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CONTRACT TITLE: The Kinetics of Sulfation of Calcium Oxide

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1. INTRODUCTION.

Sulfur emissions control is important for many fossil fuel applications, and mandatory to comply with environmental standards. Many techniques are available for the desulfurization of coal combustion processes. What is generally known as the LIMB process (Lime Injection Multistage Burner), however, carries great promises for an easy implementation and a low cost.

Temperatures found in coal-fired boilers are usually rather high (1500-2000°C), but the residence time is less than 2 seconds. The temperature history the limestone is subject to will have a determining effect on its reactivity. This can be attributed to changes in physical structure (sintering). Several investigators (Borgwardt, 1987; Sarofim et al, 1987) showed that the composition of the original stone is also very important: hydrates react much faster than carbonates, and, to a lesser extent, the concentration of other oxides affected the reaction.

Studies of the sulfation rate behavior show an initial fast rate followed by a rate decrease. This behavior has generally been interpreted as product layer diffusion limitations taking over after an initial kinetic rate regime. Many investigators tried to model this observed rate change. As pore diffusion was a limiting phenomenon in most of the experiments, authors have used several pore models to describe this complication, more or less succesfully. Product layer diffusivity has been assumed to be constant as conversion increased; however, there is no general agreement as to its value.

In this work we are investigating the mechanism of this process with emphasis on measurement of product layer diffusivity and the surface reaction rate. In the last quarter, some additional experimental work was done to investigate the order and activation energy of the sulfation under different conditions. The effect of additives was studied again, by sprinkling some KCl or NaCl salt on top of partially reacted synthetic lime, in an effort to change the surface reaction rate rather than the diffusion rate.

In order to better understand the composition of the product layer, more experimental work was performed using Electron Spectroscopy for Chemical Analysis (ESCA). The three different samples studied in this work were thus analyzed. Finally, an attempt was made to summarize the observations made so far, and to explain them in a framework consistent with the gas-solid reaction theories developed by other investigators. In order to compare with the data provided elsewhere, a computer model is being developed, capable of describing several different rate-limiting regimes.

2. Experimental Results

The previous report provided an overview of the most significant results obtained at that time. Table 1 was then presented, shown here again with some updated information. It describes the results of three types of measurements on the four different samples used in this study. The initial rates show

TABLE 1: Experimental Results

(the Rates are given at standard conditions, i.e. 800°C and 3000ppm SO_2)

Samples:	Single Crystals	Submicron Ash	Iceland Spar	Synthetic Lime
Surface Area:	0.18 m^2/g	30 m^2/g	30m^2/g	3-6 m^2/g
Initial Rates				
Rate (mol/s m^2)	$7.3*10^{-6}$	$22*10^{-6}$	-	$8.4*10^{-6}$
E_a (kcal/mol)	24.2	20.8	-	19.2
SO_2 order	-	-	-	0.5
Rates at High Conversion				
	15%, 240min		41%, 51min	40%, 20min
Rate (mol/s m^2)	$0.68*10^{-6}$	-	$0.34*10^{-6}$	$0.55*10^{-6}$
E_a (kcal/mol)	22.0	-	31.0	38.0
SO_2 order	0.2	-	-	0.23
Combination Runs				
	5%, 10min		36%, 5min	25%, 10min
Rate (mol/s m^2)	$2.89*10^{-6}$	-	$2.43*10^{-6}$	$1.17*10^{-6}$
E_a (kcal/mol)	-	-	24.0	24.9
SO_2 order	0.2	-	0.2	0.25

essentially the slope of the conversion versus time plots at the origin, under standard conditions (800°C, 3000ppm SO_2, 5% O_2 in He at 1 atm.). The high conversion results were also presented in terms of rate per unit surface area as it is the presentation closest to the experimental observation, and therefore least dependent on the assumed rate-limiting mechanism. On this basis,the rates varied by a factor of two. If the calculated product layer diffusivity had been used, a difference of almost two orders of magnitude among the different samples would have appeared. A more detailed discussion of the possible mechanisms will be proposed in section 3. For now, the fact that these high conversion rates don't vary more than an order of magnitude, while the particle sizes, and hence the product layer thicknesses, vary widely, indicates that either diffusivity vary widely with time and conversion, or that another mechanism, such as surface reaction, may control the rate.

The last section of table 1 concerns experiments that were performed in two steps. The sample was sulfated for a fixed amount of time, under a first set of conditions, and subsequently under different sets of conditions. This way, the product layer composition was known to be similar independent of the conditions subsequently studied.

2.2. Recent TGA runs.

As more experimental information was needed to determine the sulfation mechanism, another batch of the synthetic sample was prepared and characterized (Sample R1189). Its porosity and surface area are compared with other similar samples in Table 2, and its porosity presented in Figure 1. No significant difference from the other R-type synthetic lime samples was found. The only parameter needed for further analysis, then, is the surface area, obtained with BET nitrogen adsorption.

First, a few sulfation experiments were performed to determine whether gas phase mass transfer was rate limiting (Figure 2). Once this was ruled out, runs at temperatures up to 1000°C were performed in order to broaden the activation energy data obtained so far. As seen in Figure 3, the recent results compare quite well with previous ones, yielding, however, a slightly higher activation energy. At 1000°C, the rate appears to go down, probably due to a sintering effect. As the larger activation energy corresponds better to the observations made with the submicron ash, it is probably a more accurate result.

The same runs allowed us to obtain activation energy values at higher conversions. They appeared to be higher than the activation energy of the initial rate (see Table 5). They are too low, however, (30 +/- 5 kcal/mol) to explain crystal lattice diffusion as the only mechanism, since typical values for ionic diffusion in ceramics vary between 50 and 90 kcal/mol (Kingery et al., 1976).

