₂O₃ according to (31). In the range of 880 – 1050 °C, Mn₂O₃ decomposes into Mn₃O₄ as exposed in (32). And above 1300 °C MnO is the only substance present following the reaction in (33).

The high pressure and temperature quench experiments up to 5 GPa and 700 °C showed that the decomposition temperature of MnO₂ increases with pressure [77].

The mechanism for each of the steps in the thermal decomposition of Mn-O is known to be related to the origin and history of the material, as well as the reactive gas atmospheres under which the reduction takes place [73], [78].

In oxygen rich atmosphere, the formation of Mn₅O₈ from MnO₂ is slightly retarded and the formation of Mn₃O₄ is considerably retarded – occurs at 1050 °C - compared to those taking place in regular air.

If the reaction takes place in nitrogen atmosphere, there is an appreciable acceleration of the Mn_3O_4 formation right after the appearance of Mn_2O_3 at temperatures as low as 880 °C.

Pure Mn_3O_4 is obtainable in nitrogen atmosphere, whereas in oxygen and air atmospheres, the formation of Mn_2O_3 (excess oxygen containing product) is favoured at an appreciably lower temperature.

The obvious sensitivity of the formation of Mn_3O_4 to the operational range of temperature and to the availability of oxygen in the surrounding gas atmosphere may account for a strongly reversible reaction, which takes place between 520 °C and 600 °C:

The mixed valence that Mn_3O_4 has, is an electron-mobile environment very promising regarding their potential catalytic activity in oxidation/reduction reactions.

When the reaction is chemically-driven under the reductive influence of the hydrogen atmosphere, the MnO_2 goes down to MnO directly; the intermediate compositions being unstable [78].

The influence of mechanical activation on Mn_3O_4 reaction mechanism by high energy milling has been studied [79]. The main conclusion of this work is that milling has an effect on the solid-state reactions of Mn_3O_4 when heated in air between room temperature and 1100 °C.

In the commercial sample, Mn_3O_4 oxidizes to Mn_2O_3 at 520 - 600 °C and Mn_2O_3 reduces to Mn_3O_4 at 930 - 1000 °C. The milled Mn_3O_4 does not oxidize during the mechanical process, but around 250 °C there is an early partial oxidation of Mn_3O_4 to MnO_2 . When the temperature rises up to 485 °C, Mn_3O_4 becomes Mn_5O_8 , at about 615 °C all the species are reduced to Mn_2O_3 and in the range of 900 - 1000 °C the reduction of Mn_2O_3 to Mn_3O_4 takes place. It has also been observed that the extent of the early Mn_3O_4 oxidation increases with milling time of the studied sample [79].

As far as it has been reported, the results convey that none of the MnO_x compositions encountered during MnO_2 decomposition in air can be described as redox, except for Mn_3O_4 . It is also known that subsequent oxidation / reduction cycles lead to an increase in reduction temperature, probably due to a higher crystallinity [72].

2.3.1. *Synthesis methods*

There are several manganese oxide production methods; some consist in the oxidation of metallic manganese, others, in the decomposition / reaction of different manganese chemical compounds. Depending on the production process, different manganese oxidation degree with distinct properties would be obtained.

Oxidation of metallic manganese

Metallic manganese would react in oxidising atmospheres at high temperature to reach different oxidation stages [80]. In an oxygen atmosphere, the reactions shown in (35) take place. In this case, the desired ore would be obtained controlling the reaction temperature by subsequent oxidation reactions. Really high temperatures are required to obtain the highest oxidation stage ore.

In a carbon dioxide atmosphere, the reaction mechanism proposed is shown in (36). Over 90 % of the product obtained is high quality MnO and the process requires considerably lower reaction temperatures, but MnO₂ and Mn₂O₃ cannot be produced.

Decomposition of manganese compounds

Thermal decomposition of manganese carbonate (MnCO₃) in a regular air atmosphere produces manganese dioxide in a temperature range from 300 °C to 440 °C, according to (37). By higher temperature application Mn₂O₃ and Mn₃O₄ could be obtained [81].

Figure 2.14 shows the thermogravimetric (TG) and differential temperature analysis (DTA) experimental curves, black and red lines respectively. From these analyses, three weight changes in the mass sample are identified at 330 °C, 535 °C and 950 °C temperatures. These weight losses of 24.30, 31.22 and 33.57 % respectively, correspond to the MnCO₃ decomposition, and the Mn₂O₃ and Mn₃O₄ formation.

Figure 2.14. DTA and TG analysis of manganese carbonate.

Also the thermal decomposition of various manganese (II) dicarboxylate anhydrides has been studied in air, argon and carbonate dioxide atmospheres [82]. In the range 250 - 350 °C the decomposition in Ar and CO₂ atmospheres would produce MnO, while in air atmosphere the manganese ore present would be Mn₂O₃. In all cases, there is carbon deposits formation as side product, the amount of carbon would depend on the number of CH₂ groups present in the initial manganese dicarboxylate.

Manganese dioxide can be produced by pyrolytic decomposition of manganese nitrate solution [83]. An anode form with aluminium and tantalum with a thin layer of manganese dioxide is immersed in an aqueous solution of manganese nitrate. Then it is heated to about 130 - 350 °C either in a hot-air conveying or circulating furnace or in an electric furnace causing the pyrolytic decomposition of the adhering manganese nitrate to manganese dioxide.

Reaction of different manganese chemical compounds

Manganese dioxide can be produce by hydrothermal synthesis with a mixture of monohydrated MnSO₄ and KMnO₄, which is introduced in a Teflon-line pressure vessel at

140 °C. The effect of varying the hydrothermal time was studied in [84], where larger nanostructures of MnO₂ were found for increasing treatment times from 1 hour to 18 hours.

Mn₃O₄ and MnO₂ can be synthesized from MnCl₂ mixed with ethanol amine. In [85], the crystal structure, phase and the electrochemical performance were found to be dependent on the preparation conditions: MnO₂ was synthesized by stirring the mixture for 12 h and a posterior hydrolyzation at room temperature for five hours. By substituting the stirring of the mixture for different times of ultrasonication, Mn₃O₄ was obtained. A mixture of both manganese ores was the result of the ultrasonication follow by hydrolyzation in a Teflon-line autoclave at 140 - 180 °C for the same five hours.

Manganese oxide can be obtained by sol-gel synthesis by precipitation with ammonia solution. In [86], manganese oxide precursor, Mn(NO₃)₂·4H₂O, is diluted in Milli-Q[®] water. After homogenization, ammonia hydroxide is slowly added and, over stirring, the solution reposes for twenty hours. The solid formed is filtered, washed and dried at 80 °C. The dried solid is pulverized and calcined at 700 °C for four hours with a heating ramp of 2 °C/min to obtain the Mn₃O₄. In this study, it was shown the precursor solution concentration influence in the characteristics of the manganese oxide properties: a higher concentration of the precursor solution shows a bigger particle diameter and better cyclability, but the porosity and the specific surface of the particles decreases.

Mn₃O₄ was also prepared by sol-gel synthesis at a low temperature in [87], where the mixing of citric or tartaric acid with Mn(NO₃)₂ and the precipitation by adjusting the pH at a value of 11 through NH₃ addition was studied. The results indicate that the addition of citric acid and tartaric acid remarkably reduced the particle size and increased the specific surface area of Mn₃O₄ nanoparticles.

2.3.2. Manganese oxide physical properties

The Mn-O system is rather complex as it can be appreciated in the phase diagram of Figure 2.15, in which the variation of composition and crystalline structure with temperature and oxygen partial pressure is shown [88].

Figure 2.15. Calculated potential phase diagram of the Mn-O system [88].

Crystal structures

The Mn-O system contains the phases manganosite (Mn_{1-x}O); α -hausmannite ($\alpha\text{-Mn}_3\text{O}_4$) that transforms to $\beta\text{-Mn}_3\text{O}_4$ at high temperatures; β -bixbyite ($\beta\text{-Mn}_2\text{O}_3$) that transforms to $\alpha\text{-Mn}_2\text{O}_3$ at about ambient temperature; and pyrolusite (MnO_2).

Apart from these phases, quite a number of metastable modifications exist that have been reviewed by Post [89] and are not further discussed here. The crystal structures of the stable phases are summarized in Table 2.3.

Manganese exists in four modifications: α -Mn (up to 707 °C), β -Mn (up to 1087 °C), γ -Mn (up to 1138 °C), and δ -Mn (up to the melting temperature of 1246 °C). Three of these modifications (α -, β -, and δ -Mn) contain a magnetic transition.

Table 2.3. Crystal structures of the stable phases in the Mn-O system.

Name	Composition	Structure type	Ref.
Pyrolusite	MnO_2	Rutile	[90]
β -Bixbyite	$\beta\text{-Mn}_2\text{O}_3$	Bixbyite	[91]
α -Hausmannite	$\alpha\text{-Mn}_3\text{O}_4$	Spinel with Jahn-Teller distortion	[92]
β -Hausmannite	$\beta\text{-Mn}_3\text{O}_4$		[93]
Manganosite	Mn_{1-x}O	Halite	[94]
α -Mn	Mn	α -Mn	[95]
β -Mn	Mn	β -Mn	[95]
γ -Mn	Mn	Cu	[95]
δ -Mn	Mn	W	[95]

The thermodynamic description of solid and liquid manganese is taken from Fernández Guillermet and Huang [96]. Pyrolusite (MnO_2), β -bixbyite ($\beta\text{-Mn}_2\text{O}_3$), and α - and β -hausmannite (α - and $\beta\text{-Mn}_3\text{O}_4$) are described as stoichiometric phases. Manganosite (Mn_{1-x}O) is described using the compound-energy model [97], [98] and the ionic liquid is described with the two-sublattice model for ionic liquids [99], [100].

With increasing temperature, Mn_3O_4 undergoes a polymorphic transition from tetragonal $\alpha\text{-Mn}_3\text{O}_4$ to cubic $\beta\text{-Mn}_3\text{O}_4$. With decreasing temperature that modification is undone, $\alpha\text{-Mn}_3\text{O}_4$ is distorted from cubic to tetragonal symmetry by Jahn–Teller distortions of octahedral sites occupied by Mn^{3+} ions. The measured temperatures at which this transformation takes place are between 1170 and 1177 °C [101]. Keller and Dieckmann [102], who modelled the defect structure of Mn_3O_4 , state that the α - β transformation temperature varies as a function of the oxygen partial pressure and, therefore, also of the oxygen content of Mn_3O_4 .

Orthorhombic α -bixbyite ($\alpha\text{-Mn}_2\text{O}_3$) transforms to cubic β -bixbyite [103] at around 27 °C [104]. This transformation is not shown in Figure 2.15 given to the relatively low temperature at which it takes place.

Thermodynamic data

Thermodynamic properties of Mn_3O_4 , Mn_2O_3 and MnO_2 were reassessed based on new measurements and selected data from literature in [105] the main results are included in Table 2.4, Table 2.5 and Table 2.6.

Table 2.4. Thermodynamic data for MnO_2 [105].

T (K)	C_p^0 (J/K·mol)	$H_T^0 - H_{298.15}^0$ (J/mol)	S_T^0 (J/K·mol)	$-(G_T^0 - H_{298.15}^0)/T$ (J/K·mol)	$\Delta_f H^0$ (kJ/mol)	$\Delta_f G^0$ (kJ/mol)
298.15	54.77	0	52.75	52.75	-521.449	-466.405
300	54.95	102	53.09	52.75	-521.450	-466.064
400	63.22	6038	70.11	55.02	-521.220	-447.620
500	68.34	12639	84.82	59.54	-520.615	-429.286
600	71.21	19632	97.56	64.84	-519.895	-411.088
700	72.68	26835	108.66	70.33	-519.216	-393.009
800	73.34	34140	118.42	75.74	-518.659	-375.018

Table 2.5. Thermodynamic data for Mn_2O_3 [105].

T (K)	C_p^0 (J/K·mol)	$H_T^0 - H_{298.15}^0$ (J/mol)	S_T^0 (J/K·mol)	$-(G_T^0 - H_{298.15}^0)/T$ (J/K·mol)	$\Delta_f H^0$ (kJ/mol)	$\Delta_f G^0$ (kJ/mol)
298.15	109.4	0	113.70	113.70	-961.536	-884.475
300	109.8	203	114.38	113.70	-961.513	-883.998
400	108.4	10823	144.93	117.87	-960.818	-858.275
500	114.6	21978	169.79	125.84	-960.126	-832.719
600	120.0	33711	191.17	134.98	-959.359	-807.309
700	124.9	45959	210.04	144.38	-958.531	-782.033
800	129.3	58672	227.01	153.67	-957.646	-756.877
900	133.4	71813	242.48	162.69	-956.698	-731.839
980	136.6	82614	253.98	169.68	-955.869	-711.977
980	136.6	82614	253.98	169.68	-960.319	-711.978
1000	137.3	85353	256.75	171.39	-960.149	-706.820
1100	141.0	99271	270.01	179.76	-959.071	-681.537
1200	144.6	113552	282.43	187.80	-957.778	-656.365
1300	148.0	128183	294.14	195.54	-956.269	-631.302
1360	150.1	137127	300.87	200.04	-955.260	-616.425
1360	150.1	137127	300.87	200.04	-959.500	-616.424
1400	151.4	143157	305.24	202.98	-959.086	-606.242

Table 2.6. Thermodynamic data for Mn_3O_4 [105].

T (K)	C_p^0 (J/K·mol)	$H_T^0 - H_{298.15}^0$ (J/mol)	S_T^0 (J/K·mol)	$-(G_T^0 - H_{298.15}^0)/T$ (J/K·mol)	$\Delta_f H^0$ (kJ/mol)	$\Delta_f G^0$ (kJ/mol)
298.15	142.36	0	165.60	165.60	-1386.185	-1284.409
300	142.67	264	166.48	165.60	-1386.176	-1283.779
400	155.26	15215	209.41	171.37	-1385.372	-1249.751
500	163.75	31185	245.01	182.64	-1384.332	-1215.966
600	170.61	47911	275.48	195.63	-1383.264	-1182.394
700	176.72	65282	302.25	208.99	-1382.210	-1149.001
800	182.42	83241	326.22	222.17	-1381.159	-1115.755
900	187.88	101757	348.03	234.96	-1380.081	-1082.647
980	192.14	116958	364.20	244.86	-1379.150	-1056.369
980	192.14	116958	364.20	244.86	-1385.825	-1056.370
1000	193.19	120812	368.10	247.28	-1385.648	-1049.525
1100	198.41	140392	386.75	259.12	-1384.449	-1015.969
1200	203.56	160490	404.24	270.50	-1382.945	-982.538
1300	208.66	181102	420.73	281.42	-1381.121	-949.236
1360	211.71	193713	430.22	287.78	-1379.872	-929.462
1360	211.71	193713	430.22	287.78	-1386.232	-929.462
1400	213.74	202222	436.38	291.94	-1385.785	-915.903

T (K)	C_p^0 (J/K·mol)	$H_T^0 - H_{298.15}^0$ (J/mol)	S_T^0 (J/K·mol)	$-(G_T^0 - H_{298.15}^0)/T$ (J/K·mol)	$\Delta_f H^0$ (kJ/mol)	$\Delta_f G^0$ (kJ/mol)
1411	214.29	204576	438.06	293.07	-1385.713	-912.238
1411	214.29	204576	438.06	293.07	-1391.353	-912.240
1445	216.01	211891	443.18	296.45	-1391.195	-900.813
1445	210.90	229615	455.43	296.53	-1373.471	-900.788
1500	210.90	241214	463.31	302.50	-1373.337	-882.651
1519	210.90	245222	465.96	304.53	-1373.442	-876.614
1519	210.90	245222	465.96	304.53	-1406.442	-876.612
1600	210.90	262304	476.92	312.98	-1406.393	-848.179
1700	210.90	283394	489.71	323.00	-1406.499	-813.289
1800	210.90	304484	501.76	332.60	-1406.651	-778.391

Morphology of manganese oxide particles

Most manganese oxide minerals are brown-black and typically occur as intimately intermixed, fine-grained, poorly crystalline masses or coatings. Not surprisingly, identifying the particular mineral(s) in a manganese oxide specimen can pose quite a challenge. Hence many scientists report simply “manganese oxide”, rather than a particular mineral phase. Of course, this also affects to the manganese oxide particle sizes.

Depending of the production method, the manganese ores produced have different particle size. The manganese oxides produced at industrial scale have a particle size above 2-8 μm [83].

Small scale manganese oxide production processes entails different specifications because of each process characteristics, even modifications of a same process imply particle differences: nanoparticles were synthesized by sol-gel process were measured to have diameters between 65-265 nm in [86], while adding citric or tartaric acid, at the same process with the same precursor, $\text{Mn}(\text{NO}_3)_2$, resulted in particle's sizes between 5-50 nm [87]. Nanocrystalline cubic bixbyite $\alpha\text{-Mn}_2\text{O}_3$ was synthesized by diluting manganese (II) chloride in methanol via sol-gel method calcined at 400 $^\circ\text{C}$. Transmission electron microscopy revealed that the as-synthesized ultra-fine consist of crystalline particles of 30 nm [106].

These particle size variations affect critically to the materials surface area, which is a very important factor in several applications, affecting directly to the material efficiency in processes like adsorption and catalytic processes. For instance, in [107] the surface and redox properties of Mn_3O_4 , Mn_2O_3 , and MnO_2 , were investigated and it was found that the bulk oxygen diffusion rate had an effect on the catalytic oxidation rate of propane.

Optical, electric and magnetic properties

Optical properties of $\alpha\text{-Mn}_2\text{O}_3$ were studied in a nanocrystalline sample produced by sol-gel method [106]. The sample show very good crystallinity. The absorbance and photoluminescence spectra, obtained in the wavelength range 200-900 nm, are shown in Figure 2.16. $\alpha\text{-Mn}_2\text{O}_3$ nanostructures with nearly pure band gap emission should be of importance for their applications as UV emitters. The band gap in the material is above 3.27 eV, which is the energy to promote an electron from the valence band to a higher energetic band.

Figure 2.16. (a) Absorbance and (b) photoluminescence spectrum of the α - Mn_2O_3 [106].

The electrical conductivity of various manganese oxides was discussed in [108]. MnO , which is antiferromagnetic with five electrons in the 3d shell, is a bad conductor because electrons cannot move down the chain of ions coupled antiferromagnetically without violating Pauli's exclusion principle. Nevertheless, an increasing tendency is observed in MnO conductivity at higher temperatures and above $10^{-9} \Omega^{-1} \cdot cm^{-1}$.

MnO_2 is a good conductor, its ferroelectric behaviour has been observed, showing a conductivity in the semiconducting range over $27^\circ C$ and $327^\circ C$. Since MnO_2 has three electrons in the 3d shell, the migration of electrons down the chain of antiferromagnetically coupled ions is possible. This process has been shown to involve activation energy.

Finally Mn_3O_4 , which has a spinel structure, was found to be a bad conductor, with electrical conductivity above $10^{-7} \Omega^{-1} \cdot cm^{-1}$.

Manganese ores have different magnetic properties depending on their oxidation state [109] and particle diameter [110]. The magnetic susceptibility data reveals (i) antiferromagnetic nature for Mn_2O_3 , Mn_5O_8 and MnO with Néel temperatures of $-198^\circ C$, $-142^\circ C$ and $-158^\circ C$, respectively, (ii) orthorhombic to cubic crystallographic transition in Mn_2O_3 at $37^\circ C$ for the first time, and (iii) ferrimagnetic character for Mn_3O_4 with Curie temperature of $-227^\circ C$. Mn_3O_4 exhibits a decreasing tendency in magnetism with decreasing particle diameters while MnO shows the opposite tendency its magnetism increases with decreasing particle diameters. MnO presents anti-ferromagnetism before the Néel temperature ($-148^\circ C$), changing to paramagnetism for higher values.

2.3.3. Manganese oxide redox reaction's kinetics

Thermochemical energy storage consist in storing heat in chemical form, so a perfect knowledge of the kinetics of the manganese redox reactions, shown in (38), would be decisive for its future implementation as storage material in CSP plants.

Reduction reaction kinetics

Reduction reaction kinetics has been studied by few authors. Zaki et al. [78] examined the reduction of Mn_2O_3 to Mn_3O_4 under air atmosphere using dynamic (non-isothermal)

thermogravimetric analysis (TGA) reporting an 0.6 - kinetic order model and an activation energy (E) of 538 kJ/mol, calculated by the Ozawa method [111].

The reduction kinetics of the reaction $\text{Mn}_2\text{O}_3/\text{MnO}$ has been studied as one of the steps involved in the thermochemical cycle to produce hydrogen by water splitting. Firstly, Francis et al. [112] measured the kinetic rate parameters at oxygen concentrations of 0.25 and 1 % in volume, using an aerosol flow reactor. They considered a dual reaction mechanism combining Avrami-Erofeev with an order of reaction with the transition occurring approximately at a 0.6 extent of reaction. Botas et al. [113] analysed the kinetics of the dissociation using data collected from dynamic TGA at constant heating rate under nitrogen atmosphere. The model-fitting showed that either a first-order (F1) or a contracting volume (R3) model could describe the reaction mechanism. A good fitting was observed for each experiment, although a significant disparity in the values estimated for activation energies and pre-exponential factors (A) was found. Unique values for the kinetic parameters have been calculated by application of a multivariate non-linear regression method for the simultaneous fitting of data from all the experiments carried out at different heating ramps. However, also in this case the values of the Arrhenius parameters were significantly different depending on the chosen kinetic equation. Optimal kinetic parameters were finally calculated through the estimation of activation energy values by model-free isoconversional methods and using a rigorous multivariate nonlinear regression for the calculation of the model-dependent pre-exponential factors. The activation energy values obtained for the reduction of Mn_2O_3 to form Mn_3O_4 , using the isoconversional methods of Ozawa [111] and Friedman [114], were 254.14 kJ/mol and 246.27 kJ/mol respectively.

More recently, Alonso et al. [115], with a solar-driven thermogravimeter and under concentrated thermal radiative flux, indicated that the reduction of Mn_2O_3 to form Mn_3O_4 followed a n th-order mechanism, where $n = 0.93$.

The algebraic form of the abovementioned fitting functions is given in Table 2.7.

Table 2.7. Algebraic expressions for the most common f-function mechanisms in solid-state reactions [116].

Name of function	Kinetic mechanism	Function $f(\alpha)$	Notation
First order		$1 - \alpha$	F1
Second order		$(1 - \alpha)^2$	F2
n^{th} order		$(1 - \alpha)^n$	F n
Contracting area		$(1 - \alpha)^{1/2}$	R2
Contracting volume	Phase boundary controlled reaction	$(1 - \alpha)^{2/3}$	R3
Random nucleation and growth of nuclei (Avrami-Erofeev equation)	n -dimensional nucleation and growth	$n(1 - \alpha)[\ln(1 - \alpha)]^{(n-1)}$	Am
Parabola law	One-dimensional diffusion	$1/2\alpha$	D1
Valensi equation	Two-dimensional diffusion (two-dimensional particle shape)	$-1/\ln(1 - \alpha)$	D2
Jander equation	Three-dimensional diffusion	$1.5(1 - \alpha)^{2/3}[1 - (1 - \alpha)^{1/3}]^{-1}$	D3
Ginstein-Brounshtein equation	Three-dimensional diffusion	$1.5[(1 - \alpha)^{-1/3} - 1]^{-1}$	D4

Oxidation reaction kinetics

The oxidation reaction kinetics, has just been studied by Gillot et al. [117] under isothermal conditions; at rather low temperatures (162-202 °C). In that range they observed the formation of metastable manganese oxides when the oxidation of nano-particle Mn_3O_4 (32 nm) was carried out using extremely low heating rates (0.05 °C/min).

Some experimental observations related to the manganese oxide cycling properties, point to the oxidation reaction kinetics as a key aspect for its future application in TCS [118]. For that reason, a careful analysis of the oxidation kinetics at conditions similar to the working temperatures in thermochemical storage will provide the necessary information for a total understanding of the whole process and for the future scale-up of this technology.

Kinetic study for heterogeneous reactions

The so-called kinetic triplet (reaction model, $f(\alpha)$, activation energy, and pre-exponential factor) of solid-state reactions is usually estimated by either model-fitting or isoconversional methods [119].

Through isoconversional methods, also known as model-free, the activation energy E is easily calculated without assuming any reaction mechanism. Nevertheless, a further estimation of the reaction model is needed to complete the analysis, using mathematical fitting processes that could add complexity to the study.

On the other hand, master plots based model-fitting methods are a faster option to discern with accuracy the reaction model with the data collected by TGA, by either dynamic or isothermal assays. Master plots are theoretical reference curves depending on the kinetic model but independent of the kinetic parameters [116]. For instance, they have been used to study the kinetics of oxides reduction [115], dehydration [120], polymer degradation [121] or pyrolysis [122] processes.

For the kinetic study, it is commonly assumed that reaction kinetics for a solid decomposition is described by equation (39).

$$\frac{d\alpha}{dt} = k(T) \cdot f(\alpha) \quad (39)$$

Where α is the fractional conversion; k is the reaction rate coefficient, and $f(\alpha)$ is the kinetic mechanism that establishes the reaction kinetic behaviour. Fractional conversion is simply calculated from experimental data as indicated in (40).

$$\alpha = \frac{m - m_i}{m_f - m_i} \quad (40)$$

Here, m is the sample mass measured from TGA, and the indexes f and i correspond to initial and final states.

For the experimental kinetic data under isothermal conditions, using a reference point at $\alpha = 0.5$, the following equation, (41), is easily derived from equation (39).

$$\frac{d\alpha/dt}{(d\alpha/dt)_{\alpha=0.5}} = \frac{f(\alpha)}{f(0.5)} \quad (41)$$

Where $f(0.5)$ is a constant for a given kinetic model function.

Most suitable kinetic mechanism can be identified by comparing experimental data expressed according to equation (41) versus α in a master plot. A set of tentative kinetic mechanisms selected for comparison is shown in Table 2.7.

Opfermann [123] showed that virtually any model could fit an experimental TGA experiment changing the duplet E and A. This is due to the strong correlation existing between both kinetic parameters. A linear relationship between $\log A$ and E, referred as the kinetic compensation effect (KCE), has been widely reported in literature in many areas of chemistry, especially in heterogeneous catalysis [19]. In fact, several authors have proposed that the kinetic parameters lose their relevance in heterogeneous reactions in solid state, because the concepts of “order of reaction” and “concentration” are not applicable [20]. Thus, the parameters of the KCE, slope and interception in the linear regression, can be used as more realistic kinetic parameters describing the reactions [126].

CHAPTER III

3. EXPERIMENTAL TEST RIG

This chapter deals with the laboratory-scale test rig especially designed to test materials for thermochemical heat storage recreating the physically working conditions of a volumetric air central receiver CSP plant, where the storage system would be integrated. The test rig has been designed to use air as heat transfer fluid and to make experiments at different air flow rates, temperature and pressure conditions.

Although manganese oxide redox reaction is supposed to work in the temperature range between 500 - 1000 °C, the working temperature range for the workbench will be from ambient to 1100 °C to allow the testing of other metallic oxides. Being the main challenge to operate a fluidized reactor at high temperature, the working pressure is initially defined slightly over 1 bar. The facility which has been designed, built and tuned-up ex-novo for this application, is currently located at the IMDEA Energy Institute (Mostoles, Madrid).

Section 3.1 addresses the reactor design. Considering the technical specifications in terms pellet size distribution and kinetics of the manganese oxide provided for this application, the reactor concept is defined and its main dimensions as well as the requirements for the test bench are calculated. Section 3.2 deals with the definition and dimensioning of the subsystems: gas supply and gas exhaust units and electricity requirements. Section 3.3 describes the commissioning of the test rig. Section 3.4. includes a detailed description of the selection of the control variables, alerts, control parameters and the development of the data acquisition system.

3.1. Reactor development

The most suitable reactor concepts were retained from a critical analysis of the advantages and disadvantages of the reactors presented in section 2.1. Therefore, gas-solid reactor concepts should be analysed assuming either stationary reactants (fixed bed) or in motion (fluidized bed and moving bed).

3.1.1. *Evaluation of reactor concepts*

Fixed bed reactors

Thermal charging and discharging of the metal oxide reactions is made with a mixture of oxygen and nitrogen in air proportions; there is no difference in composition between transporting and reaction gases, this implies the discard of the indirect fixed bed reactor concept.

Material shaping such as into a monolith form may imply the addition of some structural material which would affect the chemical reactivity and the energy density, hence, this option would be rejected. For the same reason, the addition of any material to modify porosity of the storage material is initially discarded as well.

The regenerator concept could be considered if the size of the installation to be developed were bigger, but as it is not, it would be discarded.

Therefore, from fix bed reactors, only the direct concept with metal oxides in pellet form - size from 1 to 10 mm in diameter – could be feasible and is retained for further consideration.

Fluidized bed reactors

The same material configuration, pellets, would be of application in fluidized bed reactors. In this case, the particle size range would have its low limit in 0.5 mm of diameter, instead of 1 mm, and the high limit would be reduced to a reasonable air flow rate needed for fluidization.

The reaction time of the redox system considered is longer than few seconds so, circulating fluidized bed and pneumatic transport reactor cannot be consider, as they are suitable for faster reactions.

Moving bed reactors

Agitation assisted reactors use moving parts to procure relative particle movement, whose elements are temperature sensitive. These reactor concepts could be found in industry up to a maximum application temperature of 400 °C. Taking into account the wide reduction reaction temperatures, up to 900 °C for the manganese oxide system, this type of reactors do not fulfil the process requirements.

Gravity assisted reactors do not have moving heat sensible parts, however given the initial scale of the laboratory setup, only the vertical column reactor could be taken into account.

Comparison among the retained reactor concepts and final decision

So far, the reactor concepts retained are direct contact fixed bed, fluidized bed and the vertical column reactor, pros and cons, and a comparison among them is mandatory.

Direct contact fixed bed concept may have diffusion limitations that would affect the efficient contact between the gas reactants and the solids. By introducing relative solids movement, heat transfer and gas/solid contact improves, but abrasion is also higher. Fluidized bed concept makes it possible to increase heat and mass transfer which would improve the overall reaction rate. Vertical column reactor is the third candidate. On it, the abrasion – compared to the fluidized bed reactors – would be reduced and, thermal efficiency and gas/solid contact – compared to the fixed bed reactors – would be improved.

The final choice is related to the metal oxides shaping (spherical, cylindrical, cubic granules...) and its mechanical and thermal behaviour during consecutive charging/discharging cycles. In this case, the fluidized bed concept is retained and developed. This concept has slightly higher abrasion than that of the vertical column, but also higher heat transfer efficiency is expected.

Besides, fluidized bed is mechanically simpler and would be extensible to the pilot scale reactor, and process control with unstable granules is probably easier to handle with fluidized beds compared to vertical moving columns. It is also important to consider that working at low gas velocities, would permit us to have a fixed bed reactor also available.

3.1.2. Reactor sizing

The reactor sizing is approached by solving first the solid-related parameters in particular for the manganese oxide material and by calculating in a second step the gaseous flow rates required for fluidization.

Solid-related parameters

For laboratory scale in the framework of the European project, a storage capacity of 100 Wh is settled. Considering the theoretical enthalpy of the manganese oxide (III) redox reaction, 31.8 kJ/mol of Mn_2O_3 , the amount of material required for the settled storage capacity is estimated to be 1.8 kg of Mn_2O_3 . To be on the safe side, a conversion rate of 80 % is assumed, which implies a total mass of 2.25 kg of Mn_2O_3 .

With the assumption of a particle density of 2100 kg/m^3 and a measured bulk density of 1100 kg/m^3 , a bed porosity of 48 % results. This is a reasonable value for a loose bed with a vertical gas flow. Considering the bulk density to be constant, a volume of 2.04 l is required for the solid material in the lab-scale reactor.

By simplicity reasons, a cylindrical geometry for the reactor is chosen. Its dimensions are settled considering a static bed which internal volume is equal to that of the solid calculated above and assuming that the cylinder diameter and height are equal. This assumption is normally made in design in order to minimize surface and therefore losses. This leads to a 140 mm reactor diameter. In order to reduce material entrainment, a ratio height/diameter of five units is defined, which results in a reactor height of 700 mm.

Gaseous flow rates

Once the solid-related dimensions have been defined, the minimum amount of gas to transport the required heat for the reaction is calculated through a heat balance.

The heat capacity for temperatures in the range of 750 - 1000 °C of the $\text{Mn}_2\text{O}_3/\text{Mn}_3\text{O}_4$ system is around 800 - 900 J/(kg·K) [105]. For simplifying the sizing calculations a constant mean value of 850 J/(kg·K) is fixed for both oxides.

In the frame of the European project, the reactor capacity is settled on 10 W as a design parameter. Considering an oxidation reaction temperature of 750 °C, and a temperature difference of 100 °C from inlet to outlet gas, the resulting minimum air flow rate is 0.31 kg/h. Considering 1 bar and 25 °C as standard reference conditions, an air flow rate of 0.27 Nm^3/h would provide the heat required for reaction. This minimum gas flow rate for heat transport, considering the reactor cross section area, results in a mean gas velocity of 0.02 m/s.

Particle fluidization behaviour has been widely studied, even though it is still difficult to predict. Based on the Geldart's classification and on the equations included in section 2.1.2, an analysis on particles fluidization has been performed considering particle sizes in the range from 0.5 mm to 5 mm.

For the calculus, the particles are considered to be spherical and of the same dimension, also ideal air properties have been used. The temperature range goes from 25 °C up to 1100 °C and the pressures considered are 1, 5 and 10 bar.

Numerical results of minimal fluidization and terminal velocities, from equation (6), as well as the code implemented in Engineering Equation Solver, are included in ANNEX I Experimental test rig: design and constructive details and, plotted in Figure 3.1 and Figure 3.2 respectively.

On these figures it is reasonable to see how bigger particles require higher minimum fluidization and terminal velocities; because higher diameter imply bigger weights. Also, the increase of the air pressure has an effect shown in the results: increasing the pressure of the system, results in smaller amounts of air needed due to the variations on the air properties.

The initial decreasing trend in U_{mf} with temperature shown in Figure 3.1 for 0.5 mm particles does not have any physical meaning; it results from the relation between dynamic viscosity and density, which changes of tendency for small particles up to 0.75 mm approx.

In Figure 3.2, the corresponding curves for 0.5 mm 1bar, 2.5mm 5 bar and, 5mm 10 bar, are superposed, which is the reason why apparently there are only seven lines in the graph.

Figure 3.1. Variation of minimum fluidization velocity with temperature for a pressure range 1-10 bar and particle diameter between 0.5 and 5 mm

Figure 3.2. Variation of terminal velocity with temperature for a pressure range 1-10 bar and particle diameter between 0.5 and 5 mm

As mentioned above, the minimal gas flow rate required for the heat transport implies a mean gas velocity of 0.02 m/s. The minimum fluidization velocity, observed for 0.5 mm diameter particles is higher than 0.02 m/s, so even for the smallest particle size, also fixed bed behaviour could be studied.

Minimum fluidization and terminal velocities obtained for the minimum and maximum particle diameter at ambient pressure are shown in Figure 3.3. This data will be used later for the workbench dimensioning.

Figure 3.3. Minimum fluidization and terminal velocities as a function of temperature for 1 bar pressure and a particle range diameter of 2 mm and 5 mm.

In order to work in stable conditions, a particle size distribution as narrow as possible would help to achieve a well-defined fluidization regime, avoiding particles segregation and promoting equal heat and mass transfer to or from the solids.

3.1.3. Specifications for constructive materials of the reactor

Once the reactor dimensions are defined, the materials for its construction are considered. In order to withstand the gas tightness, pressure and temperature process conditions, a reactor design formed by three concentric layers is developed. The main requirements of these three layers are explained next:

- The internal layer, which is in direct contact with the material particles to be tested, must be made out of a material that would minimize erosion by wall collision. This layer has to resist the hardest thermal conditions in the system and should not be permeable to the gas.
- The intermediate lining consists of different isolating materials which diminish the temperature conditions to be withstood by the last layer, making it possible to maintain the heat losses by conduction in a reasonable level.
- The external layer consists of a metallic material that would provide the requirement in terms of pressure and gas tightness of the system.

The criteria and the assumptions made to design the insulation of the reactor are as follows:

- The inner layer thickness is assumed to be a cylinder 1 cm thick made out of alumina.

-
- The intermediate layer is formed by two different materials: one with enough structural strength to contain and keep in place the inner cylinder and the second one, just to diminish the heat losses by conduction. The first material selected is a ceramic brick and the second a ceramic blanket.
 - The relative thickness of these two materials is defined setting a maximum temperature of 60 °C at their outside diameter.
 - The previous calculation defines the diameter of the metallic envelop. Its thickness is then defined in order to withstand a working pressure of 10 bar at a maximum temperature of 400 °C. This temperature is defined for safety reasons.
 - The heat losses in the reactor are constant through the different layers and equal to the heat lost by radiation and convection from the metallic envelop to the ambient.
 - The heat losses of the reactor to the ambient are calculated assuming an emissivity of 0.9 for the metallic material and a wind velocity of 0.2 m/s for the interior of the building where the reactor will be located.
 - The ambient conditions considered are temperature and pressure of 20 °C and 1 atm respectively.
 - The inner face of the alumina cylinder is at a constant and uniform temperature of 1100 °C.

