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OF KRAFT BLACK LIQUOR**

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Sulfur Release During the Pyrolysis of Kraft Black Liquor

by

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Abstract

Sulfur release during kraft black liquor combustion occurs during the pyrolysis stage of burning, with the sulfur being released in the form of reduced sulfur compounds. Despite the importance of this phenomenon, much of the information available on sulfur release during black liquor pyrolysis is incomplete or contradictory. This work develops a model that predicts the amount of sulfur volatilized from a black liquor drop during pyrolysis as a function of important compositional and physical variables.

To determine the effect of compositional variables on the amount of sulfur released, soda liquors containing a single sulfur species were pyrolyzed in a captive sample reactor and the amount of released sulfur measured. Very little (<2%) sulfur was released during pyrolysis of liquors containing sodium sulfate or sodium sulfite. About 40 percent of the sulfur could be released from liquors containing sodium thiosulfate or sodium sulfide. Sulfur release was found to decrease with increasing temperature for pyrolysis temperatures above 490° C. Equations based on a modified first order decomposition model predict the amount of sulfur released from thiosulfate and sulfide as a function of pyrolysis, time, and temperature. The results of the study show that, although the amount of sulfur that can be released from either sodium thiosulfate or sodium sulfide is similar, the thiosulfate release rate is much lower.

Introduction

Sulphur release is a major problem encountered during the burning of kraft black liquor in a recovery boiler. Much of this sulphur is emitted during the pyrolysis stage of burning, when the liquor's organic compounds decompose and volatile gases are produced. During pyrolysis, 70 percent or more [1,2] of the black liquor's sulphur can be released in the form of reduced sulphur compounds, most notably hydrogen sulphide (H_2S). In addition to causing an odor problem if they are released from the boiler, these compounds can react with oxygen to form sulphur dioxide (SO_2), which has been implicated in several serious boiler problems, such as aiding the formation of sticky deposits in the convective heat recovery section and corrosion throughout the boiler [3]. Much of this SO_2 can be recaptured by reacting it with sodium carbonate fume and oxygen to form sodium sulphate which is collected by electrostatic precipitators and returned to the boiler with the incoming black liquor. This process, however, can result in handling problems associated with the high particulate recycle rate.

Despite the importance of sulphur release, there is a lack of understanding of the factors affecting it. Among these factors is the contribution to sulphur release by the various sulphur-containing species present in kraft black liquor. The major sulphur species present in black liquor is sodium sulphide or sodium thiosulphate, depending on the degree of oxidation of the liquor. Other sulphur compounds, such as sodium sulphate and

sodium sulphite are also present. In addition, 10 to 20 percent of a liquor's sulphur may be present in the form of organic sulphur, which is thought to be chemically bonded to the dissolved lignin [3]. These various compounds are expected to behave differently with respect to sulphur volatilization during pyrolysis.

Previous studies have examined the amounts of sulphur released by the different sulphur species during pyrolysis. Douglas and Price [4] pyrolyzed sodium sulphate, sodium sulphite, sodium thiosulphate, sodium sulphide, and elemental sulphur in the presence of glucose or soda lignin at 600° C and measured the amount of H₂S produced. They found that little or no sulphur was released from sodium sulphate or sodium sulphite. However, 30 to 75 percent of the sulphur present was released during pyrolysis of sodium sulphide, sodium thiosulphate, and elemental sulphur. The amount released from these species depended on the organic compound present. Sodium sulphide and sodium thiosulphate released similar amounts of volatile sulphur during pyrolysis with both glucose and soda lignin.

Strohbeen and Grace [5] studied the pyrolysis of sodium sulphate, sodium sulphite, sodium sulphide, and sodium thiosulphate in the presence of sodium gluconate or vanillic acid. The inorganic/model compound mixture was heated to a final temperature of 550° C and the resulting sulphur gases analyzed. As did Douglas and Price, Strohbeen and Grace found that sodium sulphate and sodium sulphite released little sulphur during

pyrolysis, while pyrolysis of sodium thiosulphate and sodium sulphide produced large amounts of volatile sulphur compounds. However, Strohbeen and Grace found that sulphide and thiosulphate behaved quite differently during pyrolysis. Sodium sulphide released over 90 percent of its sulphur during pyrolysis with either organic compound. This amount of volatile sulphur was more than twice the 25 to 40 percent of the total sulphur that was released during the pyrolysis of sodium thiosulphate. The results of their study led Strohbeen and Grace to conclude that black liquor oxidation, which converts the sulphide in black liquor to thiosulphate, could significantly reduce the amount of sulphur released in the recovery boiler during black liquor combustion.

Pyrolysis temperature has also been shown to affect black liquor's sulphur volatilization behavior. Several studies [1,2,6,7], employing a variety of experimental reactors, have shown that pyrolysis temperatures above a certain level tend to suppress sulphur release. Clay, *et al.* [6], who used a single particle reactor to study pyrolysis of black liquor drops at temperatures ranging from 300 to 1100° C, concluded that the maximum sulphur release occurred at temperatures between 450 and 600° C.

A model predicting the release of sulphur from black liquor as a function of liquor composition and pyrolysis temperature would be a valuable asset in efforts to control the volatilization of sulphur during black liquor combustion. The

present study was undertaken to provide such a model and to clarify uncertainties concerning the amount of sulphur released by the various sulphur species during black liquor pyrolysis.

Sample Preparation

Because it was desirable to use a material similar to kraft black liquor and necessary to control the amount and species of the sulphur contained in the pyrolysis material, a soda black liquor was chosen as the organic substrate. Solutions of sodium sulphate, sodium sulphite, sodium thiosulphate, and sodium sulphide were added to samples of soda black liquor in quantities to produce liquors that contained approximately three percent sulphur. The liquors were then concentrated to about 65 percent solids.

Apparatus and Procedure

The pyrolysis experiments were performed in a captive sample reactor. Similar reactors have been used to study the pyrolysis of coal [8] and kraft lignin [9]. The reactor, pictured in Figure 1, was chosen for its ability to provide high heating rates and to maintain stable temperatures during pyrolysis. The black liquor sample (equivalent to approximately 7 mg of solids) was held in a folded strip of 250 mesh stainless steel wire screen that was clamped between two brass electrodes. Because the liquor was pyrolyzed as a thin film, heat transfer resistances were minimized.