Subsequently, some combination runs were performed to study the reaction order at various temperatures. The concept of combination runs was explained in the previous report. The order at 600°C, 800°C and 1000°C was found to be 0.24, 0.25 and 0.43 respectively, as shown in Figure 4. All of these orders were

TABLE 2

CHARACTERIZATION OF THE MATERIAL

Sample ID	ca/Ca(NO3)2	Calcin Temp (oC)	Calcin time (hours)	Conc Additives M/Ca	AA Conc M/Ca	BET sa m2/g	Pore Volume cc/g
R1088	1:1	1000	4	-	-	6.3	4.4
R289	1:1	1000	3.5	-	-	3.9	4.8
R489	1:1	1100	6	-	-	4.0	4.6
R1189	1:1	1100	3	-	-	4.9	5.2
L1088	1:1	1000	8	-	-	5.3	3.5
D1088	2:1	1000	4	-	-	5.4	-
15Na	1:1	1000	4	Na 21.9	Na 0.3	2.0	1.5
15Cr	1:1	1000	4	Cr 16.9	Cr 11.9	1.3	1.9
10Ce	1:1	1000	4	Ce 12.5	Ce 9.0	5.4	3.7

measured after 5 minutes sulfation at 800°C in 3000ppm SO_2, which corresponds to approximately 25% conversion. It was already noted in the last report that the classical Langmuir isotherm, assuming a single energy for all adsorption sites, could not be used to explain the observed fractional order. The upward trend of order with temperature confirms the observation that a distribution of adsorption energy sites must be involved.

Finally, a limited number of experiments were performed to obtain information on the effect of additives in contact with the calcium sulfate product layer. After an initial five minute sulfation, the sample was cooled back to room temperature and sprinkled with a few milligrams of chloride salt (NaCl or KCl). These salts were chosen because they melt at 800°C, and hence are expected to wet the sulfate surface. The sample was then again heated to 800°C. A weight loss was observed during the heatup period, probably due to the evaporation of some of the salt. As shown in Table 3, enough salt was left to observe its effect. A blank run without catalyst was performed to make sure that the cooling and heating did not affect the result.

TABLE 3

Results of Combination Runs with Use of Additives After 5 Minutes Sulfation

Sample R1189, 53-90 μm, at 800°C; 3000ppm SO_2; 5% O_2; in 1 atm He

Sample wt. mg	Rate before treatment 10^{-6} mol/s g	Additive	Additive weight mg	Rate after treatment 10^{-6} mol/s g
0.20	5.5	--	--	6.6
0.22	6.3	KCl	0.58	8.1
0.25	4.9	NaCl	0.04	44.1

From this table, it appears that KCl has no effect, but NaCl does enhance the rate by a factor 5. After an additional 16% has reacted, however, the sulfation rate slows down again, resuming its rate before the addition of the additive.

These results can be compared to sulfation data, obtained earlier in this work, by using a sample, prepared by mixing some extraneous cations in the original citrate solution. This synthetic lime thus consists of a solid solution of extraneous cations in a CaO matrix. The thickness of the product layer for these samples as a function of sulfation time is shown in Figure 5. In these samples, the sodium appeared to have entirely evaporated during the calcination process, explaining why the sulfation curve is essentially that for the non-dop experiments. The effects of Cerium and of Chromium on the sulfation behavior, however, can be observed throughout the reaction.

Results obtained by Borgwardt (1984) by physically mixing the NaCl (grinding in a mortar) with precalcined lime show at a reaction temperature of 1125°C a lower rate than without additives (ratio 0.4). This was attributed to the negative effect of the Cl^- ion, since Na_2SO_4 enhanced the rate (ratio 3.7 at 1125°C, and 13 at 800°C). In order to model the rate, Borgwardt assumed the product layer diffusion regime. Hence, the ratios mentioned above are taken from a best fit of the entire conversion curve. The results obtained with Na_2SO_4 show a rate enhancement up to 45% conversion or 300 seconds (at 800°C).

2.3. Observations from the experiments

In order to construct a physical model it is useful to summarize the data obtained. Table 1 attempts to give this information. Additional information concerning the order and the activation energy at various conversions is given in Tables 4 and 5.

TABLE 4

Reaction Order for SO_2 as a Function of Conversion, as Measured with various Synthetic Limes and with Single Crystals

Sample	Conversion					
ID /	0%	16%	22%	30%	40%	50%
L1088	0.38	0.31	0.20		0.23	
R289	$0.61^{\#}$	$0.46;0.35^{*\#}$		0.38		0.24
R1189			0.25^{*}			
Sgle Cryst.	0.20^{*}	0.19^{*}				

NOTES: * : Data obtained in Combination Experiments. For the Single Crystals, the orders refer to 5% and 9% conversion respectively

\# : Order shown is an average of 2 slopes: high at low concentration, and almost zero at high concentrations

TABLE 5

Apparent Activation Energies (in kcal/mol) at Different Conversion Levels as Measured with Various Synthetic Limes

Sample ID	Temp. Range(°C)	Conversion 0%	15%	40%
R1088	500-800	16.2	29.5	
R489	700-1000	19.5	35.9	37.9
R1189	700-1000	21.9		

While the results are complex, a few observations can be highlighted to guide us in developing a model.

* The order of the reaction varies a bit from one sample to the other, but on average, the order of the initial rate is 0.5. At high conversion, the order systematically decreases down to a value of approximately 0.2. For very thick product layers, as in the case of single crystals, the same value of 0.2 was observed independently of conversion.