The properties used for the materials, as well as the code implemented in Engineering Equation Solver to solve the isolating layers design for the reactor are included in ANNEX I Experimental test rig: design and constructive details.

The compromise results are a thickness of 140 mm and 85 mm for the ceramic bricks and blanket respectively. The selected values result in a maximum temperature at the external wall of 56.6 °C. The chosen thickness for the metal enclosure is 4 mm and its final diameter is then 648 mm. The metallic layer selected will withstand working pressures over 10 bar at a temperature of 480 °C.

3.1.4. Final design

The reactor has been designed to work at pressures between 1 bar and 10 bar and to withstand temperatures above 1100 °C. Figure 3.4 (c) illustrates the final reactor design: It is a cylindrical vessel composed of three stacked bodies joined vertically by flanges in order to (i) allow an easy mounting/dismounting process and (ii) maintain vessel pressure and gas tightness.

The soft expansion at the top of the reactor, in the body 1, allows a diminution of the velocity at the reaction chamber exit, decreasing the particles entrainment (see construction details in Figure 3.4 (a), (b) and (d)). Bodies 2 and 3 accommodate the ceramic cylinder that constitutes the main part of the reactor. Body 3 is attached to the workbench outlet and contains the gas distributor plate.

In the radial direction, each body is composed by an internal ceramic piece, an intermediate insulating lining and an external metallic housing:

- The inner cylinder is a non-porous high quality alumina with a high temperature glaze in the inside to improve its softness. This ceramic piece is composed by a 650 mm

cylindrical ceramic tube and a conical ceramic top. The internal diameter of the tube is 142 mm and it is 20 mm thick. A constructive detail is shown in Figure 3.4 (a) and (d).

- The intermediate layer is composed of an external cover of Promaglaf HTI 1260, 45 mm of thickness, (see Figure 3.4 (d)), and an internal cylinder, 130 mm of thickness made out of fireproof ceramic bricks JM 26 (see Figure 3.4 (b)).
- The metallic enclosure is a welded stainless steel pipe, according to DIN 17440, the external diameter of the reactor body is 647.8 mm with a thickness of 4.0 mm. This thickness allows the system to work up to 10 bar up to a maximum temperature of 480 °C.

The internal distribution of components inside the reactor is designed taking into account the thermal expansions of the different components during the reactor heating and cooling.

Figure 3.4. Construction details of the reactor final design: (a) detail of body 1, (b) internal brick layer, (c) axial cross section and scheme of the different reactor body parts for manufacturing (d) construction detail of the isolating blanket and non-porous alumina material, and (e) cordierite rings use to ensure the mechanical stability of the reactor's bodies.

Some cordierite rings were inserted in the bottom of each body in order to secure their mechanical stability. The constructive detail is shown in Figure 3.4 (e). The gas distributor, shown in Figure 3.4 (c), is a porous alumina dish, 150 mm external diameter, with squared cross section of 1 mm and 25 mm thickness.

Figure 3.5 and Table 3.1 indicate the exact position of the temperature and pressure sensors distributed at different heights in the vertical axis of the reactor and at a different radius positions. Most of the thermocouples installed are K type with 310 stainless steel sheath and a characteristic accuracy of ± 0.6 °C. The exceptions are for the thermocouple number 1 which is

a type K with ceramic shell, characteristic accuracy of ± 1.0 °C, and thermocouples 12 and 13, which have type K exposed junctions and ceramic shell with a characteristic accuracy of ± 0.8 °C.

There is also a six-measure points thermocouple, own design, located at the centre of the reactor. The location of this device is shown in the cross section and scheme presented in Figure 3.4 (c). As mention it is an in-house design and manufacture device which characteristic accuracy was unknown at the time of the trials but it was evaluated during the experiments, as it will be explained in Chapter V.

Pressure drop through the reactor column is measured with an *IXLdp* manometer from *Ashcroft*, is settled between 0 - 50 mbar, with a maximum working pressure of 10 bar. The pressure variations are caused by the different air flow rates used, temperature changes and the characteristics of the test material used. Pressure drop data is used to study the fluidization properties of the material in evaluation.

Figure 3.5. Scheme of the reactor with the location of temperature and pressure drop sensors .

Table 3.1. Detailed list of thermocouple and pressure drop measurement positions in the reactor.

Number	Axial position (mm)	Radial position (mm)
1	0	0
2	225	214
3	320	214
4	445	226
5	620	166
6	620	0

Number	Axial position (mm)	Radial position (mm)
7	775	214
8	900	226
9	1020	53
10	1145	166
11	1270	166
12	1270	33
13	1270	33
14	1200	330
ΔP high	190	140
ΔP low	650	140

3.2. Workbench development

The assembly of subsystems aims to recreate the physical working conditions of a volumetric air receiver CSP plant, where the thermochemical storage system would be integrated. The test rig has been designed to use air as heat transfer fluid and to make experiments at different air flow rates, temperature and pressure conditions.

Although manganese oxide redox reaction is supposed to work in the temperature range between 500 - 1000 °C, the working temperature range for the workbench will be from ambient to 1100 °C to allow the testing of other metallic oxides. Being the main challenge to operate a fluidized reactor at high temperature, the working pressure is initially defined slightly over 1 bar.

Considering the sieve squared cross section of 1 mm, pellets minimum diameter will be 2 mm for experiments in the reactor. So, adjusting this parameter in the calculus of fluidization and terminal velocities given in section 3.1.2, the gas velocity working range is obtained.

Considering the typical gas flow range for operation as fixed to bubbling bed to be in the range of 0.5 - 50 kg/h, the maximum air flow rate for the installation would be settled at 76.5 kg/h to be on the safe side, which corresponds to 60 Nm³/h.

Taking into account the reactor cross section area and the density variation of air with temperature, the maximum velocity reached by the air in the reactor, noted by U_{max} , is shown and compared to the gas velocities working range in Figure 3.6.

As shown in Figure 3.6, small manganese oxide pellets would be theoretically fluidized for most of the temperature working range. Bigger pellets will have a smaller temperature range to be fluidized, nevertheless that range of temperatures would be adequate because it is consistent to the working temperatures required for the reaction.

Figure 3.6. Minimum fluidization and terminal velocities as a function of temperature for 1 bar pressure and pellet diameter of 2 mm and 5 mm.

3.2.1. Sub-systems definition

Figure 3.7 shows the process flow diagram of the test rig. Excluding the reactor, the workbench is formed by four different sub-systems.

Figure 3.7. Process flow diagram.

A short description of the four sub-systems is included next:

- Gas supply unit. It is located at the reactor upstream and it is composed of a dried-air compressor, air flow control system and an air-heating device. Its objective is to provide air at the required flow rate and temperature.
- Gas exhaust unit. It is located at the reactor downstream and it is composed of a gas extraction for gas analysis, a gas analyser bench and a cooling system to cool down the air before being released to the ambient.

- Control, monitoring and data acquisition unit. It is composed of temperature probes, pressure gauges, control valves and additional equipment for data acquisition and recording. Detailed information on this sub-system is included in section 3.4.
- Electricity supply system, which safely supplies the electrical power to the different elements of the workbench.

3.2.2. Gas supply unit

It is able to provide the installation with an air flow rate in the range from 0 Nm³/h to 60 Nm³/h at a specified temperature in the range from ambient to 1100 °C. To meet this objective, the atmospheric air is filtered, dried and compressed, and then the air flow rate is settled by using an air flow control system, and heated up to the desired temperature in an air heating device.

Air compressor

Compressed dried air is provided by using an oil-free *Tooth Compressors ZT-15ID/10 (Atlas Copco)*. This device includes an integrated cooling dryer and it provides air 100 % free of oils at flow rates between 0 and 100 Nm³/h at a pressure of 9.75 bar.

During the TCS Power project, the air compressor was acquired and installed on the roof of the Farrington Daniels pilot plant building of IMDEA Energy Institute, where the testing plant is located (see Figure 3.8).

Figure 3.8. Air compressor installed on the Farrington Daniels pilot plant building roof at the IMDEA Energy Institute.

In addition, an air pipe line was installed between the compressor and the test rig location. At the end of this line there is a pressure regulator and manual on-off valves that connect to the air flow control system (see Figure 3.9).

Figure 3.9. Air connections to the workbench.

Air flow control system

In order to achieve good accuracy in the whole range of air delivered, the air flow rate is divided into two streams. Then compressed air leaves the air pipe line through two quick connection fittings and flexible hoses and flows through two independent mass flow controllers before entering in the air heating device.

The mass flow controllers are F-203AV from the series *EL-FLOW* of Bronkhorst High-Tech B.V. (see Figure 3.10). Each mass flow controller require a minimum of 2 bar air pressure at their inlet in order to ensure the demanded air flow rate in the range of 0.06 to 30 Nm³/h, being 10 bar their maximum working pressure .

Figure 3.10. Mass flow controllers.

Air heating device

The heating unit is the main challenging component of the workbench. This unit enables to heat air up to 1100 °C whatever the air flow rate required and independently of the air inlet temperature. The heating device is composed of two stages:

-
- Peripheral electric resistors or preheaters: consist of two commercial devices from *Osram Sylvania*, which are used for the most demanding experiment conditions. It comprises two 8kW high-temperature inline heaters, model *F076339* (see Figure 3.11). Each one is able to heat air up to 400 °C at a flow rate of 30 Nm³/h and up to 600 °C for air flow rates smaller than 18 Nm³/h. The connection to the mass flow controllers is done through flexible hoses.

Figure 3.11. Inline heater, model *F076339* from *Osram Sylvania*.

- Three-phase electric furnace: It is the main heating stage and has been designed ad hoc for the workbench. Due to the complexity of the design, the complete information of this system has been separately included in section 3.2.5. Figure 3.12 shows a detail of the designed air heating device, where the preheaters are welded to the casing of the furnace.

Figure 3.12. Detail of the air heating device construction.

3.2.3. Gas exhaust unit

The gas exhaust unit is composed of a gas extraction, located downstream of the reactor, for gas composition analysis in a gas analyser bench, and a cooling system to cool down the air prior to its release to the ambient.

Gas analysis

Gas outlet composition is continuously monitored by extracting a small constant volume flow rate at the reactor exit. Molecular oxygen, CO, CO₂ and CH₄ are detected using the gas analyser *Ultramat 23* from *Siemens* (see Figure 3.13).

Figure 3.13. Gas analyser *Ultramat 23* from *Siemens* used for exhaust gases.

Oxygen concentration monitoring allows identifying the redox chemical reaction. While, CO, CO₂ and CH₄ traces indicate parallel reactions that could occurs related to the sample or to possible degradation of some insulating materials of the plant.

Cooling system

The cooling system adequate the temperature of the exhaust gas prior to its release: The hot gas, mainly air, comes out the reactor and is mixed with room temperature air before entering in a high-temperature chimney that leads the air to outside, see Figure 3.14 (c), while reducing its temperature to ambient values.

Figure 3.14. (a) Hot-air chimney inside the pilot plant building, (b) Air-cooling chamber by hot and cold air mix and, (c) Hot-air chimney on the building roof.

The gas mixing element (Figure 3.14 (b)) contains two air blowers, alternating current (AC) centrifugal fans from EBM, which provide 680 m³/h each at 300 Pa. The chimney, shown in Figure 3.14 (a), is also designed and installed for this workbench and is able to withstand operating temperatures of 350 °C.

3.2.4. Electricity supply system

Three electrical single-phase circuits 32 A / 240 V AC are built to feed each of the peripheral electric resistors and a combination of the air blowers, relays, controllers and, a 24 V direct current (DC) power source. An independent three-phase circuit 63 A / 240-415 V AC is developed to meet the electricity requirements of the furnace. Each circuit has its own breaker and differential switch, as shown in Figure 3.15. The devices connected to each of the power points are summarized in Table 3.2.

Table 3.2. Detail of electrical connections.

Power source	Electric Devices
32 A / 240 V AC 1 Phase (1)	Peripheral electric resistance 1
32 A / 240 V AC 1 Phase (2)	Peripheral electric resistance 2
32 A / 240 V AC 1 Phase (3)	Air blowers, relays, controllers, gas composition analyser and a 24 V DC power source
63 A / 240 -440 V AC 3 Phase	Three-phase electric furnace

Figure 3.15. Electrical panel boards.

3.2.5. Three-phase electric furnace

The three-phase electric furnace has the objective of heating the required air flow to the temperature specified in each moment of the experiment. For safety reasons, this furnace includes a shelter volume to contain the material pellets in case of a sieve breaking in the reactor.

The furnace shell must ensure pressure conditions in the system and have the mechanical strength to support the weight of the reactor. In order make this system temperature safe, the insulation disposition develop for the reactor is of application. Accordingly, the insulation of the furnace is composed of an external lateral cover of *Promaglaf HTI 1260*, with 45 mm of thickness and an internal structure made out of fireproof ceramic bricks *JM 26*.

In the initial design, which was subcontracted, metal resistors were located aligned on the core of the insulating material structure which has an inside-tunnel configuration (see Figure 3.16 (a)). The tunnel was filled up with alumina balls that were supposed to increase the heat transfer rate to the air by increasing the exchange surface area (see Figure 3.16 (b)).

Figure 3.16. Detail of the furnace during construction; (a) electrical resistances aligned in the air circuit tunnel, (b) filling with the alumina spheres in process.

This design presented thermal issues associated to the presence of hot spots, which were due to poor refrigeration of the resistors caused by the existence of preferential air paths. This caused the melting of the resistors in several points and also part of the alumina elements were melted, as it is shown in Figure 3.17.

Figure 3.17. Detail of the first design of the furnace during dismantling; (a) burned electrical resistances, (b) detail of a melted alumina and resistor part.

Due to the observed problems, a new design was mandatory. In the new furnace configuration, the alumina balls were removed and the initial inner-tunnel configuration and the insulating material structure were retained.

Furnace power and resistors sizing

The considerations took into account to calculate the furnace's power are described next:

- Temperature step is defined from ambient temperature up to 1100 °C.
- Air flow rates from 1 up to 150 Nm³/h.
- Pressure of the air is initially considered as 1 bar.
- Air flow properties of density and heat capacity are calculated for average temperature of 562.5 °C, resulting in 0.422 kg/m³ and 1043 J/kg·K respectively.
- The thermal power needed is calculated according to equation (42)

$$P = Q_v \cdot \rho \cdot c_p \cdot \Delta T \quad (42)$$

where P is the power of the furnace, Q_v is the volumetric air flow rate, ρ and c_p are the average density and specific heat capacity of the air and ΔT is the temperature step.

The gathered results, included in Table 3.3, show that a power about 13 kW would be enough to heat an air flow rate over 100 Nm³/h, which is the maximum capacity of the installed compressor.

Table 3.3. Required electricity power to heat up the different air flow rates.

Air flow rate (Nm ³ /h)	Furnace power (kW)
150	19.71
125	16.43
100	13.14
75	9.86
60	7.88
50	6.57
40	5.26
30	3.94
20	2.63
15	1.97
10	1.31
8	1.05
6	0.79
5	0.66
4	0.53
3	0.39
2	0.26

To be in the safe side, a furnace power of 16 kW is defined. This power would be provided by a set of three resistors arranged in star connection. The resistors were made out of *Resistohm*® *PRM* from *Aperam* and have a diameter of 2.5 mm. This material has better performances and allows a maximum working temperature of 1400 °C with a melting point of 1500 °C.

Knowing the electric power to be dissipated, the electrical resistance R of the material may be calculated with a combination of the Ohm's Law (43) and the active power expression for alternating current included in (44).

$$R = \frac{V}{I} \quad (43)$$

$$P = V \cdot I \cdot \cos \theta \quad (44)$$

Where P is the power per resistor, V is the voltage across the resistor, I is the electrical current through the resistor and θ is the phase angle between the current and voltage sine waves.

The resistance R of a conductor of uniform cross-section area S , length L and resistivity φ can be computed from

$$R = \varphi \frac{L}{S} \quad (45)$$

Considering that for electric circuits with mainly resistance loads $\cos \theta$ can be approximated as unity and taking into account (46) , the length of each resistor is calculated from expression (47):

$$L = \frac{V^2 S}{P \varphi} \quad (47)$$

With a voltage across the resistor of 220 V, a power per resistor of 5333 W, the cross-section and the resistivity of the material, according to the supplier, being $S = 4.91 \text{ mm}^2$ and $\varphi = 1.45 \text{ } \Omega \cdot \text{mm}^2/\text{m}$ respectively, results in a length of 30.72 m. Each resistor is rolled up in an extended coil which is divided in a total of 14 sub-units, 200 mm long with 20 mm of diameter.

Computational fluid dynamics (CFD) simulation of fins

Different fins and resistors disposition have been evaluated through CFD simulations to maximize heat transfer coefficients and to avoid preferential paths. The study is focussed in the straight sections of the furnace, where the main heat transfer problems were found.

Five cases of study are implemented in COMSOL Multiphysics. As common criteria: the air inlet temperature assumed is 500 °C. Six resistor's sub-units are simulated in each case, which implies different length of the simulated section depending on the resistors and fins disposition. The air flow conditions chosen are 15 m³/h and 1 bar of pressure. And, the total electric power is 96 W per sub-unit, which corresponds to double the value calculated in Table 3.3 for the set air flow. The reason to set a small air flow rate and to double the electric power is to provide critical conditions for the simulation. The five configurations considered are:

- Linear disposition of the resistor's sub-units and rectangular fins disposed perpendicularly to the air flow.
- Linear disposition of the resistor's sub-units and rectangular fins disposed in a 45 degrees angle to the air flow.
- Linear disposition of the resistor's sub-units and triangular fins disposed perpendicularly to the air flow.
- Zigzag disposition of the resistor's sub-units and triangular fins disposed perpendicularly to the air flow.
- Zigzag disposition of the resistor's sub-units and polygonal fins.

Among other useful results the simulation provides relevant information about the velocity and temperature distributions predicted for each configuration. Some of the velocity and temperature maps obtained are given in Figure 3.18 to Figure 3.24 and the conclusions drawn from them are detailed below.

Figure 3.18 shows the velocity profiles obtained for the linear disposition of the resistor's sub-units, while the numerical results for the maximum velocities observed are gathered in Table 3.4. Figure 3.18 (a) shows rectangular fins disposed perpendicularly to the air flow, in this case approximately 50 % of the resistor's surface show zero air velocity, this un-refrigerated area is surrounded by two zones of high air velocity and will suffer important temperature gradients. Figure 3.18 (b) shows rectangular fins disposed in a 45 degrees angle to the air flow, the

refrigerated surface of the resistor is similar to the first case of study, the velocities reached by the air are a little higher but there are big dead-zone areas and a small trail between consecutive resistor's units. Figure 3.18 (c) shows triangular fins, the death-zones are greatly reduced, air velocities increase slightly but the shadow effect, the preferential paths and the un-refrigerated resistor's surface are significantly increased.

Figure 3.18. Velocity profiles (m/s) for the linear disposition of the resistor's sub-units.

Figure 3.19 shows the velocity profiles obtained for the zigzag disposition of the resistor's sub-units, numerical results are included in Table 3.4. Figure 3.19 (a) shows a reduction of the un-refrigerated surface to the 25 % of the resistor's surface, the maximum velocities value has decreased but the velocity in the outskirts of the resistor has increased, improving the refrigeration. Figure 3.19 (b) shows an improvement of the fins in the zigzag disposition where the maximum air velocity has slightly increased. An additional advantage in this case is that polygonal fins are easier to construct and imply smaller death-volumes.

Figure 3.19. Velocity profiles (m/s) for the zigzag disposition of the resistor's sub-units.

The disposition of the fins and resistor's sub-unit also has a straight forward effect on the temperature of the air at the outlet and of the resistor's sub-units. It is graphically shown in Figure 3.20 and Figure 3.21. The differences among cases of study are quantified in Table 3.4.

Figure 3.20. Temperature profiles ($^{\circ}\text{C}$) for the linear disposition of the resistor's sub-units: rectangular fins disposed (a) perpendicularly and, (b) in a 45 degrees angle to the air flow; (c) triangular fins.

Figure 3.21. Temperature profiles ($^{\circ}\text{C}$) for the zigzag disposition of the resistor's sub-units: (a) triangular fins, and (b) polygonal fins.

Table 3.4. Results of the fins and resistor's sub-units disposition.

Outlet average temperature ($^{\circ}\text{C}$)	Maximum air velocity (m/s)	Air outlet average temperature ($^{\circ}\text{C}$)	Resistor's maximum temperature ($^{\circ}\text{C}$)
Linear rectangle 90°	1.70	510.4	526.5
Linear rectangle 45°	2.60	508.1	522.4
Linear triangular	2.66	508.9	520.9
Zigzag triangular	1.90	511.6	523.2
Zigzag polygonal fins	1.92	511.2	524.5

As shown in Table 3.4, the differences among the resulting air outlet temperatures are not really big. But there are also differences between air temperature and resistor's temperature. Due to the poor resistor's refrigeration observed in the linear disposition cases, the zigzag disposition would be chosen. Both zigzag resistor's sub-units disposition cases of study have similar air outlet temperatures, even though the resistor maximum temperature is smaller for triangular fins, the polygonal fins disposition is easier to construct, therefore, it is the case retained for further studies.

The effect of variation in the power of the resistor is evaluated for the case of study. Figure 3.22 shows the temperature profile for 96 W, 576 W and 1000 W electric power through the resistors. The inlet conditions considered are retained: temperature of 500 °C, air flow rate of 15 m³/h and 1 bar of pressure. Velocity profile data are included in ANNEX I Experimental test rig: design and constructive details.

The air average temperature increases and the maximum temperature observed in the simulations for each power evaluated are included in Table 3.5. The study demonstrates that the maximum temperature values in the system are far from the melting point of the resistor's material.

Figure 3.22. Temperature profiles (°C) for the zigzag disposition of the resistor's sub-units with polygonal fins at different power values: (a) 96 W, (b) 576 W and, (c) 1000 W.

Table 3.5. Results of the variation power through resistor's study.

Electric power to resistors (W)	Air outlet average temperature increase (°C)	Resistor's maximum temperature (°C)
96	11.2	524.5
576	67.3	642.5
1000	116.4	741.8

In order to spread the study, different air flow rates are studied in a simulation of the last straight part of the furnace. In this area the most demanding thermal conditions take place so, 875 °C is defined as the average inlet temperature of the air and the power through resistors is

set to 1000 W. The resulting temperature maps are given in Figure 3.23. Velocity profile data is included in ANNEX I Experimental test rig: design and constructive details.

Figure 3.23. Temperature profiles ($^{\circ}\text{C}$) for the zigzag disposition of the resistor's sub-units with polygonal fins with different air flow rates: (a) $10 \text{ m}^3/\text{h}$, (b) $25 \text{ m}^3/\text{h}$ and, (c) $60 \text{ m}^3/\text{h}$.

Table 3.6 shows the air outlet average temperature and the maximum temperature simulated for each air flow rate evaluated. The maximum temperature is observed on the top-right-quarter of the last whole resistor sub-unit, where the lowest air velocities are obtained and the maximum temperatures of the system take place.

Table 3.6. Results of the variation of air flow rate's study.

Air flow rates (m^3/h)	Air outlet average temperature increase ($^{\circ}\text{C}$)	Resistor's maximum temperature ($^{\circ}\text{C}$)
10	1092.4	1187.8
25	970.2	1068.9
60	920.7	995.8

From the simulations, it is observed that the temperature for the manganese oxide reduction reaction will be reached for the complete air flow working range. Nevertheless, the simulations were made considering 1000 W per 6 resistor units, which corresponds to 167 W per resistor unit. According to the system specifications, a total power of 381 W per resistor unit is allowed. So, there will be no problems in reaching the target of 1100°C .

A constructive modification consisting in the addition of a triangle in the rectangular side of the fin was included. This modification would ease the stability of the fins and, according to the velocity and temperature profiles shown in Figure 3.24, will have a minimum effect in the heat transfer from the resistor to the air. The study was performed considering an air flow rate of $10 \text{ m}^3/\text{h}$, inlet temperature of 875°C and, 1000 W of electric power through the resistors.

Figure 3.24. (a) Velocity (m/s) and (b) temperature ($^{\circ}\text{C}$) profiles for the final fins and resistor's sub-units disposition.

Final design

The design of the furnace finally adopted is shown in Figure 3.25: The gas stream flows from right to left while its temperature is raised up, maintained or decreased according to the experiment requirements.

Figure 3.25. Vertical (a) and horizontal (b) cross sections of the three-phase electric furnace.

In the constructed furnace, shown in Figure 3.26, there are five temperature measurements points distributed in different places of the air path at the same vertical height. There are two temperature measurement points located close to the air exit, one to notice risk of damage by high temperature and the other one used for control purposes. Pressure drop through the device is also measured. Detailed information about the sensing and monitoring of the furnace is included in section 3.4.1.

Figure 3.26. Three-phase furnace: (a) constructed device, (b) internal detailed of the furnace.

3.3. Commissioning of the installation

The assembly process started with the site conditioning which consisted in the installation of the air compressor, the air pipe line, the exhaust chimney and the electricity panels. During this first stage a mobile crane was designed and constructed to allow the safety mounting and/or dismantling of the reactor. A picture of this first stage is shown in Figure 3.27 (a).

Figure 3.27. First step of the assembly; (a) mobile crane and, (b) heating device supporting structure.

The assembly process continued with the setup of the air flow controllers, the control boxes, the heating device, the reactor and the gas cooling system. The air flow controllers, the air cooling system and four control boxes were held to the wall. A four-wheel structure, shown in Figure 3.27 (b), was constructed to allow the mobility of the heating device.

The latest step to complete the installation, shown in Figure 3.28, consisted in the connection of the temperature and pressure meters, the gas analysis extraction and the control panels.

Figure 3.28. Completed test installation.

3.4. Control and data acquisition: Design and development

The control and data acquisition system is designed to perform heat storage material tests. The initial material to be used is the redox couple of manganese oxide, which requires temperatures in the range of 500 - 1000 °C. Nevertheless, the workbench may be used to test other substances, so the control of the system would allow the user to vary the air temperature and flow rate in the ranges from ambient to 1100 °C and from 1.2 to 60 Nm³/h.

3.4.1. Hardware description

The hardware description and measurement points are detailed next in order of sub-systems appearance, from the air pipe line to the gases exhaust system.

The air mass flow controllers installed include all-in-one the air flow sensor, control valve and regulator. They are adjusted to receive the setpoint and to send the actual air flow measured, by analogic 4 - 20 mA signals.

The preheaters are controlled by a commercial *SureHeat JET* controller each. This device is based on an *Innovative 3200* temperature regulator from *Eurotherm*. It receives the setpoint by an analogic 4 - 20 mA signal and two temperature signals, one for high temperature damage risk and the other for control purposes. The thermocouples installed here are K-type exposed junction with ceramic shell and a characteristic accuracy of ± 0.8 °C.

The three-phase electric furnace is equipped with a total of seven ceramic shell type K thermocouples with a characteristic accuracy of ± 1.0 °C. As indicated in Figure 3.29, five of them are placed at mid-height at different points of the gas path, one is used to activate an alarm in case of risk of high temperature damage and, the remaining one, is used for control purposes.

Figure 3.29. Thermocouples disposition in the Furnace.

The power through the resistors is regulated by a commercial three-phase power regulator from *SRC* shown in Figure 3.30. This controller is based on phase-angle control; it works by delaying the trigger pulse to some point in the half cycle of the AC wave. It accepts a 4 - 20 mA signal as input control signal.

Figure 3.30. Three phase power regulator and relays box.

The power supplied to each of the resistor of the furnace - named as u, v and w - as function of the control input signal is slight different for each resistor, as shown in Figure 3.31. It is also noticeable from this figure than the current intensity remains constant from 80 to 100 % of the controller signal, therefore, concerned about safety, the working control range is settled from 0 to 80 % of the furnace power.

Figure 3.31. Electric current supplied to the furnace vs. controller signal.

Reactor and furnace are equipped with a differential pressure meter each. The range of these manometers, *IXLdp* from *Ashcroft*, is settled between 0 - 50 mbar, being 10 bar their maximum working pressure. There is a relative pressure meter, *S04* from *STW*, located underneath of the reactor sieve. It has a measure range between 0 and 10 bar. These three pressure meter devices, shown in Figure 3.32, have a 4 - 20 mA output signal.

Figure 3.32. Pressure meters installed: (a) differential pressure meter, (b) relative pressure meter.

The reactor is equipped with a total of nineteen type K thermocouples located at different heights and depths of the reactor body. All details about location and type of thermocouples were included in section 3.1.4.

The exhaust unit is equipped with a gas analysis unit which output signal is a 4 - 20 mA signal. The power of the air blowers is manually regulated by a *HHR 04* regulator each from *Eclipse*, see Figure 3.33.

Figure 3.33. Air blower regulator.

The foregoing mentioned control and data variables are processed in a CompactRIO 9074 (cRIO) from National Instrument (NI), supplemented with the required input/output modules. These elements are shown in Figure 3.34 and are shortly described in Table 3.7.

Figure 3.34. cRIO and input/output modules.

Table 3.7. Compact RIO modules.

Module	Units	Type	Description
NI 9265	2	Analog Output	4 - Channel - 0 to 20 mA output range
NI 9472	1	High-Voltage Digital Output	8 sourcing digital output channels with 24 V logic levels
NI 9203	1	Analog Current Input	8 channels - 0 to 20 mA
NI 9214	2	Isothermal Thermocouple Input	16 - Channel high precision

The control hardware scheme, the interrelations among the air flow and temperature controllers of the above described equipment and the measurement points in the system are detailed in the piping and instrumentation diagram - P&ID - shown in Figure 3.35.

Figure 3.35. P&ID of the research facility.

Detailed information about the variable connections to each channel of the modules can be found in ANNEX I Experimental test rig: design and constructive details.

3.4.2. Software description

This section presents the software architecture of the control and data acquisition system as well as the definition of the control design criteria. Subsequently, the LabVIEW[®] project developed to meet those criteria and its operation is explained by unified modelling language (UML). Finally, a detailed description of the human-machine interface (HMI) is included.

LabVIEW architecture

The program for control and data acquisition has been implemented under *LabVIEW 2012* environment: The *cRIO* and the host personal computer (PC), must have the same *LabVIEW* version and drivers installed for the code to run. As shown in Figure 3.36, the host PC runs a HMI on Window operating system (OS), and on the cRIO, the real time (RT) processor runs the deterministic and non-deterministic loops, and the field programmable gate array (FPGA) runs in RIO scan interface mode to check the input / output (I/O) modules.

The deterministic loop executes time consuming tasks like reading and writing the I/O variables, the control loops and the on/off switching of instruments. The non-deterministic loop executes time independent tasks like reading the RT-FIFO data or network-published shared variables.

Figure 3.36. Software architecture.

The physical communication between the host PC and cRIO is done over Ethernet and the networking protocols are based on network published shared variables or network streams functions.

Network streams functions are designed and optimized for lossless, high-throughput data communication, and they feature enhanced connection management that automatically restores network connectivity if a disconnection occurs due to a network outage or other system failure. It ensures that the data written to the stream is never lost, so that it is particularly useful for sending and receiving commands.

Network-published shared variables are straightforward to implement and support most LabVIEW data types and custom type definitions. This protocol allows efficiently and reliably transmission of data over the network but, it does not guarantee lossless data transfer. Therefore, it is mainly utilized for monitoring and not for managing command.

The communication between the RT processor and the FPGA is done through the NI scan engine, which is a software component that enables efficient access to coherent sets of I/O channels, using a scan that stores data in a global memory map and updates all values at a single rate, known as the scan period. It allows working speed of 1 kHz, which fulfils the present project requirements.

The communication between the deterministic and no deterministic loops is done by RT first-in first-out (FIFO) data.

Design criteria

The host PC or facility computer must be able to switch on and off all devices directly connected to the workbench, including the control program, implementation of the experimental test and visualization of the experimental data in real time. All the data acquired, should be accessible in a txt file for consulting and analysing purposes.

In the experiment programming, the operator should be able to:

- Define the name of the file and the path where the data would be stored.
- Switch on and off one or both stages of the heating system and the air blowers.
- Set the air flow rate, heat velocities for increasing/decreasing temperature ramps and plateaus of different length of time and at different temperatures in the whole range of the air flow rate.
- Have access to the PID control parameters of the three-phase furnace.
- Set the temperature value for high temperature risk control alarms.

Visualization of the data is done on the computer monitor in independent flow sheets for the furnace, preheaters, reactor, and xy-plots of various pressure variables and air composition. This visualization includes both, current value of the variable and its trend.

LabVIEW project

The structure of the LabVIEW project developed to fulfil the control design criteria exposed above is shown in .

Figure 3.37. LabVIEW project structure of the DAC system.

The files hanging from *My Computer* constituted the part of the project code executed in Window OS; the main virtual instrument (VI) executed in Windows is “RLF¹ Main Host”. The remaining files are executed in the cRIO; the main VI of this part is “RLF RT Main”. The project variables shared between Windows and the cRIO are defined in the cRIO, as well as the I/O variables related to the cRIO modules.

The “RLF Main Host” is the VI supporting the HMI. It uses network streams functions to write the data on the text file and, network-published shared variables to show the data in the graphs and indicators. The UML diagram of this program is illustrated in Figure 3.38.

Figure 3.38. UML diagram of the RLF Main Host VI.

¹ RLF means fluidized bed reactor from Spanish “reactor de lecho fluidizado”.

The aim of the HMI is to allow human operator to set experimental conditions and monitor the experiment progress.

The HMI developed for the workbench is organized in five different panels. The first one is related to the experiment management. The second, third and fourth screens display the information acquired from the workbench related to the air heating furnace, the preheaters and the reactor, respectively. Finally, the fifth panel monitors the pressure and gas composition.

Figure 3.39 shows the experiment management panel of the HMI, named “Process”. Here, the operator can start the program, by introducing a password, and define the file path to the txt file where the experimental data are stored. The operator can also handle various aspects of the experiment:

- Switch on/off the furnace, preheaters and air blowers.
- Define the air flow setpoint; it is possible to set a total air flow or an individual setpoint for each flow controller.
- Define the temperature setpoint for the preheaters as well as for the furnace. There are two options setting a fixed temperature value or a profile. The profile would include different heating or cooling ramps and temperature plateaus.
- Selection of manual or automatic operation mode for the furnace. In the automatic operation mode, operator can choose P, PI or PID control or on/off control.
- Set the controller parameters for a P, PI or PID control in each of the three air flow ranges defined.
- Set a temperature threshold in order to avoid any risk associated to high temperature. If any of the thermocouples measure a temperature higher than the defined one, the system is automatically switched off for the equipment protection.

Figure 3.39. Screenshot from the “Process” panel of the HMI application.

“Process” panel of the HMI shows the real total or individual air flow rates and the temperature gathered from the two K-type thermocouples fixed to the external metallic surface of the three phase electric furnace.

Figure 3.40 shows the data visualization panels of the HMI: (a) furnace, (b) preheaters, (c) reactor and (d) pressure and gas analysis panels. Each panel presents one or various graphs plotting the variables as a function of time and a component layout with displays showing instant values of the variables.

Figure 3.40. Screenshot from the data display panels of the HMI application: (a) furnace, (b) preheaters, (c) reactor and (d) pressure and gas analysis data.

The UML diagram of the RLF RT Main VI executed in cRIO is shown in Figure 3.41. This program executes successively the starting sequence, the deterministic and non-deterministic loops and the stop sequence.

The deterministic loop executes time consuming tasks like reading and writing the I/O module variables, the control loops and the on/off switching of instruments. The non-deterministic loop executes time independent tasks like reading the RT-FIFO data or network-published shared variables.

The deterministic loop has a fixed time of 0.1 seconds to execute its tasks. Nevertheless, the program has been designed to finish before, so the non-deterministic loop can be executed in the remaining time.

Figure 3.41. UML diagram of the RLF RT Main VI.

The Initialize VI implements the starting sequence of the cRIO. It starts the process to reliable initial values, creates the writing node for network stream communication and waits for establishing the connection to the host PC to start the process and emptying the buffer between processes. The UML diagram of this VI is shown in Figure 3.42.

Figure 3.42. UML diagram of the initialize VI.

Chamber control VI, which UML diagram is shown in Figure 3.43, implements the deterministic loop of the cRIO. It reads variables from the project, like setpoints or on-off commands, and input from the modules, like temperatures or pressures. It implements control loops, filters and sorts the obtained data. It also writes variables to the project and output to the modules.

Figure 3.43. UML diagram of the chamber control VI.

Logging and network communication VI implements the non-deterministic loop which reads the data from the deterministic loop through the RT-FIFO data and sends it to the host PC through both network publish shared variables and network streams functions. Its UML diagram is shown in Figure 3.44.

Figure 3.44. UML diagram of the logging and network communication VI.

Shutdown VI implements the stop sequence for the cRIO. It will be executed at the end of every experimental test or in case of an error of the program. Its UML diagram is shown in Figure 3.45. This VI set reliable values for setpoints and on/off commands when the program stops for an error or for an operator command.

Figure 3.45. UML diagram of the shutdown VI.

To complete this LabVIEW project description, additional VIs have also been implemented:

- *File module* that creates, writes and closes a text file.
- *Read NS Write text file* that reads data from network streams and writes it to the text file.
- *Clear specific error*, which is used to delete the underflow errors in the communication buffers
- *TCsErrorHandler* that deletes the open thermocouple error and the voltage error in common mode, in the thermocouple modules, avoiding the loss of data read following these errors. It also generates a Boolean signal, which is useful for alarm implementation.

