

A SIMULATION STUDY OF THE SILICOTHERMIC PRODUCTION OF MAGNESIUM

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INTRODUCTION

Magnesium is a metal of wide commercial interest, and thus considerable interest exists in improving production methods. Approximately 20 percent of the western world's primary magnesium is produced by the direct reduction of calcined dolomite at high temperatures, using ferrosilicon as the reducing agent.

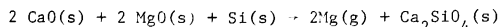
The commercial process (1) consists of finely grinding the reactants, mixing and briquetting these, and then carrying out the reaction in vacuum in relatively small metallic retorts heated in furnaces. The magnesium is evolved as a vapour and is collected in water cooled condensers. The entire process is labour-intensive, particularly in charging and discharging the retorts, is awkward to operate, and difficult to mechanize and automate. The mechanical strength of the metal retorts at elevated temperatures limits the temperature at which the reaction can be carried out, and thus limits the rate at which magnesium can be produced.

If one is to improve this process of magnesium production one must obtain a good theoretical understanding of the chemical processes involved, in order to be able to carry out model studies and optimization. Ultimately one wants a model of the industrial reactor, but before this can be achieved one must have an understanding of the reaction of a single briquette under various conditions.

This paper deals with a mathematical model for a single spherical briquette of calcined dolomite and ferrosilicon being heated by radiation in vacuum, under conditions similar to those encountered in industrial practice. The model yields curves of degree of conversion versus time at various points along a radius of the briquette, as well as total conversion versus time. A series of laboratory experiments were carried out, and confirmed the essential correctness of the model.

CHEMISTRY OF THE REACTION

The overall equation describing the reduction of calcined dolomite with ferrosilicon is



This reaction is highly endothermic, with a heat of reaction of about 50 kilocalories per gram mole of magnesium produced.

The chemistry and thermodynamics of this reaction are reasonably well understood (2), however knowledge of the kinetics and mechanism of the reaction is very limited. The mechanism is evidently very complicated; three solids react to produce a gas and a fourth solid. Most solid-solid reactions are thought to be diffusion controlled, and much of the available work in thermal magnesium production assumes diffusion control.

There are, however, experimental data (3) which indicate that diffusion control cannot be the major rate-limiting factor. These are:

1. The reaction rate increases monotonically with briquetting pressure and briquette density. Increased density however implies decreased pore volume and permeability, and should lead to a rate decrease, if the rate is diffusion controlled.

2. Finer particle size of the reactants either increases the rate or leaves it unaffected, yet finer particles decrease pore size and should decrease the rate, were it diffusion controlled.
3. Better mixing of reactants increases the reaction rate at a fixed briquetting pressure. In general, better mixing leads to denser briquettes, and a reduction in rate would be expected if diffusion were rate limiting.

While all of these experimental results suggest that diffusion of magnesium from the briquette interior cannot be the major rate-limiting process, they are not inconsistent with heat transfer to the briquette interior being rate-limiting. If one considers the very high endothermicity of the reaction this becomes an ever more obvious possibility.

Hence, a model of the reaction of a dolomite-ferrosilicon briquette, with heat transfer to the briquette interior explicitly considered, was developed in order to test the hypothesis that heat transfer is the major reaction rate-limiting step.

HEAT TRANSFER MODEL OF MAGNESIUM PRODUCTION

Consider a spherical briquette of the reactants, characterized by the following parameters and properties:

R	the radius in cm
$\bar{\rho}$	the average density in g mol/cm ³
\bar{c}_p	the average specific heat in cal/gmol°C
$\bar{\epsilon}$	the average surface emissivity

These properties are assumed to be independent of temperature and composition of the briquette. In addition, the following assumptions are made:

- a) heat transfer to the surface of the briquette is by radiation only,
- b) magnesium vapour diffusing from the briquette does so instantaneously and carries negligible thermal energy,
- c) heating is uniform from all directions, and the properties of the briquette are uniform; thus spherical symmetry is maintained.