The sample was heated by electrical resistance. Two parallel heating/timing circuits were employed, one to heat the liquor to the desired temperature, the other to maintain the temperature at this level. The heating circuits allowed fast heating times (4000° C/second) and could maintain temperatures of greater than 1000° C.

The gases produced during pyrolysis were transported by a nitrogen purge to a quartz combustion tube contained in a tube furnace. There the pyrolysis gases were mixed with air and the reduced sulphur compounds oxidized to SO₂. The sulphur dioxide concentration was measured by an ultraviolet absorption SO₂ analyzer (Teledyne Model 6000). The pyrolysis reactor system is shown in Figure 2.

The sulphur-containing liquors were pyrolyzed in the reactor at temperatures ranging from 250 to 750° C. Pyrolysis times of up to 15 seconds were employed.

Results and Discussion

As was expected, little sulphur (2% or less) was released from the sulphate or sulphite liquors, even at pyrolysis times of 15 seconds. However, both the thiosulphate- and sulphide-containing liquors released large quantities of sulphur during pyrolysis.

The results from the thiosulphate pyrolysis are shown in Figures 3-6. The figures show a great deal of scatter in the sulphur release data. The reasons for this scatter are discussed

elsewhere [10]. Sulphur release began at temperatures above 250° C and increased with increasing temperature up to about 450° C. At this temperature, and the maximum pyrolysis time of 15 seconds, 40 to 50 percent of the thiosulphate's sulphur was volatilized. At temperatures above 500 degrees, the amount of sulphur volatilized decreased with increasing temperature.

Figures 7-9 show the results of the pyrolysis experiments with liquor containing sulphide. Sulphur release began at temperatures of approximately 300° C. Maximum release occurred at temperatures of 450-500° C. At these temperatures an average of 40 percent of the sulphur present as sulphide was volatilized. Some individual sulphide tests resulted in a release of 60 to 70 percent of the sulphide sulphur. This result is in contrast to the results obtained from the thiosulphate pyrolysis tests, for which the maximum release was 50 percent or less. Sulphur release from sulphide-containing liquor declined when the pyrolysis temperature was increased above 500 degrees.

The reason for the lower sulphur release at high pyrolysis temperatures is not clear. Thermodynamic calculations for sulphur release reactions between sodium sulphide and black liquor pyrolysis products (chiefly CO_2 and H_2O) indicate that, at higher temperatures, the condensed sulphur compounds are favored. However, as the experimental apparatus employed in these experiments did not allow an equilibrium to be established between the condensed and gaseous sulphur species, such an explanation does not directly apply.

Another explanation for the decline of sulphur release at higher temperatures is the presence of a competing reaction which converts the sulphur to a compound that does not release sulphur. Still another possibility is the exhaustion of co-reactants necessary for sulphur release. Many of the proposed mechanisms for sulphur volatilization during black liquor pyrolysis require the presence of other pyrolysis products, such as carbon dioxide and water. If these products were released quickly during pyrolysis, the volatilization of sulphur could be diminished at high temperatures. This explanation could account for the differences seen between the results of the present study and those obtained in previous pyrolysis studies [1,2] where up to 70 percent of the liquor's sulphur was volatilized. In the previous studies, there was ample opportunity for reaction between the released pyrolysis products and the liquor's sulphur compounds. In the present study, pyrolysis of the liquor as a thin film and the rapid removal of the pyrolysis products by the purge gas minimized the opportunity for additional reaction. The presence of both sodium sulphate (a non-volatile sulphur species) and sodium sulfide (a volatile one) in completely pyrolyzed kraft chars [11], provides evidence that both of these mechanisms may be responsible for the decline in sulphur release at high pyrolysis temperatures.

Model

A common method of modeling the kinetics of pyrolysis reactions is to treat the reaction as a first order decomposition [8]. The amount of volatiles (or, one or more of the pyrolysis products) produced is calculated by:

$$dV/dt = K(V^* - V) \quad (1)$$

where:

V = amount of volatiles emitted at time t (usually expressed as a fraction of initial volatiles content)

V* = maximum fraction that can be volatilized

K = rate constant.

The rate constant, K, is usually correlated using an Arrhenius-type expression:

$$K = K_0 e^{-E/RT} \quad (2)$$

where:

K₀ = pre-exponential factor

E = activation energy

R = gas constant

T = absolute temperature.

This equation can be solved for the amount of volatiles emitted to obtain:

$$V = V^* - V^* \exp\left(\int_0^t K dt\right) \quad (3)$$

where the integral describes the sample's time-temperature history.

The results of the pyrolysis experiments were examined with the view of fitting a first order decomposition model to the

measured releases. Because of the low amounts of sulphur released during pyrolysis of liquors containing sodium sulphate or sodium sulphite, these compounds were modeled as being stable during black liquor pyrolysis.

It is apparent from Figures 3-9 that a first order decomposition model would not, by itself, adequately describe sulphur release from thiosulphate- and sulphide-containing liquors. The first order decomposition model predicts a rise in the amount of sulphur released during a given pyrolysis interval with increasing temperature until the upper limit, V^* , is reached. After this limit is reached, further increases in temperature will have no effect on the amount of sulphur volatilized. However, for both the thiosulphate- and sulphide-containing liquors, the amount of sulphur released during a given interval was lower at high ($>500^\circ \text{C}$) temperatures.

To model the behavior of the thiosulphate and sulphide liquors at high temperatures, the maximum amount of sulphur that could be released, V^* , was modified by multiplying it by an empirical factor, F , that was defined as the fraction of V^* that can be released. F was assumed to be a function of temperature of the form

$$\ln(F) = A/T + B \quad (4)$$

where T is the absolute temperature and A and B are constants. At low temperatures, F is equal to one.

Computer programs were written to determine the optimal values of the kinetic constants K_0 , E , V^* , A , and B . The program

inputs were pyrolysis time, pyrolysis temperature, and fraction of sulphur released. A least squares method was used to select the best values for the five constants. These values for pyrolysis of sodium thiosulphate and sodium sulphide are shown in Table I.

The results of the pyrolysis kinetics experiments compared to the model predictions are shown in Figures 3-9.

To test the models developed, two soda liquors to which thiosulphate and sulphide had been added and four kraft liquors were pyrolyzed in the captive sample reactor and the amount of sulphur released measured. This amount of sulphur is compared to the model's predictions in Table II.