3.4.3. Control strategy

As explained in the state of the art, industrial heating processes using electric-resistance furnaces are usually characterised by slow response time and non-linear features. Thus, obtaining the physical model that mathematically describes the system is usually discarded, because of its high complexity, in favour of the black box approach for process identification described in section 2.2.

Based on practical knowledge of the air heating system, the plant can be identified as a multiple input single output (MISO) nonlinear plant: the outlet temperature depends on the air inlet temperature, the air flow rate and the electric power provided to the furnace resistors, as shown in Figure 3.46.

Figure 3.46. MISO system diagram.

The air pre-heaters are only used for extreme experimental requirements. So, in order to develop the control of the three-phase electric furnace, the air inlet temperature can initially be considered as a simple perturbation on the system.

Besides, several additional simplifications have been used in order to remove non-linear dependences in the system. Firstly, by discretizing the air flow rates in three different ranges, the effects of nonlinear distortion get small enough to be considered as a disturbance for the system. Therefore, a single input single output (SISO) non-linear system, where the air outlet temperature depends only on the furnace electric power can be applied (see Figure 3.47).

Figure 3.47. SISO system diagram.

Secondly, the working temperature range is divided in various consecutive intervals, where the dynamic response of the heating system is considered to be linear, for each mass flow rate range.

A gain schedule (GS) of PID controller is implemented to soften the switch between the working temperature sections in each of the air flow ranges (see Figure 3.48). The working temperature sections are defined during the identification process of the plant.

Figure 3.48. Block diagram of a GS - PID controller.

In summary, the methodology applied to define the heating process control is to regulate the MISO non-linear plant using several SISO linear controllers. This is done in two steps: First, system identification of the plant is done for each of the air flow ranges and their corresponding temperature sections. And second, control parameter values are determined by control tuning.

3.4.4. System identification

System identification consists in building mathematical models of a given system based on measured data. These models would forecast the response $y(s)$ of the system to a variation input $u(s)$ over a time interval. In our case, the input data is the electrical power supplied to the furnace and the output data is the outlet air temperature reached at the furnace exit.

The experiments conducted for data collection consists of several open-loop responses to step variation of the furnace power. Three air flow rate intervals are defined: 10 - 20 Nm^3/h , 20 - 40 Nm^3/h and 40 - 60 Nm^3/h . The temperature sections for each air flow range are determined by the temperature at which steady state is reached.

Figure 3.49. Identification process scheme.

Figure 3.49 shows the working scheme developed for the identification process. The flow rate used in each experiment is set to the mean value, i.e., 15, 30 and 50 Nm³/h, respectively. Experiment progress consecutively from the lowest interval to the highest one. A new mass flow rate set point (and consequently the mass flow rate interval) is established once the steady state has been achieved in the previous interval.

Figure 3.50 shows the data collected for the lowest air flow rate. In this case, the temperature sections resulted to be from ambient temperature to 210 °C, 210 - 475 °C, 475 - 810 °C and 810 - 1000 °C.

Figure 3.50. Step response for 10 - 20 Nm³/h flow range.

Figure 3.51 shows the step-response experiment conducted for data collection in the intermediate air flow range. In this case, the temperature sections resulted to be from ambient temperature to 240 °C, 240 - 420 °C, 420 - 745 °C and 745 - 1000 °C.

Figure 3.51. Step response for 20 - 40 Nm³/h flow range.

Figure 3.52 shows the data collected for the highest air flow rate. In this case the temperature sections resulted to be from ambient temperature to 210 °C, 210 - 510 °C, 510 - 780 °C and 780 - 1000 °C.

Figure 3.52. Step response for 40 -60 Nm³/h flow range.

Matlab[®] System Identification Toolbox was used to evaluate first, second and third order plus time delay process models for each step response:

- In each air flow range, the experimental data collected is divided into the corresponding four step responses obtained. For each step response two data points prior to the step signal generation are maintained.
- The data are polished by removing the initial value of the temperature just before the step response is generated by subtracting the average value of the two initial temperature points.
- The time delay of the system is graphically determined for each step response and introduced as known parameter in the system identification tool.
- The FOPTD, SOPTD and TOPTD described in section 2.2.1 are estimated by running the process model with one, two and three poles respectively.
- The models validation is done by comparing each model output with the corresponding measured output data.

The best fitting model to experimental data is selected in order to design the controller. The selected models and their corresponding parameters (K_c , T_{p1} , T_{p2} , T_{p3} and T_d) for each step response are shown in Table 3.8, Table 3.9 and Table 3.10. Information related to discarded models can be found in [17].

Table 3.8. Step response model parameters for the 10 - 20 Nm³/h air flow range.

Model	TOPTD	SOPTD	SOPTD	SOPTD
Temperature section (°C)	Amb T - 210	210 - 475	475 - 810	810 - 1000
K_c	9.25	26.62	33.81	37.14
T_{p1}	14720	29722	27816	16042
T_{p2}	1795.9	6339.7	6081.2	1776
T_{p3}	98.00	-	-	-
T_d	8	4	24	12

Table 3.9. Step response model parameters for the 20 - 30 Nm³/h air flow range.

Model	TOPTD	SOPTD	SOPTD	SOPTD
Temperature section (°C)	Amb T - 240	240 - 420	420 - 745	745 - 1000
K _c	7.46	18.39	24.78	22.89
T _{p1}	2171.9	8170.7	7622.6	21951
T _{p2}	7633.3	1556.1	1150.5	3781.9
T _{p3}	198.36	-	-	-
T _d	5	6	12	14

Table 3.10. Step response model parameters for the 40 - 60 Nm³/h air flow range.

Model	SOPTD	SOPTD	SOPTD	SOPTD
Temperature section (°C)	Amb T - 200	200 - 510	510 - 760	760 - 1000
K _c	5.64	14.73	15.28	9.89
T _{p1}	3739.1	5176.5	7820.5	10453
T _{p2}	875.37	1042.6	1464.7	2813.8
T _d	8	2	3	8

3.4.5. Control tuning

The Ziegler-Nichols open-loop method is applied to design the PID controllers for each temperature section of the three flow ranges. It consists in approaching the step response models of the plant to a first order plus time delay model, which is subsequently used to calculate the process gain, delay and time constant to find PID parameters.

In order to calculate the FOPTD models parameters a Matlab[®] code to implement the maximum slope method was developed. The code is included in ANNEX I Experimental test rig: design and constructive details.

The parameters shown in Table 3.11, Table 3.12 and Table 3.13 contain the result for the three air flow ranges considered.

Table 3.11. FOPTD and PID parameters for the 10 - 20 Nm³/h air flow range.

Temperature sections	FOPTD Model			P	PI		PID		
	K _c	T _{p1}	T _d	K _p	K _p	T _i	K _p	T _i	T _d
AmbT - 210 °C	9.25	1168	19938	1.84	1.66	3890	2.21	2336	584.2
210 - 475 °C	26.62	3250	45578	0.53	0.47	10821	0.63	6499	1625
475 - 810 °C	33.81	3130	42861	0.40	0.36	10422	0.49	6259	1565
810 - 1100 °C	36.94	7369	53247	0.20	0.18	24538	0.23	14737	3684

Table 3.12. FOPTD and PID parameters for the 20 - 40 Nm³/h air flow range.

Temperature sections	FOPTD Model			P	PI		PID		
	K _c	T _{p1}	T _d	K _p	K _p	T _i	K _p	T _i	T _d
AmbT - 240 °C	7.41	1374	15366	1.51	1.36	4576	1.81	2748	687.1
240 - 420 °C	18.39	851	12071	0.77	0.69	2832	0.92	1701	425.3
420 - 745 °C	24.78	6791	10669	0.63	0.57	2262	0.76	1358	339.6
745 - 1100 °C	22.89	2127	31659	0.65	0.58	7083	0.78	4254	1064

Table 3.13. FOPTD and PID parameters for the 40 - 60 Nm³/h air flow range.

Temperature sections	FOPTD Model			P	PI		PID		
	K _c	T _{p1}	T _d	K _p	K _p	T _i	K _p	T _i	T _d
AmbT - 200 °C	5.64	453.85	5829	2.28	2.05	1511	2.73	907.7	226.9
200 - 510 °C	14.73	558.43	7756	0.94	0.85	1860	1.13	1117	279.2
510 - 760 °C	15.28	802.03	11506	0.94	0.85	2671	1.12	1604	401.0
760 - 1100 °C	9.89	1377.1	16951	1.24	1.12	4586	1.49	2754	688.6

3.4.6. System verification

Several experiments were conducted to evaluate the performance of the control strategy for PI and PID controllers. P controllers are discarded, since material evaluation experiments require a defined temperature, and P controllers have a steady-state error associated to them.

The experiments are devised to check the developed PI and PID parameters' controls in every flow rate and temperature ranges. Therefore, for different constant air flow rates within each range, experiments using various temperature setpoints, such as heating/cooling rates and isotherms, were carried out. The faster heating ramp required for material evaluation experiments is 5 °C/min, so this value is defined for the control test experiments. In order to reach this heating rate, preheaters were set to 300 °C and 500 °C for the intermediate and highest air flow ranges respectively, they were off for the lowest air flow range. Isotherms were set at temperatures close to the maximum value for each temperature section defined in the air flow range. Each temperature setpoint related to an isotherm was maintained fixed until the system reached steady state conditions.

Figure 3.53 illustrates the PI and PID experiments conducted for each air flow range: Figure 3.53 (a) and (b) show the outlet air temperature as a function of time using the PI and PID controllers, respectively. Here the air flow rate was maintained at 15 Nm³/h and temperature plateaus were defined at 190, 455, 790 and 1000 °C. Figure 3.53 (c) and (d) correspond to an air flow rate of 30 Nm³/h and temperature plateaus were defined at 220, 400, 730 and 1000 °C. Finally, Figure 3.53 (e) and (f) show the experiment progress at 50 Nm³/h and temperature plateaus at 180, 500, 750 and 1000 °C.

Figure 3.53. (a) PI and (b) PID controller evaluation in the air flow rate interval 10 - 20 Nm³/h. (c) PI and (d) PID controller evaluation in the air flow rate interval 20 - 40 Nm³/h. (e) PI and (f) PID controller evaluation in the air flow rate interval 40 - 60 Nm³/h.

Qualitatively, it can be seen that the temperature tracking improves with higher air flow rates. This tendency, observed both in PI and PID controllers, is related to intrinsic behaviour of the air heating furnace. Heat transfer processes have three well-known mechanisms: radiation, convection and conduction. In a specific device, variations in the gas flow rate would affect mainly to the heat transferred by convection. Higher gas flow rates would produce higher turbulence into the device, which implies better convective coefficients. It should also be taken into account that this particular unit has been designed to meet the highest experimental requirements which appear at the highest air flow rates, so its performance is optimized for the highest working air flow range.

PI and PID controller performances are quantitatively evaluated attending to the maximum overshoot (MOS) and the settling time (ST). MOS is defined as the difference between the maximum temperature value reached and the temperature setpoint in each temperature plateau. ST is the time required for the temperature to reach and stay into the ± 1 °C band around the temperature setpoint.

The results obtained from the analysis of the control experiments are listed in Table 3.14, Table 3.15 and Table 3.16.

Table 3.14. Controllers evaluation for the 10 - 20 Nm³/h air flow range.

Temperature plateau (°C)	PI		PID	
	MOS (°C)	ST (s)	MOS (°C)	ST (s)
190	4.97	1062	7.05	460
455	26.59	6314	38.22	6157
790	27.99	7490	25.17	9240
1000	33.63	4076	21.78	2666

Table 3.15. Controllers evaluation for the 20 - 40 Nm³/h air flow range.

Temperature plateau (°C)	PI		PID	
	MOS (°C)	ST (s)	MOS (°C)	ST (s)
220	5.81	1722	7.85	633
400	9.78	1505	9.28	1005
730	13.1	1742	10.09	1024
1000	22.21	3750	14.52	4461

Table 3.16. Controllers evaluation for the 40 - 60 Nm³/h air flow range.

Temperature plateau (°C)	PI		PID	
	MOS (°C)	ST (s)	MOS (°C)	ST (s)
180	3.39	266	2.81	287
500	7.04	718	5.29	350
750	8.18	817	6.28	478
1000	8.75	1379	6.42	803

Comparison between air flow ranges shows a general trend in which smaller air flow rates have bigger MOS and ST. The reason for this behaviour, independently from the control scheme, is that higher air flow rates improve heat transfer processes in the system.

In each particular experiment, there is an upward trend for the MOS and the ST with increasing temperature. This general behaviour, shown in both controllers, is also related to the intrinsic heat transfer process taking place in the workbench, whose complexity is enhanced when more demanding temperatures are required.

Comparing between the two control schemes, PID controllers seem to have better performances than PI controllers since they show smaller MOS and ST. This improvement in the performance should be attributed to the derivative control term and its anticipative action.

Considering that the installation aims at characterising thermochemical heat storage materials, both PI and PID controls options are useful; as far as a temperature value is reached and maintained for a certain period of time, the materials will react. Therefore the temperature overshoot will seldom be a constraint.

In any case, at this point of the analysis, it is also necessary to take into account the dynamic controller output behaviour, i.e. the variation of the regulator and the power sent to the furnace resistors. In order to do so, Figure 3.54 shows an enlargement of the PI and PID, corresponding to the third temperature plateau, where the furnace temperature setpoint, the furnace actual temperature and the power sent to the furnace resistors are displayed for each one of the three air flow.

Figure 3.54. Control of the third temperature plateau for different air flow ranges: (a) PI and (b) PID for controller for $[10, 20] \text{ Nm}^3/\text{h}$. (c) PI and (d) PID controller for $[20, 40] \text{ Nm}^3/\text{h}$. (e) PI and (f) PID controller for $[40, 60] \text{ Nm}^3/\text{h}$.

Output behaviour of the PI controllers is similar for the three air flow ranges studied while, for the PID controllers, it depends on the air flow range. For the highest range, PI and PID output performance are comparable, but with lower air flow ranges, PID controllers show bigger and more frequent variations between consecutive signals.

This behaviour is known as derivative kick and it is an undesirable behaviour of PID controllers. Notice that the derivative kick does not impact overall PID control performance since, the gathered MOS and ST are smaller than the ones found for the PI control, but it has a negative effect on the lifetime of the resistors due to the strong current intensity variations.

Hence, aiming to maximize the installation lifetime, while observing the temperature accuracy required, PID controllers would be considered for the highest air flow rates and, PI controllers would be applied for the intermediate and lower air ranges. In the exceptional cases in which the evaluated material may have special accuracy requirements, PID controllers would be considered for the intermediate air flow range, and in very rare cases for the lowest air flow range.

3.5. Summary and conclusions

The design, construction and commissioning of the chemical reactor and the associated workbench have been a very challenging task. Lot of effort and implementation of various strategies have been made mainly in regard to the development of the ex-novo air heating stages, and the definition of the technical specifications of the workbench requirement definition and the safety working conditions. The created workbench constitutes a really flexible system that will allow the characterization of many different materials in fluidized bed conditions.

The air heating furnace control developed allows great flexibility during operation with the 100-Wh multi-purpose particle reactor for thermochemical heat storage evaluation in concentrating solar power plants. By providing air mass flow rates between 10 Nm³/h and 60 Nm³/h at temperatures from ambient temperature up to 1100 °C, the testing plant will allow the evaluation of different parameters for thermochemical storage such as reaction yield, particle size, and successive oxidation / reduction cycles on the process cyclability, the mechanical strength and abrasion resistance of the storing materials, etc.

The divide-and-conquer techniques applied to the system control discretizing the air flow rates and working temperatures in intervals have simplified the initial design of a MISO non-linear plant into a SISO linear plant. A multiple controller has been designed, optimized and tested under real conditions.

The control performance evaluation has allowed defining a set of twelve PI and PID controllers to meet the application requirements. It has been demonstrated that the air temperature control also meet the performance required for the material characterization experiments.

Aiming to have the temperature accuracy required while maximizing the installation lifetime, PID controllers will be chosen for the highest air flow rates and PI controllers will be selected for the intermediate and lower air ranges. In exceptional cases in which the evaluated material may have special accuracy requirements, PID controllers would be consider for the intermediate air flow range, and in very rare cases, for the lowest air flow range.

CHAPTER IV

4. MATERIAL CHARACTERIZATION

This chapter focuses on the material characterisation of manganese oxides. The kinetics of the redox reaction are analysed, but also other physico-chemical properties as thermal conductivity, reactivity analysis, or morphology of the powder material are studied.

The material development achieved is determined by the industrial process of application done by the manganese oxide manufacturer, *Erachem Comilog S.A.*, during the time basis of the TCS Power project.

Considering that for heat storage application the material needs to be shaped to form pellets, *Erachem Comilog S.A.* developed scalable palletisation processes. In the frame of this Thesis a complete new methodology has been created to measure the evolution of the pelletized material in terms of hardness, density, porosity, volume, morphology and reactivity, with the different thermal cycles applied. Through this exhaustive analysis, a base line of the material characteristics is gathered. The compiled information will be used as reference in order to evaluate the effect of the thermochemical storage cycle on the material when using a fixed/fluidized bed reactor.

4.1. Manganese oxide: powder material

The material selected at the first stage for the experimental is the commercial manganese oxide Mn_3O_4LH grade, manufactured by *Erachem Comilog S.A.* Table 4.1 shows the chemical composition of the manganese oxide and the typical physical properties.

Technical specifications of the commercial Mn_3O_4LH material according to the manufacturer are: minimum content of manganese of 70.5%, maximum content of water - once calcined at 120 °C- of 0.6%, maximum content of K_2O , Na_2O , SiO_2 and CaO of 50 ppm each, and maximum content of MgO of 100 ppm.

Table 4.1. Manganese oxide (Mn_3O_4LH) chemical composition.

Chemical Element		Mass-%
Mn	Min.	70.5
Na_2O	Max.	0.005
K_2O	Max.	0.005
CaO	Max.	0.005
MgO	Max.	0.010
SiO_2	Max.	0.005
S	Max.	0.060
H_2O (120 °C)		0.6
Particle diameter (Typical value)	dp, 10%	0.2 μm
	dp, 50%	1.1 μm
	dp, 90%	3.4 μm
Pure density at 25 °C	ρ	4856 kg/m^3
Bulk density at 25 °C	ρ bulk	575 kg/m^3
Porosity	ϵ	0.88

4.1.1. Thermal conductivity / diffusivity

Thermal diffusivity was measured by submersion in a thermostatic bath for temperatures smaller than 100 °C and in a Laser Flash - *LFA 457 Micro Flash* from *Netzsch* for the range of 200 to 700 °C. For the thermostatic bath method, the material was placed in an aluminium tube - dimensions 20 mm of diameter and 150 mm long-, a thermocouple was inserted in the centre of the sample and the temperature was monitored since the tube was introduced in the bath until the system reached stationary temperature. For the Laser Flash measurements, the sample was placed in a Pt/Rd crucible and measured in the range of temperature from 200 °C to 700 °C. Experimental data vs. temperature are plotted in Figure 4.1.

Figure 4.1. Thermal diffusivity versus temperature of the Mn_3O_4LH powder material.

It is clear that the thermal diffusivity values in the low temperature range are higher and have a different tendency compared to the values measured in the high temperature range. This discordance may be related to the different measurement protocol, with different sample size, compacting and heat inertias. Nevertheless, for the present application only data in the high temperature range will be used, that data is fitted to a first-order polynomial:

$$\alpha = 4.5594 \cdot 10^{-11}T + 1.3178 \cdot 10^{-7} \quad (48)$$

where temperature is given in degree Celsius. Assuming an average thermal diffusivity obtained by the Laser Flash method of $\alpha \sim 1.55 \cdot 10^{-07} \text{ m}^2/\text{s}$ in the interval 200 - 700 °C, effective thermal conductivity value at 500 °C is calculated as follow:

$$\begin{aligned} \lambda &= \alpha \rho c_p = 1.55 \cdot 10^{-7} (\text{m}^2/\text{s}) \cdot 4856 (\text{kg}/\text{m}^3) \cdot 790.53 (\text{J}/\text{kg} \cdot \text{K}) \\ &= 0.60 (\text{W}/\text{m} \cdot \text{K}) \end{aligned} \quad (49)$$

where ρ , the density of Mn_3O_4 , is assumed to be constant and given in Table 4.1, and c_p , the specific heat capacity, is obtained from Table 2.4.

4.1.2. Reactivity analysis

The chemical reaction of interest for thermochemical storage purposes involving manganese oxide is:

Which stoichiometric relative mass variation from Mn_2O_3 to Mn_3O_4 is 3.38%. The reactivity of the power material is monitored by TGA using an *SDT Q-600* from *TA Instruments*. The weight change of the sample placed into a 90mL alumina crucible is recorded for fifty thermal cycles between 1000 °C and 550 °C, with a heating/cooling ramp of 10 °C/min and a constant air flow of 100 mL/min. Prior to the first heating ramp, a 60 minutes plateau at ambient temperature is accomplished for homogenizing purposes. The results are shown in Figure 4.2.

Figure 4.2. Reactivity study of the $\text{Mn}_3\text{O}_4\text{LH}$ powder material.

According to the results, $\text{Mn}_3\text{O}_4\text{LH}$ in powder form presents good cyclability since the weight change remains close to the theoretical value during the assay. Representing velocity of weight variation over time, see Figure 4.3, it is shown that the velocity remains constant during the reduction stage, while it decreases during the oxidation until reach a steady value around the 25th cycle.

Figure 4.3. Redox cycles: weigh variation derivative rate versus time of the $\text{Mn}_3\text{O}_4\text{LH}$ powder material.

It is important to explain that the oxidation reaction starts when the temperature is decreasing. After several thermal cycles, the full re-oxidation of the sample takes longer, which

means that the oxidation reaction takes place not only during the cooling but while the temperature rises up to the reduction reaction.

From Figure 4.2, it is also observed that the weight change in the first thermal cycle evolves in a different way to the remaining cycles. This event has been noticed in all the experiments performed in the present work.

A magnification of the first cycle is included in Figure 4.4. Below 400 °C, a small loss of weight in two steps is observed. It corresponds to the loss of some volatiles, free water and some of the combined water (OH^- groups). Between 400 °C and 650 °C, a weight gain in two steps is observed; it corresponds to the oxidation of the different manganese species present in the sample, and to the oxidation of Mn_3O_4 to Mn_2O_3 . Above 900 °C, the weight loss observed corresponds to the reduction of Mn_2O_3 into Mn_3O_4 according to the chemical reaction presented in (50).

Figure 4.4. First cycle magnification of the reactivity assay of the $\text{Mn}_3\text{O}_4\text{LH}$ powder material.

4.1.3. First heating ramp study

In order to evaluate if the first heating ramp affects the material reactivity, several TGA experiments programming different heating ramps from 2 to 10 °C/min were performed. The sample weight, around 30 mg, was monitored for 16 thermal cycles between 1050 °C and 650 °C varying the first heating ramp and using heating/cooling velocities of 10 °C/min for the rest of the assay. A 30 min-plateau at ambient temperature was implemented at the beginning of each assay for homogenizing purposes. The results are included in Figure 4.5.

It is important to mention here, that due to the slowdown of the oxidation reaction velocity, when the inferior temperature limit is increased of, in a hundred degrees compared to the previous experiment, the re-oxidation of the sample is not completed. There is not enough time to get to full re-oxidation, for this reason in Figure 4.5 all the samples seem to deactivate.

Nevertheless, as all the experiments are performed in the same temperature conditions, the experiment is valid in order to evaluate the effect of different heating ramps.

Figure 4.5. TG analysis for various heating ramps of the $\text{Mn}_3\text{O}_4\text{LH}$ powder material: (a) 2 °C/min, (b) 4 °C/min, (c) 6 °C/min, (d) 8 °C/min and (e) 10 °C/min.

By analysing the data, the weight percent change for reduction and oxidation reactions in each cycle is obtained. The corresponding data is plotted in Figure 4.6 and Figure 4.7, respectively.

Figure 4.6. Weight percent change in reduction reaction of the $\text{Mn}_3\text{O}_4\text{LH}$ powder material.

Figure 4.7. Weight percent change in oxidation reaction of the Mn_3O_4LH powder material.

For the two lower heating rates, the decrease in weight gain of the material is faster. For the higher heating ramps, there is no difference in the reaction progress. It could have been expected that lower heating rates will present better reaction rates but, as it will be explained further on, there is a sintering factor to be considered, smaller heating rates favour the sintering processes negatively affecting to the redox reaction. Thus, for next experiment a first heating rate higher than 4 °C/min will be used.

Also, comparing reduction and oxidation, excluding the first cycle, it is observed that both reactions are equally affected by the initial heating ramp, so forward analyses will only focused on one of them. Also, the first cycle will be considered as material activation and it will not be considered for further analyses.

4.1.4. Oxidation reaction kinetics

As explained in section 2.3 of the state of the art, some works report studies on the kinetics of the reduction reaction, but no information has been found in literature about the oxidation kinetic mechanism. Therefore, a series of TGA isothermal assays at different temperatures are performed to study the kinetics of the oxidation of Mn_3O_4 to form Mn_2O_3 .

First, the kinetic model is estimated using master plots based on the differential form of the kinetic equation. Once the model has been discerned, reaction rate coefficient, activation energy and pre-exponential factors, KCE slope and intersection, and the effective time of the reaction are evaluated.

TG analyses were performed using a *Netzsch STA 409C*. Each experiment uses a fresh sample of about 1 g of Mn_3O_4LH which is placed into an alumina crucible and the air flow rate is set to 75 ml/min. Figure 4.8 shows a typical thermogram obtained in these thermal analyses. The sample is first subjected to a 20 °C/min heating ramp from room temperature to 1050 °C, followed by a 60 minutes isotherm. Afterwards, the system is cooled down until the oxidation temperature is reached. This step is done at 50 °C/min under inert gas to prevent oxidation. Once temperature plateau is stabilized, the inert atmosphere is change back to air and the isothermal conditions are hold during 240 minutes.

The initial sample material is a mixture of Mn_3O_4 and Mn_2O_3 ; during the first heating ramp, the Mn_3O_4 contained in the sample is transformed into Mn_2O_3 , which is later reduced into Mn_3O_4 completing the first thermochemical cycle. Once the oxidation temperature is stable, at about minute 130 in the experiment shown in Figure 4.8, the Mn_3O_4 is oxidized to Mn_2O_3 .

Figure 4.8. Data acquisition procedure isotherm temperature 600 °C in air (75 ml/min ~ 1 atm) of the $\text{Mn}_3\text{O}_4\text{LH}$ powder material.

The assay is repeated at different fixed temperatures. The collected data, once removed the first cycle, is shown in Figure 4.9.

Special attention must be paid to ensure the same experimental conditions in all assays, except the temperature setpoint that defines the isotherm plateau. Figure 4.10 illustrates the master plots obtained at the different studied temperatures; red dots are calculated from the experimental data and compared with the most common f-function mechanisms in solid-state reactions, included in Table 2.7.

Figure 4.9. Re-oxidation kinetics in air (75 ml/min ~ 1 atm) of the $\text{Mn}_3\text{O}_4\text{LH}$ powder material at different temperatures.

complete conversion during the isotherm period. From these data, a common order of reaction of $n = 2.89 \pm 0.24$ is obtained.

Following the same experimental procedure explained for the assays in air, the manganese oxide oxidation is evaluated in pure oxygen atmosphere at 500, 600, 700 and 800 °C. The data obtained is shown in Figure 4.11. As the oxidation in oxygen is faster than in the air experiments the time of isotherm is set shorter for 700 °C and 800 °C experiments.

Figure 4.11. Re-oxidation kinetics in oxygen (75ml/min ~1atm) of the Mn_3O_4LH powder material at different temperatures.

Figure 4.12 shows the master plot for the experiments performed in oxygen atmosphere. An Avrami-Erofeev mechanism also seems to be the most suitable kinetics for describing the chemical reaction with another order of reaction of $n = 3.18 \pm 0.35$.

Figure 4.12. Master plots using data from TGA of the Mn_3O_4LH powder material oxidation in oxygen (see Table 2.7 for functions description).

The rate of reaction is calculated from the experimental data by applying equation (39) in the form shown in equation (51). The corresponding data are plotted versus the inverse of the temperature (expressed in K) in Figure 4.13.

$$k(T) = \frac{d\alpha}{dt} / f(\alpha) \quad (51)$$

Mn₃O₄ oxidation in air has an exponential behaviour at low temperatures. Nevertheless, it does not progress according to the exponential law when the temperature increases and the slope of the reaction rate decreases becoming negative at high temperature. These results suggest that a new mechanism takes place even if the global kinetics continues being the Avrami-Erofeev mechanism; again at high temperatures there is some competing between reduction and oxidation reactions. Notice that this effect is clearly observed in Figure 4.9, where re-oxidation time at 800 °C is longer than that at 550 °C. It is opportune to remember here, as it was set in the estate of the art, that some authors have also point to Avrami-Erofeev mechanism for the reduction reaction.

Figure 4.13. Velocity constant k versus $1/T$ from TGA of the Mn₃O₄LH powder material oxidation in air and oxygen.

Assuming that $k(T)$ is described by two different exponential functions, k_1 and k_2 , each of them as equation (52), one at low and the other at high temperatures, the general formula (53) is proposed:

$$k_i = A_i \cdot \exp(B_i/T) \text{ for } i = 1,2 \quad (52)$$

$$\frac{1}{k} = \sqrt{\frac{1}{k_1^2} + \frac{1}{k_2^2}} \quad (53)$$

The coefficients of the corresponding exponential functions are given in Table 4.2.

Table 4.2. Fitted parameters for calculating velocity constant of manganese oxide oxidation in air.

A_i	B_i
$1.122 \cdot 10^{-1}$	$-5.293 \cdot 10^3$
$1.217 \cdot 10^{-11}$	$1.747 \cdot 10^4$

Finally, Figure 4.14 shows the effective reaction time versus the inverse of the absolute temperature, $1/T$. This variable is defined as the time required for a fractional conversion between 0.01 and 0.99. Therefore, it is representative of the characteristic time of the re-oxidation reaction in working conditions closed to those use in TGA. Fitted curves are given by (54) and (55) expressions:

$$\frac{1}{t_{eff}^{O_2}} = 2.882122 \cdot \exp(-7237.99/T) \quad (54)$$

$$\frac{1}{t_{eff}^{air}} = \left[\frac{1}{(0.722240 \cdot \exp(-7237.99/T))^{1.432941}} + \frac{1}{(5.602306 \cdot 10^{-13} \cdot \exp(20234.16/T))^{1.432941}} \right]^{1.432941} \quad (55)$$

They correspond to solid and dashed lines in Figure 4.14, respectively. These expressions point out that the characteristic time has the same intrinsic behaviour, which is modified at high temperatures under air.

Figure 4.14. Effective reaction time of the Mn_3O_4LH powder material.

For practical reasons the use of air will be necessary for the economy of the process, so that following experiments will be done in air.

4.1.5. Morphological modifications with thermal treatments

The structure and morphology changes were studied over different samples of the material subjected to an increasing number of thermal cycles (from “as received” powder material up to ten cycles). The thermal cycles were performed in a *Carbolite CWF11/5* muffle furnace. Each cycle consisted of a heating step up to 1000 °C followed by a 360 minutes isotherm and a cooling step down to 500 °C ended by a isotherm of 360 minutes. The heating and cooling rates were 10 °C/min. This protocol was developed to maximize the effect of the thermal treatment in the structure and morphology of the samples using long isotherms duration.

The morphology study is carried out by scanning electron microscopy (SEM) using a *Hitachi TM-100*.

Figure 4.15 corresponds to a micrograph of the “as received” powder manganese oxide, which would be used as point zero for the comparison. No clear geometry in the material is perceptible; the particles seem to be heterogeneous in form and size.

Figure 4.15. SEM micrograph of the Mn_3O_4LH powder material in reception conditions.

Figure 4.16 show the micrographs obtained for the cycled samples. Already from the first cycle, there is an important variation in the morphology of the material. Figure 4.16 (a) shows the appearance of a kind of coral structure. This structure is maintained and grows with the number of thermal cycles applied.

Because of the heat received, the sample is thermally activated and capable to reach a lower internal energy level state, increasing the cohesion of the particles by solid-state sintering.

It is clear that the material suffers a sintering process because of the neck formation observed with the application of the thermal cycles. From cycle one to five There is an important “finger structure growth” as a result of the sintering, while from fifth cycle on this growth seems to slow down. The system could be approaching to the equilibrium state with a possible growth of the grains and the corresponding particle densification.

Figure 4.16. SEM micrographs of the Mn_3O_4LH powder material subjected from one to ten cycles: (a) 1 cycle, (b) 2 cycles, (c) 3 cycles, (d) 4 cycles, (e) 5 cycles, (f) 6 cycles, (g) 7 cycles, (h) 8 cycles, (i) 9 cycles and, (j) 10 cycles.

4.1.6. X-Ray diffraction analyses

X-ray diffraction (XRD) analyses were carried out employing an *Empyrean de PANalytical* diffractometer using $\text{CuK}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) at a scanning rate of $0.1^\circ/\text{s}$ and using a secondary monochromator. The sample sweep covered the 2-theta range of $10\text{--}75^\circ$ with a step size of 0.01° and a rotating speed of 20 rpm. The subsequently analysis is done with the commercial software *X'Pert Highscore Plus*.

The XRD spectra of the samples subjected to the thermal cycles are compared in Figure 4.17. Diffractograms indicate that the oxidation is uncompleted. The amount of Mn_3O_4 present in the sample increases with the number of thermal cycles applied.

Figure 4.17. X-ray diffraction phase composition comparison for the morphologic study for the $\text{Mn}_3\text{O}_4\text{LH}$ powder samples after 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 cycles: (a) $10\text{--}75^\circ$; and (b) $28\text{--}39^\circ$.

These results are coherent with previous experimental observations, where the pointed explanation has been the slowdown of the oxidation reaction velocity. In order to ensure that the material has not suffered deactivation, a fraction of the material subjected to 10 thermal cycles is collected and placed in the thermogravimeter. Five thermal cycles are applied to this sample, each of them consist of a heating step up to 1050°C , 30 minutes isotherm, cooling step up to 500°C and 50 minutes isotherm with $10^\circ\text{C}/\text{min}$ heating/cooling ramps.

Figure 4.18. Cyclability analysis for the 10 thermal cycles $\text{Mn}_3\text{O}_4\text{LH}$ powder sample.

Figure 4.18 shows the results; the sample shows weight variations close to the theoretical value. It is noticed that the oxidation reaction progress is slow. It starts when the temperature is diminishing, lasts for the isotherm time and ends when the temperature is rising again. There is also some effect in the reduction reaction speed: it seems to slow down, no as much as the oxidation, but it indicates that the morphology changes as also influence in the reduction reaction.

4.2. Manganese oxide: pelletized material

Once evaluated the manganese oxide $\text{Mn}_3\text{O}_4\text{LH}$ in powder form, the material must be characterised in its final shape. *Erachem Comilog S.A.* provides the $\text{Mn}_3\text{O}_4\text{LH}$ material in spherical pellets obtained with a drum granulator and dried at 120°C in two diameter size ranges: [2, 3.6] and [3.6, 5] mm. The pellet apparent average density results in 2100 kg/m^3 and the pellet porosity of 57 %. The granulation technique only adds water, thus it produces minimum alterations of the chemical properties of the material, and, thanks to its simplicity, this shape would be economically viable for industrial production.

Prior to perform the experiments in the reactor it is necessary to determine the possible effects of the pellet shape process and final pellet size on the material performance. Thus, density and hardness study is performed in both size ranges, to evaluate the evolution of these properties with temperature treatments. Also the pellets reactivity is checked by subjecting a sample of each size range to TGA.

As a result of the aforementioned experiments, small spherical pellets are selected in order to operate in fluidised and/or packed bed reactors under suitable pressure drop through the system.

To conclude the study, the optimized material is subjected to 10, 20, 30, 40 and 50 thermal treatments cycles between 1050°C and 650°C in a furnace to evaluate its evolution in terms of density, hardness, porosity, reactivity, composition and morphology variations.

4.2.1. Reactivity analyses

The reactivity of the material is monitored by TGA using an *SDT Q-600* from *TA Instruments*. The weight change of the sample placed into a 90 mL alumina crucible is register for six thermal cycles between 1050°C and 650°C , maintaining isothermal condition for 50 and 100 minutes respectively, with a heating/cooling ramp of $10^\circ\text{C}/\text{min}$ with a constant air flow of $100\text{ ml}/\text{min}$. Prior to the heating ramps, a 30 minutes plateau at ambient temperature is accomplished for homogenizing purposes.

Figure 4.19 shows the relative weight loss of $\text{Mn}_3\text{O}_4\text{LH}$ pellets recorded for [2, 3.6] mm and [3.6, 5] mm size distributions respectively.

Both sizes ranges of pellets present very similar cyclability performances. The weight variation is approximately 3.4 %, except in the sixth cycle due to the reduction in the oxidation reaction rate. At the same time, reduction reaction shows to maintain its performance.

Figure 4.19. Reactivity study for Mn_3O_4LH pelletized material in the different size ranges: (a) [2, 3.6] mm and (b) [3.6, 5] mm.

4.2.2. Hardness and density study

According to standard ASTM D4179 – 11, the raw material is initially subjected to a drying cycle, in which it is heated in a furnace up to 400 °C, the temperature is hold at that value during three hours. Once removed from the furnace, the sample is placed in a desiccator until the hardness or crush strength test is performed.

