IR 72-47 September 1, 1972

AN EVALUATION OF THE SOLID STATE CARBONATION

PROCESS FOR THE RECOVERY OF SODIUM SULFITE

FROM WASTE SULFITE PULP LIQUORS

by

R.C. Kerby and T.R. Ingraham

EXTRACTION METALLURGY DIVISION

Mines Branch Investigation Report IR 72-47

AN EVALUATION OF THE SOLID STATE CARBONATION PROCESS

FOR THE RECOVERY OF SODIUM SULFITE FROM WASTE

SULFITE PULP LIQUORS

by

R.C. Kerby* and T.R. Ingraham**

ABSTRACT

A study was made of several aspects of the solid-state carbonation process for recovering sodium sulfite from waste sulfite pulping liquors. In particular, the kinetics of the solid-state carbonation step of the process were examined in detail. The experimental results indicated that the optimum conditions for the solid-state carbonation of synthetic smelts are temperatures between 150° and 200°C, with a CO_2 partial pressure greater than 0.4 atm. and a water vapour partial pressure between 0.05 and 0.10 atm. The reaction is dependent on an adequate supply of CO_2 and H_2O to the reacting smelt and the rapid removal of the product gas, H_2S, from the reaction site.

*Research Scientist, Extraction Metallurgy Research Section, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada.
**Formerly Head, Extraction Metallurgy Research Section, and now Director, Technology Development Branch (Air), Environmental Protection Service, Department of the Environment, Ottawa, Canada.

INTRODUCTION

Sulfite pulp mills based in Canada are now faced with a number of stringent controls which will regulate the amount of pollutants that they will be allowed to release to the watershed. Consequently, a number of processes which should be capable of reducing pulp mill liquid wastes are under review at the present time. Recognizing a need for consultation on several recovery processes which involved metallurgical type operations, the Process Development Division of the Canadian International Paper Company in Hawkesbury, Ontario, approached the Mines Branch's Extractive Metallurgy Division for advice[1]. Following a visit on March 23, 1971, to the Research Laboratories of the Process Development Division by the authors, it was agreed that the Mines Branch would undertake some preliminary work to determine whether a feasible method could be devised for recovering sodium sulfite from the waste liquors of the sodium-based sulfite pulping process.

A review of the literature concerning sodium sulfite recovery methods[2] indicated that, although a number of processes are under development, none have gained general acceptance by the sodium-based sulfite pulping industry. Most processes involved the pyrolysis of the waste sulfite liquors, followed by chemical conversion of the resulting smelt to

sodium sulfite and the return of the sodium sulfite to the pulping circuit.

A preliminary study[3] indicated that a process using a solid state carbonation step to convert the smelt to sodium sulfite was feasible. The results showed that sodium sulfide, which is present in the smelts resulting from the pyrolysis of the waste sulfite liquors, was quickly and efficiently converted to sodium carbonate in the presence of carbon dioxide and water vapour. In the present report, the rates of carbonation of artificial smelts composed of sodium sulfide and sodium carbonate are reported.

EXPERIMENTAL

Preparation of Materials

Anhydrous reagent grade Na_2S and a variety of its hydrates were studied to determine the nature of the carbonation reaction. The hydrates were obtained by dehydrating reagent grade $Na_2S \cdot 9H_2O$ under partial vacuum and with controlled heating. Synthetic smelts were prepared from reagent grade anhydrous Na_2S and Na_2CO_3. Various ratios of sulfide to carbonate were used and the melts were heated to 900°C before cooling and crushing. A dry argon atmosphere was used to protect the sulfide from oxidation and hydration on cooling.

Apparatus and Method

The rates of reaction were determined by two methods; the first by weight change, and the second by evolution of gaseous H_2S. A Cahn electrobalance was used for observing the weight change of both compressed cylindrical pellets and powdered samples. The pellets were 0.5 inch in diameter, 0.04 inch in height and were prepared at 100,000 psi from minus 48-mesh powder. The density (d_o) of the pellets varied between 70 and 80% of the theoretical density.