* The activation energy of the initial rate is approximately 21 kcal/mol (+/- 3kcal/mol). At higher conversion, the temperature dependence can be described with an activation energy of 28 kcal/mol. The combination runs provide an activation energy of 25 kcal/mol (see Table 1).

* Annealing seems to be a likely mechanism for diffusivity reduction for thick product layers. This is especially clear for the data presented in the last report showing how product layer diffusion can vary with the temperature at which the product layer was formed (Figure 6).

* The synthetic lime behaves differently from the sample

composed of large CaO grains, pointing towards a different mechanism limiting the rate through thin product layers versus thick layers.

* The additives that were investigated have been observed to enhance the rate per unit surface in all cases. When calcination was caried out in the presence of these additives, however, they also increased the degree of sintering thus decreasing the amount of surface available. As a result, the conversion rates are not always faster. When the additive was added on the lime surface (sulfated or not), the rate increase, if any, was only temporary. When the additive was incorporated in the CaO crystals (as in our synthetic lime), a rate increase was observed throughout the range of conversions studied.

3. Modeling and Mechanism Studies

When measuring the conversion profile of the sulfation reaction, many different phenomena happen simultaneously, each of which we would like to describe separately. The purpose of the model is to describe mathematically how these phenomena interact.

3.1. Traditional Description

Most commonly, a gas solid reaction is considered as consisting of the following subsequent stages:

1) Diffusion from the bulk gas to the particle surface
2) Diffusion in the porous structure
3) Adsorption of reactant gases on the solid surface
4) Surface Reaction to an activated compound

5) Diffusion of sulfur compound through the product layer

6) Formation of the stable sulfate at the CaO surface

Each of these steps needs a driving force in order to proceed. If the resistance to reaction is small enough, however, the driving force needed will be negligible and equilibrium may be assumed. This is the case for step 1. Step 2 can be rate-limiting in cases where the reaction rate is very fast and the porosity and pore radius are small. It is an important step in most natural stones. However, our samples were chosen so as not to be limited by this step. When steps 1 and 2 are not rate limiting, the gas concentration at the reacting surface is equal to that in the bulk.

Step 3 is a surface phenomenon that is also taken to be at equilibrium. This assumption is based on the order less than unity observed for SO_2. Thermodynamic equilibrium for this step doesn't necessarily imply that the surface coverage of SO_2 is proportional to the gas concentration. Adsorption theories provide different adsorption isotherms that yield different relationships between surface coverage and gas concentration. The observed large range of SO_2 pressures over which a fractional and constant order is observed rules out theories based on monoenergetic adsorption sites and requires the use of theories that incorporate a distribution of site energies.

The possibility of step 4 being rate limiting was suggested in the last report. It must be considered seriously as it would allow us to describe the reaction rate of our different samples (synthetic lime as well as single crystals) in a similar manner.

Nevertheless, the behavior during sulfation, as well as the change in order and activation energy pointed out earlier, do not permit us to consider this as the only important step.

If step 4 is not rate limiting, we can assume that the chemical potential of the system is similar before and after reaction. The relative concentration of reactant and reagent can then be obtained from the stoichiometry of the reaction. The most probable complex to be formed here is SO_4^{--} (see Borgwardt, 1984). In this case the reaction would be

$$SO_2(ads) + 1/2\ O_2(ads) + O^{--} \rightarrow SO_4^{--}$$

However, there is no evidence supporting any particular complex as the diffusing compound.

Most authors take step 5, the diffusion through the product layer, as being rate limiting. After an initial fast rate, the rate decreases as the product layer builds up. This step is described analytically with Fick's law, using a diffusivity and a concentration gradient for the diffusing compound. Even though no argument exists as to what this compound is, its gradient can be approximated knowing its concentration at either boundary.

If the diffusion occurs in ionic form, which was proposed by several authors (Borgwardt, 1984,1987), these boundary values are determined by stoichiometric composition on the one hand, and defect concentration on the other. Hence, a zero order dependence on surface concentration would result, which was not observed. For a nonzero order to be interpreted in the product layer diffusion regime, the concentration of the diffusing compound at the outer boundary must be related to the surface concentration of SO_2.

The last step, the formation of a stable product at the product layer-reagent interphase is really a recrystallization reaction if we take the sulfate complex as having formed at the outer surface. Once it has diffused through the product layer, it will replace an O^{--} ion and preferentially take the $CaSO_4$ crystal structure of an existing crystal, or start a nucleus for a new crystal to grow on. In case sulfur diffuses in some other form, this last step would involve an actual chemical reaction. Whether this reaction is fast or rate limiting can be investigated from the comparison between the rate obtained from different materials, and in particular porous versus non-porous materials. As was argued in the last report, it appears not to be rate-limiting.

3.2 Alternative Mechanism

The above description assumes that the sulfur compound diffused, although in different forms. The following sequence, however, cannot be ruled out either:

1) Diffusion from the bulk gas to the particle surface
2) Diffusion in the porous structure
3) Adsorption of reactant gases on the solid surface
4) Surface Reaction to $CaSO_4$
5) Diffusion of Ca and O through the product layer
6) Decomposition of the underlying oxide

Hence, in this case, the CaO diffuses in some form through the sulfate product layer, such that the sulfur reacts directly to the final product on top of the product layer. No sulfur diffusion is needed. The description of steps 1 through 3 is similar to the traditional approach. Even step 4, the reaction of CaO with the adsorbed gaseous compounds must formally be described in the same fashion. The reactions occurring on the virgin oxide surface can continue, while where a diffusing sulfur species must be formed, one cannot assume that the reactions are the same.

