Schools of
Mechanical and Chemical Engineering

The University of Adelaide

Investigating the use of Concentrated Solar Energy to Thermally Decompose Limestone

Richard Alexander Craig

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Calcination

Splendor Solis (1532-35)

Abstract

The objectives of this research investigation are to answer fundamental questions regarding the effectiveness of using concentrated solar energy as the sole heating source for the thermo-chemical decomposition of limestone-marble, supplied by Penrice, Angaston. Specifically, scientific analyses are used to investigate the energy requirements for the efficient manufacture of quicklime using solar thermal energy. To achieve these aims, the energy requirements for an industrial scale solar lime manufacturing system were first evaluated. The main conclusion from this analysis is that the thermal efficiency of a solar energy supplied lime manufacture system compares favourably with the best fossil fuelled system. A good heat recovery system as well as a comprehensive preheating system is recommended to minimise the energy losses from the system.

A zero dimensional model was then used to determine that the most energy efficient shape for a travelling grate solar furnace is a triangular cross section. This shape maximise the exposure of the limestone to the radiant energy while minimising structural heat losses. This analytical evaluation also identified that the open area of entrance and exit openings, which allow the process materials to flow through the kiln and for the exhaust gases to escape the kiln, should be minimised. Thirty three times more heat flux is lost through these openings than through the kiln structure. Minimising the openings area therefore improves kiln thermal efficiency.

This investigation then evaluated the maximum bed thickness for the limestone when using a grate bed system within the proposed solar furnace. Due to the nature of radiation it is recommended that the limestone layer be no thicker than 2.5 times the nominal diameter of the limestone in use. This thickness optimises the exposure of the stone to the direct radiation and increases the heat transfer to the stones lower within the bed and allows for the unrestricted diffusion of CO_2 away from these stones.

The investigation then experimentally quantified the effects of radiant heat flux intensity on the calcination kinetics of the Penrice, Angaston marble as a function of stone size. This experimental investigation involved comparing results from an electric muffle furnace, an atmospherically open solar radiation furnace, and an enclosed triangular shaped solar radiation furnace. The muffle furnace provided a baseline values to which the solar calcination rates could be compared.

The open system solar calcination experiments showed that the preheating time of the stone is directly proportional to the illuminated surface area of the stone and the intensity of the heat flux to which it is exposed. Additionally, the reaction rate is directly proportional to the radiant heat flux, and is independent of the stone size for heat fluxes greater than 430kW/m^2.

The enclosed solar furnace experiments identified a 45% improvement in decomposition time could be achieved by using the triangular shaped solar furnace compared to the open solar system calcination. This benefit to the calcination time is best for the more intense heat fluxes and for the larger stone sizes. The measured calcination times were similar to those found for a conventional rotary kiln. This demonstrates the practicalities of using solar radiation technology for interchange with, or as a supplementary heating source to, a combustion driven lime manufacturing industrial plant.

A multi-zone two dimensional mathematical model was then used to evaluate the radiant heat exchange within the triangular solar furnace. The developed mathematical scheme provides a comprehensive package with a validated base model for future evaluations of solar furnace designs. A modified shrinking core calcination model was then developed, which uses an energy balance approach to calculate the preheating times and calcination rates for the Penrice marble exposed to various intensities of radiant heat flux. This version of the heat transfer based shrinking core model was used after considering the one sided heating of the stone from the point source radiation.

Declaration of Originality

This work contains no material that has been accepted for the award of any other degree or diploma in any university or other tertiary institution and, to the best of my knowledge and belief, contains no material previously published or written by another person, except where due reference has been made in the text.

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Signed:

Richard Alexander Craig

on this 1st day of May, 2010

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Nomenclature

Abbreviations and Constants

°C	Degrees centigrade
$CaCO_3$	Calcium Carbonate, Limestone, Marble
CaO	Calcium Oxide, Lime, Quicklime
CMOS	Complementary Metal Oxide Semiconductor
CO_2	Carbon Dioxide
ETSF	Enclosed Triangular Solar Furnace
g	grams
K	Kelvin
kg	kilograms
kW	kilowatt
m	metre
MJ	megajoule
mm	millimetre
N_2	Nitrogen
0-D	Zero-Dimensional
OSS	Open Solar System
SCM	Shrinking Core Model
TGA	Thermogravimetric Analyser
TIFF	Tagged Image Files Format (also TIF)