The rate of evolution of gaseous H_2S was determined by bubbling the reaction product gases through a 1N NaOH solution and measuring the increase in the sulfide ion concentration with a sulfide ion electrode. The reaction gases were also analyzed by standard wet-chemical techniques. The reaction products were identified by X-ray diffraction analysis and standard wet-chemical analysis.

Reaction temperatures were measured by thermocouples located within 1 cm. of the pellets, and in several cases by very fine (0.002 in.) thermocouples placed on the surface of the pellets. The reaction temperatures shown in the tables are those at the pellet surface.

Data Analysis

The results from the weight change experiments were normalized to obtain the rate of movement of the reactant-

product interface into the pellet[4]. The rate of migration

is given as $r_o f$, where r_o is the equivalent radius and f the

fractional penetration for a given geometry. The product,

$r_o d_o f$ is the weight change per unit area that occured as the

interface advanced.

RESULTS AND DISCUSSION

Stoichiometry and Rate Equation

The carbonation of sodium sulfide in the presence of

carbon dioxide and water vapour can be represented by the

reaction:

$$Na_2 S \cdot xH_2 O + yH_2 O + CO_2 \rightleftharpoons Na_2 CO_3 \cdot (x+y-1)H_2 O + H_2 S \qquad [1]$$
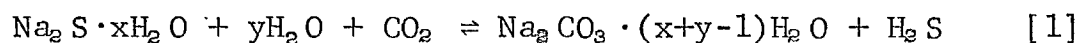
At least one mole of water is required for the conversion of

one mole of sodium sulfide to sodium carbonate. This water

can be supplied either as water vapour or as water of hydration

associated with the sodium sulfide. The sodium carbonate which

is formed will be present either in the anhydrous state or

the hydrated state, depending on the temperature at which the

reaction occurs.

The carbonation of anhydrous sodium sulfide to yield

anhydrous sodium carbonate is exothermic, with a heat of

reaction of 22 kcal/mole at 100°C[5]. Preliminary experi-

ments[3] indicated that sodium sulfide monohydrate reacted

at a significantly greater rate than either anhydrous sodium

sulfide or the higher hydrates of sodium sulfide. Sodium carbonate was the principal product, but small amounts (1-3%) of Na_2SO_3 were also detected in some of the experiments. Hydrogen sulfide was the only product gas found in the effluent gas stream, although previous studies have reported trace amounts of CO, COS, and H_2 [5]. Similar analyses were made on the reaction products resulting from the studies recorded in this report. The same products were found in both cases.

The general rate equation applicable to a cylindrical pellet of pressed powder which undergoes a heterogeneous reaction along an advancing interface is [4].

$$\alpha = 1-(1-f)^2(a-f)/a \qquad [2]$$

where α is the fractional decomposition, f is the fractional thickness of the layer of reacted material, and a is the ratio of the pellet height to pellet diameter. This equation was used to normalize the observed reaction rates for the change in interfacial area which occurred as the reaction proceeded. A surface roughness factor of unity was assumed. The rate of migration of the reaction interface was calculated as r_0f. The carbonation rates were calculated from the product r_0d_0f, which is the weight change per unit area that takes place as the interface advances. Visual examination of the sectioned pellets after reaction confirmed that the carbonation reaction occurred along a well-defined interface.

Influence of Composition on the Carbonation Reaction

Comparable initial rates of carbonation in the temperature range 80 to 180°C were found for three synthetic smelts composed of sodium sulfide and sodium carbonate (Table 1). The rate of carbonation of sodium sulfide monohydrate was 60% greater under the same conditions. The initial rates of reaction were best represented by the parabolic rate equation:

$$(r_o d_o f)^2 = K_p t \qquad [3]$$

where $r_o d_o f$ is the weight change per unit area, t is the time in minutes and K_p is the parabolic rate constant with units of $mg^2 \cdot cm^{-4} \cdot min^{-1}$.

