

# HETEROGENEOUS THERMOCHEMICAL DECOMPOSITION UNDER DIRECT IRRADIATION

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Radiative heat transfer in a chemical reacting system directly exposed to an external source of high-flux radiation is considered. The endothermic decomposition of  $\text{CaCO}_3(\text{s})$  into  $\text{CaO}(\text{s})$  and  $\text{CO}_2(\text{g})$  is selected as the model heterogeneous reaction. Experimentation using an Ar arc as the radiation source was carried out in which powder samples were subjected to radiative power fluxes in the range  $400\text{--}930\text{ kW/m}^2$ . A 3D transient heat transfer model that links conduction-convection-radiation heat transfer to the chemical kinetics is formulated using wavelength and chemical composition dependent material properties. Monte-Carlo ray tracing and the Rosseland diffusion approximation are employed to obtain the radiative transport. The unsteady energy equation is solved by finite volume technique. The model is validated by comparing the computed reaction extent variation with time to the values experimentally measured.

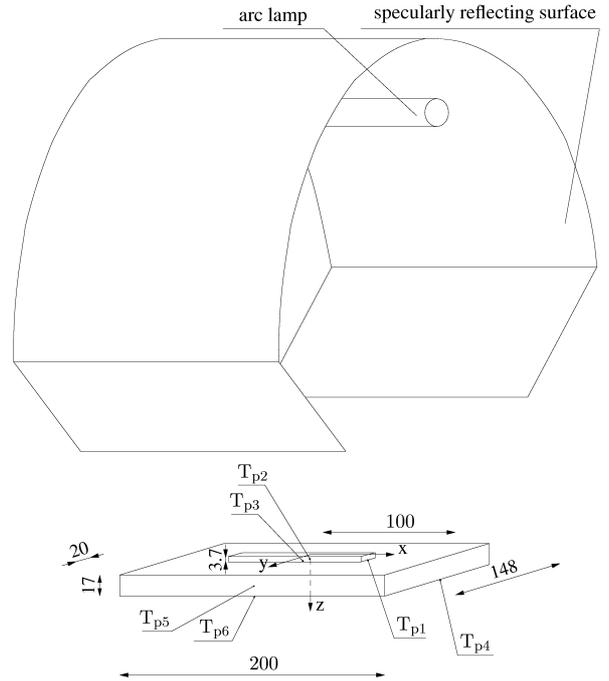
## 1 INTRODUCTION

High temperature endothermic chemical processes involving solid and gases are found in a wide range of industrial applications, e.g. extractive metallurgy, ceramic material processing, and calcination. These processes are characterized by their high energy consumption and their concomitant emission of pollutants, derived mainly from the combustion of fossil fuels for heat generation. The use of an external source of concentrated radiative energy for supplying the process heat offers several advantages, namely: 1) the products are not contaminated by combustion by-products; 2) heat is efficiently transferred by direct irradiation of reactants, and 3) if the radiation source is derived from renewable energy, e.g. concentrated solar energy, the emission of greenhouse gases is avoided. Chemical reactors based on the concept of direct irradiation require matching the rate of radiation heat transfer to the rate of the chemical reaction. Modeling such an interaction is needed to anticipate the consequences of a given design decision on the reactor's performance.

This note presents an analysis of radiative heat transfer in a non-gray, non-isothermal solid undergoing heterogeneous thermochemical decomposition. A 3D model that couples the rate of radiative transfer to the chemical reaction kinetics is formulated, and the experimental set-up and measurements conducted for its validation are described [1,2].

## 2 DIRECT IRRADIATION EXPERIMENTAL SET-UP

Tests were conducted at the ETH's high-flux solar simulator [3]. The experimental set-up is shown in Figure 1. A  $100 \times 20 \times 3.7\text{ mm}$  prism made of  $\text{CaCO}_3$  particles was positioned on top of a  $200\text{ mm}$ -length  $148\text{ mm}$ -width  $17\text{ mm}$ -depth refractory SiC plate, and mounted at the focal plane of the solar simulator. Thermocouples type-K were used to measure temperatures of the plate and plate-sample interface at various locations, as indicated in Figure 2. Samples were irradiated at constant power fluxes during controlled intervals of time, weighted before and after each run to determine their mass loss, and finally completely calcined in an electrical furnace after each run to verify their degree of calcination.



**Fig. 1:** Scheme of experimental set-up. Indicated are the positions of the temperature measurements. Dimensions in mm.