Roman Symbols

b_d	limestone bed depth (mm)
C_A	reactant gas concentration
d_c	marble / limestone nominal diameter (mm)
D	furnace/kiln diameter (m or mm)
D'	dimensionless firing density
D_e	effective diffusivity through the product layer (mm^{-1})
D_{eq}	furnace/kiln characteristic equivalent diameter (mm)
D_b	radiation beam diameter (mm)
dm	conversion gradient of $CaCO_3$ to CaO
E_a	activation energy of the reaction (kJ/kg or kJ/mol)
gg, GG	gas to gas heat exchange
gs, GS	gas to surface heat exchange
$(GS_1)_R$	total exchange area with allowance for effect of surface zones in radiative equilibrium
g	gas phase (Italic)
h	enthalpy (J)
H	kiln height (m or mm)
H_F	enthalpy flux in the feed stream entering the chamber per hour
$I_{measured}$	bit level of each pixel within the image
I_n	irradiation normal to the surface
k	Arrhenius rate constant (sec^{-1})
K	attenuation factor (extinction coefficient) (m^{-1})
K_p	equilibrium constant
k_s	reaction rate constant
L	kiln length (m or mm)

Roman Symbols (Cont)

L	number of volume elements
M_B	molecular weight of the solid reactant (g/mol)
M	number of surface elements
m_o	initial mass of limestone (g)
m_t	mass of calcining sample at any time (t)
m_3	mass of calcining sample equal to 3% of the stones final mass (g)
m_{50}	mass of calcining sample equal to 50% of the stones final mass (g)
m_{75}	mass of calcining sample equal to 75% of the stones final mass (g)
m_{100}	final mass of calcining sample at 100% calcination (g)
N_g	number of gray gases
P	total resistance pressure (pa)
P_{CO2}	partial pressure of CO_2 (pa)
P_v	vapour pressure (pa)
q	radiant heat flux (W/m^2)
Q	heat (or power), (W)
Q'	dimensionless furnace efficiency
Q_{out}	energy leaving a surface or gas zone (J/s)
R	Universal Gas Constant = 8.314 J/ K. mol
R^2	coefficient of determination
r	distance between each zone (m)
r_c	radius of the un-reacted limestone core at any time (mm)
r_o	initial radius of the solid limestone (mm)
S	distance from the focal point along radiation beam (m)
Ss, SS	surface to surface heat exchange
sg, SG	surface to gas heat exchange
T	temperature (K)
t	time (s or min)
t_{50}	time to achieve 50% calcination (s or min)
t_{75}	time to achieve 75% calcination (s or min)
t_{100}	time to complete (100%) calcination (s or min)
T_{AF}	adiabatic flame temperature (K)
$T_{ambient}$	ambient temperature (K)
T_{board}	measured board temperature (K)
T_o	base temperature (K)
$T_{Platform}$	temperature of calcination platform (K)
T_F	muffle furnace temperature (K)
W	kiln width (m or mm)
X	fractional calcination
X_{CO2}	molar fraction of carbon dioxide
X_{ls}	rate of conversion of limestone used in Arrhenius equation
X_{N2}	molar fraction of nitrogen
y_1	constant mole fraction of CO_2

Greek Symbols

α	absorptivity
ε	emissivity
ρ_m	bulk density of the reacting particle
ρ	reflectivity
σ	Stefan-Boltzmann constant = 5.67×10^{-8} $W/m^2.K^4$

Greek Symbols (Cont)

Δ	Change in Parameter
θ	Roof angle for triangular shaped furnace (deg)
τ	transmissivity factor

Subscripts

Air	ambient air
B	bulk phase
b	stoichiometric coefficient
beam	within the radiation beam
d,c	calculated bed depth
d,m	measured bed depth
elec	calculated from electrical power
Ex	exhaust gases
g	gas phase
Lime	quicklime
LS	limestone
m1	mirror position 1
m2	mirror position 2
max	maximum
os	open system
React	calcination reaction
s	solid phase
temp	calculated from temperature measurement
TSF	triangular solar furnace

Superscripts

e	equilibrium
i	interfacial