For the pelletized sodium sulfide smelts, the rate of reaction changed after approximately ten minutes to a logarithmic rate of the form:

$$r_o d_o f = K' \log t \qquad [4]$$

where K' is the logarithmic rate constant with units of $mg \cdot cm^{-2} \cdot (\log min)^{-1}$. The sodium sulfide monohydrate pellets did not show this behaviour until after the carbonation reaction had proceeded for approximately 30 minutes. However, anhydrous sodium sulfide, which reacted very slowly, only showed logarithmic rate kinetics during the course of carbonation (Table 1).

An Arrhenius plot of the parabolic rate data listed in Table 1 indicated that the activation energy of the initial

Table 1

Effect of Temperatures on the Rate of Carbonation of Sodium Sulfide

Gas flow rate: 50 ml min^{-1}. Gas composition: CO_2, 0.520 atm; N_2, 0.448 atm; H_2O, 0.032 atm.

I: Anhydrous Sodium Sulphide. II: Sodium sulphide monohydrate
III: Smelt (50 mole % Na_2S, 50 mole % Na_2CO_3). IV: Smelt
(10 mole % Na_2S, 90 mole % Na_2CO_3. V: Smelt (20 mole % Na_2S,
80 mole % Na_2CO_3).

Composition	Temperature (°C)	Parabolic Rate ($mg^2/cm^4 \cdot min$)	Logarithmic Rate (mg/cm^2 (log min))
I	81	--	0.064
	94	--	0.072
	112	--	0.14
	157	--	0.18
II	88	7.2	8.6
	108	14.5	11.6
	121	19.1	12.8
	143	29.0	14.6
	150	29.5	14.7
III	83	4.4	1.9
	96	6.9	2.3
	104	9.2	2.4
	122	12.0	2.4
IV	81	4.0	2.1
	103	10.4	2.6
	137	11.2	2.7
	159	17	2.9
V	81	4.6	1.68
	98	6.9	1.77
	118	10.0	1.92
	139	15.1	2.12
	174	32.1	2.29
		Linear Rate ($mg/cm^2 \cdot min$)	
	25	0.049	2.03
	33	0.024	2.14
	45	0.043	3.36
	54	0.064	3.72
	62	0.116	4.70

carbonation reaction was 6.8 ± 0.3 kcal/mole for the sodium sulfide-sodium carbonate smelts and for sodium sulfide monohydrate (Figure 1). This would indicate that the carbonation reaction is similar in these cases and is not affected by the initial presence of sodium carbonate. The faster reaction rates observed for the monohydrate were probably due to the fact that the water required for the carbonation reaction was already present in the sulfide compound. However, only very slow reaction rates were found for pelleted sulfide smelts which had been hydrated.

Because the carbonation reaction is exothermic, there is a tendency for the reacting pellet to become hotter than its surroundings. In some experiments, temperature increases of 5 to 10°C were found. The temperatures given in Table 1 have been corrected for this increase. The activation energy for the logarithmic carbonation rate found for anhydrous sodium sulfide was approximately 4 kcal/mole.