## 3 HEAT TRANSFER MODEL

The general energy conservation law for a differential solid is given by:

$$\frac{\partial U}{\partial t} = -\nabla \cdot \vec{q}'' + q''' \quad (1)$$

where  $U$  is the internal energy,  $q''$  is the heat flux by radiation, convection, and conduction, and  $q'''$  is the heat sink/source per unit volume. The directional distribution of the radiative heat flux incident on the sample was modeled by Monte Carlo ray-tracing method. The spectral distribution is assumed equivalent to Planck's blackbody distribution at  $5780\text{ K}$ , which corresponds to an approximation of the solar spectrum. Using Fourier's law, the conductive heat transfer through the sample is given by:

$$q_c'' = -k_c \nabla T \quad (2)$$

The radiative heat transfer inside the porous sample is determined assuming the Rosseland diffusion approximation for an optically thick medium:

$$q_r'' = -k_r \nabla T \quad (3)$$

where  $k_r$  is calculated using the gray band model by

$$k_r = -\frac{4}{3} \sigma T^3 \left\{ \frac{1}{K_{0-\lambda_1}} \left[ 4F_{0-\lambda_1 T} + \frac{15}{\pi^4} \frac{\zeta_1^3}{e^{\zeta_1} - 1} \right] + \dots + \frac{1}{K_{\lambda_n - \infty}} \left[ 4F_{\lambda_n - \infty} - \frac{15}{\pi^4} \frac{\zeta_n^3}{e^{\zeta_n} - 1} \right] \right\} \quad (4)$$

Finally, the energy sink due to chemistry in the sample is given by

$$q_{ch} = \Delta H_T^o \frac{dn_{CaCO_3}}{dt} = -\Delta H_T^o \frac{dx}{dt} n_{0,CaCO_3} \quad (5)$$

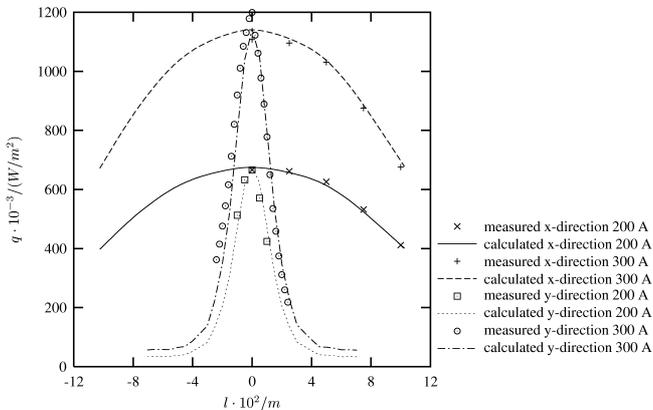
where

$$\frac{dx}{dt} = 6.45 \cdot 10^5 \text{ s}^{-1} \cdot \exp\left(-\frac{187.3 \text{ kJ} \cdot \text{mol}^{-1}}{RT}\right) (1-x)^{0.5} \quad (6)$$

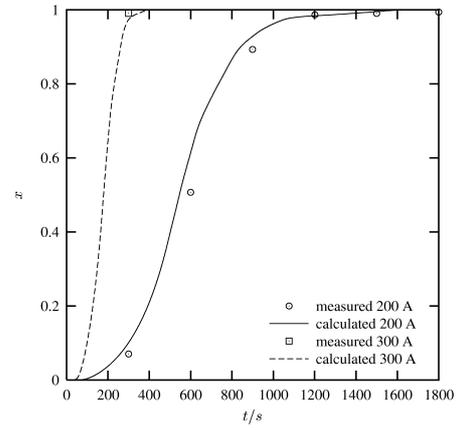
is the kinetic reaction rate ( $x$  = reaction extent), determined by thermogravimetry.

## 4 RESULTS

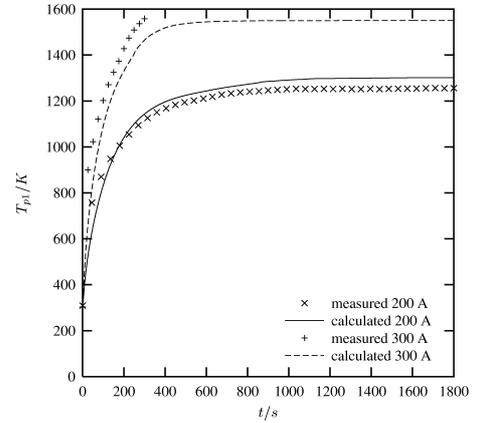
Experimental runs were performed with arc currents of 200 and 300 A. The calculated and measured power flux distribution at the focal plane is shown in Figure 2. The calculated and measured extent of the reaction as a function of time is shown in Figure 3. The calculated and measured variation of temperature with time is shown in Figure 4. The agreement is reasonably good. Differences are mainly the result of discrepancies between the real material properties ( $C_p$ ,  $k$ , and  $\varepsilon$ ) of the actual experimental system and those employed in the modeled system, extracted from the literature. This model enables to treat a non-isothermal non-grey chemical system with a time-dependent chemical composition. It can be applied in the treatment of transient problems involving solid reactants directly exposed to an external source of concentrated thermal radiation and undergoing thermochemical decomposition.



**Fig. 2:** Optically measured and calculated distribution of the radiative flux across the  $x$ - and  $y$ -axis at the focal plane of the high-flux solar simulator for arc currents 200 and 300 A.



**Fig. 3:** Extent of the reaction as a function of time for arc currents 200 and 300 A: measured values (data points) and calculated curves.



**Fig. 4:** Calculated and measured (data points) variation of temperature ( $T_{p1}$ ) with time, for arc currents 200 and 300 A.

## 5 ACKNOWLEDGEMENTS

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## 6 REFERENCES

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