In order to study the hardness and density variation with thermal cycles, the standard drying temperature is modified: the original material, pre-treated at 120 °C, is subjected to heat treatments consisting of sample heating at 10 °C/min until achieving the temperature setpoint which is hold for three hours. Thermal treatments were carried out with temperatures of 200, 400, 600, 800, 1000, 1200 and 1400 °C.

Evaluation of pellets size is done by measurement of their diameter. Initially, every pellet is measured manually in its three dimensions and the diameter of the pellet is calculated as the average of those values. Improving this procedure of obtaining reliable data is mandatory in order to optimize work time. So an image processing method was developed and validated.

A representative sample is photographed and this image is processed with *Image J* software to obtain the pellet area, considering their spherical shape, the diameter and volume of each pellet is obtained. For average diameter estimation, around 80 pellets are used. Detailed information about the developed image processing methodology, as well as its validation, is included in ANNEX II Material characterization.

The density of the material is calculated considering the total mass of the representative sample over its volume. The total volume is obtained by addition of the calculated single pellet volumes in the sample.

The hardness of the samples is evaluated with a *DSFII* dynamometer from *Ametek* by application of the Standard ASTM D4179 – 11 crush strength method adapted to the thermal treatments. The standard method only considers a drying process at 120 °C to eliminated water, in our case this drying process is substituted by the heating process at the studied temperature. In the crush test, five pellets are broken to obtain an initial estimation value and other 15 pellets are broken to get the average hardness value and its standard deviation.

The analysis is carried out for both diameter size ranges: [2, 3.6] and [3.6, 5] mm. For comparison purposes, it is remembered here that the pellet apparent average density is 2100 kg/m³. The resulting data are included in Table 4.3 and Table 4.4 and graphically presented in Figure 4.20 and Figure 4.21.

Table 4.3. Hardness and density results for the [2, 3.6] mm diameter pelletized Mn₃O₄LH.

Heat treatment T (°C)	Diameter (mm)	Density (kg/m ³)	Hardness (N)	Appearance
120	3.2 (±0.4)	2200 (±170)	10 (±3)	Uniform matte light brown
200	3.0 (±0.5)	2150 (±270)	13 (±4)	Uniform matte light brown
400	3.2 (±0.3)	2200 (±170)	32 (±10)	Uniform matte black
600	2.5 (±0.4)	2300 (±300)	15 (±6)	Uniform matte black
800	2.6 (±0.4)	2200 (±270)	24 (±6)	Uniform matte black
1000	2.7 (±0.4)	2700 (±400)	65 (±20)	Uniform matte black
1200	2.2 (±0.4)	4100 (±700)	446 (±74)	Uniform matte grey
1400	2.0 (±0.3)	5500 (±850)	420 (±110)	Uniform shiny grey

Table 4.4. Hardness and density results for the [3.6, 5] mm diameter for pelletized Mn₃O₄LH

Heat treatment T (°C)	Diameter (mm)	Density (kg/m ³)	Hardness (N)	Appearance
120	4.4 (±0.6)	2050 (±160)	11 (±4)	Uniform matte light brown
200	4.4 (±0.6)	1980 (±200)	18 (±3)	Uniform matte light brown
400	4.1 (±0.4)	2250 (±170)	44 (±10)	Uniform matte black
600	4.3 (±0.6)	2100 (±260)	28 (±9)	Uniform matte black
800	4.1 (±0.4)	2100 (±170)	40 (±8)	Uniform matte black
1000	4.1 (±0.5)	2500 (±170)	47 (±10)	Uniform matte black
1200	3.3 (±0.4)	4200 (±500)	-	Uniform matte grey
1400	3.0 (±0.3)	5100 (±540)	-	Uniform shiny grey

The global tendency of the diameter is decreasing with the thermal cycles. Nevertheless, for both ranges of diameters considered, there is a break of the tendency for the 400 °C heat treatment and a clear decrease for the thermal treatments at 1200 °C and 1400 °C.

Figure 4.20. Diameter evolution with the thermal treatments for pelletized Mn_3O_4LH

Figure 4.21 shows that the density, independently of the pellet diameter studied, is constant from 120 to 1000 °C and increases for thermal treatments at temperatures higher than 1000 °C. The comparison between the two size distribution samples shows that generally particles with smaller diameter have slightly higher densities.

Figure 4.21. Density evolution with the thermal treatments for pelletized Mn_3O_4LH

The results of the pellets hardness study are shown in Figure 4.22. Small diameter pellets treated at 1200 °C and 1400 °C were close, and some above, the maximum of the dynamometer measuring range (500 N). The hardness of the higher range pellets was always higher than 500 N. The important increase observed in the hardness of the samples thermally treated at 1200 °C and 1400 °C complicates the appreciation of the tendency obtained for lower temperatures.

Figure 4.22. Hardness evolution with the thermal treatments for pelletized Mn_3O_4LH

Figure 4.23 presents the hardness results excluding the aforementioned data showing an increasing tendency of this physical property with higher temperature treatments. It is also appreciable how the 400 °C sample shows a peak in the hardness value independently of the pellet diameter studied. The comparison between both size distributions indicates that the hardness generally increases with the pellet diameter.

Figure 4.23. Hardness evolution from 120 °C to 1000 °C for pelletized Mn_3O_4LH

Considering the variation in diameter, density and hardness, it seems that a reduction on diameter due to the thermal treatments is directly related with a slight increase in density and important increases in hardness of the pellets. Exceptional values are observed in the three properties evaluated for the case of thermal treatment at 400 °C.

X-Ray diffraction analyses

Crystalline phases are identified by powder XRD analyses for each sample after the heat treatment. The analyses are carried out employing the experimental method described in section 4.1.6. The three crystalline phases identified, are listed in Table 4.5. Detailed information about diffractograms analyses is included in ANNEX II Material characterization.

Table 4.5. Crystalline phases found in x-ray diffraction analysis for pelletized Mn_3O_4LH

Chemical formula	Mineral name	Crystal system	Reference number
Mn_3O_4	Hausmannite	Tetragonal	98-010-0054
Mn_5O_8	Manganese Oxide (5/8)	Monoclinic	98-000-4829
Mn_2O_3	Bixbyite C	Cubic	98-008-1762

Table 4.6 presents the results of the heat treated samples for both pellet size ranges. The presence of Mn_5O_8 is noteworthy, considering that the aforesaid substance is a metastable structure and it is present in a high percentage in both samples treated at 400 °C.

Considering the results obtain for the hardness in the case of the experiments at 400 °C, the increment in hardness of the pellet can be related to the presence of Mn_5O_8 .

Table 4.6. Chemical composition found in the heat treated samples of pelletized Mn_3O_4LH

	Diameter [2, 3.6] mm			Diameter [3.6, 5] mm		
	Ratio	Chemical formula	Crystal system	Ratio	Chemical formula	Crystal system
120 °C	100 %	Mn_3O_4	Tetragonal	100%	Mn_3O_4	Tetragonal
200 °C	100 %	Mn_3O_4	Tetragonal	100%	Mn_3O_4	Tetragonal
400 °C	54 %	Mn_3O_4	Tetragonal	55%	Mn_3O_4	Tetragonal
	46 %	Mn_5O_8	Monoclinic	45%	Mn_5O_8	Monoclinic
600 °C	100 %	Mn_2O_3	Cubic	100%	Mn_2O_3	Cubic
800 °C	100 %	Mn_2O_3	Cubic	100%	Mn_2O_3	Cubic
1000 °C	100 %	Mn_2O_3	Cubic	100%	Mn_2O_3	Cubic
1200 °C	100 %	Mn_3O_4	Tetragonal	100%	Mn_3O_4	Tetragonal
1400 °C	100 %	Mn_3O_4	Tetragonal	100%	Mn_3O_4	Tetragonal

The results obtained are in agreement with the expected kinetics of manganese oxides. Heat treatments below 600 °C result in Mn_3O_4 because the oxidation rate is almost zero. Thermal treatments at 600 and 800 °C results in Mn_2O_3 because they are between oxidation and reduction temperatures. In the case of 1000 °C the resulting material is Mn_2O_3 because re-oxidation took place in the cooling process, which was hold in air atmosphere.

The two highest temperature assays resulted in Mn_3O_4 though theoretically, for thermal treatments over 1050 °C, the substance present would be MnO. A possible explanation for the Mn_3O_4 presence is that this crystalline structure is energetically favoured, so there is a transformation from MnO into Mn_3O_4 during the cooling process as it is hold in an air atmosphere. The manganese does not react to form Mn_2O_3 because of the densification of the material and the reduction of its porosity as it is demonstrated in section 4.2.4.

Morphology study

In order to detect material morphology changes due to the performed thermal treatments SEM images of the samples surface and interior are taken with a *XL 30 ESEM Philips* microscope.

The first sample analysed was the pelletized manganese oxide of small diameter range in reception conditions, dried at 120 °C, which would be used as point zero for the comparison. In its micrograph shown in Figure 4.24 a non-homogeneous surface is shown. As it was observed in the power material (Figure 4.15), there is no clear geometry and the particles seem to be heterogeneous in form and in size.

Figure 4.24. SEM micrograph of Mn₃O₄LH pelletized material in reception conditions.

Figure 4.25 shows the morphology variation of the samples with the heat treatments, up to 800 °C there is no a clear structure definition, as is appreciable in Figure 4.25 (e). Figure 4.25 (f) shows a small coral-like structure. Micrographs of Figure 4.25 (g) and (h), show really big particles with some porous and grain separations due to the sintering process. This would explain the hardness results obtained and would be in agreement with the MnO formation hypothesis.

Several pellets of each thermal treatment sample were broken to analyse the pellet internal morphology. The corresponding micrographs are shown in Figure 4.26.

The morphology observed in the interior of the pellets agrees with the surface's one. The only remarkable difference is the presence of gaseous bubbles, presumably formed during the shaping process.

The same study was performed for the big diameter pellet material subjected to the thermal treatments. The results do not provide any new information, so the micrographs have been directly included in the ANNEX II Material characterization.

Figure 4.25. SEM micrographs of $\text{Mn}_3\text{O}_4\text{LH}$ pelletized material surfaces subjected to different temperatures thermal treatments: (a) 120 $^{\circ}\text{C}$, (b) 200 $^{\circ}\text{C}$, (c) 400 $^{\circ}\text{C}$, (d) 600 $^{\circ}\text{C}$, (e) 800 $^{\circ}\text{C}$, (f) 1000 $^{\circ}\text{C}$, (g) 1200 $^{\circ}\text{C}$ and, (h) 1400 $^{\circ}\text{C}$.

Figure 4.26. SEM micrographs of fragments of $\text{Mn}_3\text{O}_4\text{LH}$ pelletized material internal surfaces subjected to different temperatures thermal treatments: (a) 120 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C, (f) 1000 °C, (g) 1200 °C and, (h) 1400 °C.

Reactivity analysis for samples subjected to 1200 °C and 1400 °C heat treatments

According to the micrographs, the samples treated at 1200 °C and 1400 °C show great differences compared to those treated at other temperatures. According to the scientific literature, when manganese oxide is heated over 1050 °C it reacts to produce MnO [77], [80], [88]. Taking into account that XRD analysis identifies those samples as Mn_3O_4 , it is reasonable to assume that there has been a transformation to MnO, and a later re-oxidation to Mn_3O_4 . This re-oxidation would have taken place during the cooling process, which was held in ambient air. The reason is that Mn_3O_4 has a lower energetic structure compared to MnO. To support this theory, a reactivity analysis is performed for the samples heated at 1000 °C and over. Samples treated at 1200 °C and 1400 °C do not have any cycling capacity, as shown in Figure 4.27.

Figure 4.27. TG analyses for $\text{Mn}_3\text{O}_4/\text{LH}$ pelletized material of both diameters ranges subjected to different temperature thermal treatments: (a) [2, 3.6] mm at 1000 °C, (b) [3.6, 5] mm at 1000 °C, (c) [2, 3.6] mm at 1200 °C, (d) [3.6, 5] mm at 1200 °C, (e) [2, 3.6] mm at 1400 °C and, (f) [3.6, 5] mm at 1400 °C.

4.2.3. Cyclability as function of pellet diameter

The cyclability of the material is monitored by TGA using an *SDT Q-600* from *TA Instruments*. The weight change of the sample placed into a 90 mL alumina crucible is register for 15 thermal cycles between 1050 °C and 650 °C, without any isothermal plateau, with a heating/cooling ramp of 5 °C/min and a constant air flow of 100 mL/min. Prior to the heating ramps, a 30 minutes plateau at ambient temperature is conducted for homogenizing purposes.

The pellet diameters available for the study are 2 mm, 2.5 mm, 3 mm, 3.6 mm, 4 mm and 4.5 mm. The maximum sample diameter is defined by the alumina crucible dimensions, so 5 mm diameter pellets have to be discarded. The resulting TG weight variation curves are shown in Figure 4.28.

Figure 4.28. TG analysis for the Mn_3O_4LH pelletized material different diameter pellets (a) 2 mm, (b) 2.5 mm, (c) 3 mm, (d) 3.6 mm and (e) 4 mm and (f) 4.5 mm.

The absence of isothermal plateaus and the use of a slower heating ramp constitute a bad reaction scenario. These conditions are used with the purpose to stand out the diameter effect on the material reaction.

Figure 4.29. Weight change percent variation with the thermal cycles, for Mn_3O_4LH pelletized material with different diameter pellets.

Attending to Figure 4.29, there is not a clear trend of the weight change with the pellet diameters. Pellet diameters of 2 and 4 mm show the quickest reaction decay while 4.5 mm diameters would show the slowest reaction decay, the rest of the diameter are among the mentioned values.

4.2.4. Multi-cycle thermal treatments

From the pelletized material information obtained in above sections and considering reasonable compressed air consumptions for the later fluidization stage, the analysis will be done on the small range diameter pellets from now on.

In order to avoid entrainment in the reactor and pellet abrasion by particles collision among then and with the reactor wall, a thermal treatment is applied. The pellets are subjected to a curing-hardening step at 700 °C during three hours to increase their hardness. The calcination temperature results from a compromise between the hardness increase with temperature and the energy required for the treatment. Bearing in mind the amount of manganese oxide required for a hypothetical storage in a plant, this temperature had to be optimized.

A reactivity analysis is performed in order to check that the performance of the reaction is not affected by the calcination. The reactivity of the material is monitored by TGA using an *SDT Q-600* from *TA Instruments*. The weight change of the sample placed into a 90 mL alumina crucible is registered for seven thermal cycles between 1050 °C and 650 °C, with a heating/cooling ramp of 10 °C/min with a constant air flow of 100 mL/min. Prior to the heating ramps, a 30 minutes plateau at ambient temperature is conducted for homogenizing purposes. The results of this analysis are shown in Figure 4.30.

Figure 4.30. Reactivity study of pelletized Mn_3O_4LH [2, 3.6] mm calcined three hours at 700 °C.

Comparing to the reactivity analyses performed in section 4.2.1, it is noticeable how the presence of isothermal plateaus at maximum and minimum temperatures affects to the oxidation reaction performance.

To complete the material analysis, cyclic thermal treatments are applied to the 2 - 3.6 mm spherical pellets calcined at 700 °C. The samples are subjected to 10, 20, 30, 40 and 50 thermal cycles between 1000 °C and 500 °C in a furnace with a heating/cooling velocity of 10 °C/min and six hours plateau at each temperature. The resulting samples are named MnOx - 10 cycles, MnOx-20 cycles, MnOx-30 cycles, MnOx-40 cycles and MnOx-50 cycles respectively.

Hardness and density study

The evaluation of diameter, density and hardness is done by applying the same protocol explained in section 4.2.2. The results obtained are included in Table 4.7.

Table 4.7. Hardness and density results for the Mn_3O_4LH pelletized material cycled material.

Sample	Diameter (mm)	Density (kg/m ³)	Hardness (N)	Appearance
MnOx - 700°C	2.5 (±0.3)	2200 (±280)	33 (±9)	Uniform matte black
MnOx - 10 cycles	2.8 (±0.4)	2100 (±330)	75 (±13)	Uniform matte brown-red
MnOx - 20 cycles	2.4 (±0.4)	2100 (±300)	70 (±21)	Uniform matte brown-red
MnOx - 30 cycles	2.8 (±0.4)	2140 (±350)	70 (±12)	Uniform matte brown-red
MnOx - 40 cycles	2.6 (±0.4)	2300 (±340)	63 (±16)	Uniform matte brown-red
MnOx - 50 cycles	2.4 (±0.4)	2300 (±300)	63 (±14)	Uniform matte brown-red

Figure 4.31 shows a global constant tendency of the diameter with the number of thermal cycles. In view of the decreasing diameter trend obtained in the pelletized manganese oxide (Figure 4.20), together with the constant trend obtained for the density values shown in Figure 4.32, this new result indicates the deceleration of the sintering process. From Figure 4.31 it can be also pointed out that the samples subjected to 10 and 30 thermal cycles have a slightly bigger diameter value according to the global trend. Considering the associated error this deviation may not have physical meaning and it could be explained because slightly bigger particles were used in the measurement.

Figure 4.31. Diameter evolution for Mn_3O_4LH pelletized material with the multi-cycle thermal treatments.

Figure 4.32. Density evolution for Mn_3O_4LH pelletized material with the multi-cycle thermal treatments.

Figure 4.33 shows the hardness variation with the thermal cycles. There is an increment from the un-cycled to the cycled samples and, a slight decreasing tendency for longer cycling tests.

Figure 4.33. Hardness evolution for Mn_3O_4LH pelletized material with the multi-cycle thermal treatments.

X-Ray diffraction analyses

Crystalline phases are identified by powder XRD analyses for each sample after the heat treatment. Details of the experimental method are included in section 4.1.6. Two crystalline phases are identified in the subsequent analysis done with the commercial software *X'Pert Highscore Plus*; their information is included in Table 4.8.

Table 4.8. Crystalline phases found in x-ray diffraction analysis for Mn_3O_4 LH pelletized material in multi-cycle thermal treatment.

Chemical formula	Mineral name	Crystal system	Reference number
Mn_3O_4	Hausmannite	Tetragonal	98-010-0054
Mn_2O_3	Bixbyite C	Cubic	98-008-1762

Table 4.6 presents the results of the thermally cycled samples. Detailed information about diffractograms analyses is included in ANNEX II Material characterization.

Table 4.9. Chemical composition found in the heat treated samples of Mn_3O_4 LH pelletized material in multi-cycle thermal treatment.

	Diameter [2, 3.6] mm		
	Ratio	Mineral	Crystal system
700 °C	100 %	Mn_2O_3	Cubic
10 cycles	94 %	Mn_3O_4	Tetragonal
	6 %	Mn_2O_3	Cubic
20 cycles	98 %	Mn_3O_4	Tetragonal
	2 %	Mn_2O_3	Cubic
30 cycles	100 %	Mn_3O_4	Tetragonal
40 cycles	100 %	Mn_3O_4	Tetragonal
50 cycles	100 %	Mn_3O_4	Tetragonal

Morphology study

In order to detect material morphology changes due to the performed cyclic thermal treatments SEM images of the samples surface and interior are taken with a XL 30 ESEM Philips microscope.

First sample to be analysed is the optimized material: pelletized manganese oxide small diameter range calcined at 700 °C, which would be used as the zero-point for the comparison. In its micrograph shown in Figure 4.34 a non-homogeneous surface is shown, according to what is expected from Figure 4.25 (d) and (e) micrographs.

Figure 4.35 shows the morphology variation of the samples with the cyclic heat treatments, there is a coral-like structure that grows in size through the thermal cycles applied to the material. This growth seems to be faster for the first cycles, and slowly decreases with the number of thermal cycles applied, which is congruent with the results obtained in the diameter and density tendencies found.

Figure 4.34. SEM micrograph of the [2, 3.6] mm Mn₃O₄LH pelletized material calcined at 700 °C.

Figure 4.35. SEM micrographs of pelletized Mn₃O₄LH surfaces subjected to several multi-cycle thermal treatments: (a) MnOx 700°C, (b) MnOx-10 cycles, (c) MnOx-20 cycles, (d) MnOx-30 cycles, (e) MnOx-40 cycles and (f) MnOx-50 cycles.

Several pellets of each cyclic thermal treatment sample were broken to analyse the pellet internal morphology. Results are given in Figure 4.36.

The tendency in the internal structure of the material is the same shown for its surface. Except for the initial material micrograph, it can be concluded that the morphological variation of the material due to the thermal treatments is uniform through the pellet. Figure 4.36 (a) apart of showing the presence of a gaseous bubble, shows a different structure than Figure 4.35 (a). This is explained because the calcination process lasts for three hours instated of six and the temperatures achieved are smaller. It is relevant to point out the presence of what seem to be a cut of a pore, appreciable as a shadow in the right part of Figure 4.36 (e).

Figure 4.36. SEM micrographs of pelletized $\text{Mn}_3\text{O}_4\text{LH}$ material internal surfaces subjected to several multi-cycle thermal treatments: (a) MnOx 700°C, (b) MnOx -10 cycles, (c) MnOx -20 cycles, (d) MnOx -30 cycles, (e) MnOx -40 cycles and (f) MnOx -50 cycles.

Porosity evaluation

The porosity and its evolution with thermal treatments are studied by mercury intrusion porosimetry. The samples have been analysed at the “Centro Superior de Investigaciones Científicas” (CSIC). This study has been performed with an *AutoPore IV Series* from *Micromeritics* under the next analysis conditions: surface tension of 0.484 N/m, contact angle of 141° and maximum pressure of 4.08 atm. The results of the analysed samples are shown in Figure 4.37.

Figure 4.37. Mercury porosimetry for pelletized Mn_3O_4LH samples subjected from 0 to 40 thermal cycles.

The results show good agreement with the previous analyses, the biggest change occurs between the initial material and the 10 cycle sample. The median pore diameter increases from 270 to 2200 nm within the first cycles, while from 10 to 40 the increasing trend is much slower. The opposite behaviour is shown in the total pore area; there is an important reduction between the initial material and the 10 cycle sample, from 4.4 to 0.5 m²/g, and a light decreasing trend with the rest of the cycles.

Reactivity analysis

To conclude the section, the reactivity of the samples subjected to thermal cycles is studied by application of the reactivity protocol detailed in section 4.2.4. Due to the negative results obtained (see Figure 4.38) only the first two samples are analysed, assuming the cyclability of the material is lost.

Figure 4.38. Reactivity study for [2, 3.6] mm Mn_3O_4LH pelletized material subject to: (a) 10 thermal cycles and (b) 20 thermal cycles.

4.3. Manganese oxide – 5% iron

An approach to improve the cyclability performance of the commercial manganese oxide is based on doping this material with transition metals that substitute manganese atoms in the solid lattice. An analysis on various candidates was carried in the frame of the EU FP7 TCSPower project using various synthesis routes. A summary of main results can be found in the Alfonso Carrillo's PhD Thesis [127] and the associated publications [128], [129] and [86].

The analysis using the commercial manganese oxide $\text{Mn}_3\text{O}_4\text{LH}$ demonstrated that 5 mol % Fe doping was a good trade-off between cyclability and production cost. Indeed, iron is an excellent candidate due to its demonstrated redox behaviour, abundance, and low price. *Erachem Comilog S.A.* provided pseudo-spherical pellets made of manganese oxide, $\text{Mn}_3\text{O}_4\text{LH}$ grade, doped with 5 mol % of iron and mean diameter between 2 and 3.6 mm.

The addition of iron into the manganese oxide entailed certain degree of complexity in the shaping process. It modifies the powder characteristics and powder aggregation using water was not as satisfactory as with pure $\text{Mn}_3\text{O}_4\text{LH}$. Two batches of material are prepared with mean sphericity of 88 % and 80 % respectively. Pictures of both materials are shown in Figure 4.39.

The 88 % sphericity material at reception conditions had been calcined at 700 °C, so it was used for the cyclic thermal treatment study and for the analysis of reactivity in different particle sizes.

Part of the 80 % sphericity material received had been calcined at 120 °C and the rest at 700 °C. Best sphericity pellets are selected among the 80%-sphericity material calcined at 120 °C, the result of this preselection reaches a sphericity of 88 %. This selected sample is used for the hardness and density study.

Figure 4.39. Pelletized $\text{MnOx5\%Fe}$ material: (a) high-sphericity and (b) low-sphericity batches.

4.3.1. Material reactivity

The reactivity of the pelletized doped material is monitored by TGA using an *SDT Q-600* from *TA Instruments*. The experimental method performed is explained in section 4.2.4. Due to the sample change in composition the temperature range is defined between 1050 °C and 500 °C. Results are shown in Figure 4.40.

Figure 4.40. Reactivity study for MnOx5%Fe pelletized material in the size range [2, 3.6] mm.

The material presents a weight change above 3% and, comparing to Figure 4.19, it is clear that the oxidation reaction proceeds at higher temperatures and has better performances in this doped material, compared to the initial one.

4.3.2. Hardness and density

In order to know the doped material density and hardness changes with temperature treatments, their evolution is studied. For comparison purposes, the parameters and experimental method of this study are the same used for the manganese oxide material. They are described in detail in section 4.2.2.

The resulting data is included in Table 4.10 and graphically analysed next:

Table 4.10. Hardness and density for [2, 3.6] mm pellets of MnOx5%Fe.

Heat treatment T (°C)	Diameter (mm)	Density (kg/m ³)	Hardness (N)	Appearance
120	2.7 (±0.3)	1920 (±230)	11 (±4)	Uniform matte dark brown
200	2.6 (±0.4)	2100 (±350)	16 (±4)	Uniform matte brown-black
400	2.6 (±0.3)	2100 (±300)	17 (±4)	Uniform matte black
600	2.6 (±0.3)	2000 (±250)	17 (±5)	Uniform matte black
800	2.7 (±0.4)	2000 (±300)	17 (±9)	Uniform matte black
1000	2.3 (±0.4)	3100 (±500)	46 (±11)	Uniform matte black-grey
1200	2.0 (±0.3)	3800 (±550)	252 (±68)	Uniform shiny dark grey
1400	2.0 (±0.3)	3400 (±450)	211 (±53)	Uniform shiny dark grey

Figure 4.41 shows the mean pellet diameter as a function of the plateau temperature in the heat treatment. The diameter seems to be constant from 200 to 800 °C and then decreases when the temperature rises up. Figure 4.42 shows how the density tendency is to remain stable from 120 °C to 800 °C and to increase for temperature treatments higher than 800 °C.

The results of the pellets hardness study are shown in Figure 4.43. There is an important increase observed in the hardness of the samples thermally treated at 1200 °C and 1400 °C, it hinders the study of the hardness tendency obtained for lower temperature treatments.

Figure 4.41. Diameter evolution of MnOx5%Fe pellets with the thermal treatments.

Figure 4.42. Density evolution of MnOx5%Fe pellets with the thermal treatments.

Figure 4.43. Hardness evolution of MnOx5%Fe pellets with the thermal treatments.

Figure 4.44 shows the hardness test results excluding the aforementioned data. There is a small increase of this property with the first heating treatment at 200 °C, from that

temperature up to 800 °C the hardness remains more or less constant and sharply increases with the 1000 °C heat treatment.

Figure 4.44. Hardness evolution of MnOx5%Fe pellets with the thermal treatments from 120 °C to 1000 °C.

Considering the variation in diameter, density and hardness, it seems that a reduction on diameter due to the thermal treatments is directly related with a slight increase in density and important increases in hardness of the pellets.

Compared to the original manganese oxide, the inclusion of iron atoms in the crystalline structure of the manganese oxide causes a decrease in density and hardness of the particles. This was the expected behaviour and it is easily explained by the distortion in the crystalline structure caused by the introduction of iron in the original material.

X-Ray diffraction analyses

Crystalline phases are identified by powder XRD analyses for each sample after the heat treatment. The analyses are carried out employing the experimental method described in section 4.1.6. The crystalline phases identified, are listed in Table 4.11.

Table 4.11. Crystalline phases found in X-ray diffraction analysis.

Chemical formula	Mineral name	Crystal system	Reference number
Mn ₃ O ₄	Hausmannite	Tetragonal	98-002-8708
Mn ₃ O ₄	Hausmannite	Tetragonal	98-008-9971
MnO ₂	Pyrolusite	Tetragonal	98-003-5156
Fe _{0.84} Mn _{1.16} O ₃	Bixbyite	Cubic	98-010-6539
Fe _{1.26} Mn _{0.74} O ₃	Manganese(III) Iron(III) Oxide (0.7/1.3/3)	Cubic	98-000-2391
Fe _{0.03} Mn _{2.97} O ₄	Hausmannite, ferric	Tetragonal	98-006-1837

Table 4.12 presents the percentage of each crystalline phase identified in each of the heat thermally treated samples. Detailed information about diffractograms analyses is included in ANNEX II Material characterization.

Even though the manganese oxide is doped with five percent of iron, the X-ray diffractograms analyses for temperatures lower than 600 °C, identify tetragonal structures without iron in the chemical composition. In any case, there is distortion in the diffractogram and, comparing to the crystalline structures found in the un-doped material, the only change is the distance among the atoms in the tetragonal structures. This indicates that the iron is very well located into the crystalline lattice.

When the thermal treatment temperature value is between 600 °C and 1000 °C, the material changes into a cubic structure where iron is identified.

At the highest temperatures, 1200 °C and 1400 °C, the identified structure is tetragonal, which would indicate a lack of reactivity. The identification of iron in the highest temperature treatment would point to a segregation or migration of the iron with temperature.

This theory is also supported in the case of the cubic structures obtained, where the iron is identified and its content in the crystalline phases increases with temperature treatments.

Table 4.12. Chemical composition found in the heat treated samples of MnOx5%Fe pellets.

Temperature	Diameter [2, 3.6] mm			
	Ratio	Chemical formula	Crystal system	Reference number
120 °C	85 %	Mn ₃ O ₄	Tetragonal	98-002-8708
	15 %	Mn ₃ O ₄	Tetragonal	98-008-9971
200 °C	88 %	Mn ₃ O ₄	Tetragonal	98-002-8708
	12 %	MnO ₂	Tetragonal	98-003-5156
400 °C	89 %	Mn ₃ O ₄	Tetragonal	98-002-8708
	11 %	MnO ₂	Tetragonal	98-003-5156
600 °C	100 %	Fe _{0.84} Mn _{1.16} O ₃	Cubic	98-010-6539
800 °C	100 %	Fe _{0.84} Mn _{1.16} O ₃	Cubic	98-010-6539
1000 °C	100 %	Fe _{1.26} Mn _{0.74} O ₃	Cubic	98-000-2391
1200 °C	57 %	Mn ₃ O ₄	Tetragonal	98-002-8708
	43 %	Mn ₃ O ₄	Tetragonal	98-008-9971
1400 °C	69 %	Mn ₃ O ₄	Tetragonal	98-002-8708
	31 %	Fe _{0.03} Mn _{2.97} O ₄	Tetragonal	98-006-1837

Morphology study

In order to detect material morphology changes after being subjected to thermal treatments SEM images of the samples surface and interior are taken with a XL 30 ESEM Philips microscope.

First sample to be analysed is the pelletized doped manganese oxide in reception conditions, dried at 120 °C, which would be used as the zero-point for the comparison. In its micrograph shown in Figure 4.45 a non-homogeneous surface appears. There is no clear geometry and the particles seem to be heterogeneous in form and in size.

Figure 4.45. SEM micrograph of MnOx5%Fe - 120 °C pellet on the surface in reception conditions.

Figure 4.46 shows the morphology variation of the samples with the heat treatments. Up to 800 °C there is no a clear structure definition, as is appreciable in Figure 4.46 (e). Figure 4.46 (f) shows a coral-like structure and micrographs shown in Figure 4.46 (g) and (h), display really big particles, some porous and grain separations due to sintering process. This would explain the hardness results obtained.

Figure 4.46. SEM micrographs of MnOx5%Fe pellets surfaces subjected to different temperatures thermal treatments: (a) 120 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C, (f) 1000 °C, (g) 1200 °C and, (h) 1400 °C.

Comparing to the same study performed for manganese oxide without iron (see Figure 4.25), the global tendency is similar, but the size of the particles, particularly in the two last micrographs is much bigger for the doped manganese oxide than for the original one.

Several pellets of each thermal treatment sample were broken to analyse the pellet internal morphology. The results are presented in Figure 4.47. The general morphology observed in the interior of the pellets agrees with that observed for the surface. Nevertheless, the presence of pores should be pointed out.

Figure 4.47. SEM micrographs of MnOx5%Fe pellets internal surfaces subjected to different temperatures thermal treatments: (a) 120 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C, (f) 1000 °C, (g) 1200 °C and, (h) 1400 °C.

4.3.3. Cyclability as function of pellet diameter

The cyclability of the material is monitored by TGA using an *SDT Q-600* from *TA Instruments*. The experiment consists in performing 25 thermal cycles following the experimental methodology already described in section 4.2.3.

The pellet diameters available for the study are 1 mm, 1.5 mm, 2 mm, 2.5 mm, 3 mm and 3.5 mm. The material retained its cyclability for the whole experiment independently of the pellet diameter. The TGA results have been included in ANNEX II Material characterization.

4.3.4. Multi-cycle thermal treatment

In the hardness and density study, it was shown how the doped manganese oxide hardness remains constant from 200 °C to 800 °C, nevertheless, in order to keep similarity with the study of the original manganese oxide, the doped material is subjected to the same calcine step at 700 °C during three hours.

A reactivity analysis, whose experimental details are included in section 4.2.4, is performed in order to check that the performance of the reaction is not affected by the calcination. This fact is confirmed from the results contained in in Figure 4.48.

Figure 4.48. Reactivity study for [2, 3.6] mm MnOx5%Fe pellets calcined at 700 °C for three hours.

To complete the material analysis, multi-cycle thermal treatments has been applied to the 2-3.6 mm spherical pellets calcined at 700 °C. The experimental methodology was described in section 4.2.4. The resulting samples are named MnOxFe-10 cycles, MnOxFe-20 cycles, MnOxFe-30 cycles, MnOxFe-40 cycles and MnOxFe-50 cycles respectively.

Hardness and density study

The evaluation of diameter, density and hardness is done by applying the same protocol explained in section 4.3.2. The results obtained are included in Table 4.13.

Table 4.13. Hardness and density results for the MnOx5%Fe cycled pellets.

Sample	Diameter (mm)	Density (kg/m ³)	Hardness (N)	Appearance
MnO _x Fe - 700 °C	2.9 (±0.3)	2500 (±300)	51 (±15)	Uniform matte black
MnO _x Fe - 10cycles	3.3 (±0.4)	1800 (±250)	34 (±8)	Uniform shiny black -grey
MnO _x Fe - 20cycles	3.2 (±0.4)	1800 (±200)	26 (±7)	Uniform shiny black -grey
MnO _x Fe - 30cycles	3.4 (±0.4)	1550 (±190)	16 (±3)	Uniform shiny black -grey
MnO _x Fe - 40cycles	3.1 (±0.4)	1700 (±220)	11 (±2)	Uniform matte black -grey
MnO _x Fe - 50cycles	3.3 (±0.5)	1500 (±320)	9 (±2)	Uniform matte black -grey

Figure 4.49 shows that the diameter is more or less constant for the cycled doped material, as it happened in the pelletized manganese oxide (See Figure 4.31). By the contrary, if the density

in the pelletized manganese oxide showed an increasing trend with thermal treatments (See Figure 4.32), in Figure 4.50, the cycled doped material shows an opposite trend.

Figure 4.49. Diameter evolution of the MnOx5%Fe pellets with the cyclic thermal treatments.

Figure 4.50. Density evolution of the MnOx5%Fe pellets with the cyclic thermal treatments.

Figure 4.51. Hardness evolution of the MnOx5%Fe pellets with the cyclic thermal treatments.

Figure 4.51 shows an important decrease of the hardness with the number of thermal cycles to which the material has been subjected. It is worth to mention here that the reason why the hardness of the initial sample treated at 700 °C is above the average hardness found in the hardness and density study is because the assay has been performed on materials obtained through different pelletization processes.

X-Ray diffraction analyses

Crystalline phases are identified by powder XRD analyses for each sample after the heat treatment. The analyses are carried out employing the experimental method described in section 4.1.6. The crystalline phases identified are listed in Table 4.14.

Table 4.14. Crystalline phases proposed from XRD analysis.

Chemical formula	Mineral name	Crystal system	Reference number
$\text{Fe}_{0.84}\text{Mn}_{1.16}\text{O}_3$	Bixbyite	Cubic	98-010-6539
Mn_3O_4	Hausmannite	Tetragonal	98-002-8708
$\text{Fe}_{1.26}\text{Mn}_{0.74}\text{O}_3$	Manganese(III) Iron(III) Oxide (0.7/1.3/3)	Cubic	98-000-2391
Mn_3O_4	Hausmannite	Tetragonal	98-001-7918

Table 4.15 presents the percentage of each crystalline phase identified in each of the heat treated samples. Detailed information about diffractograms analyses is included in ANNEX II Material characterization. As observed in the X-ray analyses performed in the hardness and density study, the iron is identified in the cubic structures but not in the tetragonal ones, where some distortion is found.

Table 4.15. Chemical composition in cycled of the MnOx5%Fe pellets from XRD analysis.