With these assumptions, from a differential energy balance, the equation giving the temperature, T , as a function of time, t , and radius from the centre of the pellet, r , becomes (4):

$$\frac{\partial^2 T}{\partial r^2} + \frac{2}{r} \frac{\partial T}{\partial r} = \frac{1}{\alpha_e} \frac{\partial T}{\partial t} + \frac{(-r_A)(\Delta H_r)}{k_e} \quad (1)$$

where

$\alpha_e = k_e / \bar{c}_p \bar{\rho}$	the effective thermal diffusivity in cm ² /s
k_e	the effective thermal conductivity in cal/cm·s·K
$-r_A$	the reaction rate in gmol Mg/cm ³ ·s
ΔH_r	the heat of reaction in cal/gmol Mg

Equation (1) can be generalized to a dimensionless form by defining:

$\rho = r/R$ the dimensionless radius
 $\theta = (T - T_R)/(T_W - T_R)$ the dimensionless temperature
 T_R the initial or reference temperature of the briquette
 T_W the temperature of the furnace wall
 $\tau = \alpha_e t/R^2$ the dimensionless time

With these definitions, the energy balance equation becomes:

$$\frac{\partial^2 \theta}{\partial \rho^2} + \frac{2}{\rho} \frac{\partial \theta}{\partial \rho} = \frac{\partial \theta}{\partial \tau} + \frac{(-r_A)(\Delta H_r)R^2}{k_e(T_W - T_R)} \quad (2)$$

Initial and Boundary Conditions

Initial Condition Experimental confirmation of the model was to be carried out in a long tube furnace at temperatures above 1050°C. Initially, the temperature of the briquette would be constant, and relatively low, in an upper, preheat zone. Thus, an initial condition for equation (1) is:

$$T = T_R ; \tau = 0 ; 0 \leq r \leq R \quad (3)$$

or, in non-dimensional form:

$$\theta = 0 ; \tau = 0 ; 0 \leq \rho \leq 1 \quad (4)$$

Flux Boundary Condition To carry out the reaction the briquette was to be moved into the hot zone of the furnace essentially instantaneously. The surface temperature of the briquette thereafter is determined by the balance between

- heat flux from the furnace wall to briquette surface by radiation
- heat flux from the briquette surface to the interior by conduction through the porous solid, and radiation between particle surfaces in the interior.

Thus, the boundary condition at the surface of the briquette is:

$$H(T_W - T_S) = -k_e \left. \frac{\partial T}{\partial r} \right|_{r=R} \quad (5a)$$

where T_S is the temperature of the briquette at $r = R$ and H is given by:

$$H = \frac{\bar{\epsilon} \sigma F_{W-S}(T_W^4 - T_S^4)}{(T_W - T_S)} \quad (5b)$$

where

- H is the radiation heat transfer coefficient in $\text{cal/s}\cdot\text{cm}^2\cdot\text{K}$
 σ the Stefan-Boltzmann constant, 1.37×10^{-12} $\text{cal/s}\cdot\text{cm}^2\cdot\text{K}^4$
 F_{W-S} the configuration factor for radiation heat transfer from furnace wall to briquette

In non-dimensional form this boundary condition becomes:

$$H(T_W - T_S) = -\frac{k_e(T_W - T_R)}{R} \left. \frac{\partial \theta}{\partial \rho} \right|_{\rho=1} \quad (6)$$

Symmetry Condition Under the conditions of the experiment, the radiation flux to the surface of the briquette is uniform at all points, thus the temperature distribution within the briquette is symmetric with respect to the centre. This leads to the boundary condition

$$\left. \frac{\partial T}{\partial r} \right|_{r=0} = 0 \quad (7)$$

or in non-dimensional form

$$\left. \frac{\partial \theta}{\partial \rho} \right|_{\rho=0} = 0 \quad (8)$$

Rate of Reaction

In order to solve equation (2) with initial and boundary conditions (4), (6) and (8), one must obtain an expression for the reaction rate, $-r_A$. Several semi-empirical models exist for the degree of conversion as a function of time and temperature for reactions between powdered solids under isothermal conditions. Of these, the so-called Jander model

$$[1 - (1-X)^{1/3}]^2 = Kt \quad (9)$$

where X is the rate of conversion
and K is the reaction rate constant in s^{-1}

fits the available data best (3). The rate constant, K , follows the Arrhenius relation

$$K = K_0 \exp(-E/R'T) \quad (10)$$

where K_0 is the preexponential factor in s^{-1}
 E the activation energy for the reaction in cal/gmol Mg
 R' the gas constant, $1.98 \text{ cal/gmol}\cdot\text{K}$

The concentration of unreduced magnesium at any point in the briquette at a particular time is:

$$C = C_0(1-X) \quad (11)$$

where X is to be considered the conversion at the point of interest. The rate of reaction then is:

$$\begin{aligned} (-r_A) &= -\frac{d}{dt} [C_0(1-X)] \\ &= C_0 \frac{dX}{dt} \end{aligned} \quad (12)$$

where C_0 is the initial concentration of unreduced magnesium in gmol/cm^3 .