The main difference between the two approaches, however, is the product layer diffusion step. While in the traditional description, sulfur and oxygen are regarded as diffusing (in ionic form), this analysis would have Ca^{++} cations, along with O^{--}, diffusing to the external surface, in a similar fashion as metals were observed to diffuse through their oxide layer (Kirk & Huber, 1968; Jost, 1952). The analytical description of the diffusion process, however, is very similar to the one mentioned above. The concentration gradient describing the diffusion will be determined by two boundary conditions: maximum solubility of the rate-limiting ion in the product layer on the one hand, and stoichiometric composition on the other. If this step is controlling the sulfation, it is clear that a zero order dependence on SO_2 partial pressure is expected, which is not observed.

Step 6 is, following this analysis, the decomposition of the CaO crystal. Similar phenomena have been described in the case of tarnishing, or oxidation reactions (Cabrera & Mott, 1949). This reaction was not observed to be rate-limiting, as mentioned in the previous analysis.

It appears that even though two different approaches can be used for describing the sulfation reaction, they will result in similar analytical rate expressions, and hence it is impossible, with the information available, to make a definitive decision as to which is the true mechanism.

4. Conclusion and Future Work

In this work, an attempt was made to reconcile the data obtained earlier with a mechanistic model. Some additional experiments we performed to complete the picture, and help identify some trends. The description of the various possible steps occurring in this gas-solid reaction highlighted the complexity of the problem.

It is important to describe our results in the light of the existing literature, such that a more complete critical study can be performed. Although not described in this report, a mathematical model, following the lines of the mechanism described in section 3, is being developed. It allows for the description of surface reaction, product layer diffusion and interphase reaction, with or without pore diffusion limitation.

In the coming quarter, it is the purpose to improve this model to describe as correctly as possible the experimental observations, and to use it to compare our data with the literature. The difference in behavior between thin and thick product layers may open new insights for the use of small limestone particles.

5. References

Bhatia S.K.& D.D. Perlmutter: "A Random Pore Model for Fluid-Solid Reactions: Isothermal, Kinetic Control" AIChE. J., 26, 379 (1980)

Borgwardt R., R. Bruce and J. Blake: "EPA Experimental Studies of the mechanisms of Sulfur Capture by Limestone", presented at the 1st Joint Symposium on Simultaneous SO_2/NOx Control Technologies, 1984

Borgwardt,R., K. Bruce & J. Blake: "An Investigation of Product Layer Diffusivity for CaO Sulfation" Ind. Eng. Chem. Res. 26, 1993 (1987)

Cabrera,N. & N.F.Mott: "Theory of the Oxidation of Metals", Report on Progress in Physics, 12, 163 (1949)

Fergusson,O.L. & E.F. Rissman: "An Infrared Kinetic Study of Mechanisms Involved in the Dry Limestone SO_2 removal Process": Proceedings of the 2nd International Clean Air Congress, by H.M. Englund & W.T Berry (editors), Academic Press, NY, 1971

Froment,G. & Bischoff: "Chemical Reactors, Analysis and Design", J.Wiley & Son, 1979

Halsey, G.: "The Role of Surface Heterogeneity in Adsorption" Adv. in Cat., 4, 259 (1952)

Ishida,M & C.Y. Wen: "Comparison of Zone-Reaction and Unreacted Core Shrinking Model in Gas-Solid Reactions: I Isothermal Analysis" Chem Eng Sci, 26, 1031 (1971)

Jost,W : "Diffusion in Solids, Liquids and Gases" Academic Press, New York, 1952

Kingery,W.D., Bowen & Uhlman: "Introduction to Ceramics", John Wiley & Sons, 1976

Kirk,C.T. & E.E.Huber,Jr. : "The Oxidation of Aluminum Films in Low Pressure Oxygen Atmospheres" Surface Science, 9, 217 (1968)

Kocaefe,D., D. Karman & F.R. Steward: "Comparison of the Sulfation Rate of Calcium, Magnesium and Zinc Oxides with SO_2 and SO_3" Can. J. of Chem. Eng., 63, 971 (1985)

Lindner,B. & D. Simonsson: "Comparison of Structural Models for Gas-Solid Reactions Undergoing Structural Changes" Chem. Eng. Sci., 36, 9 1519 (1981)

Low, M.J.D., A.J. Goodsel, N. Takezawa: "Reactions of Gaseous Pollutants with Solids: Infrared Study of the Sorption of SO_2 on CaO" Env. Sci. & Tech., 5, 12, 1191 (1971)

Marsch, D.W. & D.L. Ulrichson: "Rate and Diffusional Study of the Reaction of Calcium Oxide with Sulfur Dioxide" Chem. Eng. Sci., 40, 3, 423 (1985)

Mess, D.: "Product Layer Diffusion in the Carbonation of Calcium Oxide", PhD Thesis, MIT, 1989

Sarofim, A.F., J.P. Longwell, G.A. Simons, D.Ham, J.C. Kramlich & G.H. Newton: "Kinetics of Sulfur and Nirtogen Reactions in Combustion Systems" Proceedings of the AR&TD Direct Utilization and Instrumentation and Diagnostics Contractors Review Meeting, 1987

Simons, G.A.: " The Pore Tree Structure of Porous Char" 19th International Symposium on Combustion pp1067-1076 (1982)

Steward, F.R., D.Karman, D.Kocaefe: "A Comparison of the Reactivity of Various Metal Oxides with SO_3", The Can. J. of Chem. Eng., 65, 342 (1987)

Szekely, J., J. Evans and H.Y. Sohn: "Gas Solid Reactions", Academic Press, New York, 1976