The percentage conversion of sodium sulfide to sodium carbonate for sodium sulfide smelts, and for sodium sulfide monohydrate in pellet form, can be found as a function of the parabolic rate and the reaction time from the chart shown in Figure 2. For example, 19% of the sodium sulfide present in a pellet (diameter = 0.50 in., height = 0.04 in.) of any of the above four compositions will be converted to sodium carbonate after ten minutes when the parabolic rate is
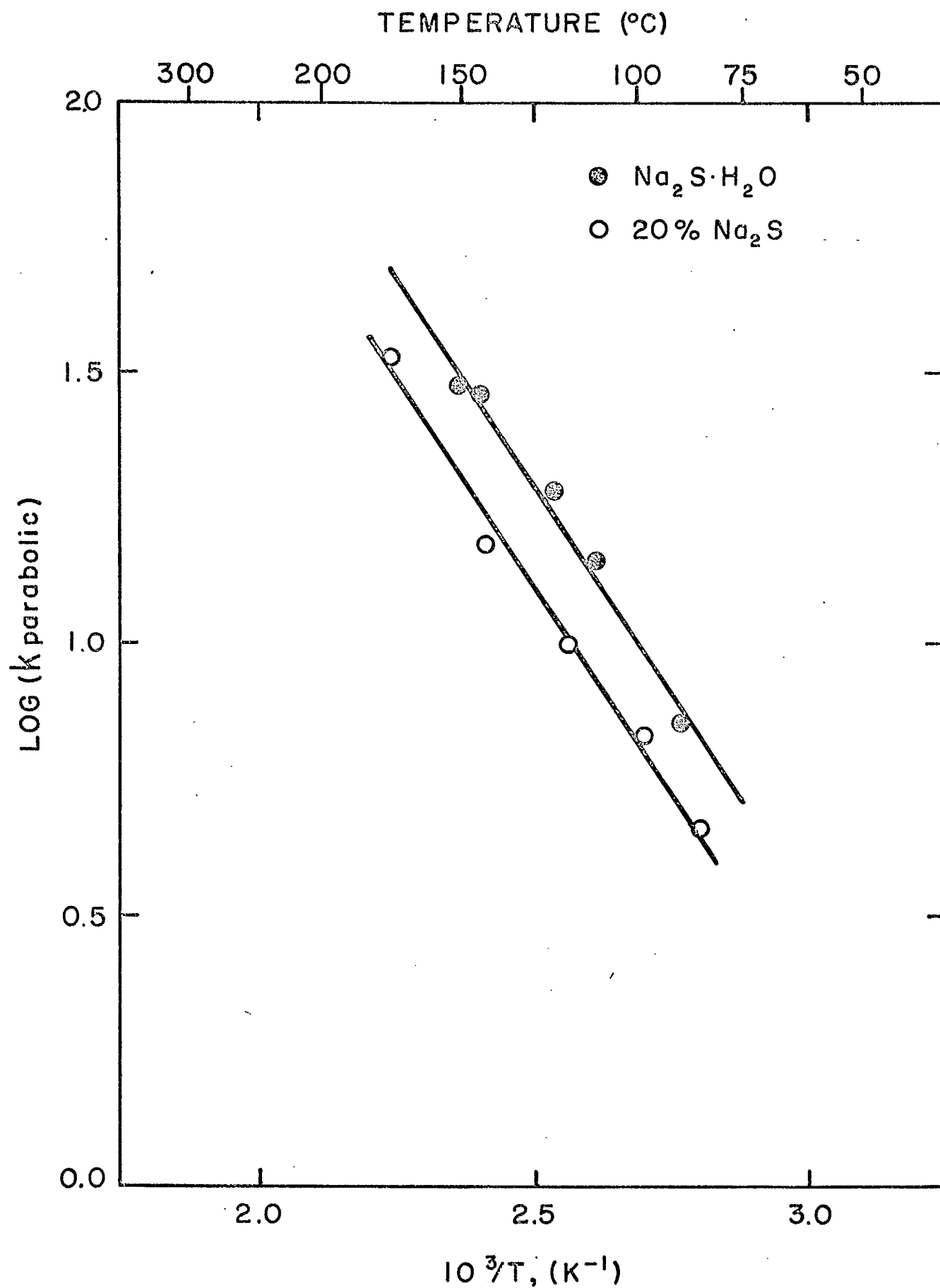
Figure 1: Effect of Temperature on the Rate of Carbonation of Sodium Sulfide Monohydrate and Pelletized 20% Na₂S Smelt.

30 mg^2/cm^4 sec. Tests made with two different sizes of pellets indicated that a decrease in the total surface area of the pellets had no effect on the reaction rate (Table 2). Thus a finely ground powder of the sodium sulfide smelts or of the monohydrate, could be expected to convert to sodium carbonate in a much shorter time than the pellets, because there is a much larger surface area relative to the amount of sodium sulfide present.