If one assumes the Jander model applies at each point in the briquette, one can solve equation (9) explicitly for X

$$X = 1 - (1 - \sqrt{Kt})^3 \quad (13)$$

which then, together with (12) and (10) gives the reaction rate as a function of time and temperature.

NUMERICAL SOLUTION OF MODEL EQUATIONS

Table I lists the physical parameters used for the numerical solution of the model equation. Some of these were arbitrarily chosen, some taken from the best available literature data (3), and others estimated in the laboratory.

The dimensionless model equations, initial and boundary conditions were converted to finite difference form and solved numerically by the Crank-Nicholson method (5,6). The difference equations were written for six spatial points in the briquette; the centre and surface, and four interior points. The size of the time step was adjusted to give good convergence without unduly long computation time.

Solution times were 15 to 30 seconds on an IBM 360/75 for solutions of 60 to 120 minutes of real time. Results were temperature and conversion profiles at various times, and some typical results are shown in figures 1 to 4. Figures 1 and 2 show typical temperature and conversion profiles at various times; figure 3 shows the effect of the thermal conductivity on temperature and conversion profiles; while, figure 4 shows the effect of briquette diameter on temperature and conversion profiles.

Table I

Physical Parameters for Magnesium Reduction Model

Symbol	Quantity	Value
R	radius of briquette	1.0 and 1.5 cm
$\bar{\rho}$	average density of briquette	1.5 g/cm ³
k_e	effective thermal conductivity	(1.0 to 1.5) x 10 ⁻⁴ cal/s·cm·K
C ₀	initial magnesium concentration	1.1 x 10 ⁻² g mol/cm ³
\bar{c}_p	mean specific heat	0.27 cal/g·K
ϵ	emissivity	0.7
ΔH	heat of reaction	5.0 x 10 ⁴ cal/gmol Mg
K ₀	preexponential in Arrhenius law	exp(7.51) s ⁻¹
E	activation energy	5.42 x 10 ⁴ cal/gmol
T _w	furnace temperature	1450 K(1177°C)
T _R	briquette preheat temperature	873 K (600°C)

EXPERIMENTAL WORK

In order to obtain experimental confirmation of the model two sets of experiments were carried out. It proved impossible to measure temperature profiles inside a reacting briquette, however it was possible to obtain total magnesium evolved from a briquette as a function of time, and to obtain conversion profiles as functions of time.

Total magnesium evolved from a reacting briquette was obtained from continuous weight loss measurements during reaction by suspending the briquette from a strain gauge transducer. Conversion profiles from the model were converted to magnesium evolved as a function of time, and thus could be compared to actual measurements.

Conversion profiles as a function of time were obtained by reacting several briquettes for various lengths of time. The briquettes were then impregnated with a paraffin, and sectioned in such a manner that very small samples could be obtained along a radius. These were dissolved and analyzed for magnesium content by atomic absorption. From these measurements conversion profiles were calculated at various times. Figure 5 shows such data together with profiles predicted by the model.

DISCUSSION

Model results, in general, were consistent with the best available data and results obtained in the laboratory. The model predicts that the reaction of a briquette is characterized by a gradual conversion profile without a sharply unreacted core. For example, the model predicts that the centre of a 1 cm briquette begins to react at about 15 minutes, while the surface is still not completely reacted after 30 minutes. This is observed experimentally. Total conversion measurements are also well predicted by the model, as is the observed dependence of reaction rate on briquetting pressure. Greater pressure affects k_e primarily and as shown in Figure 3, a higher k_e results in a flatter conversion profile, and higher reaction rate.

Since diffusion of magnesium from the briquette is unlikely to explain the observed conversion profiles, and since the heat transfer model predicts correctly the experimentally observed conversion profiles, it is suggested that reaction to heat transfer in the briquette is a major rate-limiting factor in the production of magnesium.

CURRENT WORK

To complete the model described above, an additional partial differential equation describing the diffusion of magnesium vapour from the briquette is currently being added. This equation will allow inclusion of the equilibrium relationship between the magnesium vapour and unreacted magnesium to be included in the calculation of reaction rate, as well as including the thermal energy carried away by magnesium vapour. This extended model should allow prediction of the effect of magnesium diffusion rate on reaction rate, and allow judgement of its importance relative to thermal resistance as a factor in limiting conversion.

Also being developed is a model of the industrial reactor, which involves unsteady heat transfer with reaction in a packed bed of particles which are large relative to the bed diameter. It is hoped that this model will allow consideration of the optimal policies for operating the industrial reactor.