Diameter [2, 3.6] mm				
	Ratio	Mineral	Crystal system	Reference number
700 °C	100 %	$\text{Fe}_{0.84}\text{Mn}_{1.16}\text{O}_3$	Cubic	98-010-6539
10 cycles	83 %	$\text{Fe}_{0.84}\text{Mn}_{1.16}\text{O}_3$	Cubic	98-010-6539
	17 %	Mn_3O_4	Tetragonal	98-002-8708
20 cycles	96 %	$\text{Fe}_{1.26}\text{Mn}_{0.74}\text{O}_3$	Cubic	98-000-2391
	4 %	Mn_3O_4	Tetragonal	98-001-7918
30 cycles	93 %	$\text{Fe}_{0.84}\text{Mn}_{1.16}\text{O}_3$	Cubic	98-010-6539
	7 %	Mn_3O_4	Tetragonal	98-001-7918
40 cycles	87 %	$\text{Fe}_{0.84}\text{Mn}_{1.16}\text{O}_3$	Cubic	98-010-6539
	13 %	Mn_3O_4	Tetragonal	98-002-8708
50 cycles	85 %	$\text{Fe}_{0.84}\text{Mn}_{1.16}\text{O}_3$	Cubic	98-010-6539
	15 %	Mn_3O_4	Tetragonal	98-002-8708

Morphology study

In order to detect material morphology changes due to the performed cycling thermal treatments SEM images of the samples surface and interior are taken with a XL 30 ESEM Philips microscope.

First sample to be analysed is the pelletized doped manganese oxide calcined at 700 °C, which would be used as point zero for the comparison. In its micrograph shown in Figure 4.52 a non-homogeneous surface is shown, according to the expected from Figure 4.46 (d) and (e) micrographs.

Figure 4.52. SEM micrograph of the [2, 3.6] mm of the MnOx5%Fe pellets calcined at 700 °C.

Figure 4.53 shows the morphology variation of the samples with the cyclic heat treatments. There is grain formation and an increase in size of these grains for the twenty first cycles. After that, the coral-like structure appears and the pores among the grains grow with the remaining thermal cycles applied to the material. Compared to the manganese oxide material, the pores found in the doped material are much bigger. This growth would explain the hardness decreasing observed in the present study.

Figure 4.53. SEM micrographs of the MnOx5%Fe pellets surfaces subjected to several cyclic thermal treatments: (a) MnOxFe 700°C, (b) MnOxFe-10 cycles, (c) MnOxFe-20 cycles, (d) MnOxFe-30 cycles, (e) MnOxFe-40 cycles and (f) MnOxFe-50 cycles.

Figure 4.54. SEM micrographs of the MnOx5%Fe pellets internal surfaces subjected to several cycling thermal treatments: (a) MnOxFe 700°C, (b) MnOxFe-10 cycles, (c) MnOxFe-20 cycles, (d) MnOxFe-30 cycles, (e) MnOxFe-40 cycles and (f) MnOxFe-50 cycles.

The tendency in the internal structure of the material for the 10 and 20 cycles is clearly different to that of the external one. This points to a superficial behaviour which disappears for longer cycled samples, where the same coralline structure is shown in its interior and exterior. Detailed images of the superficial behaviour are given in Figure 4.55.

Figure 4.55. SEM micrographs of the MnOx5%Fe pellets internal surfaces at the limit of the pellet: (a) MnOxFe-10 cycles 1.0k magnifications, (b) MnOxFe-10 cycles 3.0k magnifications, (c) MnOxFe-20 cycles 1.0k magnifications, (d) MnOxFe-20 cycles 3.0k magnifications (e) MnOxFe-30 cycles 1.0k magnifications and, (f) MnOxFe-30 cycles 3.0k magnifications.

From micrograph Figure 4.55 (a) to (f), the evolution of the superficial layer is observed. In the 10-cycles micrographs a thin and continuous layer is observed. For the 20-cycles material, the layer gets thicker and some holes start appearing in its interior. In the 30-cycles images, the layer has lost its uniformity, starting the change to the coral-like structure found afterwards.

Porosity evaluation

The porosity and its evolution with thermal treatments are studied by mercury intrusion porosimetry. The samples have been analysed at CSIC. The experimental methodology applied is described in section 4.2.4. The results of the analysed samples are shown in Figure 4.56.

Figure 4.56. Mercury porosimetry results for MnOx5%Fe pellets samples subjected from 0 to 40 thermal cycles.

The total pore area rapidly decreases during the first ten cycles from 5.3 to 0.3 m²/g and then keeps a light decreasing trend with the rest of the cycles. That behaviour is similar to the one observed for Mn₃O₄LH, with slightly higher numbers (see Figure 4.37). The great difference is found in the median pore diameter evolution; instead of shown an increment within the first ten cycles and an established tendency after, it keeps an increasing tendency with the number of cycles. Also, comparing to the result obtained for Mn₃O₄LH, see Figure 4.37, the median pore diameter get to values that double those obtained for plain manganese oxide.

The results are in good agreement with previous analyses, and explained the reduction in hardness of the pellets with thermal treatments and the pores observed in the morphology study.

Reactivity analysis

To conclude this section, the reactivity of the samples subjected to thermal cycles is studied by application of the reactivity protocol detailed in section 4.2.4. From Figure 4.57, it can be concluded that the reactivity of the material, in terms of reaction speed, is much better than the obtained for plain manganese oxide. Even though, from 30 cycle experiment on the weight variation suffers a step decrease, as can be seeing in Figure 4.57 (c), (d) and (e). The oxidation reaction takes longer time with increasing number of thermal treatments, which is the reason why the decay in reactivity seems to occur by steps being constant at a lower value. The time at the reaction temperature is not long enough to allow the reaction of the material to complete. This explanation is confirmed by a last thermogravimetric assay, shown in Figure 4.57 (f), in which one hour plateau is hold at maximum temperature and two hours plateau is hold for the minimum temperature, giving rise to the cycling reaction is completed.

Figure 4.57. Reactivity study for MnOx5%Fe pellets subject to: (a) 10 thermal cycles, (b) 20 thermal cycles, (c) 30 thermal cycles, (d) 40 thermal cycles, (e) 50 thermal cycles and, (f) 50 thermal cycles with isothermal plateaus.

4.4. Summary and conclusions

Manganese oxide – powder material

Cyclability of the manganese oxide powder material has been demonstrated for fifty cycles by TGA. Besides, the thermal diffusivity and its relation with temperature have been obtained. A heating ramp study has been performed that has concluded into recommend heating/cooling ramps over 4 °C/min.

The kinetics of the oxidation reaction and the effective reaction time have been studied in air and in pure oxygen atmospheres. The apparent kinetic mechanism for the oxidation reaction in both cases is an Avrami-Erofeev mechanism.

Also the morphology evolution of the material within ten thermal cycles has been analysed. The formation of coral-like structure has been identified: the material suffers a sintering process with fast neck formation and growth for the five first cycles.

The velocity of the oxidation reaction decreases for the first few cycles until it reaches a constant value, much slower than the reduction reaction velocity.

Manganese oxide – pelletized material

In order to get reasonable pressure drops through the reactor the powder material was shaped in spherical pellets. Hardness, density and diameter evolution with thermal treatments have been studied for pellet mechanical optimization purposes in increasing temperatures from 120 °C up to 1400 °C.

The diameter evolution with the thermal cycles shows a light decreasing tendency, related to the sintering process. The density of the pellets remains constant up to 1000 °C and increases for higher temperature heat treatments. The hardness measured is bigger for the larger diameter pellets. There is an increase in hardness with increasing temperature thermal treatments up to 1000 °C and, for 1200 and 1400 °C thermal treatments, the hardness sharply increases. The presence of the metastable Mn_5O_8 found by XRD in the samples treated at 400 °C is noteworthy. As it is the results for the samples treated at 1200 and 1400 °C, which marks a clear limit for the upper reaction temperature range.

Morphological study of the ten-cycle assay showed how the structure variations affect to the whole particle without difference between surfaces or pellet inside areas.

A long-term cycling-thermal assay was also performed over the [2, 3.6] mm diameter pellets calcined at 700 °C for three hours. The global constant tendency of the diameter and density values with the thermal cycles indicates the deceleration of the sintering process. The morphology study performed shows that the structure variation with thermal cycles is uniform through the pellet. The porosity evaluation of samples shows a big change occurring between the initial material and the 10 cycle sample while from ten to forty the increasing trend is much slower. These porosity trends could explain the loss of reactivity of the samples.

Manganese oxide – 5% iron

A way to improve the manganese oxide cyclability is to dope the material with iron. By doing so, a shift towards higher reduction reaction temperatures was found.

Hardness, density and diameter evolution with thermal treatments have been studied for the doped material by increasing temperatures from 120 °C up to 1400 °C in pellet size range [2, 3.6] mm.

In view of the variation in diameter, density and hardness, it seems that a reduction on diameter due to the thermal treatments is directly related with a slight increase in density and important increases in hardness of the pellets.

Compared to the original manganese oxide, the inclusion of iron atoms in the crystalline structure of the manganese oxide has caused a decrease in density and hardness of the particles.

Even though the manganese oxide is doped with five percent of iron, the X-ray diffraction analyses for temperatures lower than 600 °C identify tetragonal structures without iron in the chemical composition. For thermal treatment temperatures between 600 °C and 1000 °C, the

material changes into a cubic structure where iron is identified. In the highest temperatures, 1200 °C and 1400 °C, the identified structure is tetragonal, without identification of iron. As in the case of un-doped material, it indicates a lack of reactivity of the samples thermally treated at the highest temperature.

The morphological study shows a coral-like structure for the sample heated at 800 °C, similar to the structure variation found in the un-doped material but with bigger particle sizes. The morphology evolution of the material was uniform along the pellet, but unlike the un-doped material, in the interior of the doped manganese oxide, the existence of porosity is perceptible.

The cyclability as function of the pellet diameter study showed that the pellets retain its reactivity for twenty-five cycles.

The long-term cycling-thermal assay for the doped material is performed over the [2, 3.6] mm diameter pellets calcined at 700 °C for three hours.

The XRD study shows a mixture of cubic and tetragonal structures with an eight to one proportion.

The morphology study shows a superficial phenomenon: the ten-cycle sample, has a thin homogeneous surface layer which grows and decompose in the twenty and thirty cycles sample, leading to a homogeneous material without difference between inside and outside surfaces and with a noteworthy porosity.

The porosity evaluation shows a big reduction in the total pore area occurring between the initial material and the ten cycle sample, with a posterior light decreasing trend for the rest of the cycles.

The reactivity analysis performed for the samples show that the samples retain their cycling capability but it also shows a deceleration of the oxidation reaction.

Conclusions

Great differences between manganese oxide and manganese oxide doped material have been found. Manganese oxide has good mechanical qualities to face abrasion and collision involved in fluidization experiments performed in the reactor. On the other hand, the cyclability of the un-doped manganese oxide is lost in less than 15 cycles. By the contrary, it has been demonstrated that the cyclability of the doped manganese oxide last longer, whereas it has worse mechanical properties.

The cyclability of both materials has been found to be close related to the size of the pore diameter: being inversely proportional in the case of the manganese oxide.

Both materials suffer a sintering process with thermal treatments and both present the growth of a coral-like structure. This morphology is stronger in the case of the doped manganese oxide, which also presents a superficial morphology phenomenon that do not affect to its cyclability.

For both materials a deceleration has been found in the velocity of the oxidation reaction. In the case of the manganese oxide this implies the loss of cyclability whereas in the case of the doped manganese oxide, it just means longer reaction times.

CHAPTER V

5. EXPERIMENTAL TESTS IN THE REACTOR

This Chapter presents the results gathered from the experimental tests performed in the reactor. First, the reactor is characterized by using inert materials consisting in alumina pellets. Second, pure and doped manganese oxide pellets are tested in fixed and fluidized bed conditions. Last, to complete the gathered information, the effect of the testing in the manganese material is analysed and measured in comparison to the base investigation performed in Chapter IV.

As mentioned in Chapter III, section 3.1.4, the reactor was designed to test thermochemical storage materials in fixed and/or fluidized bed conditions for temperatures between ambient and 1100 °C and pressures in the range of ambient up to 10 bar. The evolution of the experiments is monitored by measuring temperatures at different points, pressure drop through the particles bed and gas composition of the exhausting gases.

Even with an optimized test material, attrition would take place into the reactor due to the contact among pellets and between pellets and wall. Therefore a gentle solid handling is necessary to avoid dust formation in the reactor's charging and discharging processes. A completed working procedure has been developed. A detailed description of materials loading into the reactor and collection with a vacuum system after the trials, is included in ANNEX III Test in the reactor: working procedures, together with the maintenance protocols.

The test rig is operated as a batch where maximum gas velocities are restricted to an upper limit depending on pellets properties and size to avoid material entrainment.

5.1. Inert material assays

First test aimed at characterising the reactor performance in terms of heat and mass transfer using ideal inert material, so that phenomena related to chemical and geometrical characteristics of the pellets could be identified in the assays using metal oxides. Experiments were performed using grade alumina spheres Al_2O_3 99,5% from *Redhill Precision*. This material has a precision grade of G10; according to ISO3290 they have a mono-modal size distribution centred on 1.5 mm with an allowable diameter variation of 5 μm and an allowable deviation from spherical form of 0.5 μm . The reactor was filled with 4.263 kg, which corresponds to an effective volume of 2 L. Considering the density of 3860 kg/m^3 , the bed would have a porosity of 0.45.

Fluidization behaviour of the alumina is studied by measuring the bed pressure drop for different air flow rates at five constant temperatures. Thermal behaviour was studied by subjecting alumina pellets to ten thermal cycles between 1100 °C and 650 °C with a thermal heating/cooling rate of 5 °C/min.

5.1.1. Fluidization test on alumina pellets

Once the pellets were placed in the reactor, the air flow rate crossing the bed was set to the maximum value, 60 Nm^3/h , and a temperature setpoint was defined for each experiment. Ambient temperature, 250 °C, 500 °C, 750 °C and 1000 °C were considered. As mentioned above, the heating process was done at constant heating rate of 5 °C/min. Once the set point

temperature is reached, the system is ready for the experiment. Then, the pressure drop is measured for decreasing air flow rates in steps of 5 Nm³/h at the constant inlet air temperature defined.

The pressure drop variation with the air flow rate for the different temperatures is shown in Figure 5.1 (a). Considering the reactor geometry and the variation of the air properties with the temperature, the pressure drop variation is plotted also versus air velocity in Figure 5.1 (b). It is theoretically expected that the curves in this figure are superposed. Nevertheless, the represented values are mean values of the pressure drop for each air flow rate step, which would explain the little variation among the lines.

Figure 5.1. Pressure drop for alumina balls (a) vs. air flow rate and, (b) vs. air velocity at different temperatures.

Plots in Figure 5.4 make it possible to identify the desirable fluidization conditions with the tested material. Operation with air flow rates between 0 and 30 Nm³/h will ensure a fixed bed for every inlet air temperatures. A fluidised bed is achieved using air flow rates higher than 50 Nm³/h and temperatures higher than 1000 °C.

The theoretical fluidization values for the alumina pellets are included in Table 5.1. These values are obtained by applying the same equations and code used in CHAPTER I which are included in ANNEX I Experimental test rig: design and constructive details.

Table 5.1. Calculated minimum fluidization conditions for alumina balls of 1.5 mm in diameter.

Temperature (°C)	Fluidization velocity (m/s)	Fluidization air flow rate (Nm ³ /h)
Amb. T	1.35	74.8
250	1.54	48.6
500	1.58	33.9
750	1.56	25.2
1000	1.51	19.5

The theoretical calculations predict that the fluidization would take place in experiments conducted at 500 °C and higher temperatures. Whereas the experimental measurements indicate that fluidization is not achieved at 500 °C but at 750 °C and 1000 °C.

The experimental values are double of the theoretical ones. Even though there is a big difference, it has to be considered that the assumed average error for this type of calculations is higher than 30 %.

The difference obtained between the experimental and theoretical fluidization velocities for this ideal material, justifies the safety design decisions made in the reactor and workbench project development. Also this difference makes it necessary to repeat the assay for every material to be tested in the reactor.

5.1.2. Thermal cycles on alumina balls in semi-fluidization conditions

The alumina does not show properties variation with the thermal treatments, so the same amount and volume of 1.5 mm diameter alumina pellets are consider for the present ten thermal cycles assay.

According to the study presented in the previous section, an air flow rate of 45 Nm³/h is settled to obtain semi-fluidization conditions.

In order to keep similarity with the requirements for manganese oxide experiments, the thermal conditions selected for the present test were the following: maximum and minimum temperatures were 1100 °C and 650 °C, respectively, thermal heating/cooling rate of 5 °C/min and an initial 30 min isotherm stage at ambient temperature.

Figure 5.2 shows the evolution of temperatures at the inlet -below the gas distributor-, middle and outlet of the reactor - both above the pellets bed (See Figure 3.5 points 1, 6 and 14 respectively). Those three measurements are done with K-type thermocouples in direct contact with the air flow. The temperature setpoint programmed for the air at the inlet has also been included. As shown in the figure, there are one hour long isotherms at 1100 °C and 650 °C. In the third cycle at the highest temperature, there is a safety shut down of the air heating system, which is short enough and does not disturb the experiment.

It can be noticed how the air gets colder once it has crossed the alumina bed - with a temperature step of about 200 °C - and even colder when it reaches the exit of the reactor - with another approx. 200 °C step. Nevertheless, in every cycle the same temperature is reached at the different measurement points. It is also noticeable the crossing of the inlet and central midway temperature lines in the cooling down process being an indicator of a little sensible heat storage.

Figure 5.2. Reactor temperatures in the 10 cycles assay using alumina balls.

Figure 5.3 shows the air temperature at the entrance of the reactor versus its temperature after the alumina bed. A common pattern that repeats for all cycles is usually observed except for the first and second cycles due to the reactor heating and third cycle (indicated by a red line) related to the safety shut down of the workbench. There are two irregular zones in every cycle, one in the heating up process at around 800 °C and the second one, in the cooling process between 700 °C and 650 °C.

Figure 5.3. Reactor central vs. inlet temperatures during 10-cycles assay using alumina balls.

To gather a better understanding, the tenth cycle is analysed in detail. Figure 5.4 show the tenth cycle with four areas which have been identified for the analysis. The heating cycle starts at the point named “0” to the right, the inlet temperature increases from 650 °C up to 1100 °C going through zone 1 up to zone 2, where the highest temperature in the cycle is reached. In 2 there is a small overheating and then the inlet temperature is stabilized. The cooling process starts after zone 2 to the right, going through zone 3 and zone 4, where the isotherm at 650 °C is maintain also with a small overcooling.

Figure 5.4. Detail of the reactor central vs. inlet temperatures during the 10th cycle using alumina balls.

Zones 1 and 3 are not related to any fluctuation in the air flow rate during the assay and they are explained by the transition between fixed and fluidized beds, as shown below.

Figure 5.5 shows the reactor inlet - real and set point -, and central temperatures and the air flow rate as a function of time. The figure includes the marks used to define the zones 1-4. Mean air flow rate is almost constant in agreement with the setpoint and discards a variation in the air flow rate as possible explanation of the observed irregularities.

Figure 5.5. Air temperatures in the reactor and air gas flow rate during the 10th cycle using alumina balls.

Figure 5.6 shows the same temperature points evolution as well as the pressure drop through the bed. There are two pressure drop jumps corresponding to zones 1 and 3. In zone 1, pressure drop increases and suddenly drops; it is considered that the air velocity increases due to the diminution of its density during the heating stage. In zone 1, air reaches the minimum fluidisation velocity for the inlet temperature and fluidisation starts causing a diminution in the pressure drop. The continuous variation observed for the pressure drop between zone 1 and 3, is due to the increase/decrease of the volume of the air with increasing/decreasing temperature.

Figure 5.6. Air temperatures and pressure drop in the reactor during the 10th cycle using alumina balls.

In zone 3, due to the temperature drop, the velocity of the air decreases below the minimum fluidization velocity causing the bed to change from fluidization conditions to fixed bed with explains the sudden increase in pressure drop.

As seen in Figure 5.6, any temperature increment will promote the fluidisation regime, which explains that the temperature variation in Figure 5.3 and Figure 5.4 are due to the fluidization (zone 1) and de-fluidization (zone 3) of the pellets in the bed.

Figure 5.7 shows the temperature and the pressure drop during the 10-cycles assay. As expected, the transition between fluidisation and fixed bed occurs twice per cycle.

Figure 5.7. Air temperatures and pressure drop in the reactor during the 10-cycles assay using alumina balls.

Finally, Figure 5.8 illustrates the progress of the oxygen concentration in the gaseous flow stream at the reactor exit during the test. Filtered oxygen concentration signal, denoted as oxygen concentration MM50 and represented in dark blue, remains constant as expected, because alumina is an inert material and no oxygen is added or removed from the air flow.

Figure 5.8. Oxygen concentration during the 10-cycles assay using alumina balls.

The two different lines observed in Figure 5.8 (b) are due to the apparatus sensibility.

5.2. Reactive material tests in the reactor

Once the features of the heat transfer process related to non-chemical effects in the reactor have been established, a new analysis was performed incorporating heat and mass transfer

due to redox reactions. Tested material consisted in $\text{Mn}_3\text{O}_4\text{LH}$ pellets with a size distribution comprised between 2 - 3.6 mm in diameter calcined at 700 °C.

First step is to identify air flow rates required for operating as fixed or fluidized bed. This is done as a function of the inlet air temperature through the fluidization test. Second step would be to perform the material tests consisting in 25 consecutive thermal cycles under fixed or fluidized bed conditions.

The tests are performed for both, pure and doped, manganese oxide materials. Even though the reactivity of the pure manganese oxide has shown to shrink in few cycles, the tests will allow the assessing of the material behaviour in different experimental conditions as well as the reactor performance.

5.2.1. Manganese oxide fluidization test

The reactor is uploaded with 2.16 L of manganese oxide, which corresponds to 2.812 kg of material. The temperatures set for the assay are related to the manganese oxide temperature reaction range, 650 °C and 1000 °C. The results are shown in Figure 5.9.

Figure 5.9. Pressure drop for $\text{Mn}_3\text{O}_4\text{LH}$ pellets vs. (a) air flow rate and (b) air velocity.

Initially, the pressure drop increases with increasing air flow rates through the pellets bed. Then, there is a change in the slope of both curves which indicates the change of bed fluidization conditions at 25 Nm^3/h for 1000 °C and about 40 Nm^3/h at 650 °C. The pressure drop evolution after the fluidization point does not remain constants as it could be theoretically expected.

This increase of pressure drop after fluidization is related to the evolution of the material characteristics: the particles diameter decreases, there is sintering phenomena and the density of the particles increases. Because of reactive material restrictions, the material used in the present assay had been prior subjected to a total of 6 thermal cycles, one cycle between 650 °C and 1000 °C, and five cycles between 650 °C and 1050 °C. In order to minimize the effect of the material characteristics variations, fresh material would be used for the remaining assays performed.

Compared to the fluidization test on alumina pellets, the air flow needed to reach fluidization in a manganese oxide bed is smaller, as expected because the difference on density of the materials.

5.2.2. Manganese oxide thermal cycles test in a fixed bed

The optimized material from *Erachem Comilog* consists of manganese oxide pellets with an initial diameter in the range of 2-3.6 mm. This material has been calcined at 700 °C for three hours to improve its mechanical strength. A total volume of 2.4 L of fresh material, which corresponds to 3.190 kg, is placed in the reactor cavity.

The material is subjected to 25 thermal cycles between 1100 °C and 650 °C with a heating ramp of 5 °C/min and one hour and 30 minutes plateau at the end of each ramp. At the beginning of the experiment, a 30 minutes plateau at ambient temperature is programmed to homogenize the system. According to the data shown in Figure 5.9, the air flow rate is set to 20 Nm³/h to guarantee fixed bed conditions for the experiment.

Reactor experiment analysis

The temperature evolution at the entrance, central part and exit of the air path through the reactor is shown in Figure 5.10. It has also been included the setpoint programmed for the temperature at the inlet.

As shown in the figure, there are few safety shutdowns of the air heating system, the main one is observed at the 21st cycle where the highest temperature is briefly reached. Excluding cycle 6th, up to cycle 18th there is good repeatability and the same temperature is reached in the different measure points.

The temperature step between the temperature at the entrance and the temperature measurement point after the particles bed is of about 250 °C, bigger than the one observed in the alumina experiment. The relation between the temperature at the entrance and exit of the reactor is similar to the alumina experiment with a temperature difference of approximately 400 °C.

Figure 5.10. Reactor temperature evolution in the 25 - cycles fixed bed Mn₃O₄LH assay.

From Figure 5.10 it is also appreciable the effect of the initial heating process in the three first cycles. This, together to the air heating device safety shutdowns, make it difficult to obtain much information from Figure 5.11, where the temperature at the entrance is plotted versus the temperature of the air after going through the manganese oxide pellets bed.

Figure 5.11. Reactor temperatures relation 25 - cycles fixed bed Mn_3O_4LH assay.

Fortunately, the workbench is equipped with a gaseous analyser to measure oxygen concentration variation in the exhaust gases. The manganese oxide reaction is clearly appreciable in Figure 5.12, where on the left there is oxygen depletion related to the oxidation of the material and on the right there is an increase of oxygen due to the reduction reaction of the manganese oxide. It is necessary to mention that the steps shown in the figure are related to the sensibility of the analyser, unable to detect variation smaller than 0.1 %.

Figure 5.12. Oxygen concentration variation for the 25 - cycles fixed bed Mn_3O_4LH assay.

Figure 5.13 highlights the first cycle of the material showing that it is heated up to reduction temperature, where the oxygen concentration in the exhaust gas increases. The material is then cooled down to oxidation temperature where the oxygen concentration decreases quickly in a short temperature range.

In subsequent cycles, the oxidation of the material takes longer producing wider and flatter oxygen depletions. The peaks observed for the reduction reaction remain of the same wide, their flattering in subsequent cycles is due to the lost in reactivity of the manganese oxide.

Figure 5.13. Oxygen concentration variation for the 25 - cycles fixed bed Mn_3O_4LH assay. First cycle highlighted in brown colour

An oxygen depletion at high temperatures is also appreciable in Figure 5.12, Figure 5.13 and Figure 5.14. These data correspond to the forth cycle of the material. An explanation for this behaviour has not been found. The reaction is observed up to cycle seven. In Figure 5.14 the last cycle of the experiment is highlighted, showing clearly the deactivation of the material.

Figure 5.14. Oxygen concentration variation for the 25 - cycles fixed bed Mn_3O_4LH assay. Cycle 25th highlighted in brown colour

To complete the analysis, Figure 5.15 shows the pressure variation through the whole experiment; there are no discordances, as in the case of semi-fluidization conditions observed in the alumina experiment. The pressure drop evolution shown in the figure is explained by the temperature variations.

Figure 5.15. Reactor temperatures relation and pressure drop evolution for the 25 - cycles fixed bed Mn_3O_4LH assay.

Material characterization

Figure 5.16 shows two samples of the material: top tube contains the material discharged after the experiment, bottom one, the initial material. In the discharging process loose black-colour pellets were found forming a layer in the top part of the bed and there was a block of brown-red-colour pellets underneath. The transition between the different colour pellets was not clear and passed through a black-brown colour pellets layer, as it can be seen in the figure. The brown-red pellets block had a hole close to the axis, which corresponds to the central thermocouple. These brown-red pellets were softly stuck together, so it was easy to extract them with the vacuum system and once in the solids deposit, the pellets were all loose, there were no agglomerates (See ANNEX III Test in the reactor: working procedures for further detail on material collection).

Figure 5.16. Fixed bed material samples; discharged material into the top tube and, initial material into the bottom tube.

The amount of black pellets is about 0.15 L and around 0.211 kg, the brown-red pellets weight is 2.842 kg corresponding to a volume of 1.85 L. Considering the 13 g of material contained in the vacuum filter, the total mass variation is 124 g. The total volume of material after the experiment is 2 L which means a volume change of 0.4 L.

Diameter, density and hardness study

Diameter, density and hardness are evaluated in the material prior and after the experiment, where two different materials are considered. The results obtained are shown in Table 5.2.

Table 5.2. Mn_3O_4 LH in a fixed bed: diameter, density and hardness results.

Sample	Diameter (mm)	Density (kg/m^3)	Hardness (N)	Appearance
Initial material	2.9 (± 0.3)	2150 (± 250)	33 (± 9)	Uniform matte black
Black material	2.7 (± 0.4)	2000 (± 250)	45 (± 9)	Uniform matte black
Brown-red material	2.6 (± 0.4)	2150 (± 300)	77 (± 16)	Uniform matte brown-red

There is variation in the diameter of the three materials, the after-test materials have smaller diameter although the three material diameters remain within the standard deviation values. Figure 5.17 shows a comparative histogram of the pellets and Figure 5.18 shows the accumulative size distribution.

Figure 5.17. Pellet size distribution (a) before and (b) after testing.

Figure 5.18. Cumulative size distribution of manganese oxide pellets.

From the cumulative size distribution, it is seen that the after-test material has a lightly higher contribution of small diameter pellets compare to the initial material.

The smaller diameter found for the brown-red material, compared to the black one, indicates that the brown-red material must have suffered higher temperatures, which would explain its higher sintering and the stick together effect found in the discharge process.

The density evolution of the after-test materials is in concordance to the cycling thermal treatment study for manganese oxide pellets performed in section 4.2.4. The comparison for density and hardness of the materials is shown in Figure 5.19. Attending to the hardness, black pellets have a value definitely below the trend and, brown-red material shows a higher value included into the trend range. This hardness values can be explained by the material being exposed to different thermal treatment temperatures. In fact, this result indicates that the top material have reached smaller temperatures in the cycling than the bottom material, which is coherent with the theoretical behaviour in a fixed bed.

Figure 5.19. Comparison of Mn₃O₄LH pellets result in the fixed bed with the data obtained in cycling thermal treatment study for manganese oxide pellets: (a) density and (b) hardness.

X-Ray diffraction analyses

Crystalline phases are identified by powder XRD analyses of the samples. Details of the experimental method are included in section 4.1.6. Two crystalline phases are identified by applying the commercial software *X'Pert Highscore Plus*. Results are shown in Table 5.3 and further information is included in ANNEX IV Test in the reactor: material characterization.

Table 5.3. Chemical composition found for the Mn₃O₄LH fixed bed test in the reactor.

Sample	Ratio	Chemical formula	Crystal system	Reference number
Initial material	100 %	Mn ₂ O ₃	Cubic	98-008-1762
Black pellets	100 %	Mn ₂ O ₃	Cubic	98-008-1762
Brown-red pellets	72 %	Mn ₃ O ₄	Tetragonal	98-010-0054
	28 %	Mn ₂ O ₃	Cubic	98-008-1762

The results are in concordance to the material colours observed and they support the idea of the top material not reaching a high enough temperature for the reduction reaction to proceed.

Morphology study

The morphology of the different samples is studied by SEM of the pellets surfaces as well as of their interior at different magnifications.

Figure 5.20. SEM micrographs of Mn₃O₄LH pellets subjected to 25 cycles between 1100 and 650 °C in fixed bed conditions: (a) black material external surface, (b) brown-red material external surface, (c) black material internal surface, (d) brown-red material internal surface, (e) black material border and, (f) brown-red material border.

From Figure 5.20, it can be stated that the particles present the same morphological variation through the whole pellet and that there is no superficial phenomenon. There is not enough difference between both after-test materials as to produce a clear conclusion but it can be inferred from the surfaces micrographs that the black material presents small sintering effects.

Porosity evaluation

The porosity of the after-test samples is studied by mercury intrusion porosimetry. The experimental methodology applied is described in section 4.2.4. The results, and their comparison to the porosimetry evolution analysis performed for manganese oxide in section 4.2.4, are shown in Figure 5.21.

Figure 5.21. Mercury porosimetry results for $\text{Mn}_3\text{O}_4\text{LH}$ samples tested in a fixed bed for 25 cycles and comparison with porosimetry evolution through cycling in a furnace.

The results for the black pellets are similar to materials which have suffered less thermal cycles, the values obtained for brown-red pellets show the predictable value of materials exposed to over forty cycles. The explanation is related to the thermal treatments. Black pellets have passed through 25 cycles at tower temperatures where the sintering has little less effect. Brown-red materials have suffered 25 cycles at the same temperatures to the applied in the furnace study, but the heat transfer coefficients reached in the reactor are higher than in the furnace where there is no air flowing through the reactive pellets, so the effect of the sintering is more important.

Reactivity verification

The cyclability of the material is evaluated by thermogravimetric analysis. The weight change of the sample is calculated for seven thermal cycles between 1050 °C and 650 °C with a heating/cooling velocity of 5 °C/min. Previously to the first heating ramp, a 30 minutes plateau is introduced to homogenize.

The results included in Figure 5.22, show that none of the samples has chemical activity.

Figure 5.22. Reactivity study for $\text{Mn}_3\text{O}_4\text{LH}$ pellets subject to 25 thermal cycles in fixed bed reactor: (a) black material and (b) brown-red material.

5.2.3. Manganese oxide thermal cycles test in a fluidized bed

The reactor cavity is filled up with a total volume of 2.4 L of fresh material, which corresponds to 3.082 kg. The material used is the same optimized manganese oxide pellets from *Erachem Comilog*.

The thermal cycle test performed is basically the same as explained in section 5.2.2. The only difference is that the air flow rate for this experiment is set to 45 Nm³/h to guarantee fluidized bed conditions according to the data shown in Figure 5.9.

Reactor experiment analysis

The temperature evolution at the entrance, central part and exit of the air path through the reactor is shown in Figure 5.23. It has also been included the setpoint programmed for the temperature at the inlet.

As shown in the figure, there is good repeatability and the same temperature is reached at the different measure points. The air temperature step between the temperature at the entrance and the temperature measurement point right after the particles bed is of about 150 °C, 100 degrees smaller than the air temperature step observed in the manganese oxide fixed bed experiment, which is in good accordance to the theoretical heat transfer improvement of the fluidized bed with respect to the fixed bed. The relation between the temperature at the entrance and exit of the reactor has also been reduced, being the difference smaller than 300 °C.

Figure 5.23. Reactor temperature evolution in the 25 - cycles fluidized bed Mn₃O₄LH assay.

In Figure 5.24 the temperature of the air after going through the manganese oxide pellets bed is plotted versus the temperature at the entrance. The initial heating process is only perceptible in the first cycles, which again means that heat transfer is much faster in fluidization conditions. This, together with the absence of safety shutdowns, allows the appreciation of the temperature variations due to the reduction and oxidation reactions of the manganese oxide.

The reduction reaction, as demonstrated in the material analysis, keeps its velocity through the cycles, so, its effect on the temperature is clearly confined in a small zone of the graph. By

the contrary the oxidation velocity reaction gets smaller along the cycles, so its effect in the air temperature is spread in the low temperature zone.

Figure 5.24. Reactor temperatures relation in the 25 - cycles fluidized bed Mn_3O_4LH assay.

Furthermore, Figure 5.25 shows the oxygen concentration variation in the exhaust gases. The peaks due to the material reduction are well defined at high temperatures. By the contrary, the lack of oxygen due to the oxidation reaction is not clearly identified. The fact of the oxidation reaction taking longer with the number of thermal cycles, together with the turbulence caused by the high air flow required to reach fluidization conditions, implies more important oxygen dilution. Thus, the oxygen depletion is only clearly appreciable in the first few cycles. Nevertheless, comparing to the fix bed test, it is appreciable how fluidization conditions favour the reaction; there are oxygen peaks up to cycle ten.

Figure 5.25. Oxygen concentration variation for the 25 - cycles fluidized bed Mn_3O_4LH assay.

To complete the analysis, Figure 5.26 shows the pressure variation through the whole experiment. There is a slight increase of pressure drop cycling values in the initial cycles and a smooth decrease in the following cycles. This is related to the variation of the material properties with the thermal cycles. Nevertheless, there are no discordances in the line of the

pressure drop, which demonstrate that there has not been change in the fluidization conditions through the experiment, being completely performed in that state.

Figure 5.26. Reactor temperatures relation and pressure drop evolution for the 25 - cycles fluidized bed Mn_3O_4LH assay.

Material characterization

Figure 5.27 shows two samples of material: top tube contains the material discharged after the experiment, bottom one, the initial material. In the discharging process two different materials were found; loose shiny grey pellets forming a layer in the top part of the bed, and a block of brown-red pellets underneath. These brown-red pellets were stuck together and it was harder than in the previous experiment to extract the pellets with the vacuum system. The after-test material was detached by soft blows and once in the solids deposit, the pellets were all loose without agglomerates.

Figure 5.27. Fluidized bed material samples; discharged material into the top tube and, initial material into the bottom tube.

The amount of shine grey pellets is about 0.32 L and around 0.481 kg, the brown pellets weight is 2.464 kg corresponding to a volume of 1.62 L. Considering the 13 g of material contained in the vacuum filter, the total mass variation is 121 g. The total volume of material after the experiment is about 2 L which means a volume change of 0.4 L.

It is important to mention here that the shiny grey colour is not uniform along the pellet, it is just a superficial phenomenon. In their interior, the particles are brown-red. It is assumed that the block of brown-red material was formed during the cooling down of the system; cold air occupies smaller volumes than hot air, so its velocity through the reactor diminish producing fixed bed conditions, but the solid material retains its high temperature which permits the pellets' agglomeration.

Diameter, density and hardness study

Diameter, density and hardness are evaluated for the material prior and after the experiment. The results obtained are shown in Table 5.4.