Table 2

Effect of Surface Area on the Rate of Carbonation of Pelleted
50 mole % Na_2S, 50 mole % Na_2CO_3

Gas Flow Rate: 50 ml/min

Gas Composition: CO_2 = 0.520 atm, N_2 = 0.448 atm, H_2O = 0.032 atm

Temperature ($°C$)	Area of Pellet (cm^2)	Parabolic Rate ($mg^2/cm^4 \cdot min$)
80	2.75	4.4
83	10.53	4.4
112	2.75	9.4
122	10.53	12.0

At temperatures below 80°C the carbonation reaction product was primarily hydrated sodium carbonate. The initial rates of reaction for the 20% sodium sulfide smelt and the monohydrate are best represented by the linear rate equation:
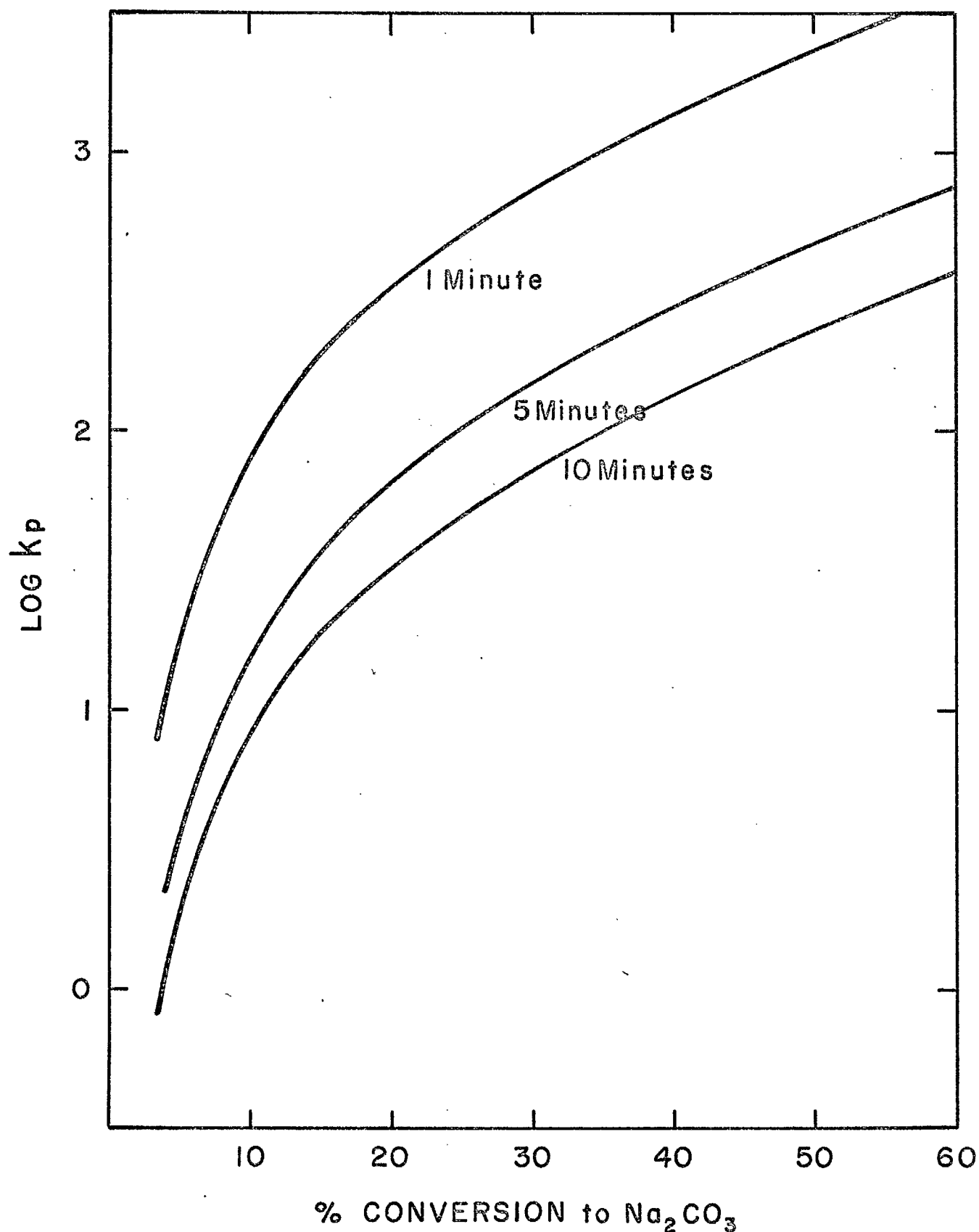
$$r_o d_o f = K_L t \qquad [5]$$