ACKNOWLEDGEMENTS

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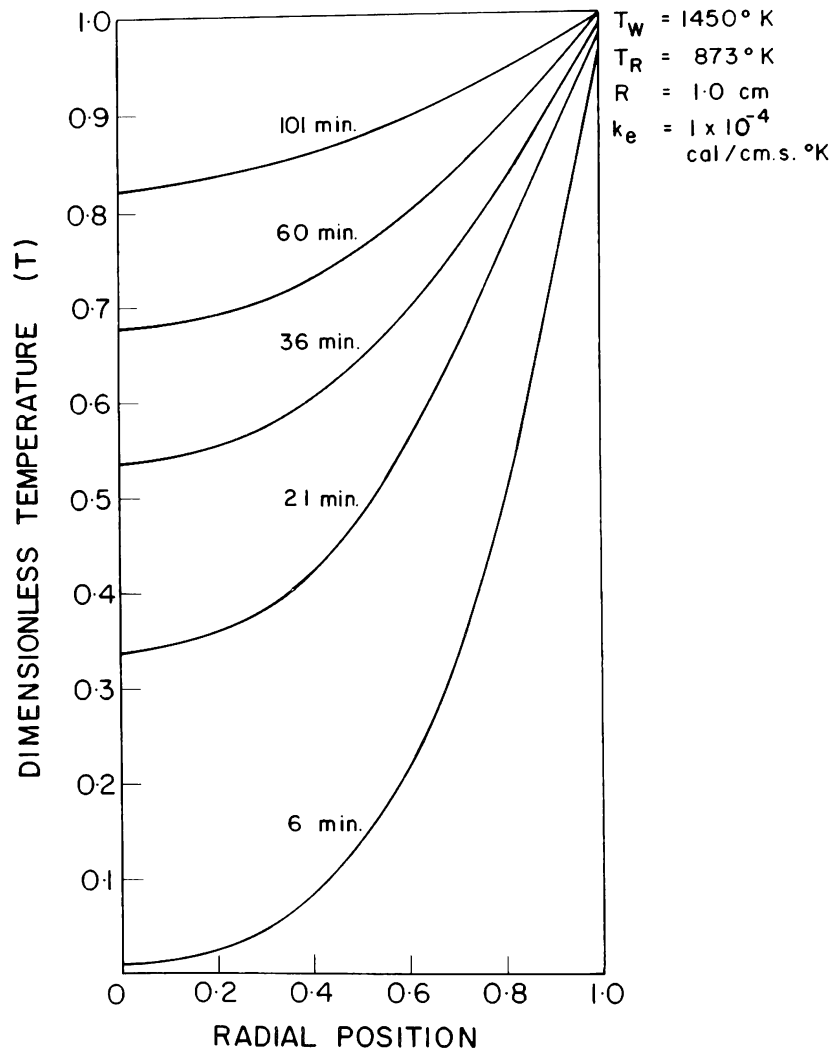