For the kraft liquors, the predicted sulphur releases are lower than those observed. There are several explanations for the differences between the predicted and calculated values. First, although kraft and soda black liquors result from similar pulping processes, there are some differences in the organic compounds present in the two liquors. The amount of sulphur released from inorganic sulphur compounds depends on the composition of the organic material with which the sulphur compounds are pyrolyzed [4,5]. Therefore, it is possible that the different organic composition of the kraft liquor results in an increased sulphur release.

Also, the pyrolysis model predicts sulphur release only from the sulphur present as thiosulphate and sulphide. Kraft liquors may contain other sulphur species, such as organic sulphur, that

may be volatile under pyrolysis conditions. Analysis of the kraft liquors tested showed the presence of 0.3-0.5 percent sulphur in forms other than sulphate, sulphite, thiosulphate, and sulphide. If it is assumed that 40% of this sulphur is volatilized, the predictions differ from the measured releases by an average of less than 10 percent.

Conclusions

The results of the pyrolysis experiments show that thiosulphate and sulphide, the two main volatile sulphur species found in black liquor, can release similar amounts of sulphur during pyrolysis. Approximately 40 percent of the sulphur present as either sulphide or thiosulphate can be volatilized during black liquor pyrolysis. At temperatures above 500° C, the amount of sulphur released from both thiosulphate and sulphide decline with increasing pyrolysis temperature.

The reasons for this decline in sulphur release at high pyrolysis temperatures are not clear. Further research, including more complete chemical analysis of the black liquor and its pyrolysis products, is required to confirm the sulphur release mechanism.

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Table I. Kinetic Constants For Thiosulphate and Sulphide Models.

	Thiosulphate	Sulphide
K_0 (1/sec)	255.1	9.692×10^6
E (kcal/mole)	10.49	24.10
V^* (fraction)	0.434	0.402
A (K)	3733.	7497.
B	-4.957	-9.785

Table II. Verification of pyrolysis kinetics model
(Pyrolysis Time = 9.0 Seconds)

Liquor Type	Thiosulphate Content (% as S)	Sulphide Content (% as S)	Pyrolysis Temp. (°C)	Sulphur Released (mg S/100 g solids)	
				Measured*	Predicted
Soda	1.40	1.00	436	804 ± 63	844
Soda	1.41	0.98	431	806 ± 121	817
Kraft	1.37	0.59	447	1092 ± 104	712
Kraft	2.14	0.33	462	1001 ± 215	927
Kraft	3.14	0.24	476	1448 ± 232	1248
Kraft	0.80	2.08	429	1432 ± 128	1023

*Average ± 95% confidence limits

Figure Captions

Fig. 1. Pyrolysis kinetics reactor - top and side view.

Fig. 2. Pyrolysis kinetics reactor system.

Fig. 3. Thiosulphate release model - 4.5 seconds.

Fig. 4. Thiosulphate release model - 9.0 seconds.

Fig. 5. Thiosulphate release model - 10.5 seconds.

Fig. 6. Thiosulphate release model - 15.0 seconds.

Fig. 7. Sulphide release model - 4.5 seconds.

Fig. 8. Sulphide release model - 9.0 seconds.

Fig. 9. Sulphide release model - 15.0 seconds.

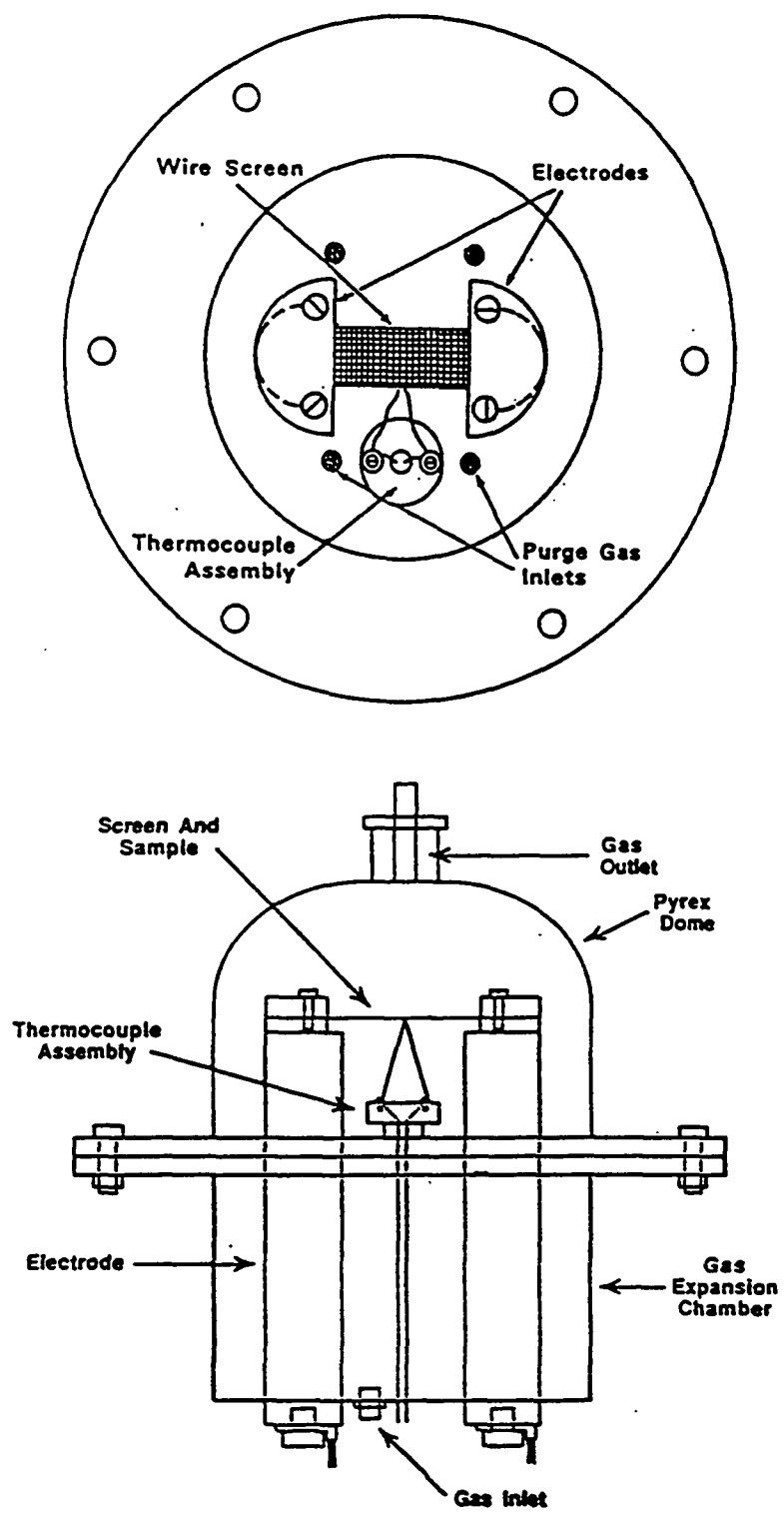


Fig. 1. Pyrolysis kinetics reactor - top and side view.