Table 5.4. Manganese oxide in a fluidized bed: diameter, density and hardness results.

Sample	Diameter (mm)	Density (kg/m ³)	Hardness (N)	Appearance
Initial material	2.9 (±0.3)	2150 (±250)	33 (±9)	Uniform matte black
Shiny grey material	2.6 (±0.4)	2550 (±400)	82 (±14)	Uniform shiny silver
Brown-red material	2.3 (±0.3)	3000 (±450)	120 (±34)	Uniform matte brown-red

Similar to the fixed bed experiment, the variation in the diameter of the materials remains within the standard deviation values. Figure 5.28 shows a comparative histogram of the pellets and Figure 5.29 shows the accumulative size distribution.

Figure 5.28. Pellet size distribution (left) before and (right) after testing.

Figure 5.29. Cumulative size distribution of Mn₃O₄LH pellets.

Looking at the cumulative size distribution, it seems that the after-test material has smaller pellet diameters, nevertheless the majority of the values are included in the initial diameter range. It is also shown bigger contribution of small pellet size in the shiny grey material, with big fines presence in the both materials. This agrees to the bigger abrasion suffered by the particles in a fluidized bed than in a fixed bed.

Attending to the density values, both after-test materials have similar values. Attending to the diameter of the material, it could indicate a kind of reorganization of the bed where the smaller and lighter pellets would have travel to the top.

A comparison with the data obtained in the cycling thermal treatment study for manganese oxide pellets is shown in Figure 5.30. The density of the after-test materials is above the general trend found in the cycling study. In the case of the hardness, the shiny grey material seem to be slightly bigger compared to the general trend, even though it remains in the expected value, while the hardness of the brown-red particles is clearly bigger than the values found in the cycling study.

Figure 5.30. Comparison of Mn_3O_4LH pellets result in the fluidized bed with the data obtained in cycling thermal treatment study for manganese oxide pellets: (a) density and (b) hardness.

These hardness and density values indicate much more efficient heat treatment processes, so the sintering suffered by the particles is of bigger importance compared to the particles tested in the furnace, where the heat transfer effectiveness is limited.

X-Ray diffraction analyses

Crystalline phases are identified by powder XRD analyses of the samples. Details of the experimental method are included in section 4.1.6. Two crystalline phases were identified by applying the commercial software *X'Pert Highscore Plus*. Results are shown in Table 5.5 and further information is included in ANNEX IV Test in the reactor: material characterization.

Table 5.5. Chemical composition found for the Mn_3O_4LH fluidized bed test in the reactor.

Sample	Ratio	Chemical formula	Crystal system	Reference number
Initial material	100 %	Mn_2O_3	Cubic	98-008-1762
Shiny-grey pellets	93 %	Mn_3O_4	Tetragonal	98-010-0054
	7 %	Mn_2O_3	Cubic	98-008-1762
Brown-red pellets	100 %	Mn_3O_4	Tetragonal	98-010-0054

The results of the shiny grey pellets did not show any different crystal system as expected from their outside colour. Considering the hypothesis of this outside layer being too thin for this structure to be detected, a sample from the fines gathered after the assay was analysed and a MnO_2 crystal system was identified. The results of the powder analysed are included in Table 5.6.

Table 5.6. Chemical composition found for the $\text{Mn}_3\text{O}_4\text{LH}$ powder gathered after the fluidized bed test in the reactor.

Sample	Ratio	Chemical formula	Crystal system	Reference number
Powder material gathered after the fluidized bed test	85 %	Mn_3O_4	Tetragonal	98-010-0054
	11 %	MnO_2	Orthorhombic	98-001-2283
	4 %	Mn_2O_3	Cubic	98-008-1762

The high percentage found for MnO_2 suggest that it was formed in the surface of most of the pellets. Due to the abrasion the majority of pellets lost this layer, which was only retained by the low density pellets that moved up to the top part of the bed where the abrasion effect is smaller.

Morphology study

The morphology of the different samples is studied by SEM of the pellets surfaces as well as of their interior at different magnifications.

Figure 5.31. SEM micrographs of $\text{Mn}_3\text{O}_4\text{LH}$ pellets subjected to 25 cycles between 1100 and 650 °C in fluidized bed conditions: (a) shiny grey material external surface, (b) brown-red material external surface, (c) shiny grey material internal surface, (d) brown-red material internal surface, (e) shiny grey material border and, (f) brown-red material border.

From Figure 5.31, the superficial phenomenon on the shiny grey material is clear, while both materials present the same morphological variation in the interior of the pellets. This indicates that the temperatures reached in the bed during the test have been uniform through the height of the test bed.

Porosity evaluation

The porosity of the after-test samples is studied by mercury intrusion porosimetry. The experimental methodology applied is described in section 4.2.4. The results, and their comparison to the porosimetry evolution analysis performed for manganese oxide in section 4.2.4, are shown in Figure 5.32.

Figure 5.32. Mercury porosimetry results for $\text{Mn}_3\text{O}_4\text{LH}$ samples tested in a fluidized bed for 25 cycles and comparison with porosimetry evolution through cycling in a furnace.

The results obtained for both after-test materials are very similar; the difference in total pore area is smaller than 0.07 nm and the difference in median pore diameter is 200 nm. These small differences indicate that both materials have suffered similar thermal processes.

In the case of the total pore area, both materials present higher sintering effects than the trend, about 10 % smaller. This could be explained by the better heat exchange conditions

reached in the reactor compared to the furnace. In the case of the median pore diameter, the brown-red material has a lower value, while the shiny-grey material has higher value compared to the trend, nevertheless the difference in percentage is smaller than 4 % so the these information cannot lead to a clear conclusion.

Reactivity verification

The cyclability of the material is evaluated by thermogravimetric analysis. The weight change of the sample is calculated for seven thermal cycles between 1050 and 650 °C with a heating/cooling velocity of 5 °C/min. Previously to the first heating ramp, a 30 minutes plateau is introduced to homogenize.

The results included in Figure 5.33, show that none of the samples has cycling activity.

Figure 5.33. Reactivity study for Mn_3O_4LH pellets subject to 25 thermal cycles in fixed bed reactor: (a) shiny grey material and (b) brown-red material.

5.2.4. 5% iron doped manganese oxide thermal cycles test in a fixed bed

The manganese oxide doped with 5 % of iron from *Erachem Comilog* used in this experiment present low sphericity and high presence of fines. This material, which has been calcined at 700 °C for three hours, is selected with a squared 1.81 mm sieve, so the initial diameter is in the range of 1.8-3.6 mm. A total volume of 2.4 L, which corresponds to 2.450 kg, is placed in the reactor cavity.

For comparison purposes, the material is subjected to the same thermal test than pure manganese oxide in the fixed bed test. Detailed description of the test is included in section 5.2.2. Due to the soft material mechanical characteristics, the experiment will not be performed in fluidized bed conditions.

Reactor experiment analysis

The temperature evolution at the entrance, central part and exit of the air path through the reactor is shown in Figure 5.34. It has also been included the setpoint programmed for the temperature at the inlet.

As shown in the figure, there are few safety shutdowns of the air heating system but, they are all short enough not to have an effect in reaching the setpoint temperature. The temperature downstream of the fixed bed shows good repeatability and reaches the same temperature in every cycle, with a temperature step with respect to the entrance of about 230 °C, which is close to the fixed bed manganese oxide experiment results.

The temperature at the reactor exit slightly decreases with de number of cycles; for the maximum value there is a variation of about 30 °C and 10 °C for the minimum one. Rather than being related to the test material, this decrease is due to heat loses at the exit of the reactor, where the insulating material was a little bit damaged. Nevertheless, the maximum temperature step to the temperature at the entrance is of about 330 °C at the middle of the experiment, which is half way between the manganese oxide fluidized and fixed bed results.

Figure 5.34. Reactor temperature evolution in the 25 - cycles fixed bed MnOx5%Fe pellets assay.

From Figure 5.34 it is also appreciable the effect of the initial heating process in the two first cycles. Figure 5.35 shows the temperature of the air after going through the manganese oxide pellets bed plotted versus the temperature at the entrance. For this assay, the controller used was a PI controller which is the reason why the minimum temperature does not reach the setpoint. This, together with the safety shutdowns, makes it difficult to gather any further information from the next figure.

Figure 5.35. Reactor temperatures relation 25 - cycles fixed bed MnOx5%Fe pellets assay.

Nevertheless, Figure 5.36 shows the oxygen concentration variation in the exhaust gases through the assay, demonstrating the manganese oxide doped material reaction. On the left of

this figure there is oxygen depletion related to the oxidation of the material and on the right there is an increase of oxygen due to the reduction reaction.

Figure 5.36. Oxygen concentration variation for the 25 - cycles fixed bed MnOx5%Fe pellets assay.

Compared to the manganese oxide, the doped material shows activity for all thermal cycles. It is also clear how the addition of iron to the material has an impact in the oxidation reaction temperature, which is higher than the one observed for the undoped material. From this figure, it can be also noticed that the reduction reaction remains stable with the number of cycles while the oxidation reaction takes longer times. The mean value for oxygen concentration is smaller than 21 % throughout the experiment, because of the oxidation reaction takes place until the reduction reaction temperature is reached.

To complete the analysis, Figure 5.37 shows the pressure variation through the whole experiment. In this graph the normal shape for the pressure drop line is found to have an increasing tendency with the number of cycles. This is related to the material variation shown in the following material characterization study.

Figure 5.37. Reactor temperatures relation and pressure drop evolution for the 25 - cycles fixed bed MnOx5%Fe pellets assay.

Material characterization

In the discharging process a black-grey uniformed material is found. The after-test and the initial conditions materials are shown in Figure 5.38.

After the test, the pellets are stuck together in a block with a hole close to the axis, which corresponds to the central thermocouple. The material is detached by blowing the pellets with the vacuum system. Once in the solids deposit, there were agglomerates among the loose pellets.

Figure 5.38. Fixed bed MnOx5%Fe samples: initial material into the top tube and, discharged material into the bottom tube.

The recovered material weight is 2.372 kg. Considering the 16 g of material contained in the vacuum filter, the total mass variation is 62 g.

The total volume of material after the experiment was about 1.4 L which means a volume change of 1 L. This volume change, approximately of the 50%, is a clear indicator of the degradation suffered by the material in the thermal process.

Diameter, density and hardness study

Diameter, density and hardness are evaluated in the material prior and after the experiment, where two different materials were found. The results obtained are shown in Table 5.7.

Table 5.7. MnOx5%Fe in a fixed bed: diameter, density and hardness results.

Sample	Diameter (mm)	Density (kg/m ³)	Hardness (N)	Appearance
Initial material	3.0 (±0.5)	1700 (±250)	10 (±3)	Uniform matte black
Black-grey material	2.6 (±0.4)	2200 (±300)	32 (±16)	Uniform matte black-grey

Similar to the fixed bed experiment, the variation in the diameter of the materials remains within the standard deviation values. Figure 5.39 shows a comparative histogram of the pellets and Figure 5.40 shows the accumulative size distribution.

Figure 5.39. Pellet size distribution (left) before and (right) after testing.

Figure 5.40. Cumulative size distribution of MnOx5%Fe pellets.

Looking at the cumulative size distribution, the after-test material presents smaller pellet diameters. In this experiment, the cumulative size distribution does indicate an important presence of fines, more important in the initial material than in the after-test material due to the sintering suffered by the material. The amount of fines is related to the quality of the material rather than to the abrasion suffered during the experiment.

Attending to the density and hardness, the black-grey material shows an increase in both properties compared to the initial material. This is the opposite behaviour to the results found in the cycling study. The comparison between both studies is included in Figure 5.41.

Figure 5.41. Comparison of MnOx5%Fe pellets results in the fixed bed with the data obtained in cycling thermal treatment study for manganese oxide 5 % iron pellets: (a) density and (b) hardness.

From this data, it is noticeable the high impact of the pelletizing process in the quality and evolution of the material. The material used for the cycling study present no agglomerates but nice spherical shaped pellets. With the number of thermal cycles it suffered of sintering and pore diameter increase, sometimes the formation for cracks in the pellets was even eye-visible, so its hardness presented a decreasing trend.

Whereas the material used for the reactor assay was a combination of agglomerates, the pellets consist of a small material agglomerates that would get loose easily. Along the thermal cycles, the agglomerates stuck strongly together, so they hardness increased, even though this increase reached a relatively low value.

X-Ray diffraction analyses

Crystalline phases are identified by powder XRD analyses of the samples. Details of the experimental method are included in section 4.1.6. Two crystalline phases are identified by applying the commercial software *X'Pert Highscore Plus*. Results are shown in Table 5.8 and further information is included in ANNEX IV Test in the reactor: material characterization.

Table 5.8. Chemical composition found for the MnOx5%Fe material fixed bed test in the reactor.

Sample	Ratio	Chemical formula	Crystal system	Reference number
Initial material	100 %	$\text{Fe}_{1.26}\text{Mn}_{0.74}\text{O}_3$	Cubic	98-000-2391
Black -grey pellets	87 %	$\text{Fe}_{1.26}\text{Mn}_{0.74}\text{O}_3$	Cubic	98-000-2391
	13 %	Mn_3O_4	Tetragonal	98-001-7918

As observed in the X-ray previous analyses performed for the doped manganese oxide characterization, the iron is identified in the cubic structures but not in the tetragonal ones, where some distortion is found. This means that the iron is well imbibed in the structure.

Morphology study

The morphology of the different samples is studied by SEM of the pellets surfaces as well as of their interior at different magnifications. From Figure 5.42 (a), a partial superficial phenomenon is observed on the tested material, this is coincident to the morphology study of the cycle thermal study performed in 4.3.4. This superficial phenomenon does not imply any appreciable colour change.

Figure 5.42. SEM micrographs of MnOx5%Fe pellets subjected to 25 cycles between 1100 and 650 °C in fixed bed conditions: black-grey external surface (a) 1.0 k magnification and (b) 3.0 k magnification, black-grey internal surface (c) 1.0 k magnification and (d) 3.0 k magnification and, black-grey border (e) 1.0 k magnification and (f) 3.0 k magnification.

Porosity evaluation

The porosity of the initial and after-test samples is studied by mercury intrusion porosimetry. The experimental methodology applied is described in section 4.2.4. The results, and their comparison to the porosimetry evolution analysis performed for doped manganese oxide in section 4.3.4, are shown in Figure 5.43.

Figure 5.43. Mercury porosimetry results for MnOx5%Fe samples: initial condition and after-test in a fixed bed for 25 cycles and comparison with porosimetry evolution through cycling in a furnace.

In this case, due to the different pelletizing process, the material in initial and after-test conditions is compared to the porosimetry evolution through cycling in a furnace. The result shows similar tendency in the porosimetry for both of the different pellets material.

The initial material tested in the reactor presents higher total pore area compared to the high sphericity material. The after-test material has a small stronger trend explained by the better heat transfer coefficients reached in the reactor.

Reactivity verification

The cyclability of the material is evaluated by thermogravimetric analysis. The weight change of the sample is calculated for seven thermal cycles between 1050 and 650 °C with a heating/cooling velocity of 5 °C/min. Previously to the first heating ramp, a 30 minutes plateau is introduced to homogenize.

The result, presented in Figure 5.44, show that the doped manganese oxide maintains its cycling activity. It also shows how the oxidation reaction velocity has slow down; it starts in the cooling process and continues while the heating process until the reduction temperature is reached.

Figure 5.44. Reactivity study for the doped manganese oxide pellets subject to 25 thermal cycles in fixed bed reactor.

5.3. Summary and conclusions

The characterization of the reactor with an inert material has provided a useful knowledge for the interpretation of the data acquired from the reactor experiments using reactive materials. The fluidization assay has helped to define the different air flow rate ranges required to work in the desired fluidization conditions.

The fact of using a material having a narrow particle size distribution has also been useful to evaluate the accuracy of the mathematical formulae used for the reactor design, which have shown to have a big deviation compared to the experimental value. The use of pellets with a wide particle size distribution would have introduced additional considerations to estimate the fluidization conditions.

The assays performing thermal cycles using inert material have provided with the knowledge to the identification of variations in the material bed fluidization conditions. This assay has also been used to evaluate the reactor experimental repeatability, which has shown good behaviour by reaching the same temperature levels in each cycle at the same observed points. The data obtained in this assay has also be taken into account for comparison to the reactive material cycling tests, where different fluidization conditions applied and chemical reactions take place.

For comparison purposes, all assays have been performed using the same temperature profiles with variations from 1100 °C to 650 °C, a 90 minutes plateau at each temperature and heating/cooling velocities of 5 °C/min. encompasses the main data considered for comparison.

Table 5.9. Experimental conditions comparison among the cycling test carried out in the reactor.

	Al ₂ O ₃	MnO _x	MnO _x	MnO _x -5%Fe
Fluidization conditions	Intermediated	Fixed bed	Fluidized bed	Fixed bed
Air flow [Nm ³ /h]	45	20	45	20
Max. air mid-height temperature [°C]	900	850	960	870
Pressure drop through the bed [mbar]	13 - 14	2.5 - 4	5 - 8	1 - 2 / 2 - 3

Due to the higher density of the alumina particles compared to the manganese oxide, an air flow rate of 45 Nm³/h provides fluidization conditions for the manganese oxide while for alumina spheres that flow rate switches between fixed and fluidized conditions.

Particle regime has an effect on the maximum air temperature reached at medium height of the reactor. The highest air temperature is observed in the manganese oxide fluidization test due to the higher heat transfer coefficient, followed by the intermediated fluidization conditions using alumina spheres. The lowest temperatures at medium height of the reactor are reached for the fixed bed test of manganese oxide and doped manganese oxide.

The pressure drop variation is also characteristic of this type of test. As expected, the pressure drop for the fixed bed is smaller than in fluidized bed conditions using manganese oxide pellets. The high pressure drop measured using alumina is not comparable due to the different material, but the pressure drop measured for the doped manganese oxide is comparable to the value obtained for the undoped material in the same fixed bed conditions.

In the reactive material tests performed, the data gathered from the experiments allows for analysing the material redox behaviour. By detecting variation of the oxygen concentration in the gaseous exit stream, it is shown that the manganese oxide pellets lose their cyclability with the number of thermal treatments, while the doped material keeps reacting for the 25 cycles assay. It is also appreciable the diminution in the oxidation reaction velocity for both materials independently of the fluidization conditions. Also, the switch to a higher oxidation reaction temperature is shown as an effect of the inclusion of iron in the manganese oxide.

In the manganese oxide fluidized bed test, where there were no safety shutdowns of the heating system, the variation on temperature due to the chemical reaction of the material is also appreciable.

The material characterization brings results in concordance to the theoretically expected for fixed and fluidized bed conditions respectively. In the manganese oxide fixed bed test, the pellets located at the top of the bed did not reach high enough temperatures as for the reduction reaction to proceed, while the pellets located at the bottom of the bed reached higher temperatures and suffered more important sintering effects. In the manganese oxide fluidized bed test, a relocation of the pellets according to their density was found: lower density material at the top and higher density material at the bottom, this was possible thanks to the mobility of the pellets in a fluidized bed. In the case of the manganese oxide doped material fixed bed test, all the pellets manage to react, and there was no appreciable distinction among top particles and bottom particles. The inclusion of iron in the manganese oxide structure has different effects on the material properties. It may most probably have an effect on the conductivity that can allow this reaction. But it must be taken into account that the diameter of the doped material pellets was smaller than the undoped material. And it also may have an effect the high impact of the heat treatments in the porosity of the doped material, which medium pore diameter doubles the value of the undoped material medium pore diameter.

Manganese oxide pellets have demonstrated good mechanical properties that would allow their use in high abrasion systems, but they suffer a loss of cyclability because of the effect of several thermal treatments in the material intrinsic characteristics.

Once the material is doped with a five percent of iron, its cyclability is maintained for at least the fifty-seven cycles studied, but its mechanical properties would need to be improved in order to ensure the mechanical performance of the material. Nevertheless the oxidation reaction velocity still decreases with the thermal treatments, so it is also a factor to be improved.

CHAPTER VI

6. CONCLUSIONS AND FURTHER WORK

6.1. Conclusions

Increasing the penetration of renewable energy in the production of the consumed electricity is mandatory. Solar energy has the potential to highly contribute to the electricity generation mix, but it is necessary to improve its dispatchability. Here thermochemical energy storage is a very promising way to reach this target due to its numerous advantages.

In order to choose an optimized substance to work as thermochemical storage material, this work has been focused on manganese oxide, since it is cheap enough and innocuous material and capable of storing thermal energy at the temperatures characteristics in current and future in central receiver solar thermal power plants.

The main conclusions and results reached during the present PhD Thesis are listed next:

- An experimental test rig has been designed and constructed. It reproduces the working conditions of a CSP plant, allowing the analysis of the potential of manganese oxides for thermochemical energy storage application in fluidized and fixed bed conditions.
- An air heating electric furnace has been built and optimized by CFD simulations to heat air, used as heat transfer and reactant fluid required for the oxidation/reduction cycles of the manganese oxide. It provides air flow rates between 10 Nm³/h and 60 Nm³/h, at temperatures from ambient temperature up to 1100 °C
- A reactor has been built and its thermal and fluidization characteristics has been defined by the used of an inert material, alumina pellets, which has provided the basic knowledge for the posterior interpretation of the data acquired from the materials tested.
- A specific control and data acquisition system has been designed; a multiple controller based in PI and PID controllers, optimized and tested under real conditions to meet the exigent application requirements. It has been demonstrated that the air temperature control developed meet the performance required for the material characterization experiments.
- The kinetics of the oxidation reaction and the effective reaction time of manganese oxide have been studied in air and in oxygen atmospheres. The apparent kinetic mechanism for the oxidation reaction in both cases is Avrami-Erofeev mechanism. It has also been found that the velocity of the oxidation reaction decreases for the first few cycles until it reaches a constant value, much slower than the reduction reaction velocity.
- The cyclability of the manganese oxide powder material has been demonstrated for fifty cycles by TGA. Besides, the thermal diffusivity and its relation with temperature have been defined. A heating ramp study has been performed and a recommendation of using heating/cooling ramps over 4 °C/min has been obtained as a result.

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- The morphology evolution of the powder manganese oxide within ten thermal cycles has been analysed. The formation of coral-like structure has been identified: the material suffers a sintering process with fast neck formation and growth for the five first cycles.
 - Pelletized manganese oxide has been characterized. Its hardness, density and diameter evolution with thermal treatments in increasing temperatures from 120 °C up to 1400 °C have been studied for pellet mechanical optimization purposes. A calcination process at 700 °C has been selected as compromise solution to optimize mechanical properties of the material taking into account production cost.
 - The behaviour of pelletized manganese oxide has been studied by a 50 thermal cycle assay in a furnace. The global constant tendency of the diameter and density values with the thermal cycles indicates the deceleration of the sintering process. The porosity evaluation of samples shows the biggest variation occurring within the first 10 cycle. The porosity trend has been pointed to explain the loss of reactivity of the pelletized manganese oxide.
 - It has been found that by doping manganese oxide with 5% iron its cyclability is greatly improved with a shift towards little higher reduction reaction temperatures. With the 50 thermal cycle assay in a furnace it has been found that doped manganese oxide also suffers sintering processes but reactivity analysis performed show that the samples retain their cycling capability with a detriment of its mechanical characteristics.
 - Pelletized pure and doped manganese oxide has been test in fluidized and fixed bed condition in the reactor. Their redox behaviour has been studied by detecting oxygen concentration variation in the gaseous exit stream, it is shown how the manganese oxide pellets lose their cyclability with the number of thermal treatments, while the doped material keeps reacting for the 25 cycles assay.
 - In the manganese oxide fixed bed test, the pellets located at the top of the bed did not reached high enough temperatures as for the reduction reaction to proceed, while the pellets located at the bottom of the bed reached higher temperatures and suffer more important sintering effects.
 - In the manganese oxide fluidized bed test, a relocation of the pellets according to their density was found; lower density material at the top and higher density material at the bottom, this was possible thanks to the mobility of the pellets in a fluidized bed.
 - In the doped manganese oxide fixed bed test, all the pellets manage to react, and there was no appreciable distinction among top particles and bottom particles. The inclusion of iron may have an effect on the conductivity that allows its reaction. But also, the smaller pellet diameter, and the important porosity increment in the doped material must be taken into account.
 - Manganese oxide pellets have demonstrated good mechanical properties that would allow their use in high abrasion systems, but they suffer a loss of cyclability because of the effect of several thermal treatments in the material intrinsic characteristics. While five percent iron doped material retains its cyclability for the fifty-seven cycles studied, but its mechanical strength would need to be improved in order to ensure the performance of the material.

6.2. Further work

With the knowledge gathered from the research work done in the present Thesis, the future research line proposed would point to two main concerns:

Firstly, optimize the properties of these redox materials by testing different dopant metallic oxides in various concentrations. In order to develop this line of investigation, the redox couple Mn_2O_3 / Mn_3O_4 reaction characteristics could be adjusted by doping or substituting of manganese by suitable element such as (but not limited to) iron, cobalt, nickel, zinc, and magnesium.

Evaluate the effect of doping in critical parameters as reaction temperatures, kinetics of the redox reaction, cycling behaviour and material aging under specific conditions (maximum and minimum cycle temperatures and heating rates). Also consider the cost variation of the active material, as key factor for the scalability of the process as well as in the economic feasibility of the material industrial production.

Secondly the selection and design of the reactor to be developed for the next scaling up. It must aim to a relative movement between the particles and the reactor but with lower abrasion rates, as it could be expected in a vertical moving bed reactor where the material would be fed on the top of the reactor and the air flow rate would come into the system through a distribution system located at the bottom of the reactor.

For a vertical moving bed reactor design the main effort would be concentrated in the solid pellets inlet and outlet in order to regulate its moving velocity. Also the inlet of the hot air needed for the reaction and its homogeneous distribution would be a great challenge.

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ANNEX I Experimental test rig: design and constructive details

I.a Code and results for fluidization and terminal velocities.

{Parametric variables}

$P_{g_in}=1$ [bar] {Pressure of the air at the inlet}

$T_{g_in} = 1100$ [°C] {Temperature of the air at the inlet}

$d_p=0,001$ [m] {Pellet diameter}

{Material propertities and constants}

$\rho_s=2100$ [Kg/m³] {Density of the manganese oxide}

$\rho_g=DENSITY(Air;T=T_{g_in};P=P_{g_in})$ {Density of the air}

$\mu_g=VISCOSITY(Air;T=T_{g_in})$ {Kinematic viscosity of the air}

$g=9,8$ [m²/s]

$fi=0,48$ {Void fraction of the bed}

$\phi=1$ {Sphericity of the pellet}

{Minimum fluidization velocity}

$Ar=d_p^3 \cdot \rho_g \cdot (\rho_s - \rho_g) \cdot g / \mu_g^2$

$Re_{p_mf}=42,9 \cdot (1-fi) \cdot ((1+fi^3/(1-fi)^2 \cdot Ar/3214)^{(1/2)}-1)$

$u_{mf}=Re_{p_mf} \cdot \mu_g / (d_p \cdot \rho_g)$

{Terminal velocity}

$Re_a= (4/3 \cdot Ar)^{(1/2)}$

$u_t=Re_a \cdot \mu_g / (d_p \cdot \rho_g)$

Table I.a.1. Fluidization (U_{mf}) and terminal (U_t) velocities for 0.5 mm particle size.

Pressure	1 bar		5 bar		10 bar	
T (°C)	U_{mf}	U_t	U_{mf}	U_t	U_{mf}	U_t
25	0.32	3.43	0.22	1.53	0.18	1.08
100	0.29	3.83	0.22	1.71	0.18	1.21
200	0.26	4.32	0.21	1.93	0.18	1.36
300	0.24	4.75	0.20	2.12	0.18	1.50
400	0.22	5.15	0.19	2.30	0.17	1.63
500	0.20	5.52	0.18	2.47	0.17	1.74
600	0.19	5.86	0.17	2.62	0.16	1.85
700	0.17	6.19	0.16	2.77	0.15	1.96

Pressure	1 bar		5 bar		10 bar	
T (°C)	Umf	Ut	Umf	Ut	Umf	Ut
800	0.17	6.50	0.16	2.91	0.15	2.05
900	0.16	6.80	0.15	3.04	0.14	2.15
1000	0.15	7.08	0.14	3.17	0.14	2.24
1100	0.14	7.35	0.14	3.29	0.13	2.32

Table I.a.2. Fluidization (Umf) and terminal (Ut) velocities for 2.5 mm particle size.

Pressure	1 bar		5 bar		10 bar	
T (°C)	Umf	Ut	Umf	Ut	Umf	Ut
25	1.53	7.66	0.72	3.42	0.51	2.42
100	1.67	8.57	0.79	3.83	0.57	2.71
200	1.81	9.65	0.88	4.31	0.63	3.05
300	1.92	10.62	0.95	4.75	0.69	3.36
400	2.01	11.51	1.02	5.15	0.74	3.64
500	2.07	12.34	1.07	5.52	0.78	3.90
600	2.12	13.11	1.12	5.86	0.82	4.14
700	2.16	13.84	1.16	6.19	0.86	4.37
800	2.19	14.54	1.20	6.50	0.89	4.59
900	2.21	15.20	1.23	6.80	0.92	4.80
1000	2.22	15.83	1.26	7.08	0.94	5.00
1100	2.23	16.44	1.29	7.35	0.97	5.20

Table I.a.3. Fluidization (Umf) and terminal (Ut) velocities for 5 mm particle size.

Pressure	1 bar		5 bar		10 bar	
T (°C)	Umf	Ut	Umf	Ut	Umf	Ut
25	2.29	10.83	1.04	4.84	0.74	3.42
100	2.54	12.12	1.16	5.42	0.82	3.83
200	2.82	13.65	1.30	6.10	0.92	4.31
300	3.07	15.02	1.42	6.71	1.01	4.74
400	3.28	16.28	1.53	7.28	1.09	5.14
500	3.47	17.45	1.63	7.80	1.17	5.51
600	3.63	18.54	1.72	8.29	1.23	5.86
700	3.78	19.57	1.81	8.75	1.30	6.19
800	3.92	20.56	1.89	9.19	1.36	6.50
900	4.04	21.49	1.96	9.61	1.41	6.79
1000	4.16	22.39	2.03	10.01	1.47	7.08
1100	4.26	23.25	2.10	10.40	1.52	7.35

I.b Code and results for the calculus of the reactor isolating layers.

```
{Function definitions}

{CONVECTION LOSSES}

FUNCTION f_perd_conv(T_ext;D_ext)
$COMMON v_air;P_amb;T_amb;L_r

{Calculus of air properties}
T_67=(T_ext+T_amb)/2 "[°C]"
K_67=Conductivity(Air;T=T_67) "[W/m·K]"
cp_67=Cp(Air;T=T_67) "[J/kg·K]"
mu_67=Viscosity(Air;T=T_67) "[kg/ms]"
rho_67=Density(Air;T=T_67;P=P_amb) "[kg/m3]"
rho_7=Density(Air;T=T_amb;P=P_amb) "[kg/m3]"
rho_6=Density(Air;T=T_ext;P=P_amb) "[kg/m3]"
mu_7=Viscosity(Air;T=T_amb) "[kg/ms]"
mu_6=Viscosity(Air;T=T_ext) "[kg/ms]"
cp_6=Cp(Air;T=T_ext) "[J/kg·K]"
cp_7=Cp(Air;T=T_amb) "[J/kg·K]"
K_6=Conductivity(Air;T=T_ext) "[W/m·K]"
K_7=Conductivity(Air;T=T_amb) "[W/m·K]"

IF (v_air<=0,1) THEN

{Coefficients to calculate Nu_D6 in natural convection}
g=9,81 "[m/s2]"
alpha_67=K_67/(rho_67*cp_67) "[m2/s]"
Pr_67=Viscosity(Air;T=T_67)*cp_67/K_67 "[dimensionless]"
beta=1/T_67 "[1/K]"
Ra_D6=abs(g*beta*(T_ext-T_amb)*((D_ext)^3)*rho_67/(alpha_67*mu_67)) "[dimensionless]"

Nu_D6= (0,6+(0,387*(Ra_D6^(1/6)))/ (1+ ((0,559/Pr_67)^(9/16)) )^(8/27) ) ^2
"[dimensionless]"

f_h=Nu_D6*K_67/(D_ext) "[W/m2K]"

ELSE

{Coefficients to calculate Nu_D6 in forced convection}
Re_D6=rho_7*D_ext*v_air/mu_7 "[ dimensionless]"
Pr_6=mu_6*cp_6/K_6 "[ dimensionless]"
Pr_7=mu_7*cp_7/K_7 "[ dimensionless]"

If (Pr_6<=10) then
  n=0,37
Else
  n=0,36
EndIf

If (Re_D6*Pr_7>0,2) then
  Nu_D6=0,3+( (0,62*Re_D6^(1/2)*Pr_7^(1/3)) / ((1+ ((0,4/Pr_7)^(2/3)) )^(1/4)) ) * ((1 +
(Re_D6/282000)^(5/8))^(4/5))
Else

  If (Re_D6<=40) then
    C=0,75
    m=0,4
    Nu_D6=C*(Re_D6^m)*(Pr_7^n)*((Pr_7/Pr_6)^(1/4)) "[adimensional]"
```

```

Else
  If (Re_D6>=40) and (Re_D6<10^3) then
    C=0,51
    m=0,5
    Nu_D6=C*(Re_D6^m)*(Pr_7^n)*((Pr_7/Pr_6)^(1/4)) "[adimensional]"

  Else
    If (Re_D6>=10^3) and (Re_D6<2*10^5) then
      C=0,26
      m=0,6
      Nu_D6=C*(Re_D6^m)*(Pr_7^n)*((Pr_7/Pr_6)^(1/4)) "[adimensional]"

    Else
      If (Re_D6>=2*10^5) and (Re_D6<10^6) then
        C=0,076
        m=0,7
        Nu_D6=C*(Re_D6^m)*(Pr_7^n)*((Pr_7/Pr_6)^(1/4)) "[adimensional]"
      EndIf
    EndIf
  EndIf

EndIf

h_conv=Nu_D6*K_67/D_ext "[W/m2K]"

Area=pi*D_ext*L_r "[m^2]"

T_sky=T_amb-8 "[°C]"

f_perd_conv=h_conv*Area*(T_ext-T_sky)

ENDIF

END

{RADIATION LOSSES}

FUNCTION f_perd_rad(T_ext;D_ext)
$COMMON emisividad; T_amb; L_r;
  sigma=5,67E-8 [W/m^2K^4]
  T_ext_K=T_ext+273,15
  T_amb_K=T_amb+273,15
  Area=pi*D_ext*L_r
  f_perd_rad=Area*sigma*emisividad*(T_ext_K^4-T_amb_K^4) "[W/m2]"
END

{ Subscript key

r      Reactor
g      Gas
s      Mn2O3
amb    Ambient
in     Inlet
out    Outlet
perd   Lost
ext    External
}

```

{Maximum operational conditions}

$P_{g_in}=1$ [bar]

$T_1=1100$ [°C]

{Reactor size and dimension data}

$D_{r_1}=0,140$ [m]

{Alumina cylinder internal diameter}

$L_r=5*D_{r_1}$

{Alumina cylinder heigh}

$A_{paso_r}=\pi/4*D_{r_1}^2$ [m²]

$D_{r_2}=D_{r_1}+2*e_{12}$

$e_{12}=0,010$ [m]

{Alumina cylinder thickness}

$D_{r_3}=D_{r_2}+2*e_{23}$

$e_{23}=0,140$ [m]

{Ceramic brick thickness}

$D_{r_4}=D_{r_3}+2*e_{34}$

$e_{34}=0,085$ [m]

{Ceramic blanket thickness}

$D_{r_5}=D_{r_4}+2*e_{45}$

$e_{45}=0,004$ [m]

{Metalic layer thickness}

{Ambient conditions definition}

$T_{amb}=20$ "[°C]"

$P_{amb}=1,01325$ "[bar]"

$v_{air}=0,2$ "[m/s]"

{Metalic layer material emisivity}

emisividad=0,9

{Heat losses calculus for the external layer to the ambient}

$q_{rad}=f_{perd_rad}(T_5;D_{r_5})$

$q_{conv}=f_{perd_conv}(T_5;D_{r_5})$

$Q_{lost}=q_{rad}+q_{conv}$

{Heat losses through the isolating materials}

$k_{12}=4,3$ "[W/m·K]"

{Alumina cylinder conductivity}

$A_{12}=\pi*L_r*(D_{r_2}-D_{r_1})/\ln(D_{r_2}/D_{r_1})$ "[m²]"

$Q_{lost}=A_{12}*k_{12}*(T_1-T_2)/e_{12}$ "[W]"

$k_{23}=0,0001*((T_1+T_2)/2+273,15) + 0,0382$ "[W/m·K]"

{Ceramic brick conductivity }

$$A_{23} = \pi \cdot L_r \cdot (D_{r_3} - D_{r_2}) / \ln(D_{r_3} / D_{r_2})$$

$$Q_{lost} = A_{23} \cdot k_{23} \cdot (T_2 - T_3) / e_{23} \text{ "[W]"}$$

$$k_{34} = 2E-07 \cdot ((T_3 + T_4) / 2 + 273,15)^2 - 7E-05 \cdot ((T_3 + T_4) / 2 + 273,15) + 0,044 \text{ "[W/m}\cdot\text{K]"}$$

{Ceramic blanket conductivity}

$$A_{34} = \pi \cdot L_r \cdot (D_{r_4} - D_{r_3}) / \ln(D_{r_4} / D_{r_3})$$

$$Q_{lost} = A_{34} \cdot k_{34} \cdot (T_3 - T_4) / e_{34}$$

$$k_{45} = 30 \text{ "[W/m}\cdot\text{K]"}$$

{Metalic layer conductivity }

$$A_{45} = \pi \cdot \{L_r\} \cdot (D_{r_5} - D_{r_4}) / \ln(D_{r_5} / D_{r_4})$$

$$Q_{lost} = A_{45} \cdot k_{45} \cdot (T_4 - T_5) / e_{45}$$

The heat losses to the ambient by convection and radiation are 126 W and 307.8 W respectively. The gathered results about the layer and temperatures are shown in the next table:

Table I.b.1. Reactor material layers sizes and temperatures to withstand.