Figure 1 - Predicted Temperature Profiles

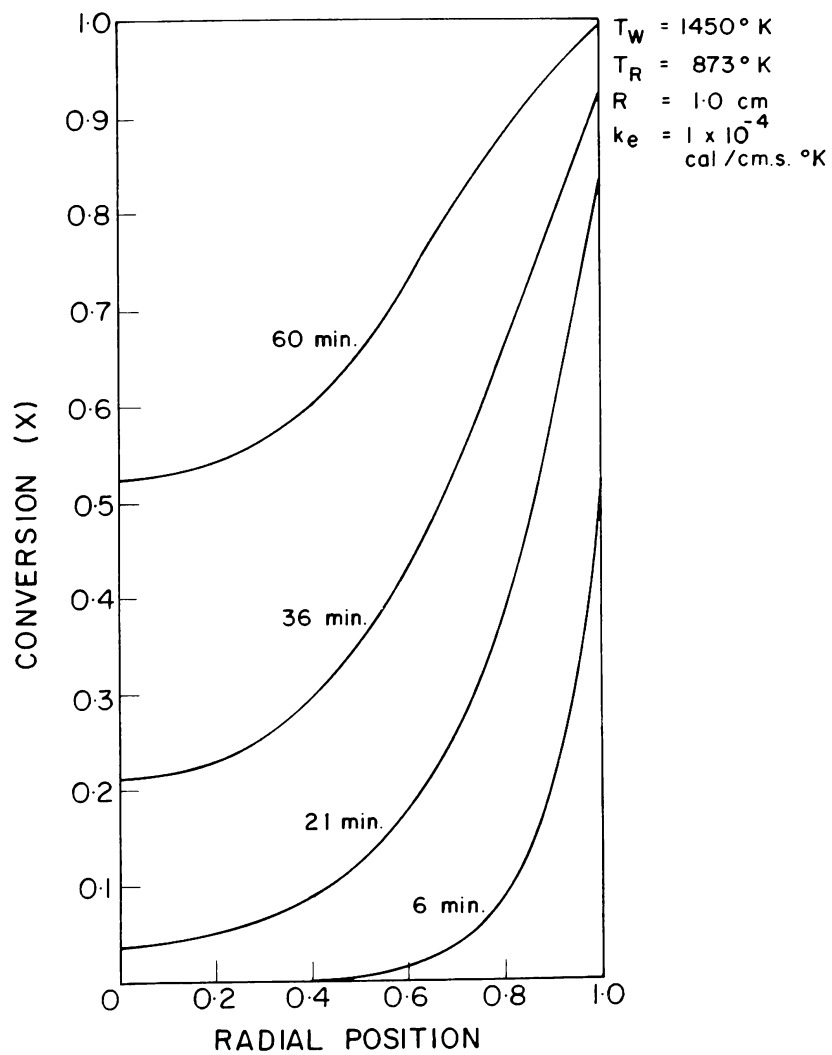


Figure 2 - Predicted Conversion Profiles

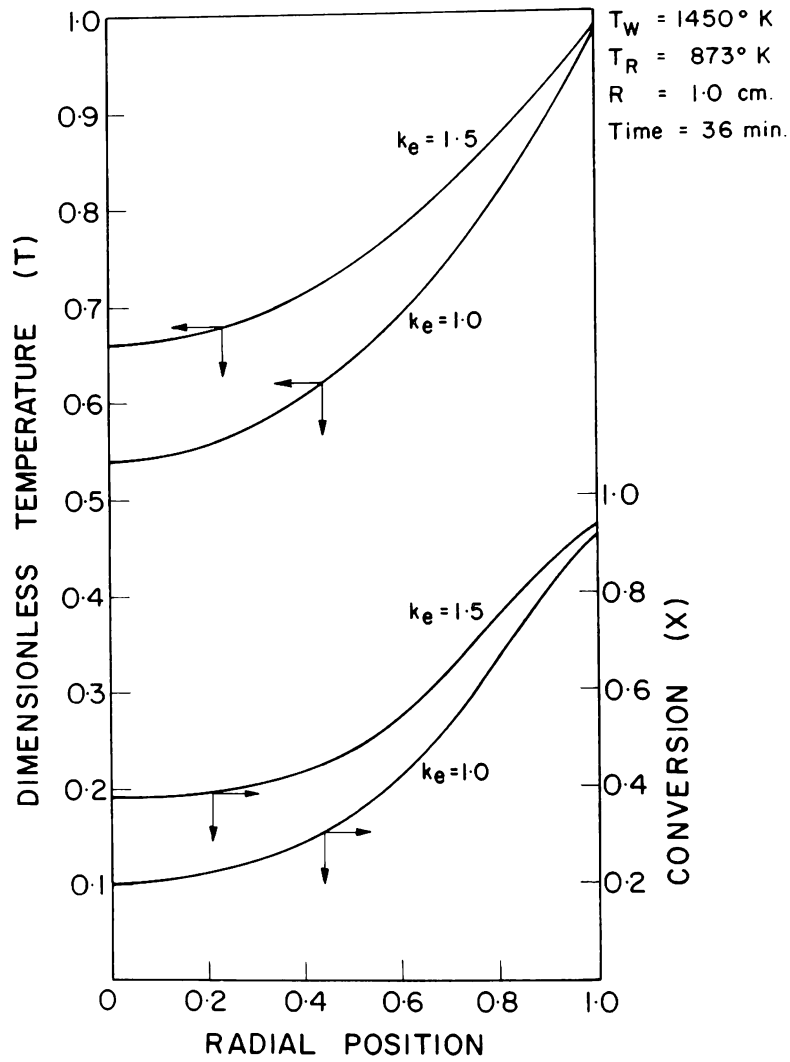


Figure 3 - Variation of Temperature and Conversion with Thermal Conductivity