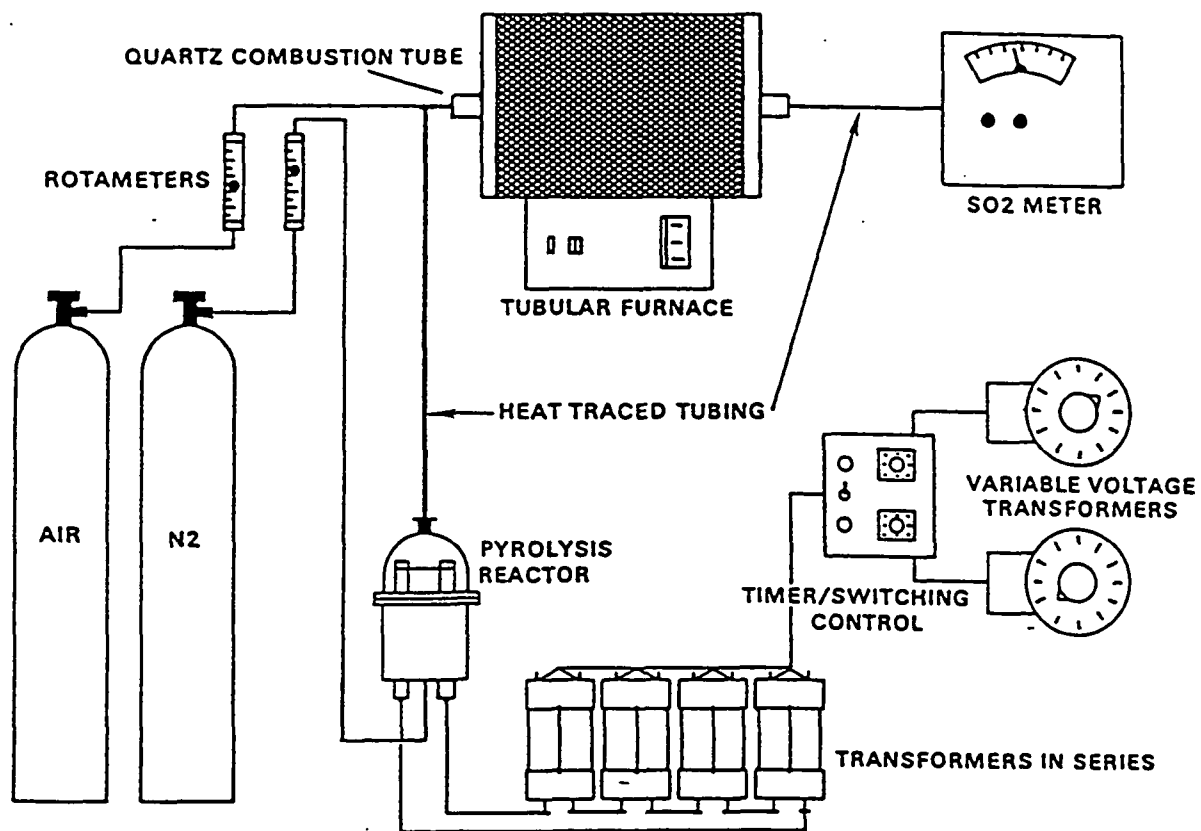


Fig. 2. Pyrolysis kinetics reactor system.