Layer	Internal diameter (mm)	Thickness (m)	Temperatures (°C)
Alumina cylinder	140	0.010	1100
Ceramic bricks	160	0.140	1097
Ceramic blanket	440	0.085	528
Metallic material	610	0.004	56.6
External surface of the reactor	618	-	56.6

I.c Complementary data for the evaluation of resistors disposition and fins design

This section includes complementary information obtained in the evaluation of the different fins and resistors disposition through CFD simulations.

The effect of variation in the power of the resistor is evaluated for the zigzag disposition of the reactor's sub-units and polygonal fins. Figure I.c.1 shows the velocity profile for 96 W, 576 W and 1000 W power through the resistors. The inlet temperature of 500 °C, air flow rate of 15 m³/h of air flow and 1 bar of pressure are retained.

Figure I.c.1. Velocity profiles (m/s) for the zigzag disposition of the resistor's sub-units with polygonal fins for (a) 96 W, (b) 576 W and (c) 1000 W.

The maximum velocities achieved in the three case of study agrees with the air volume evolution with temperature; higher power through the resistors results in higher air temperatures, as shown in Figure 3.22 of the section 3.2.5. Higher temperature implies higher air volume, as the cross area remain constant, the air velocity increases. The maximum velocity numerical values obtained are shown in Table I. c.1

Table I. c.1. Results of the fins and resistor's sub-units disposition.

Electric power to resistors (W)	Maximum air velocity (m/s)
96	1.92
500	2.02
1000	2.11

In order to spread the study, different air flow rates are studied in a simulation of the last straight part of the furnace. In this area the most demanding thermal conditions take place so, 875 °C is defined as average inlet temperature of the air and the power through resistors is set

to 1000 W. Figure 3.23 from section 3.2.5 shows the temperature profiles obtained for the study, Figure I.c.2, shows the velocity profiles gathered.

Figure I.c.2. Velocity profiles (m/s) for the zigzag disposition of the resistor's sub-units with polygonal fins with different air flow rates: (a) 10 Nm³/h, (b) 25 Nm³/h and, (c) 60 Nm³/h.

The maximum velocity numerical values obtained are shown in Table I. c.2

Table I. c.2. Results of the fins and resistor's sub-units disposition.

Air flow rate (Nm ³ /h)	Maximum air velocity (m/s)
10	1.49
25	3.36
60	7.79

I.d Detailed signals connection to the cRIO modules

Table I.d.1. Compact RIO modules signal connection.

Module	Channel	Wired signal
Analog Output 4-20mA NI 9265	1.1	Air flow meter setpoint1
	1.2	Air flow meter setpoint2
	1.3	Preheater setpoint 1
	1.4	Preheater setpoint 2
	2.1	Furnace power setpoint
	2.2-2.4	Available
Digital Output 24 V NI 9472	1	Preheater 1 On/Off
	2	Preheater 2 On/Off
	3	Air blower 1 On/Off
	4	Air blower 2 On/Off
	5	Furnace power regulator On/Off
	6-8	Available
Analog Current Input 4-20mA NI 9203	1	Air flow controller 1
	2	Air flow controller 2
	3	Furnace differential pressure meter
	4	Reactor differential pressure meter
	5	Relative pressure meter
	6	Gas analyser
Isothermal Thermocouple Input NI 9214	7-8	Available
	1.1-1.6	Reactor multipoint meter
	1.7 – 1.15	9 reactor wall thermocouples
	1.16	Inside reactor thermocouple
	2.1	Furnace control thermocouple
	2.2	Furnace alarm thermocouple
	2.3-2.7	Furnace path thermocouples
	2.8	Preheater 1 control thermocouple
	2.9	Preheater 2 control thermocouple
	2.10-2.11	2 Top reactor thermocouples
	2.12	Outlet reactor thermocouple
	2.13-2.14	Available
	2.15-2.16	2 Peripheral thermocouples

I.e Matlab® code implemented for control tuning

% Code developed by Gabriel Mollocana in the master thesis DESARROLLO DEL CONTROL DE PROCESO EN UN BANCO DE ENSAYOS DE REACTORES DE PARTÍCULAS A ALTA TEMPERATURA at the Universidad Politécnica de Madrid.

```
% The name of the model should be type idproc
plant=input('\nSet the name of the model: ')
if strcmp(plant.Type,'P1') %First order models
    s=tf('s'); G=plant.Kp.value/(1+s*plant.Tp1.value)
elseif strcmp(plant.Type,'P2') %Second order models
    s=tf('s');
    G=plant.Kp.value/((1+s*plant.Tp1.value)/(1+s*plant.Tp2.value))
elseif strcmp(plant.Type,'P2D') %SOPTD models
    s=tf('s');
    G=plant.Kp.value/((1+s*plant.Tp1.value)/(1+s*plant.Tp2.value));
    G.ioDelay=plant.Td.value
elseif strcmp(plant.Type,'P1D') %FOPTD models
    s=tf('s'); G=plant.Kp.value/(1+s*plant.Tp1.value);
    G.ioDelay=plant.Td.value
else
    fprintf('\nModelo no encontrado\n')
end
%Maximun slope method
[y,t]=step(G);k=dcgain(G);
[dydt,idx]=max(diff(y)./diff(t));
t1=t(idx)+(k-y(idx))/dydt;
t0=t(idx)-y(idx)/dydt;
plot([t0 t1],[0 k],'r--'), hold on, step(G),grid on,
title(plant.Name,'fontsize',14,'linewidth',2)
xlabel('Tiempo','fontsize',14),ylabel('Amplitud
(°C)','fontsize',14),hold off
%Zieglier-Nichols
L=t0; T=t1-L;
[Gc1,Kp1]=zn(1,[k,L,T,10]);
[Gc2,Kp2,Ti2]=zn(2,[k,L,T,10]);
[Gc3,Kp3,Ti3,Td3]=zn(3,[k,L,T,10]);
fprintf('\nL=%f - T=%f - k=%f\nP: Kp=%f\nPI: Kp=%f - Ti=%f\nPID: Kp=%f
- Ti=%f - Td=%f\n',L,T,k,Kp1,Kp2,Ti2,Kp3,Ti3,Td3)

% Ziegler-Nichols function obtained from Dc. Cecilia García Course on
System Control Practice 2.
%
function [Gc,Kp,Ti,Td,H]=zn(key,vars)
Ti=[]; Td=[]; H=1;
if length(vars)==4,
    K=vars(1); L=vars(2); T=vars(3); N=vars(4); a=K*L/T;
    if key==1, Kp=1/a;
    elseif key==2, Kp=0.9/a; Ti=3.33*L;
    elseif key==3 | key==4, Kp=1.2/a; Ti=2*L; Td=L/2; end
elseif length(vars)==3,
    K=vars(1); Tc=vars(2); N=vars(3);
    if key==1, Kp=0.5*K;
    elseif key==2, Kp=0.4*K; Ti=0.8*Tc;
    elseif key==3 | key==4, Kp=0.6*K; Ti=0.5*Tc; Td=0.12*Tc; end
elseif length(vars)==5,
    K=vars(1); Tc=vars(2); rb=vars(3); N=vars(5);
    pb=pi*vars(4)/180; Kp=K*rb*cos(pb);
```

```

        if key==2, Ti=-Tc/(2*pi*tan(pb));
        elseif key==3|key==4, Ti=Tc*(1+sin(pb))/(pi*cos(pb)); Td=Ti/4; end
    end
    [Gc,H]=escribirpid(Kp,Ti,Td,N,key);

%PID writing function obtained from Dc. Cecilia García Course on System
Control Practice 2.

function [Gc,H]=escribirpid(Kp,Ti,Td,N,key)
switch key
    case 1, Gc=Kp;H=1;
    case 2, Gc=tf(Kp*[Ti,1],[Ti,0]); H=1;
    case 3, nn=[Kp*Ti*Td*(N+1)/N,Kp*(Ti+Td/N),Kp];
    dd=Ti*[Td/N,1,0]; Gc=tf(nn,dd); H=1;
    case 4, d0=sqrt(Ti*(Ti-4*Td)); Ti0=Ti; Kp=0.5*(Ti+d0)*Kp/Ti;
    Ti=0.5*(Ti+d0); Td=Ti0-Ti; Gc=tf(Kp*[Ti,1],[Ti,0]);
    nH=[(1+Kp/N)*Ti*Td, Kp*(Ti+Td/N), Kp];
    H=tf(nH,Kp*conv([Ti,1],[Td/N,1]));
    case 5, Gc=tf(Kp*[Td*(N+1)/N,1],[Td/N,1]); H=1;
end

```

ANNEX II Material characterization

II.a Image J protocol and validation procedure

The pellets diameter is an important parameter in the performed studies. An average diameter value is manually obtained out of three longitudinal length measurements in the three perpendicular directions of the pellet. This manual measuring procedure is a tedious and slow work, in which constant attention and care should be pay in order to get accurate values.

Improving this procedure of obtaining reliable data was mandatory in order to optimize time work. So an image processing method was developed and validated.

The procedure starts by taking a picture of a representative number of pellets in a sample. The pellets are carefully allocated on a flat surface with good colour contrast with the particles; a white surface is used for our application. The number of thirty units is considered good enough for validation purposes. Figure II.a.1 (a) shows an example of the initial photograph; where each pellet is placed separated to the others. A rule should be included in the picture in order to have real lengths to dimension the pixels of the photograph. A magnification of the picture is done writing down the length of the image in the rule. By doing so, a 10 cm picture is obtained and shown in Figure II.a.1 (b).

Figure II.a.1. (a) Initial pellets 2-3.6 mm sample photograph. (b) 10 cm magnification of the initial image.

From the properties menu of the magnified picture, the width in pixels is obtained and wrote down. The ImageJ program is booted, and the magnified image is uploaded by sweeping along the image to the program's interface. See Figure II.a.2 (a).

First step now is to dimension the image, on the program menu select Analyze→Set scale the window shown in Figure II.a.2 (b) appears. The collected data of the image width is introduced in pixel and in mm.

Figure II.a.2. (a) Magnified image uploaded on ImageJ program. (b) Scale's window for ImageJ program.

Then, the image is selected through the menu Image→Adjust→Threshold... and the image will change its colour and shown in Figure II.a.3 (a). Next, the image is converted to binary by selecting Process→Binary→Make binary in the program menu. The result is shown in Figure II.a.3 (b).

Figure II.a.3. (a) Adjusted image by threshold and (b) binary image.

In Figure II.a.3 (b), we can see that there are small points which do not correspond to pellets but, to the dust spread in the pellets positioning. To eliminate these noises in the image a minimum particle size to be considered is defined in the menu Analyse→Analyze particles. The window shown in Figure II.a.4 appears.

Figure II.a.4. Pellets analyse window.

The predetermined pellet size range is 0-Infinity, so, by changing this value to a one smaller than the pellet surface, the dust on the paper would be eliminated for the analysis. On this same window, in the menu show, Outlines is selected. By clicking Ok the program returns the detected particles and their measured surface area, from which the diameter is calculated.

Table II.a.1 contains the pellets diameter data obtained by both, manual measurements and from the software information.

Table II.a.1. Pellet diameter data obtained.

Sample	Manual D _p (cm)	Software D _p (cm)	Sample	Manual D _p (cm)	Software D _p (cm)
1	0.333	0.254	16	0.353	0.325
2	0.353	0.260	17	0.358	0.326
3	0.328	0.261	18	0.3	0.332
4	0.345	0.285	19	0.357	0.333

Sample	Manual D _p (cm)	Software D _p (cm)	Sample	Manual D _p (cm)	Software D _p (cm)
5	0.288	0.287	20	0.338	0.334
6	0.318	0.293	21	0.325	0.339
7	0.308	0.293	22	0.263	0.347
8	0.323	0.300	23	0.282	0.349
9	0.348	0.306	24	0.323	0.350
10	0.33	0.308	25	0.325	0.351
11	0.263	0.310	26	0.32	0.353
12	0.313	0.315	27	0.292	0.357
13	0.277	0.316	28	0.32	0.358
14	0.348	0.317	29	0.265	0.364
15	0.315	0.319	30	0.3	0.368

For comparison purposes, Table II.a.2, shows the average diameters value and their standard deviation.

Table II.a.2. 2 - 3.6 mm pellet diameter data obtained.

	Manual D _p (cm)	Software D _p (cm)
Average (cm)	0.317±0.002	0.320
Standard deviation (cm)	0.028	0.031

The difference between the average diameter's values obtained is smaller than the data standard deviation. It can be said that the values obtained on both methods are similar. Note that the 0.002 value corresponds to the error related to the manual measurement.

This validation procedure was repeated for 3.6-5 mm pellets diameter range, the resulting data is shown in Table II.a.3.

Table II.a.3. 3.6 - 5 mm pellet diameter data obtained.

	Manual D _p (cm)	Software D _p (cm)
Average (cm)	0.425±0.002	0.416
Standard deviation (cm)	0.029	0.033

The data obtained in both methods, like in the previous analysis, shows high similarity. The difference between the methods is on the range of the standard deviation value.

To complete the validation, two samples one of each diameter range, subjected in an oven to four thermal cycles between 500 and 1000 °C with heating/cooling ramps of 10 °C/min and isothermal plateaus of six hours at each temperature, were measured. At this stage, it is known that the material suffers from sintering with thermal treatments and the objective of

this experimental work is to check if that effect is detected with the photographic method. The results included in Table II.a.4 and Table II.a.5 show, by comparison to the raw material data contained in Table II.a.2 and Table II.a.3, the detection of the expected reduction in the diameter values.

Table II.a.4. 2 - 3.6 mm heat treated pellet diameter data obtained.

	Manual	Software
	D_p (cm)	D_p (cm)
Average (cm)	0.309±0.002	0.288
Standard deviation (cm)	0.025	0.028

Table II.a.5. 3.6 - 5 mm heat treated pellet diameter data obtained.

	Manual	Software
	D_p (cm)	D_p (cm)
Average (cm)	0.410±0.002	0.398
Standard deviation (cm)	0.031	0.032

In view of the results obtained, the photographic method developed has turned to be a reliable alternative for the measurement of the pellets' diameter in an optimized work-time.

The binary conversion of the image is a key step in the photographic method to obtain good results. Figure II.a.5 shows a sample photograph and two binary images. Figure II.a.5 (b) is a binary image with an important lack of accuracy. In the right upper corner it is clear than the particles are not as big or round as in the sample photograph. Figure II.a.5 (c) shows a binary image of the same sample photograph with better accuracy. Accepting Figure II.a.5 (b) as good enough image would introduce error in the measured diameter, the corresponding values are shown in Table II.a.6

Figure II.a.5. (a) Sample photograph, (b) improvable binary image and, (c) accepted binary image.

Table II.a.6. Data error introduced by the binary conversion of the images.

	D_p (cm)	D_p (cm)	D_p (cm)
Average (cm)	0.410±0.002	0.376	0.398
Standard deviation (cm)	0.031	0.039	0.032

II.b X-Ray diffractograms for the hardness and density study of manganese oxide pellets

Figure II.b.1. Diffractograms of the 2-3,6 mm diameter sample treated at: (a) 120 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C, (f) 1000 °C, (g) 1200 °C and, (h) 1400 °C.

Figure II.b.2. Diffractograms of the 3,6-5 mm diameter sample treated at: (a) 120 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C, (f) 1000 °C, (g) 1200 °C and, (h) 1400 °C.

The data file of the crystalline phases found 98-010-0054, 98-000-4829 and 98-008-1762 are included next:

Reference code: 98-010-0054

Mineral name: Hausmannite
Compound name: Hausmannite
Chemical name: Manganese Dimanganese(III) Oxide
Common name: Hausmannite
ICSD name: Manganese Dimanganese(III) Oxide

Chemical formula: Mn_3O_4
Second chemical formula: Mn_3O_4

Crystallographic parameters

Crystal system: Tetragonal
Space group: I 41/a m d
Space group number: 141

a (Å): 5,7600
b (Å): 5,7600
c (Å): 9,4600
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 4,84
Measured density (g/cm³): 4,84
Volume of cell (10⁶ pm³): 313,86
Z: 4,00

RIR: 2,54

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Mineral
Quality: Calculated (C)

Comments

ICSD collection code: 109250
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Compound with mineral name:
Structures: CdMn₂O₄
Original ICSD space group: I41/AMDS
ICSD Collection Code: 109250

Original ICSD space group: I41/AMDS
Stable from 60 to 1443 K (2nd ref., Tomaszewski), above
Fd3-m, m.p.
1833 K
At least one temperature factor missing in the paper.
No R value given in the paper

X-ray diffraction from single crystal
Structure type: CdMn₂O₄

The structure has been assigned a PDF number (experimental powder diffraction data): 21-1152
 Compound with mineral name: Hausmannite
 Structure type: CdMn₂O₄
 Recording date: 4/1/2007
 Mineral origin: Langban, Sweden
 ANX formula: AB₂X₄
 Z: 4
 Authors density: 4.84
 Calculated density: 4.84
 Pearson code: tI28
 Wyckoff code: h d a
 PDF code: 00-021-1152
 TRANS Origin 0 3/4 5/8
 REMARK Transformed from non-centrosymmetric setting.
 Publ. title: Oxygen positional parameters of tetragonal Mn₃O₄

References

Primary reference: Satomi, K., *Golden Book of Phase Transitions, Wroclaw*, **1**, 1, (2002)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	1	1	4,91978	18,016	28,5
2	1	1	2	3,08638	28,905	39,9
3	0	2	0	2,88000	31,027	17,6
4	0	1	3	2,76597	32,340	80,9
5	1	2	1	2,48545	36,109	100,0
6	0	2	2	2,45989	36,498	14,9
7	0	0	4	2,36500	38,017	20,2
8	2	2	0	2,03647	44,451	20,8
9	1	2	3	1,99493	45,428	0,2
10	0	3	1	1,88164	48,331	0,0
11	0	2	4	1,82772	49,853	6,2
12	0	1	5	1,79751	50,749	25,7
13	1	3	2	1,69979	53,895	10,4
14	0	3	3	1,63993	56,032	7,8
15	2	3	1	1,57523	58,551	33,6
16	2	2	4	1,54319	59,889	59,0
17	1	2	5	1,52488	60,683	0,7
18	1	1	6	1,47034	63,187	2,7
19	1	3	4	1,44308	64,524	0,1
20	0	4	0	1,44000	64,678	20,1
21	2	3	3	1,42509	65,439	1,6
22	0	2	6	1,38298	67,695	3,6
23	1	4	1	1,38202	67,749	2,4
24	0	4	2	1,37758	67,997	0,1
25	0	3	5	1,34764	69,723	5,2
26	0	1	7	1,31570	71,672	0,1
27	3	3	2	1,30495	72,355	1,6
28	2	4	0	1,28798	73,464	1,3
29	1	4	3	1,27727	74,182	10,6
30	2	4	2	1,24273	76,610	5,3
31	0	4	4	1,22995	77,554	4,6
32	2	3	5	1,22061	78,259	1,4

33	1	2	7	1,19673	80,132	5,7
34	1	3	6	1,19210	80,507	3,0
35	0	0	8	1,18250	81,297	4,6
36	0	5	1	1,14355	84,691	0,6
37	2	4	4	1,13111	85,845	2,8
38	1	4	5	1,12384	86,537	7,7
39	0	3	7	1,10512	88,378	0,0
40	1	5	2	1,09873	89,028	2,2
41	0	2	8	1,09388	89,528	1,1

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,00000	0,21400	0,38400	0,5000	1,0000	16h
2	MN1	Mn	0,00000	0,25000	0,62500	0,5000	1,0000	8d
3	MN2	Mn	0,00000	0,00000	0,00000	0,5000	1,0000	4a

Stick Pattern

Reference code: 98-000-4829

Compound name: Manganese Oxide (5/8)
Chemical name: Manganese Oxide (5/8)
Common name: Manganese Oxide (5/8)
ICSD name: Manganese Oxide (5/8)

Chemical formula: Mn_5O_8
Second chemical formula: Mn_5O_8

Crystallographic parameters

Crystal system: Monoclinic
Space group: C 1 2/m 1
Space group number: 12

a (Å): 10,3470
b (Å): 5,7240
c (Å): 4,8520
Alpha (°): 90,0000
Beta (°): 109,4100
Gamma (°): 90,0000

Calculated density (g/cm³): 4,93
Measured density (g/cm³): 4,93
Volume of cell (10⁶ pm³): 271,03
Z: 2,00

RIR: 1,26

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Quality: Calculated (C)

Comments

ICSD collection code: 16956
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: The structure has been assigned a PDF number (calculated powder diffraction data):
Structures: Cd₂Mn₃O₈
Original ICSD space group: C12/M1
ICSD Collection Code: 16956

Original ICSD space group: C12/M1
X-ray diffraction from single crystal
Structure type : Cd₂Mn₃O₈
The structure has been assigned a PDF number (calculated powder diffraction data): 01-072-1427
Structure type: Cd₂Mn₃O₈
Recording date: 9/25/1986
ANX formula: A₂B₃X₈

Z: 2
 Authors density: 4.93
 Calculated density: 4.93
 R value: 0.078
 Pearson code: mS26
 Wyckoff code: j i3 g c
 TRANS Origin 0 0 1/2
 Publ. title: Die Kristallstrukturen von Mn5 O8 und Cd2 Mn3 O8

References

Primary reference: Wampetich, M.J. Oswald, H.R., *Helvetica Chimica Acta*, **50**, 2023, (1967)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	1	1	0	4,93737	17,951	24,2
2	2	0	0	4,87946	18,166	70,4
3	0	0	1	4,57623	19,381	0,0
4	2	0	-1	4,08295	21,749	36,1
5	1	1	-1	3,67882	24,173	7,4
6	1	1	1	3,10602	28,719	100,0
7	2	0	1	2,89258	30,889	25,6
8	0	2	0	2,86200	31,227	5,1
9	3	1	0	2,82817	31,610	27,7
10	3	1	-1	2,79372	32,011	75,7
11	4	0	-1	2,53004	35,451	2,7
12	2	2	0	2,46868	36,363	53,3
13	4	0	0	2,43973	36,810	23,9
14	0	2	-1	2,42653	37,017	25,4
15	2	0	-2	2,40095	37,426	17,7
16	2	2	-1	2,34358	38,378	49,2
17	0	0	2	2,28812	39,346	20,7
18	1	1	-2	2,22354	40,538	3,8
19	3	1	1	2,14461	42,100	0,3
20	3	1	-2	2,10013	43,035	15,4
21	4	0	-2	2,04148	44,336	0,5
22	2	2	1	2,03446	44,497	0,3
23	1	1	2	1,95444	46,423	21,0
24	5	1	-1	1,93760	46,851	1,6
25	4	0	1	1,90594	47,677	1,2
26	4	2	-1	1,89556	47,954	68,3
27	1	3	0	1,87255	48,581	2,3
28	4	2	0	1,85667	49,024	1,1
29	2	0	2	1,84889	49,244	35,1
30	5	1	0	1,84734	49,288	21,4
31	2	2	-2	1,83941	49,515	0,5
32	0	2	2	1,78717	51,064	5,1
33	1	3	-1	1,77315	51,497	3,4
34	5	1	-2	1,72722	52,972	0,1
35	6	0	-1	1,72398	53,079	0,4
36	1	3	1	1,69559	54,039	5,3
37	4	2	-2	1,66199	55,224	10,6
38	3	3	0	1,64579	55,815	8,5
39	3	3	-1	1,63892	56,069	9,9
40	6	0	0	1,62649	56,536	0,1
41	2	0	-3	1,61698	56,899	0,6
42	6	0	-2	1,60043	57,542	18,2

43	4	2	1	1,58636	58,100	34,5
44	3	1	2	1,57072	58,735	0,8
45	2	2	2	1,55301	59,472	2,3
46	5	1	1	1,55195	59,517	3,3
47	4	0	-3	1,54456	59,830	3,7
48	3	1	-3	1,54150	59,961	0,3
49	1	1	-3	1,53189	60,377	1,6
50	0	0	3	1,52541	60,660	5,7
51	1	3	-2	1,49666	61,952	0,0
52	6	2	-1	1,47676	62,881	14,4
53	3	3	1	1,47188	63,114	0,8
54	3	3	-2	1,45726	63,821	8,3
55	4	0	2	1,44629	64,363	5,4
56	0	4	0	1,43100	65,135	26,2
57	7	1	-1	1,43062	65,155	24,5
58	5	1	-3	1,41486	65,972	6,6
59	6	2	0	1,41409	66,013	6,7
60	2	2	-3	1,40782	66,344	35,3
61	1	3	2	1,40586	66,449	9,1
62	5	3	-1	1,39955	66,788	0,9
63	6	2	-2	1,39686	66,933	0,4
64	6	0	1	1,39339	67,122	5,1
65	1	1	3	1,39289	67,150	4,9
66	7	1	-2	1,37663	68,050	1,0
67	2	4	0	1,37317	68,245	1,6
68	0	4	-1	1,36578	68,666	0,0
69	5	3	0	1,36438	68,746	0,2
70	6	0	-3	1,36098	68,942	0,4
71	4	2	-3	1,35925	69,042	2,4
72	7	1	0	1,35453	69,317	2,5
73	2	4	-1	1,35046	69,556	1,5
74	0	2	3	1,34614	69,811	1,2
75	2	0	3	1,33505	70,477	0,1
76	5	3	-2	1,31378	71,793	0,1
77	4	2	2	1,29083	73,275	1,3
78	8	0	-1	1,29024	73,313	1,4
79	2	4	1	1,28263	73,821	2,5
80	8	0	-2	1,26502	75,023	1,8
81	5	1	2	1,25703	75,583	4,4
82	6	2	1	1,25280	75,884	3,5
83	4	4	-1	1,24557	76,403	0,2
84	3	3	2	1,24083	76,748	0,1
85	4	4	0	1,23434	77,226	4,6
86	5	3	1	1,23151	77,436	0,8
87	2	4	-2	1,22923	77,607	7,5
88	6	2	-3	1,22909	77,618	7,9
89	7	1	-3	1,22882	77,638	6,5
90	3	3	-3	1,22627	77,830	0,0
91	1	3	-3	1,22142	78,198	0,5
92	8	0	0	1,21987	78,316	4,2
93	0	4	-2	1,21326	78,825	2,7
94	2	2	3	1,20989	79,088	4,7
95	2	0	-4	1,20652	79,352	1,0
96	3	1	3	1,20497	79,475	0,1
97	4	0	-4	1,20047	79,832	1,7
98	7	1	1	1,19783	80,043	0,4
99	3	1	-4	1,18641	80,973	0,4
100	8	2	-1	1,17624	81,822	0,3
101	4	4	-2	1,17179	82,199	0,0
102	7	3	-1	1,16820	82,507	2,3
103	5	3	-3	1,15957	83,257	1,1

104	8	0	-3	1,15889	83,317	1,9
105	1	1	-4	1,15817	83,380	2,6
106	8	2	-2	1,15704	83,480	3,1
107	6	0	2	1,15655	83,523	1,9
108	5	1	-4	1,14754	84,329	2,8
109	1	3	3	1,14738	84,343	2,8
110	4	4	1	1,14435	84,618	0,4
111	0	0	4	1,14406	84,645	0,3
112	7	3	-2	1,13824	85,180	0,7
113	1	5	0	1,13700	85,294	0,1
114	4	0	3	1,13493	85,487	0,8
115	2	4	2	1,13164	85,795	6,9
116	6	0	-4	1,12878	86,066	2,8
117	7	3	0	1,12566	86,363	2,1
118	8	2	0	1,12218	86,696	0,0
119	9	1	-1	1,12166	86,747	0,1
120	9	1	-2	1,11515	87,381	0,3
121	1	5	-1	1,11359	87,534	0,0
122	2	2	-4	1,11177	87,714	0,1
123	4	2	-4	1,10703	88,186	0,7
124	6	4	-1	1,10110	88,786	0,1
125	1	5	1	1,09359	89,558	3,6
126	8	0	1	1,09185	89,739	0,1

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,61100	0,00000	0,92500	1,4000	1,0000	4i
2	O2	O	0,09300	0,00000	0,90500	1,4000	1,0000	4i
3	O3	O	0,09800	0,23400	0,39400	1,4000	1,0000	8j
4	MN1	Mn	0,73000	0,00000	0,66200	1,2000	1,0000	4i
5	MN2	Mn	0,00000	0,26200	0,00000	1,1000	1,0000	4g
6	MN3	Mn	0,00000	0,00000	0,50000	1,1000	1,0000	2c

Stick Pattern

Reference code: 98-008-1762

Mineral name: Bixbyite C
Compound name: Bixbyite C
Chemical name: Manganese(III) Oxide - Beta
Common name: Bixbyite C
ICSD name: Manganese(III) Oxide - Beta

Chemical formula: Mn_2O_3
Second chemical formula: Mn_2O_3

Crystallographic parameters

Crystal system: Cubic
Space group: $I a \bar{3}$
Space group number: 206

a (Å): 9,4100
b (Å): 9,4100
c (Å): 9,4100
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 5,03
Measured density (g/cm³): 4,72
Volume of cell (10⁶ pm³): 833,24
Z: 16,00

RIR: 5,25

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Mineral
Quality: Calculated (C)

Comments

ICSD collection code: 52348
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Compound with mineral name:
Structures: Mn_2O_3
Original ICSD space group: $IA\bar{3}$ -
ICSD Collection Code: 52348

Original ICSD space group: $IA\bar{3}$ -
Standardized by Structure Tidy
Alias type names: Yb₂S₃ (theta), Mg₃P₂, bixbyite,
sesquisulfide T;
SB:D5(3)
AE: Mn1: 6o O6; Mn2: deformed 6o O6; O: 4t Mn4
Cell of Sc₂ O₃: 9.79, of Y₂ O₃: 10.60, of In₂ O₃: 10.12, of
Ti₂ O₃:

10.57, of Sm₂ O₃: 10.85 to Lu₂ O₃: 10.37
Tetragonal bixbyite, (Mn, Fe)₂ O₃ has a= 9.50, c= 18.93
At least one temperature factor missing in the paper.
No R value given in the paper.
Unusual difference between calculated and measured density
X-ray diffraction (powder)
Structure type : Mn₂O₃
Structure type prototype : Mn₂O₃
The structure has been assigned a PDF number (experimental powder diffraction data): 41-1442
The structure has been assigned a PDF number (calculated powder diffraction data): 01-071-3820
Compound with mineral name: Bixbyite C
Structure type: Mn₂O₃
Recording date: 4/1/2003
Modification date: 2/1/2009
Mineral origin: natural
ANX formula: A₂X₃
Z: 16
Authors density: 4.72
Calculated density: 5.03
Pearson code: cI80
Wyckoff code: e d a
PDF code: 00-041-1442
Publ. title: Lattice dimensions and space group of braunite

References

Primary reference: Aminoff, G., *Kunglia Svenska Vetenskaps Akademiens Handlingar*, **9**, 14, (1931)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	0	2	4,70500	18,846	0,3
2	1	1	2	3,84162	23,134	16,5
3	0	2	2	3,32694	26,775	0,0
4	2	2	2	2,71643	32,947	100,0
5	1	2	3	2,51493	35,672	0,2
6	0	0	4	2,35250	38,227	14,3
7	1	1	4	2,21796	40,645	3,4
8	0	2	4	2,10414	42,949	0,7
9	2	3	3	2,00622	45,158	6,9
10	2	2	4	1,92081	47,285	0,6
11	1	3	4	1,84545	49,342	6,8
12	1	2	5	1,71802	53,278	1,4
13	0	4	4	1,66347	55,171	46,2
14	3	3	4	1,61380	57,021	1,4
15	0	0	6	1,56833	58,833	0,2
16	1	1	6	1,52650	60,612	3,7
17	0	2	6	1,48785	62,360	0,6
18	1	4	5	1,45199	64,080	3,0
19	2	2	6	1,41861	65,776	22,8
20	1	3	6	1,38743	67,449	5,4
21	4	4	4	1,35822	69,102	2,4
22	3	4	5	1,33077	70,737	1,1
23	0	4	6	1,30493	72,356	0,7

24	1	2	7	1,28054	73,961	2,6
25	2	4	6	1,25746	75,553	0,8
26	1	5	6	1,19507	80,266	1,6
27	0	0	8	1,17625	81,821	4,6
28	1	1	8	1,15829	83,369	2,3
29	0	2	8	1,14113	84,913	1,0
30	3	5	6	1,12471	86,454	1,1
31	0	6	6	1,10898	87,991	0,7
32	1	3	8	1,09389	89,527	2,1

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,10500	0,36500	0,13000	0,5000	1,0000	48e
2	MN1	Mn	0,28000	0,00000	0,25000	0,5000	1,0000	24d
3	MN2	Mn	0,00000	0,00000	0,00000	0,5000	1,0000	8a

Stick Pattern

II.c Complementary morphology study for manganese oxide 3.6 - 5 mm pellets for the hardness and density study

The micrograph shown in Figure II.c.1 corresponds to the manganese oxide pellet surface from the big diameter range. It shows a non-homogeneous surface, as it was observed in the power material (Figure 4.15) and in the small diameter range manganese oxide pellet surface (Figure 4.24), there is no clear geometry and the particles seem to be heterogeneous in form and in size.

Figure II.c.1. SEM micrograph of the pelletized manganese oxide in reception conditions.

Figure II.c.2 shows the morphology variation of the samples with the heat treatments, up to 800°C there is no a clear structure definition, as is appreciable in Figure II.c.2 (f). Micrographs shown in Figure II.c.2 (g) and (h), show really big particles, some porous and grain separations due to sintering process. This would explain the hardness results obtained.

Several pellets of each thermal treatment sample were broken to analyse the pellet internal morphology; results are included in Figure II.c.3.

The morphology observed in the interior of the pellets agrees with the surface's one. The only remarkable difference is the presence of gaseous bubbles, presumably formed during the shaping process.

Figure II.c.2. SEM micrographs of manganese oxide pellets surfaces subjected to different temperatures thermal treatments: (a) 120 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C, (f) 1000 °C, (g) 1200 °C, (h) 1400 °C.

Figure II.c.3. SEM micrographs of manganese oxide pellets internal surfaces subjected to different temperatures thermal treatments: (a) 120 $^{\circ}$ C, (b) 200 $^{\circ}$ C, (c) 400 $^{\circ}$ C, (d) 600 $^{\circ}$ C, (e) 800 $^{\circ}$ C, (f) 1000 $^{\circ}$ C, (g) 1200 $^{\circ}$ C, (h) 1400 $^{\circ}$ C.

II.d X-Ray diffractograms for the cycle thermal treatment study of manganese oxide pellets

Figure II.d.1. Diffractograms of the 2-3,6 mm diameter sample: (a) calcined at 700 °C, (b) subjected to 10 thermal cycles, (c) subjected to 20 thermal cycles, (d) subjected to 30 thermal cycles, (e) subjected to 40 thermal cycles and, (f) subjected to 50 thermal cycles.

The data file of the crystalline phases 98-010-0054 and 98-008-1762 were already included in X-Ray diffractograms for the hardness and density study of manganese oxide pellets

II.e X-Ray diffractograms for the hardness and density study of manganese oxide doped with iron pellets

Figure II.e.1. Diffractograms of the 2-3,6 mm diameter sample treated at: (a) 120 °C, (b) 200 °C, (c) 400 °C, (d) 600 °C, (e) 800 °C, (f) 1000 °C, (g) 1200 °C and, (h) 1400 °C.