Van Houte, G. & B. Delmon: "Kinetics of the Reaction of $CaCO_3$ with SO_2 and O_2 below 650°C", J. of The Chem. Soc., Faraday Transactions I, 75, 1593 (1979)

Figure 1

Pore Size Distribution

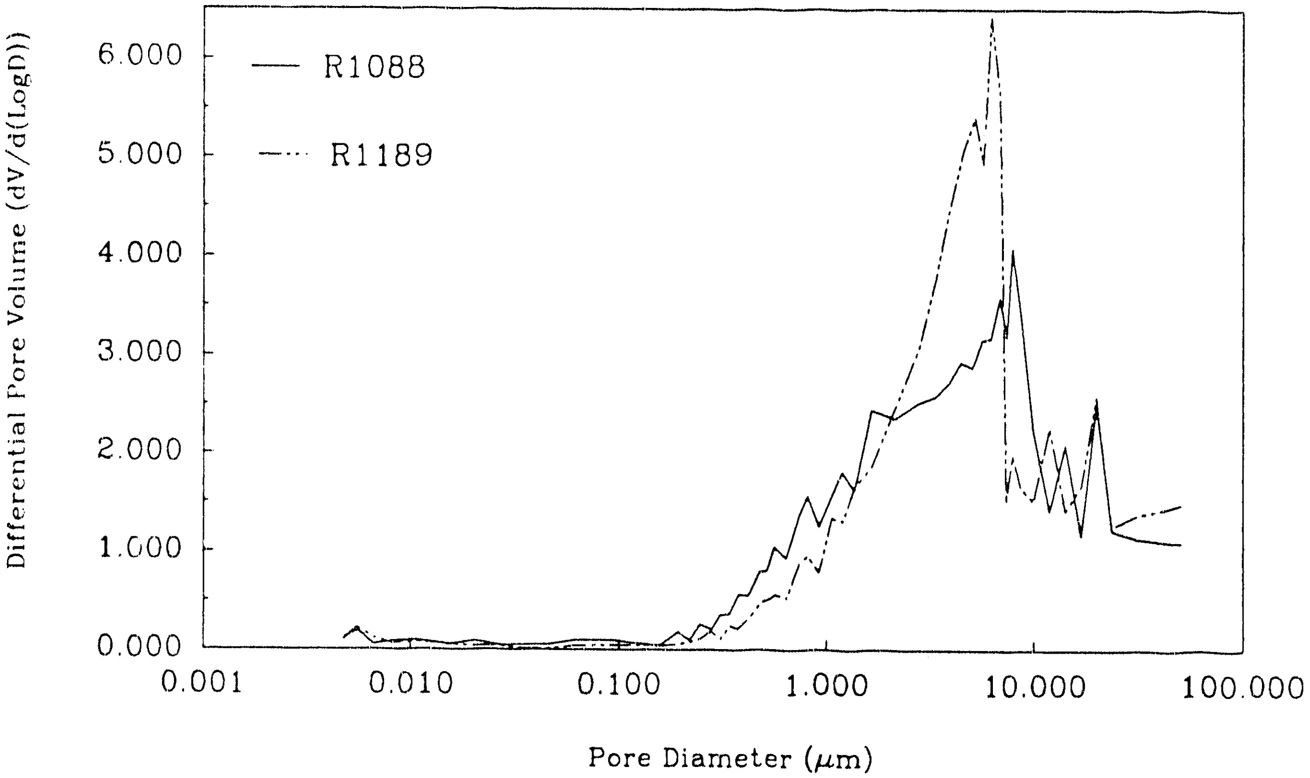


Figure 2 | Conversion Behavior of Different Size Samples, at Different Flow Rates. Other Conditions: 800°C, 3000ppm SO_2; 5% O_2 in 1atm He