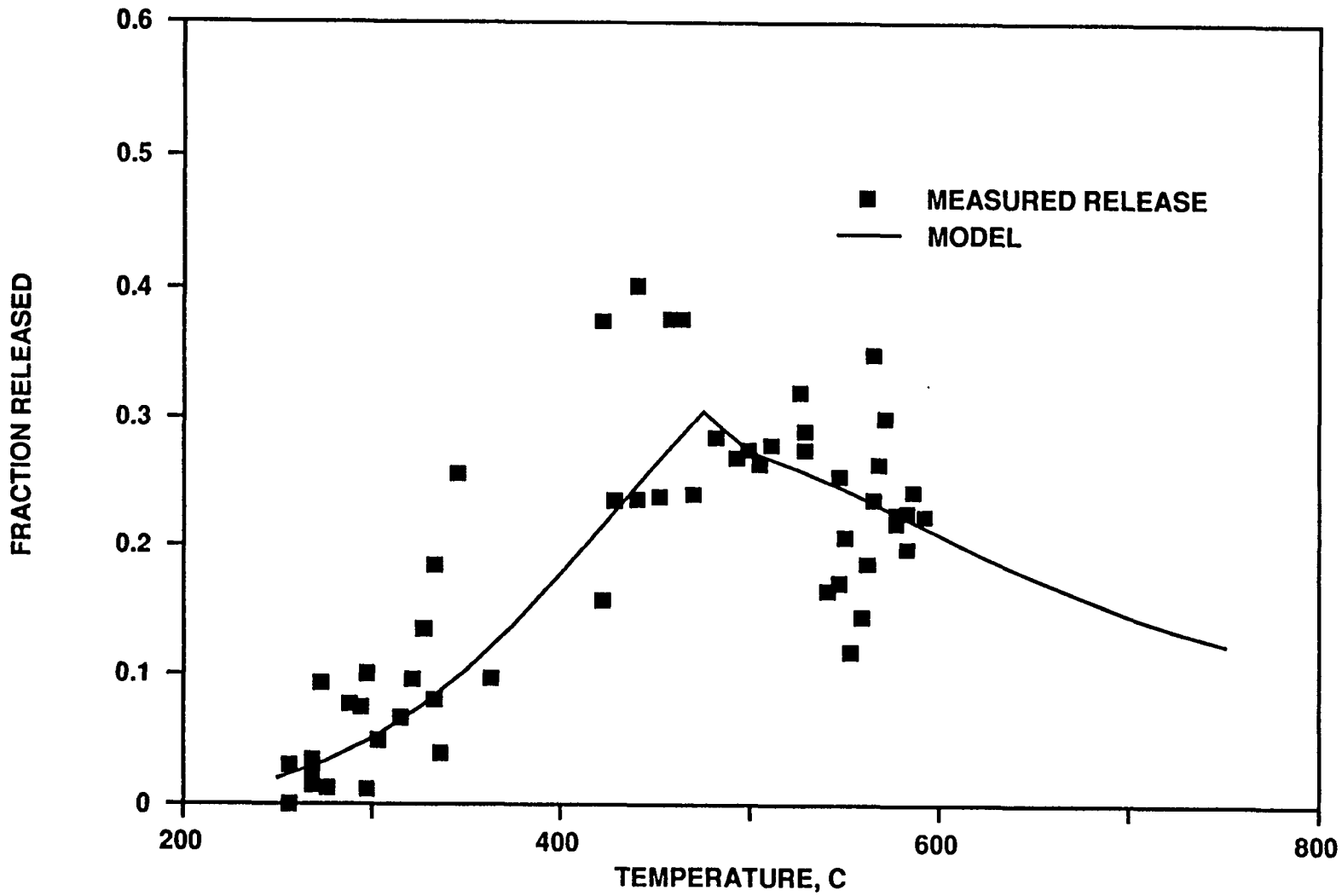


Fig. 3. Thiosulphate Release Model - 4.5 Seconds

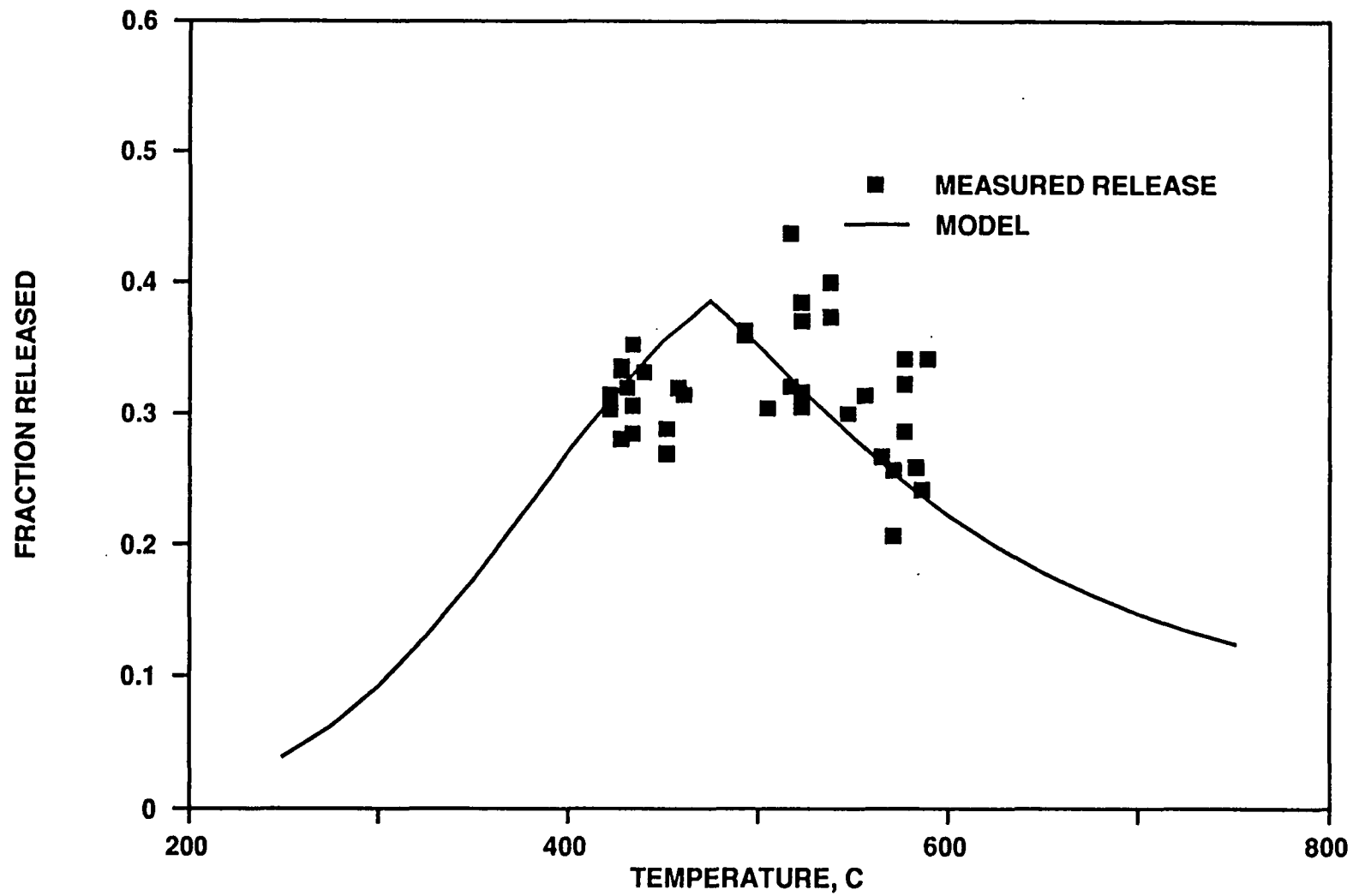