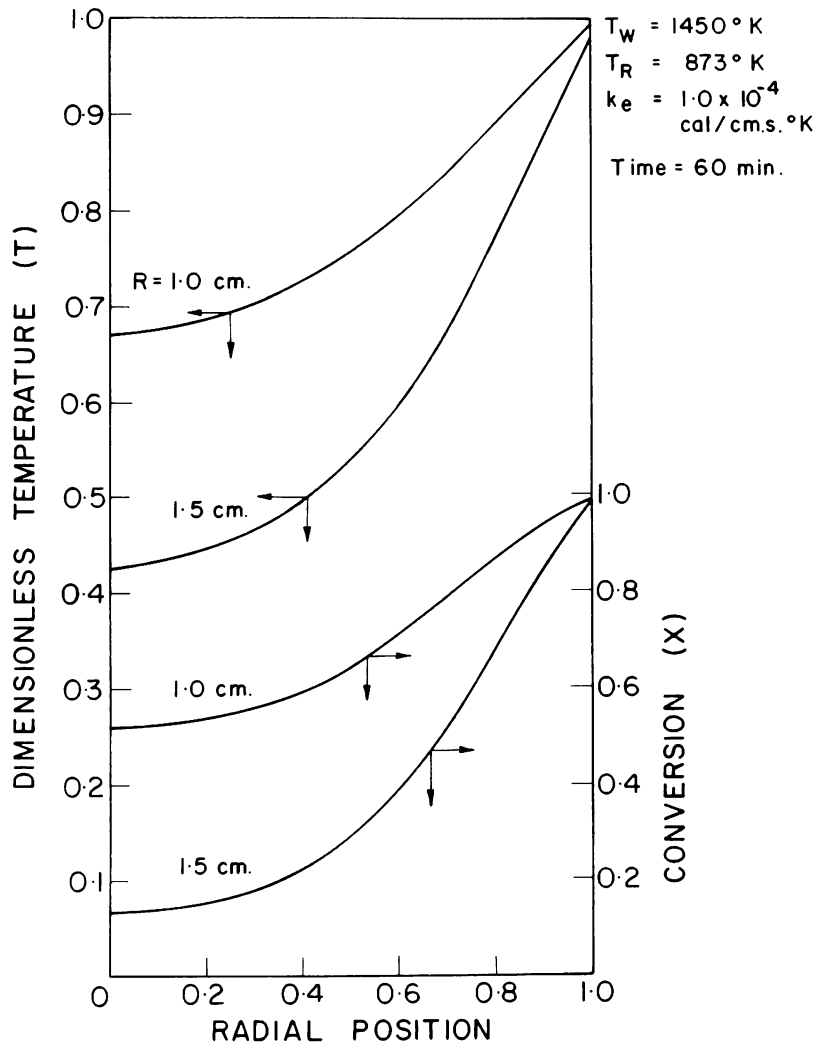


Figure 4 - Variation of Temperature and Conversion with Briquette Radius

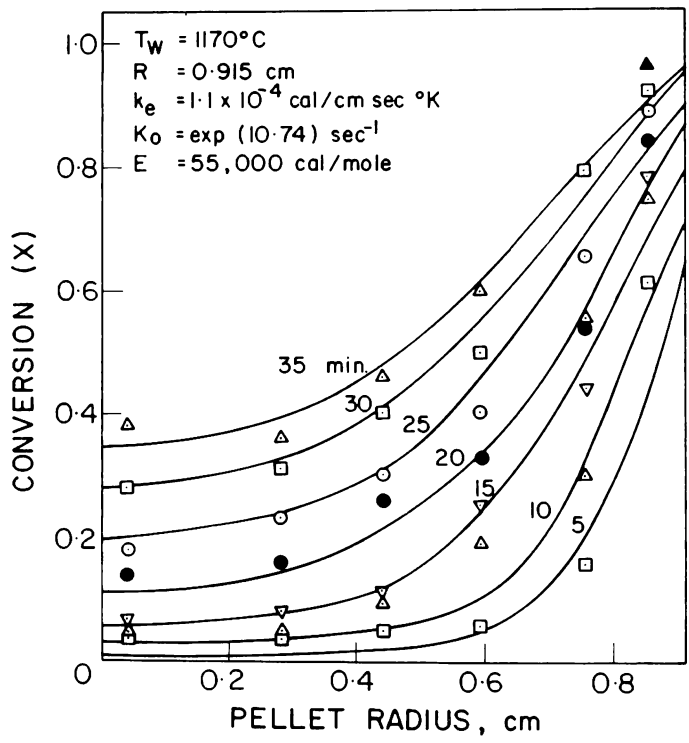


Figure 5 - Experimental and Predicted Conversion Profiles