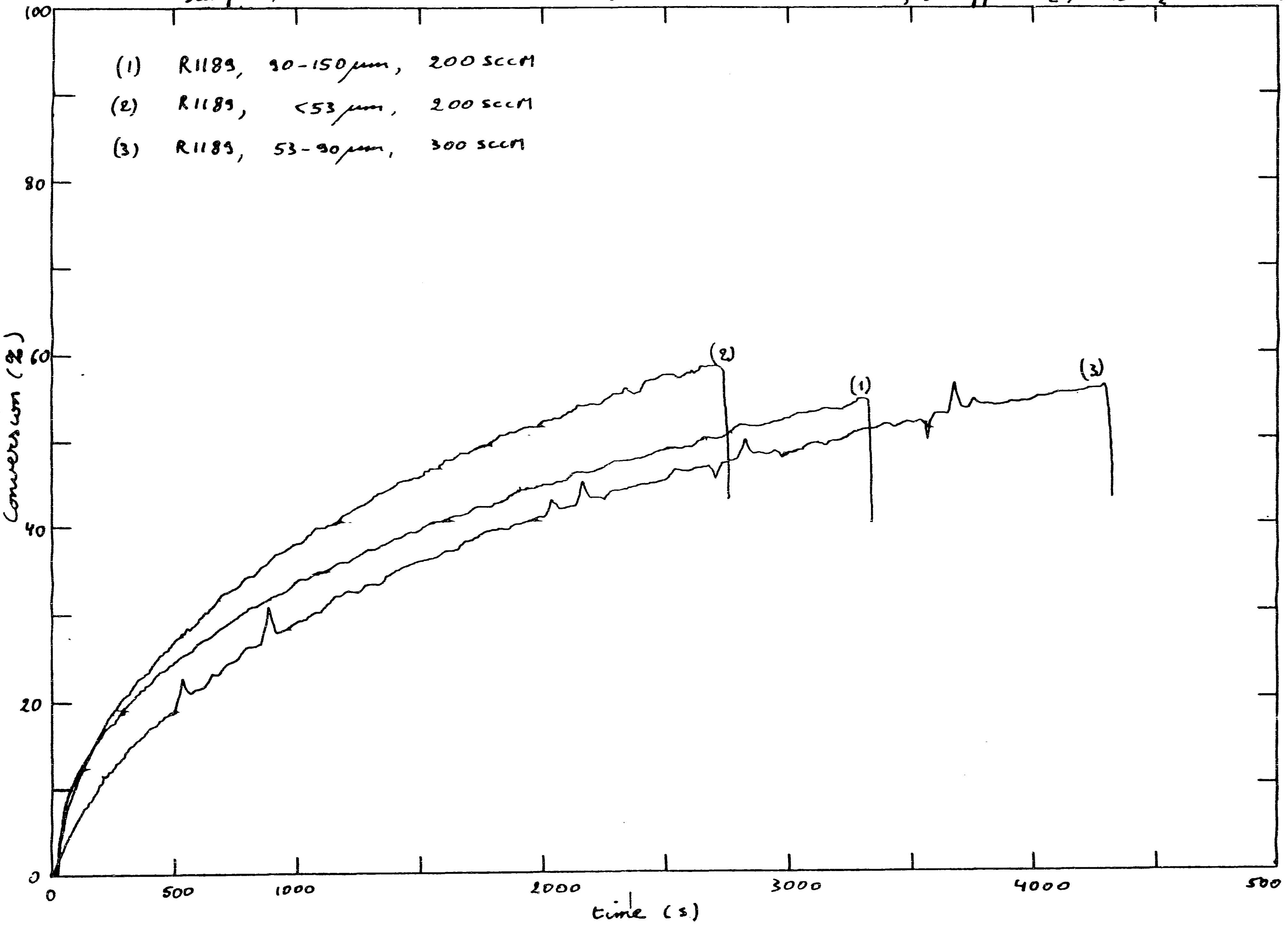


Figure 3

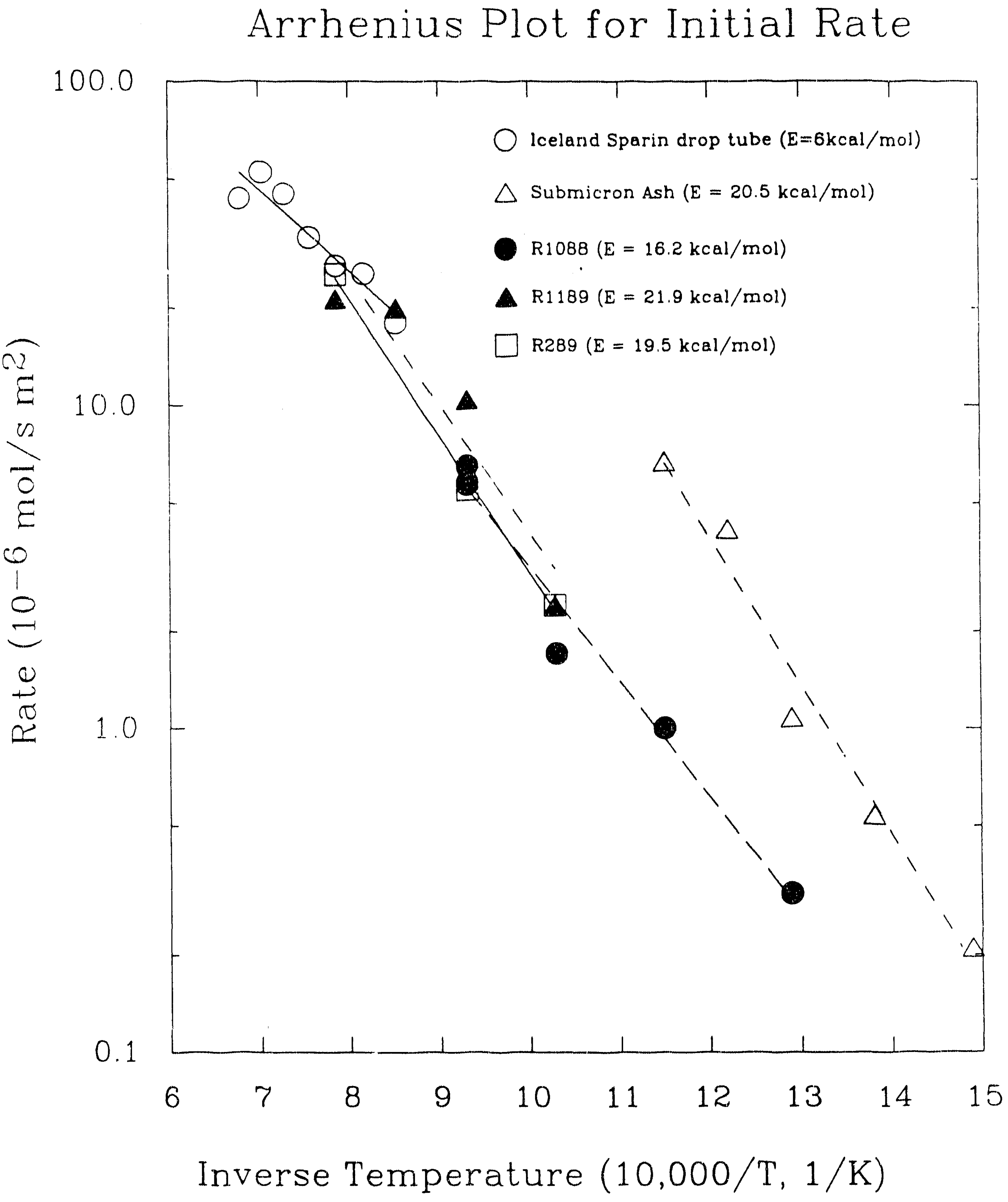

Arrhenius Plot for Initial Rate
100.0
10.0
1.0
0.1
Rate (10−6 mol/s m^2)
6
7
8
9
10
11
12
13
14
15
Inverse Temperature (10,000/T, 1/K)
○ Iceland Sparin drop tube (E=6kcal/mol)
△ Submicron Ash (E = 20.5 kcal/mol)
● R1088 (E = 16.2 kcal/mol)
▲ R1189 (E = 21.9 kcal/mol)
☐ R289 (E = 19.5 kcal/mol)