Fig. 4. Thiosulphate Release Model - 9.0 Seconds

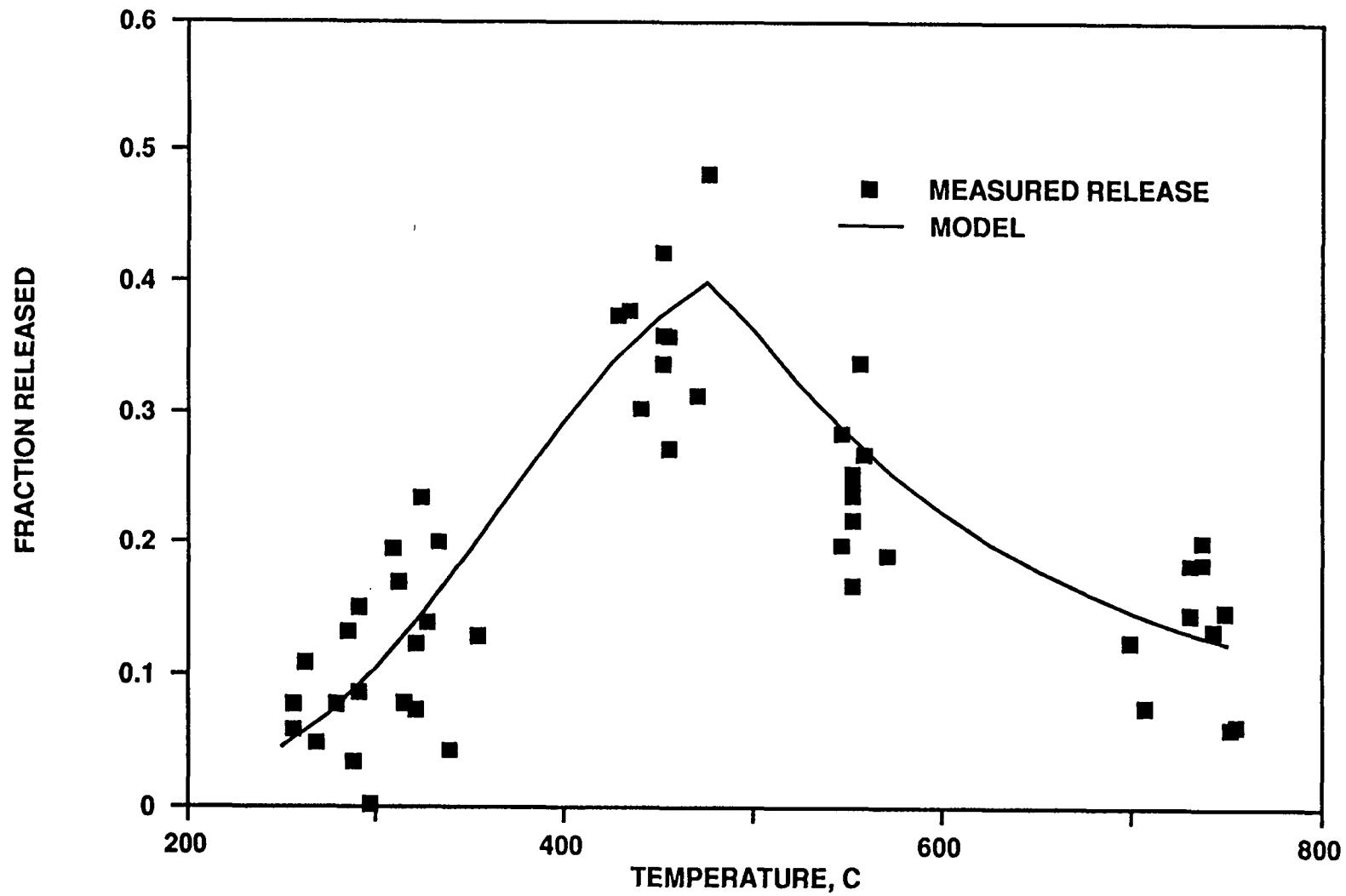


Fig. 5. Thiosulphate Release Model - 10.5 Seconds

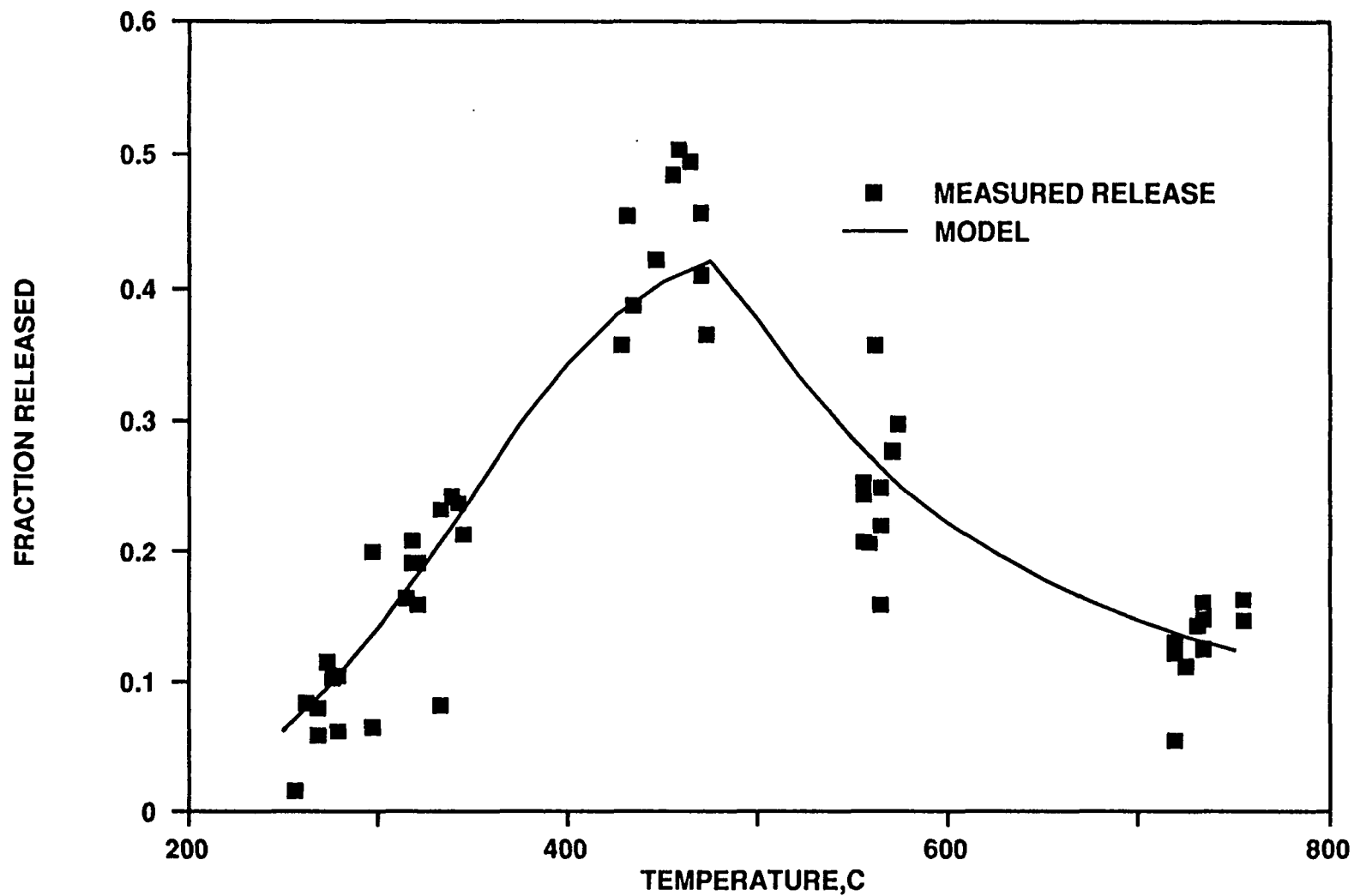