The data file of the crystalline phases found 98-002-8708, 98-008-9971, 98-003-5156, 98-010-6539, 98-000-2391 and 98-001-7918 are included next:

Reference code: 98-002-8708

Mineral name: Hausmannite
Compound name: Hausmannite
Chemical name: Dimanganese(III) Manganese Oxide
Common name: Hausmannite
ICSD name: Dimanganese(III) Manganese Oxide

Chemical formula: Mn_3O_4
Second chemical formula: Mn_3O_4

Crystallographic parameters

Crystal system: Tetragonal
Space group: I 41/a m d
Space group number: 141

a (Å): 5,7650
b (Å): 5,7650
c (Å): 9,4420
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 4,84
Volume of cell (10⁶ pm³): 313,81
Z: 4,00

RIR: 2,64

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Mineral
Quality: Calculated (C)

Comments

ICSD collection code: 68174
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Compound with mineral name:
Structures: CdMn₂O₄
Original ICSD space group: I41/AMDZ
ICSD Collection Code: 68174

Original ICSD space group: I41/AMDZ
Stable from 60 to 1443 K (3rd ref., Tomaszewski), above Fd3-
m, m.p 1833 K
F-cell from 2nd reference: 8.15(3), 9.45(3), at 1473 K cubic: 8.68(3)
Contains 1.3 wt% FeO, .7 wt% ZnO, .5 wt% MgO

X-ray diffraction from single crystal
 Structure type : CdMn₂O₄
 The structure has been assigned a PDF number (experimental powder diffraction data): 24-734
 The structure has been assigned a PDF number (calculated powder diffraction data): 01-080-0382
 Compound with mineral name: Hausmannite
 Structure type: CdMn₂O₄
 Recording date: 7/10/1991
 Modification date: 10/1/2005
 Mineral origin: Langban, Sweden
 ANX formula: AB₂X₄
 Z: 4
 Calculated density: 4.84
 R value: 0.036
 Pearson code: tI28
 Wyckoff code: h d a
 PDF code: 00-024-0734
 TRANS Origin 0 0 1/2
 Publ. title: Crystal structure refinement and reflectance measurements of hausmannite, Mn₃ O₄

References

Primary reference: Jarosch, D., *Golden Book of Phase Transitions, Wroclaw*, **1**, 1, (2002)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	1	1	4,92035	18,014	24,2
2	1	1	2	3,08541	28,915	36,6
3	0	2	0	2,88250	30,999	16,5
4	0	1	3	2,76247	32,383	78,4
5	1	2	1	2,48713	36,084	100,0
6	0	2	2	2,46018	36,493	14,3
7	0	0	4	2,36050	38,092	18,4
8	2	2	0	2,03824	44,410	23,1
9	1	2	3	1,99444	45,439	0,3
10	0	3	1	1,88306	48,293	0,0
11	0	2	4	1,82628	49,895	6,5
12	0	1	5	1,79458	50,838	24,2
13	1	3	2	1,70066	53,865	10,2
14	0	3	3	1,64012	56,025	8,8
15	2	3	1	1,57648	58,500	31,3
16	2	2	4	1,54271	59,910	55,7
17	1	2	5	1,52345	60,746	0,8
18	1	1	6	1,46807	63,296	2,6
19	1	3	4	1,44284	64,536	5,3
20	0	4	0	1,44125	64,615	20,8
21	2	3	3	1,42552	65,417	1,2
22	1	4	1	1,38313	67,687	1,2
23	0	2	6	1,38123	67,792	3,1
24	0	4	2	1,37845	67,948	0,0
25	0	3	5	1,34691	69,766	5,5
26	0	1	7	1,31339	71,818	0,1

27	3	3	2	1,30581	72,300	1,6
28	2	4	0	1,28909	73,390	1,6
29	1	4	3	1,27780	74,146	10,5
30	2	4	2	1,24357	76,549	4,9
31	0	4	4	1,23009	77,543	5,0
32	2	3	5	1,22026	78,286	1,3
33	1	2	7	1,19517	80,258	6,0
34	1	3	6	1,19124	80,577	2,8
35	0	0	8	1,18025	81,485	4,6
36	3	4	1	1,14450	84,605	0,6
37	2	4	4	1,13138	85,820	2,4
38	1	4	5	1,12372	86,549	7,6
39	0	3	7	1,10403	88,488	0,0
40	1	5	2	1,09952	88,947	2,1
41	0	2	8	1,09224	89,699	1,0

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,00000	0,47220	0,25890	0,5000	1,0000	16h
2	MN1	Mn	0,00000	0,50000	0,50000	0,5000	1,0000	8d
3	MN2	Mn	0,00000	0,25000	0,87500	0,5000	1,0000	4a

Stick Pattern

Reference code: 98-008-9971

Compound name: Manganese Dimanganese(III) Oxide
Chemical name: Manganese Dimanganese(III) Oxide
Common name: Manganese Dimanganese(III) Oxide
ICSD name: Manganese Dimanganese(III) Oxide

Chemical formula: Mn_3O_4
Second chemical formula: Mn_3O_4

Crystallographic parameters

Crystal system: Tetragonal
Space group: I 41/a m d
Space group number: 141

a (Å): 8,1600
b (Å): 8,1600
c (Å): 9,4400
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 2,42
Volume of cell (10⁶ pm³): 628,57
Z: 4,00

RIR: 4,04

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Quality: Calculated (C)

Comments

ICSD collection code: 643198
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Metals structure type
Structures: NiCr2O4
Original ICSD space group: I41/AMDS
ICSD Collection Code: 643198

Original ICSD space group: I41/AMDS
At least one temperature factor missing in the paper.
No R value given in the paper

X-ray diffraction from single crystal

Structure type: NiCr2O4
Metals structure type Mn3 O4
Structure type: NiCr2O4
Recording date: 7/7/2008
Modification date: 8/1/2009
ANX formula: AB2X4
Z: 4

Calculated density: 2.42
 Pearson code: tI28
 Wyckoff code: h d a
 TRANS Origin 0 3/4 5/8
 REMARK Transformed from non-centrosymmetric setting.
 Publ. title: Ueber die Kristallstruktur von Hausmannit (Mn Mn2 O4).

References

Primary reference:

Aminoff, G., *Zeitschrift fuer Kristallographie, Kristallgeometrie, Kristallphysik, Kristallchemie* (-144,1977), **64**, 475, (1926)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	1	1	6,17332	14,336	5,6
2	0	2	0	4,08000	21,765	12,7
3	1	1	2	3,65336	24,344	18,0
4	1	2	1	3,40378	26,159	100,0
5	0	2	2	3,08666	28,903	7,6
6	0	1	3	2,93594	30,421	21,9
7	2	2	0	2,88500	30,972	24,7
8	0	3	1	2,61367	34,282	1,9
9	1	2	3	2,38307	37,718	0,4
10	0	0	4	2,36000	38,101	5,8
11	1	3	2	2,26415	39,780	9,5
12	2	3	1	2,20081	40,975	21,0
13	0	3	3	2,05777	43,967	9,8
14	0	2	4	2,04286	44,304	13,5
15	0	4	0	2,04000	44,370	28,2
16	1	4	1	1,93698	46,867	0,5
17	0	4	2	1,87258	48,580	0,0
18	0	1	5	1,83941	49,515	8,4
19	2	3	3	1,83732	49,575	3,5
20	2	2	4	1,82668	49,883	35,5
21	2	4	0	1,82463	49,943	17,4
22	3	3	2	1,78113	51,250	2,4
23	1	3	4	1,74149	52,504	0,0
24	2	4	2	1,70189	53,823	3,5
25	1	2	5	1,67687	54,693	4,6
26	1	4	3	1,67529	54,749	7,8
27	0	5	1	1,60814	57,240	0,7
28	0	3	5	1,55098	59,558	5,3
29	0	4	4	1,54333	59,883	4,3
30	1	1	6	1,51792	60,991	1,4
31	1	5	2	1,51557	61,096	2,1
32	2	5	1	1,49612	61,977	7,9
33	0	2	6	1,46797	63,301	1,3
34	2	3	5	1,44977	64,190	4,0
35	0	5	3	1,44874	64,241	7,4
36	2	4	4	1,44351	64,502	5,6
37	4	4	0	1,44250	64,553	7,8
38	1	4	5	1,36609	68,648	5,3
39	2	5	3	1,36523	68,697	3,0
40	0	6	0	1,36000	68,999	0,4
41	1	3	6	1,34333	69,979	1,4
42	3	5	2	1,34170	70,076	1,5
43	0	1	7	1,33052	70,753	0,0
44	1	6	1	1,32815	70,898	4,3
45	1	5	4	1,32451	71,123	0,0

46	0	6	2	1,30683	72,235	0,8
47	2	6	0	1,29021	73,316	2,0
48	1	2	7	1,26496	75,028	2,2
49	4	5	1	1,26292	75,170	0,0
50	0	4	6	1,24585	76,383	0,0
51	2	6	2	1,24455	76,477	0,0
52	0	5	5	1,23466	77,202	5,6
53	1	6	3	1,23403	77,249	3,1
54	4	4	4	1,23079	77,490	1,5
55	3	3	6	1,21779	78,476	0,3
56	0	3	7	1,20822	79,218	0,0
57	3	6	1	1,20645	79,358	2,4
58	3	5	4	1,20371	79,574	0,0
59	2	4	6	1,19154	80,553	1,4
60	2	5	5	1,18174	81,360	1,3
61	4	5	3	1,18119	81,406	2,0
62	0	0	8	1,18000	81,506	1,6
63	0	6	4	1,17834	81,644	0,4
64	2	3	7	1,15849	83,352	1,4
65	0	7	1	1,15693	83,490	0,1
66	3	6	3	1,13459	85,519	0,1
67	0	2	8	1,13354	85,617	0,3
68	2	6	4	1,13208	85,755	10,3
69	4	6	0	1,13159	85,801	6,2
70	1	5	6	1,12193	86,721	1,0
71	1	7	2	1,12098	86,812	1,2
72	1	4	7	1,11444	87,450	0,0
73	2	7	1	1,11304	87,588	1,4
74	4	6	2	1,10041	88,856	0,9
75	1	6	5	1,09355	89,562	0,8
76	0	7	3	1,09312	89,608	1,2
77	2	2	8	1,09218	89,706	1,0

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,00000	0,26500	0,39000	0,5000	1,0000	16h
2	MN1	Mn	0,00000	0,25000	0,62500	0,5000	1,0000	8d
3	MN2	Mn	0,00000	0,00000	0,00000	0,5000	1,0000	4a

Stick Pattern

Reference code: 98-003-5156

Mineral name: Pyrolusite
Compound name: Pyrolusite
Chemical name: Manganese(IV) Oxide - Beta
Common name: Pyrolusite
ICSD name: Manganese(IV) Oxide - Beta

Chemical formula: Mn_2O_3
Second chemical formula: MnO_2

Crystallographic parameters

Crystal system: Tetragonal
Space group: P 42/m n m
Space group number: 136

a (Å): 4,4040
b (Å): 4,4040
c (Å): 2,8770
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 5,17
Measured density (g/cm³): 5,10
Volume of cell (10⁶ pm³): 55,80
Z: 2,00

RIR: 4,05

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Mineral
Quality: Calculated (C)

Comments

ICSD collection code: 73716
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Compound with mineral name:
Structures: TiO₂(tP6)
Original ICSD space group: P42/MNM
ICSD Collection Code: 73716

Original ICSD space group: P42/MNM
Structure type : TiO₂(tP6)
Rietveld profile refinement applied
The structure has been assigned a PDF number (experimental powder diffraction data): 24-735
The structure has been assigned a PDF number (calculated powder

diffraction data): 01-081-2261
 Neutron diffraction (powder)
 Compound with mineral name: Pyrolusite
 Structure type: TiO₂(tP6)
 Recording date: 1/10/1995
 Modification date: 10/1/2005
 Mineral origin: synthetic
 ANX formula: AX₂
 Z: 2
 Authors density: 5.1
 Calculated density: 5.17
 R value: 0.017
 Pearson code: tP6
 Wyckoff code: f a
 PDF code: 00-024-0735
 Publ. title: Powder neutron diffraction study of pyrolusite,
 beta-Mn
 O₂

References

Primary reference: Howard, C.J. Kennedy, B.J. Fong, C. Bolzan, A.A., *Australian Journal of Chemistry*, **46**, 939, (1993)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	1	1	0	3,11410	28,643	100,0
2	0	1	1	2,40860	37,303	56,4
3	0	2	0	2,20200	40,952	9,9
4	1	1	1	2,11320	42,756	14,8
5	1	2	0	1,96953	46,047	4,7
6	1	2	1	1,62519	56,585	57,9
7	2	2	0	1,55705	59,302	15,4
8	0	0	2	1,43850	64,754	8,1
9	1	3	0	1,39267	67,161	8,8
10	2	2	1	1,36936	68,461	0,4
11	0	3	1	1,30761	72,185	19,9
12	1	1	2	1,30590	72,294	12,2
13	1	3	1	1,25352	75,832	0,8
14	2	3	0	1,22145	78,195	0,2
15	0	2	2	1,20430	79,528	3,1
16	1	2	2	1,16165	83,075	0,9
17	2	3	1	1,12432	86,491	5,6
18	0	4	0	1,10100	88,796	2,9

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,30460	0,30460	0,00000	0,5000	1,0000	4f
2	MN1	Mn	0,00000	0,00000	0,00000	0,5000	1,0000	2a

Stick Pattern

Reference code: 98-010-6539

Mineral name: Bixbyite
Compound name: Bixbyite
Chemical name: Iron(III) Manganese(III) Oxide (0.84/1.16/3)
Common name: Bixbyite
ICSD name: Iron(III) Manganese(III) Oxide (0.84/1.16/3)

Chemical formula: $\text{Fe}_{0.84}\text{Mn}_{1.16}\text{O}_3$
Second chemical formula: $(\text{Fe}_{0.42}\text{Mn}_{0.58})_2\text{O}_3$

Crystallographic parameters

Crystal system: Cubic
Space group: $I a \bar{3}$
Space group number: 206

a (Å): 9,4090
b (Å): 9,4090
c (Å): 9,4090
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 5,06
Volume of cell (10⁶ pm³): 832,97
Z: 16,00

RIR: 5,23

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Mineral
Quality: Calculated (C)

Comments

ICSD collection code: 154347
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Compound with mineral name:
Structures: Mn₂O₃
Original ICSD space group: $IA\bar{3}$ -
ICSD Collection Code: 154347

Original ICSD space group: $IA\bar{3}$ -
X-ray diffraction from single crystal
Structure type : Mn₂O₃
Compound with mineral name: Bixbyite
Structure type: Mn₂O₃
Recording date: 4/1/2007
Mineral origin: Mt Tomas, Utah, USA
ANX formula: A₂X₃
Z: 16

Calculated density: 5.06
R value: 0.0263
Pearson code: cI80
Wyckoff code: e d a
Publ. title: Structure change of Mn₂ O₃ under high pressure and pressure-induced transition

References

Primary reference: Fukuda, T. Okada, T. Nagai, T. Yamanaka, T., *Zeitschrift fuer Kristallographie (149,1979-)*, **220**, 938, (2005)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	0	2	4,70450	18,848	0,7
2	1	1	2	3,84121	23,137	15,5
3	0	2	2	3,32658	26,778	0,1
4	2	2	2	2,71614	32,950	100,0
5	1	2	3	2,51466	35,676	0,9
6	0	0	4	2,35225	38,231	16,6
7	1	1	4	2,21772	40,649	2,2
8	0	2	4	2,10392	42,954	1,1
9	2	3	3	2,00601	45,163	9,2
10	2	2	4	1,92060	47,290	1,3
11	1	3	4	1,84526	49,347	10,4
12	1	2	5	1,71784	53,284	3,1
13	0	4	4	1,66329	55,177	37,6
14	3	3	4	1,61363	57,028	1,7
15	0	0	6	1,56817	58,840	0,5
16	1	1	6	1,52634	60,619	4,3
17	0	2	6	1,48769	62,367	1,1
18	1	4	5	1,45184	64,088	5,7
19	2	2	6	1,41846	65,784	18,4
20	1	3	6	1,38728	67,457	4,9
21	4	4	4	1,35807	69,111	2,6
22	3	4	5	1,33063	70,746	1,0
23	0	4	6	1,30479	72,365	1,3
24	1	2	7	1,28040	73,970	2,8
25	2	4	6	1,25733	75,562	1,2
26	1	5	6	1,19494	80,276	1,3
27	0	0	8	1,17613	81,831	2,7
28	1	1	8	1,15817	83,380	2,9
29	0	2	8	1,14101	84,924	1,6
30	3	5	6	1,12459	86,465	1,8
31	0	6	6	1,10886	88,003	1,1
32	1	3	8	1,09377	89,539	1,8

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,13470	0,14030	0,91170	0,8100	1,0000	48e
2	MN1	Mn	0,28490	0,00000	0,25000	0,6500	0,5800	24d
3	FE1	Fe	0,28490	0,00000	0,25000	0,6500	0,4200	24d
4	MN2	Mn	0,00000	0,00000	0,00000	0,6900	0,5800	8a
5	FE2	Fe	0,00000	0,00000	0,00000	0,6900	0,4200	8a

Stick Pattern

Reference code: 98-000-2391

Compound name: Manganese(III) Iron(III) Oxide (0.7/1.3/3)
Chemical name: Manganese(III) Iron(III) Oxide (0.7/1.3/3)
Common name: Manganese(III) Iron(III) Oxide (0.7/1.3/3)
ICSD name: Manganese(III) Iron(III) Oxide (0.7/1.3/3)

Chemical formula: $\text{Fe}_{1.26}\text{Mn}_{0.74}\text{O}_3$
Second chemical formula: $(\text{Mn}_{.37}\text{Fe}_{.63})_2\text{O}_3$

Crystallographic parameters

Crystal system: Cubic
Space group: $I a \bar{3}$
Space group number: 206

a (Å): 9,4130
b (Å): 9,4130
c (Å): 9,4130
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 5,06
Volume of cell (10⁶ pm³): 834,03
Z: 16,00

RIR: 4,95

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Quality: Calculated (C)

Comments

ICSD collection code: 9092
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: The structure has been assigned a PDF number (calculated powder diffraction data):
Structures: Mn₂O₃
Original ICSD space group: $IA\bar{3}$ -
ICSD Collection Code: 9092

Original ICSD space group: $IA\bar{3}$ -
X-ray diffraction from single crystal
Structure type : Mn₂O₃
The structure has been assigned a PDF number (calculated powder diffraction data): 01-071-0637
Structure type: Mn₂O₃
Recording date: 1/1/1980
ANX formula: A₂X₃
Z: 16

Calculated density: 5.06
R value: 0.027
Pearson code: cI80
Wyckoff code: e d a
Publ. title: Structures of alpha-(Mn₂ O₃), (Mn_{0.983} Fe_{0.017})₂ O₃,
(Mn_{0.37} Fe_{0.63})₂ O₃ and Relation to Magnetic Ordering

References

Primary reference: Geller, S., *Acta Crystallographica B* (24,1968-38,1982), **27**, 821, (1971)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	0	2	4,70650	18,840	0,8
2	1	1	2	3,84284	23,127	15,4
3	0	2	2	3,32800	26,766	0,1
4	2	2	2	2,71730	32,936	100,0
5	1	2	3	2,51573	35,660	0,9
6	0	0	4	2,35325	38,214	16,9
7	1	1	4	2,21867	40,631	2,6
8	0	2	4	2,10481	42,935	1,2
9	2	3	3	2,00686	45,143	9,6
10	2	2	4	1,92142	47,269	1,3
11	1	3	4	1,84604	49,325	11,2
12	1	2	5	1,71857	53,259	3,5
13	0	4	4	1,66400	55,152	41,6
14	3	3	4	1,61432	57,001	1,8
15	0	0	6	1,56883	58,813	0,6
16	1	1	6	1,52699	60,591	4,5
17	0	2	6	1,48833	62,338	1,2
18	1	4	5	1,45246	64,057	6,1
19	2	2	6	1,41906	65,752	20,5
20	1	3	6	1,38787	67,425	5,5
21	4	4	4	1,35865	69,077	3,0
22	3	4	5	1,33120	70,711	1,0
23	0	4	6	1,30535	72,330	1,4
24	1	2	7	1,28095	73,934	3,3
25	2	4	6	1,25786	75,525	1,3
26	1	5	6	1,19545	80,235	1,3
27	0	0	8	1,17663	81,789	3,3
28	1	1	8	1,15866	83,337	2,8
29	4	4	6	1,14149	84,880	1,9
30	3	5	6	1,12507	86,419	1,8
31	0	6	6	1,10933	87,956	1,1
32	1	3	8	1,09424	89,491	2,0

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,13527	0,13950	0,91170	0,5000	1,0000	48e
2	MN1	Mn	0,28473	0,00000	0,25000	0,5000	0,3700	24d
3	MN2	Mn	0,00000	0,00000	0,00000	0,5000	0,3700	8a
4	FE1	Fe	0,28473	0,00000	0,25000	0,5000	0,6300	24d
5	FE2	Fe	0,00000	0,00000	0,00000	0,5000	0,6300	8a

Stick Pattern

Reference code: 98-001-7918

Mineral name: Hausmannite
Compound name: Hausmannite
Chemical name: Manganese Dimanganese(III) Oxide
Common name: Hausmannite
ICSD name: Manganese Dimanganese(III) Oxide

Chemical formula: Mn_3O_4
Second chemical formula: Mn_3O_4

Crystallographic parameters

Crystal system: Tetragonal
Space group: I 41/a m d
Space group number: 141

a (Å): 5,7620
b (Å): 5,7620
c (Å): 9,4390
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm³): 4,85
Measured density (g/cm³): 4,84
Volume of cell (10⁶ pm³): 313,38
Z: 4,00

RIR: 3,00

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Mineral
Quality: Calculated (C)

Comments

ICSD collection code: 31094
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Compound with mineral name:
Structures: CdMn₂O₄
Original ICSD space group: I41/AMDS
ICSD Collection Code: 31094

Original ICSD space group: I41/AMDS
Stable from 60 to 1443 K (2nd ref., Tomaszewski), above
Fd3-m, m.p.
1833 K
At least one temperature factor missing in the paper.
No R value given in the paper

X-ray diffraction from single crystal

Structure type: CdMn₂O₄
 The structure has been assigned a PDF number (experimental powder diffraction data): 21-1152
 The structure has been assigned a PDF number (calculated powder diffraction data): 01-075-1560
 Compound with mineral name: Hausmannite
 Structure type: CdMn₂O₄
 Recording date: 1/1/1980
 Modification date: 10/1/2005
 Mineral origin: Langban, Sweden
 ANX formula: AB₂X₄
 Z: 4
 Authors density: 4.84
 Calculated density: 4.85
 Pearson code: tI28
 Wyckoff code: h d a
 PDF code: 00-021-1152
 TRANS Origin 0 3/4 5/8
 REMARK Transformed from non-centrosymmetric setting.
 Publ. title: Ueber die Kristallstruktur von Hausmannit (Mn Mn₂O₄).

References

Primary reference: Aminoff, G., *Golden Book of Phase Transitions*, Wroclaw, **1**, 1, (2002)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	0	1	1	4,91807	18,022	8,9
2	1	1	2	3,08407	28,927	32,3
3	0	2	0	2,88100	31,016	12,6
4	0	1	3	2,76146	32,395	65,0
5	1	2	1	2,48587	36,103	100,0
6	0	2	2	2,45903	36,511	10,8
7	0	0	4	2,35975	38,105	17,2
8	2	2	0	2,03717	44,435	20,3
9	1	2	3	1,99357	45,460	1,5
10	0	3	1	1,88210	48,319	0,6
11	0	2	4	1,82555	49,916	5,8
12	0	1	5	1,79397	50,857	16,7
13	1	3	2	1,69982	53,894	9,4
14	0	3	3	1,63935	56,053	12,0
15	2	3	1	1,57567	58,533	20,0
16	2	2	4	1,54204	59,938	50,0
17	1	2	5	1,52286	60,772	0,5
18	1	1	6	1,46757	63,321	2,5
19	1	3	4	1,44220	64,568	4,0
20	0	4	0	1,44050	64,653	19,2
21	2	3	3	1,42483	65,452	0,4
22	1	4	1	1,38242	67,726	0,7
23	0	2	6	1,38073	67,820	2,2
24	0	4	2	1,37775	67,987	0,0
25	0	3	5	1,34635	69,799	5,3
26	0	1	7	1,31296	71,845	0,1
27	3	3	2	1,30515	72,342	1,7

28	2	4	0	1,28842	73,434	1,5
29	1	4	3	1,27718	74,188	8,5
30	2	4	2	1,24294	76,595	3,2
31	0	4	4	1,22952	77,586	4,9
32	2	3	5	1,21973	78,327	0,2
33	1	2	7	1,19474	80,293	6,9
34	1	3	6	1,19076	80,616	2,3
35	0	0	8	1,17988	81,516	4,3
36	0	5	1	1,14391	84,659	0,2
37	2	4	4	1,13084	85,871	2,0
38	1	4	5	1,12321	86,597	5,3
39	0	3	7	1,10361	88,531	0,1
40	1	5	2	1,09896	89,004	1,7
41	0	2	8	1,09186	89,739	0,9

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,00000	0,25000	0,37500	0,5000	1,0000	16h
2	MN1	Mn	0,50000	0,25000	0,12500	0,5000	1,0000	8d
3	MN2	Mn	0,00000	0,00000	0,00000	0,5000	1,0000	4a

Stick Pattern

II.f X-Ray diffractograms for the cycle thermal treatment study of manganese oxide doped with iron pellets

Figure II.f.1. Diffractograms of the 2-3,6 mm diameter sample: (a) calcined at 700 °C, (b) subjected to 10 thermal cycles, (c) subjected to 20 thermal cycles, (d) subjected to 30 thermal cycles, (e) subjected to 40 thermal cycles and, (f) subjected to 50 thermal cycles.

The data file of the crystalline phases found, 98-010-6539, 98-002-8708, 98-000-2391 and 98-001-7918 were already included in X-Ray diffractograms for the hardness and density study of manganese oxide doped with iron pellets

II.g TGA results for the manganese oxide doped material in the cyclability as function of pellet diameter study

Figure II.g.1. TG analysis for the different diameter pellets (a) 1 mm, (b) 1.5 mm, (c) 2 mm, (d) 2.5 mm, (e) 3 mm and, (f) 3.5 mm.

ANNEX III Test in the reactor: working procedures

Prior to the execution of any single operation described below, the operator must ensure the next points:

- The air heating system must be switched off and the power supply of both heating stages, preheating and three-phase electric furnace, must be cut off.
- The manual valves which allow the air entrance into the system must be closed.
- All monitored temperatures must be lower than 50 °C.

III.a Material loading

Once measured its effective volume and weight, the material is introduced in the reactor through the cap located on its top. A gentle handling of the sample is required, so a funnel is used to ease the material insertion through the insulation blanket.

Due to the location of the cap, the use of a ladder is required during the material loading and collection. Special attention must be paid when the ladder is put in place due to the high amount of wires of thermocouples, pressure measurement, gas analysis, etc.

The recommended height of the fixed bed is 20 cm, which corresponds to a design volume of 2 litres of material to be tested. However, the final height could be modified depending on the properties of the material to be analysed as well as the experimental conditions.

A sample of the material to be tested should be always kept (sample control) in order to analyse the evolution of the material prior to and after the experiments. Once the reactor loaded with the material, the funnel is extracted from the reactor, the cap is closed and the ladder is removed.

III.b Material collection

The procedure for removing the material from the reactor starts by unplugging and removing the thermocouples located at the top of the reactor; identified with numbers 12, 13 and 14 in Figure 3.5. Scheme of the reactor with the location of temperature and pressure drop sensors .Figure 3.5. Next, the screws of the top cap of the reactor are removed in the order specified in Figure III.b.1. To do so, the use of the ladder is mandatory.

Figure III.b.1. Screwing and unscrewing order for the flanges of the reactor.

The isolating materials are removed to access to the reactor inside. Prior to proceed with the material vacuuming, the thermocouple identify with number 4 in Figure 3.5, which is laterally introduced up to the edge of the reactor, is protected by its partial extraction.

A vacuum system is used for the test material recuperation. First thing is to ensure is that the Hoover is clean and to check the filter to be used; new material implies a new filter, and it will be weight prior and posterior to its use, in order to know the test material mass which is trapped on it. The vacuum system is turned on; its tube is place inside the reactor and the particles are vacuumed. When the reactor is empty, the vacuum is switched off and its tube is removed. The tested material would be gathered from the vacuum system solid deposit. And the system would be keep clean and ready for next use.

At this point, a visual verification of the reactor sieve would be done. If there is any signal of damage by breaks or blocking, it would be replace. In this case, the solids safety deposit, located in the three phase electric furnace, would be access for cleaning checking if any particle has gone through the sieve. The procedure for this is explained in next section.

Once the reactor is empty, thermocouple number 4 is pushed back to its position, the insulating materials are place back in, the top cap of the reactor is screw to the reactor body and the thermocouples located at the top of the reactor are introduced. It is necessary to very careful when locating the insulating material back in place, the position must permit the introduction of the thermocouples once the cover is placed and crewed.

III.c Sieve replacement

If a change of sieve is required, the reactor must be opened between bodies two and three according to Figure 3.4. To do so, the first step is to disconnect all the instrumentation located in those bodies: thermocouples connections, top fitting for differential pressure measurement and, the gasses fitting for the analyser. Second step would consist on extracting the central thermocouple, identified as number 14 in Figure 3.5.

The flange connecting bodies two and three would be unscrewed, following the order shown in Figure III.b.1, while the flange connecting to the gasses outlet would be unscrewed following the order indicated in Figure III.c.1.

Figure III.c.1. Screwing and unscrewing order for the gases exit of the reactor.

The mobile crane, shown in Figure 3.27 (a), is located on top of the reactor, its wheels are braked and the reactor is held to the tackle in three points. The two bodies, as a whole, are rose with the tackle and insured against moving or falling.

Then, the crane is moved aside to gain access to the reactor recipient and the safety solids deposit. The reactor recipient would be removed from the third body and the sieve would be changed. The recipient containing the new filter would be put back in place.

The crane will be carefully moved back to position; bodies one and two would be carefully put in place. The two flanges would be screwed and the tackle fastening removed. The top fitting for differential pressure measurement, the exit of gasses for analysis would be connected and the thermocouples of the bodies plugged in again. The central thermocouple would be introduced through the top of the reactor, and the system would be ready again for operation.

III.d Operational procedure for the test bench

Once the sample is placed inside the reactor, a general overhaul of the system must be carried out. The electricity supply is turned on, and, all connections and fittings (gas and temperature/pressure measurement points) are checked up.

Air blowers are initially switched on at 25 % of the maximum speed. Pressure is manually settled to 3 bar in the pressure drop regulator and the valves to let the air come into the system are opened.

Control and monitoring system is turned on: the air flow rates and heating/cooling rates are fixed according to the experiment definition. For high temperature requirements, the speed of the air blowers is increased in order to maintain the outlet air temperature lower than 200 °C in the extraction chimney.

Once the experiment has been performed, the heating devices are turned off and the system is cooled down by passing air through it until the temperature achieves a value smaller than 60 °C. Then gas flow is stopped.

ANNEX IV Test in the reactor: material characterization

IV.a X-Ray diffractograms for the fixed bed test in the reactor of manganese oxide pellets

Figure IV.a.1. Diffractograms of the manganese oxide samples: (a) initial state calcined at 700 °C for three hours, (b) black material found at the top part of the bed and, (c) brown-red material found at the bottom part of the bed, after 25 cycles fixed-bed assay.

The data file of the crystalline phases 98-010-0054 and 98-008-1762 were already included in X-Ray diffractograms for the hardness and density study of manganese oxide pellets

IV.b X-Ray diffractograms for the fluidized bed test in the reactor of manganese oxide pellets

Figure IV.b.1. Diffractograms of the manganese oxide samples: (a) initial state calcined at 700 °C for three hours, (b) brown-red material found at the bottom part of the bed and, (c) shiny-grey material found at the top part of the bed, after a 25 cycles fluidized-bed assay.

Figure IV.b.2. Diffractogram of the manganese oxide powder sample from the fines gathered after the experiment of 25 cycles fluidized-bed assay.

The data file of the crystalline phases 98-010-0054 and 98-008-1762 were already included in X-Ray diffractograms for the hardness and density study of manganese oxide pellets. The data file of the 98-001-2283 is included next:

Reference code: 98-001-2283

Mineral name: Ramsdellite
Compound name: Ramsdellite
Chemical name: Manganese(IV) Oxide
Common name: Ramsdellite
ICSD name: Manganese(IV) Oxide
Chemical formula: Mn_1O_2
Second chemical formula: MnO_2

Crystallographic parameters

Crystal system: Orthorhombic
Space group: $Pnma$
Space group number: 62

a (Å): 9,2700
b (Å): 2,8660
c (Å): 4,5330
Alpha (°): 90,0000
Beta (°): 90,0000
Gamma (°): 90,0000

Calculated density (g/cm^3): 4,79
Measured density (g/cm^3): 4,83
Volume of cell (10^6 pm^3): 120,43
Z: 4,00
RIR: 3,75

Subfiles and Quality

Subfiles: ICSD Pattern
Inorganic
Mineral
Quality: Calculated (C)

Comments

ICSD collection code: 24034
Creation Date: 01/01/1970
Modification Date: 01/01/1970
Calculated Pattern Original Remarks: Compound with mineral name:
Structures: VO2
Original ICSD space group: PBNM
ICSD Collection Code: 24034

Original ICSD space group: PBNM
At least one temperature factor missing in the paper.
No R value given in the paper

X-ray diffraction from single crystal

Structure type: VO2
The structure has been assigned a PDF number (experimental powder diffraction data): 43-1455
The structure has been assigned a PDF number (calculated

powder
diffraction data): 01-073-1539
Compound with mineral name: Ramsdellite
Structure type: VO₂
Recording date: 1/1/1980
Modification date: 10/1/2005
Mineral origin: Lake Valley, New Mexico
ANX formula: AX₂
Z: 4
Authors density: 4.83
Calculated density: 4.79
Pearson code: oP12
Wyckoff code: c3
PDF code: 00-043-1455
TRANS b,c,a origin 0 1/2 1/2
REMARK Transformed from setting P b n m.
Publ. title: The crystal structure of ramsdellite, an orthorhombic modification of Mn O₂

References

Primary reference: Bystroem, A.M., *Acta Chemica Scandinavica* (1-27,1973-42,1988), **3**, 163, (1949)

Peak list

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
1	2	0	0	4,63500	19,133	2,7
2	1	0	1	4,07220	21,808	100,0
3	2	0	1	3,24078	27,500	3,0
4	3	0	1	2,55322	35,119	34,4
5	2	1	0	2,43763	36,843	26,0
6	0	1	1	2,42243	37,082	0,5
7	1	1	1	2,34373	38,375	26,6
8	4	0	0	2,31750	38,827	5,3
9	0	0	2	2,26650	39,737	5,3
10	1	0	2	2,20165	40,959	0,0
11	2	1	1	2,14690	42,053	15,0
12	4	0	1	2,06347	43,839	2,6
13	2	0	2	2,03610	44,459	1,2
14	3	1	1	1,90643	47,664	14,6
15	3	0	2	1,82758	49,857	3,0
16	4	1	0	1,80206	50,612	1,5

No.	h	k	l	d [Å]	2Theta[deg]	I [%]
17	1	1	2	1,74595	52,360	0,3
18	5	0	1	1,71602	53,345	1,2
19	4	1	1	1,67459	54,773	0,3
20	2	1	2	1,65986	55,301	28,4
21	4	0	2	1,62039	56,768	15,3
22	6	0	0	1,54500	59,812	0,5
23	3	1	2	1,54094	59,985	3,2
24	1	0	3	1,49132	62,199	1,2
25	5	1	1	1,47228	63,094	15,5
26	6	0	1	1,46239	63,571	0,0
27	2	0	3	1,43659	64,851	0,8
28	5	0	2	1,43504	64,929	1,7
29	0	2	0	1,43300	65,033	7,1
30	4	1	2	1,41055	66,200	0,4

31	2	2	0	1,36906	68,478	0,1
32	6	1	0	1,35998	69,000	9,3
33	3	0	3	1,35740	69,150	3,2
34	1	2	1	1,35175	69,480	5,3
35	0	1	3	1,33662	70,382	1,6
36	1	1	3	1,32293	71,220	8,5
37	2	2	1	1,31059	71,995	0,2
38	6	1	1	1,30262	72,506	0,2
39	2	1	3	1,28428	73,710	0,1
40	5	1	2	1,28318	73,784	0,0
41	6	0	2	1,27661	74,227	0,6
42	7	0	1	1,27115	74,600	2,8
43	4	0	3	1,26573	74,974	0,2
44	3	2	1	1,24963	76,110	5,1
45	3	1	3	1,22676	77,792	1,0
46	4	2	0	1,21882	78,397	1,3
47	0	2	2	1,21122	78,984	1,3
48	1	2	2	1,20101	79,789	0,0
49	4	2	1	1,17701	81,756	0,4
50	2	2	2	1,17187	82,193	0,9
51	5	0	3	1,17128	82,243	1,3
52	6	1	2	1,16615	82,683	2,1
53	7	1	1	1,16199	83,045	0,5
54	8	0	0	1,15875	83,329	1,2
55	4	1	3	1,15784	83,409	0,7
56	7	0	2	1,14342	84,704	0,0
57	0	0	4	1,13325	85,645	0,9
58	3	2	2	1,12768	86,170	0,8
59	1	0	4	1,12488	86,438	0,8
60	8	0	1	1,12265	86,651	0,6
61	2	0	4	1,10082	88,814	0,1
62	5	2	1	1,09992	88,906	0,5

Structure

No.	Name	Elem.	X	Y	Z	Biso	sof	Wyck.
1	O1	O	0,78900	0,96700	0,25000	0,5000	1,0000	4*
2	O2	O	0,33300	0,27500	0,25000	0,5000	1,0000	4*
3	MN1	Mn	0,02200	0,13600	0,25000	0,5000	1,0000	4*

Stick Pattern

IV.c X-Ray diffractograms for the fixed bed test in the reactor of iron-doped manganese oxide pellets

Figure IV.c.1. Diffractograms of the doped manganese oxide samples: (a) initial state calcined at 700 °C for three hours, (b) black-grey material found after 25 cycles fixed-bed assay.

The data file of the crystalline phases 98-000-2391 and 98-001-7918 were already included in X-Ray diffractograms for the hardness and density study of manganese oxide doped with iron pellets