Figure 4:
Reaction Order at Various Temperatures

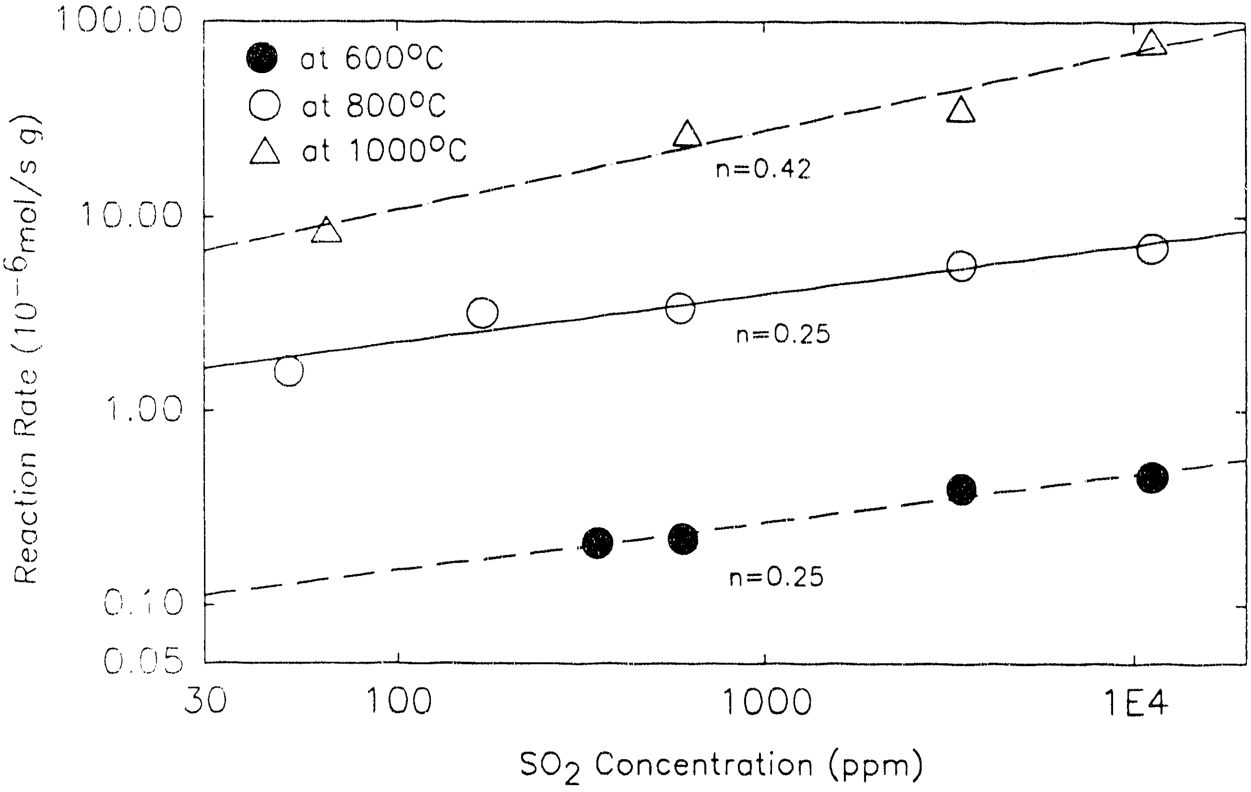
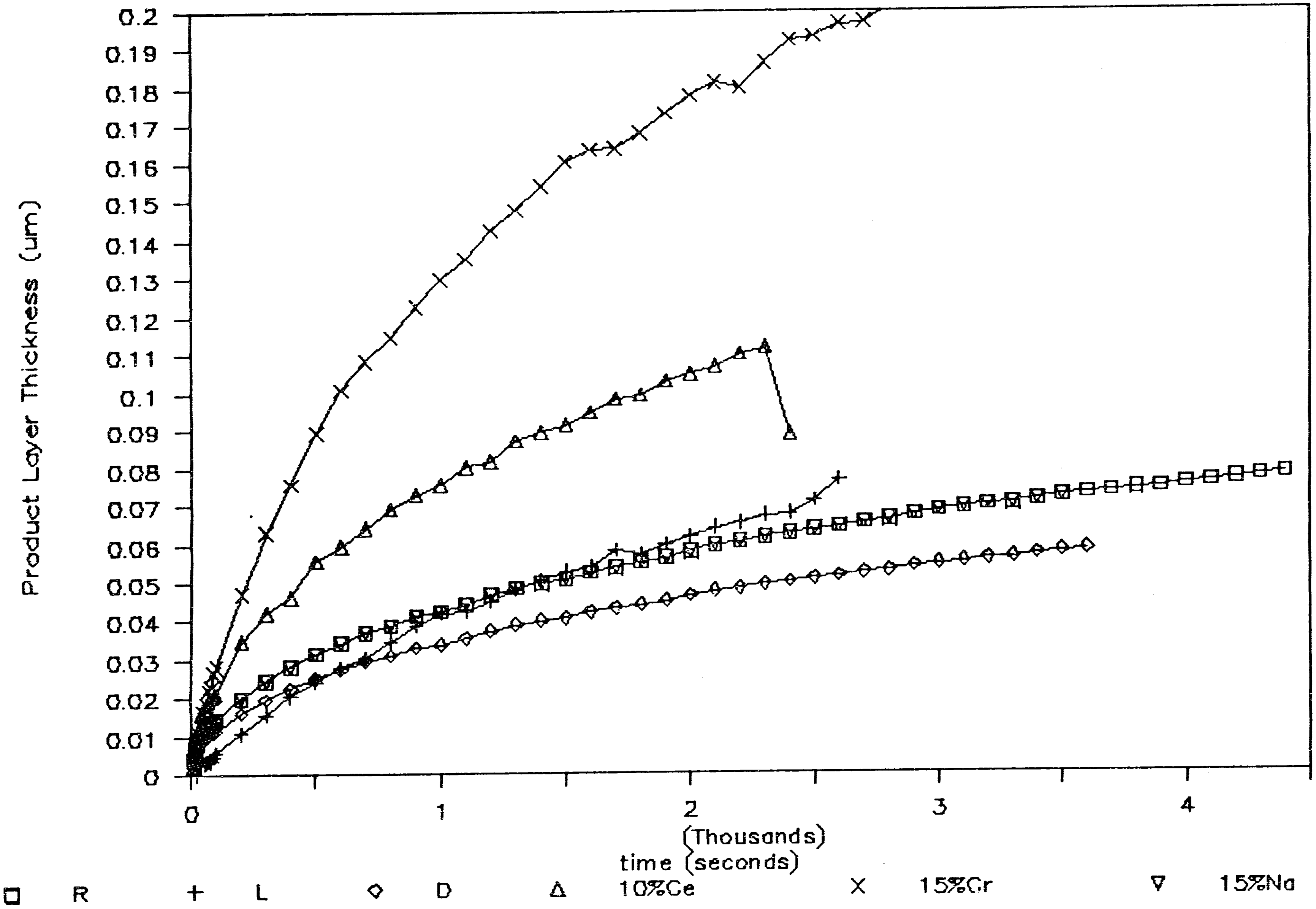