Fig. 6. Thiosulphate Release Model - 15.0 Seconds

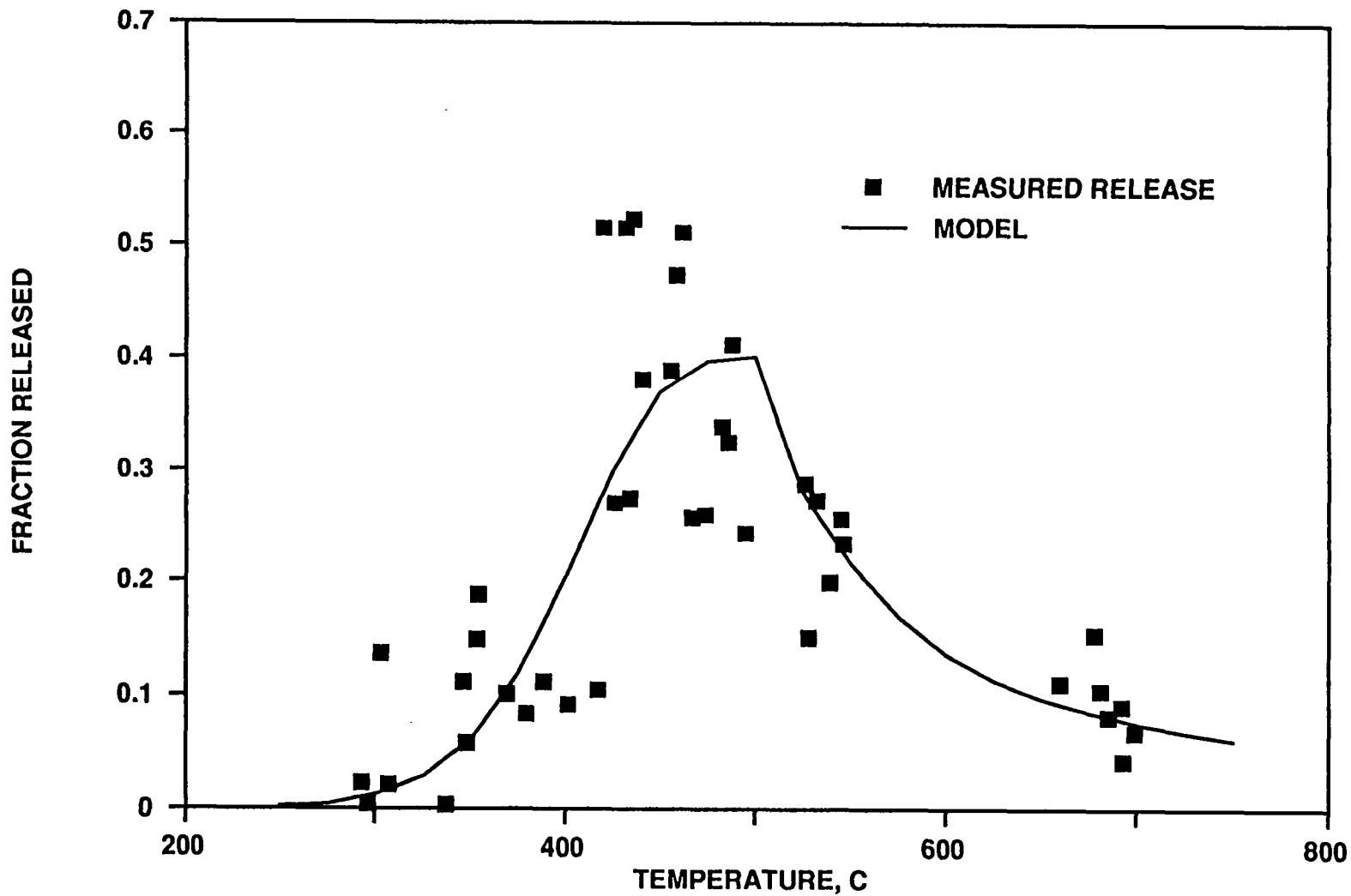


Fig. 7. Sulphide Release Model - 4.5 Seconds

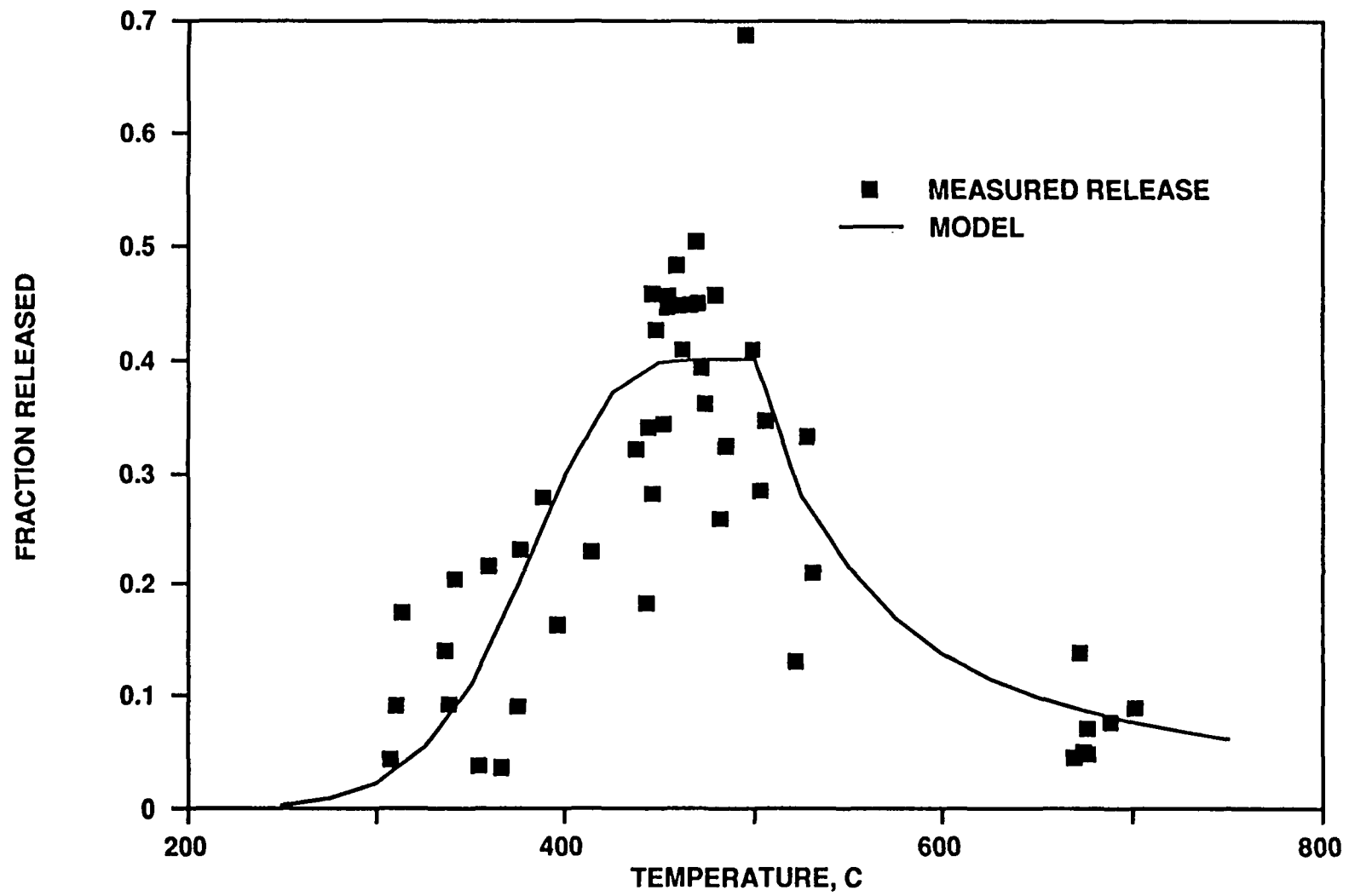


Fig. 8. Sulphide Release Model - 9.0 Seconds

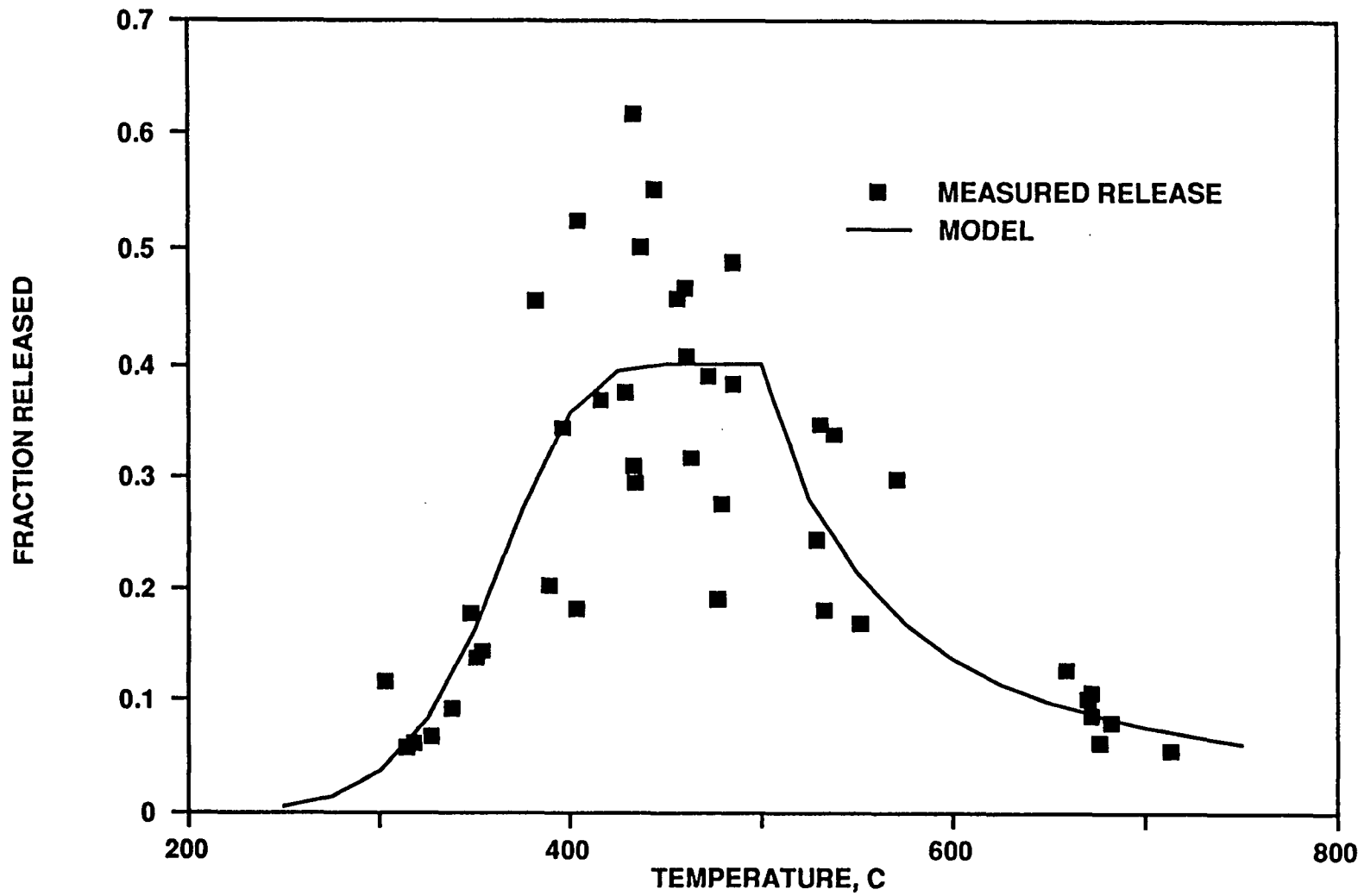


Fig. 9. Sulphide Release Model - 15.0 Seconds