Figure 5

Product Layer Thickness vs time



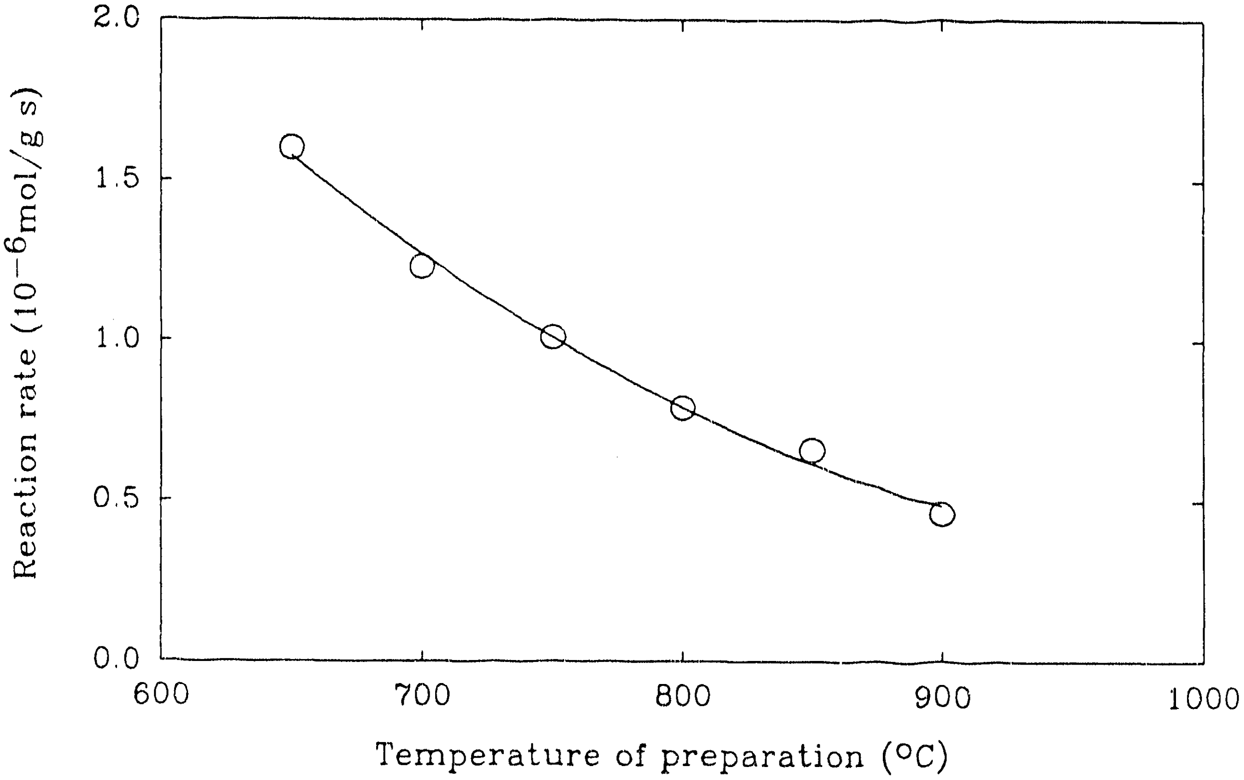


Figure 6: Reaction Rate at 800°C after Preparation at Different Temperatures

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