Figure 2: Chart for the Calculation of the Percentage Conversion of Sodium Sulfide Pellets to Sodium Carbonate For Various Parabolic Rates.

where K_L is the linear rate constant with units of $mg \cdot cm^{-2} \cdot min^{-1}$ (Table 1). After the carbonation reaction had proceeded for approximately thirty minutes, the reaction rate no longer followed a linear rate law, but was better represented by a logarithmic rate law (equation 4). Because the rate of reaction was followed by measuring the associated weight change, the measured reaction rates for temperatures below 80°C represent a combination of the carbonation rate and the hydration rate of both the sodium carbonate which is formed and the sodium carbonate originally present. Several experiments showed that the sodium carbonate present as a reaction product hydrated at a more rapid rate then the sodium carbonate that was present initially. Measurement of the hydrogen sulfide evolved from the reacting pellets gave an approximate indication that the weight change associated with the initial reaction was due primarily to the formation of sodium carbonate. The hydration of the sodium carbonate became important only after two or three minutes of reaction.

Effect of CO_2 and H_2O Partial Pressures on the Carbonation Reaction

The initial carbonation rates of both a 20% sodium sulfide smelt and the sodium sulfide monohydrate increased linearily with increasing CO_2 partial pressures, for reaction temperatures above 110°C (Figure 3). At temperatures below

110°C, no increase in initial carbonation rates were found

for CO_2 partial pressures greater than 0.5 atm (Table 3).

Because the effect of the CO_2 partial pressure on the reaction

rate differed as a function of both temperature and CO_2

partial pressure, the activation energies of the carbonation

reactions also varied. At CO_2 partial pressures less than

0.4 atm the activation energies associated with the carbonation

of 20% sulfide smelts were approximately 3 kcal/mole. When

the CO_2 partial pressure increased, the activation energies

increased to approximately 14 kcal/mole at a CO_2 partial

pressure of 1.0 atm. The activation energy of 6.8 kcal/mole

calculated previously (Figure 1) was for a CO_2 partial pressure

of 0.52 atm.

The initial carbonation rates for a 20% sulfide

smelt and for sodium sulfide monohydrate increased linearily

with increasing H_2O partial pressure for temperatures greater

than 80°C (Figure 4). Below this temperature, the initial

carbonation rate only increased for H_2O partial pressures

greater than 0.035 atm (Table 4). The activation energies

associated with the carbonation of 20% Na_2S smelts increased

slightly with increasing H_2O partial pressures.

The large effects that both the partial pressures

of CO_2 and H_2O had on the rate of carbonation of sodium

sulfide in its various forms indicates that the diffusion of

Table 3

Effect of the Parital Pressure of CO_2 on the Rate of Carbonation

Of Sodium Sulfide

Gas Flow Rate: 50 ml/min

Gas Composition: H_2O = 0.032 atm, remainder N_2 and CO_2

I: Sodium Sulfide Monohydrate ($Na_2S \cdot H_2O$)

II: Smelt (20 mole % Na_2S, 80 mole % Na_2CO_3

Composition	Temperature (°C)	P_{CO_2} (atm)	Parabolic Rate ($mg^2/cm^4 \cdot min$)	Logarithmic Rate (mg/cm^2 (log min))
I	136	0.12	9	10.2
	136	0.52	25	13.1
	136	0.71	35	13.0
	136	0.93	52	14.0
II	117	0.10	1.54	0.80
	117	0.43	7.2	1.71
	117	0.52	10.0	2.14
	117	0.75	14.1	4.20
	117	0.97	18.9	4.49
II	97	0.06	0.54	0.56
	97	0.30	5.4	2.17
	97	0.49	7.2	1.87
	97	0.52	6.8	1.77
	97	0.79	6.3	1.92
	97	0.97	5.6	1.72

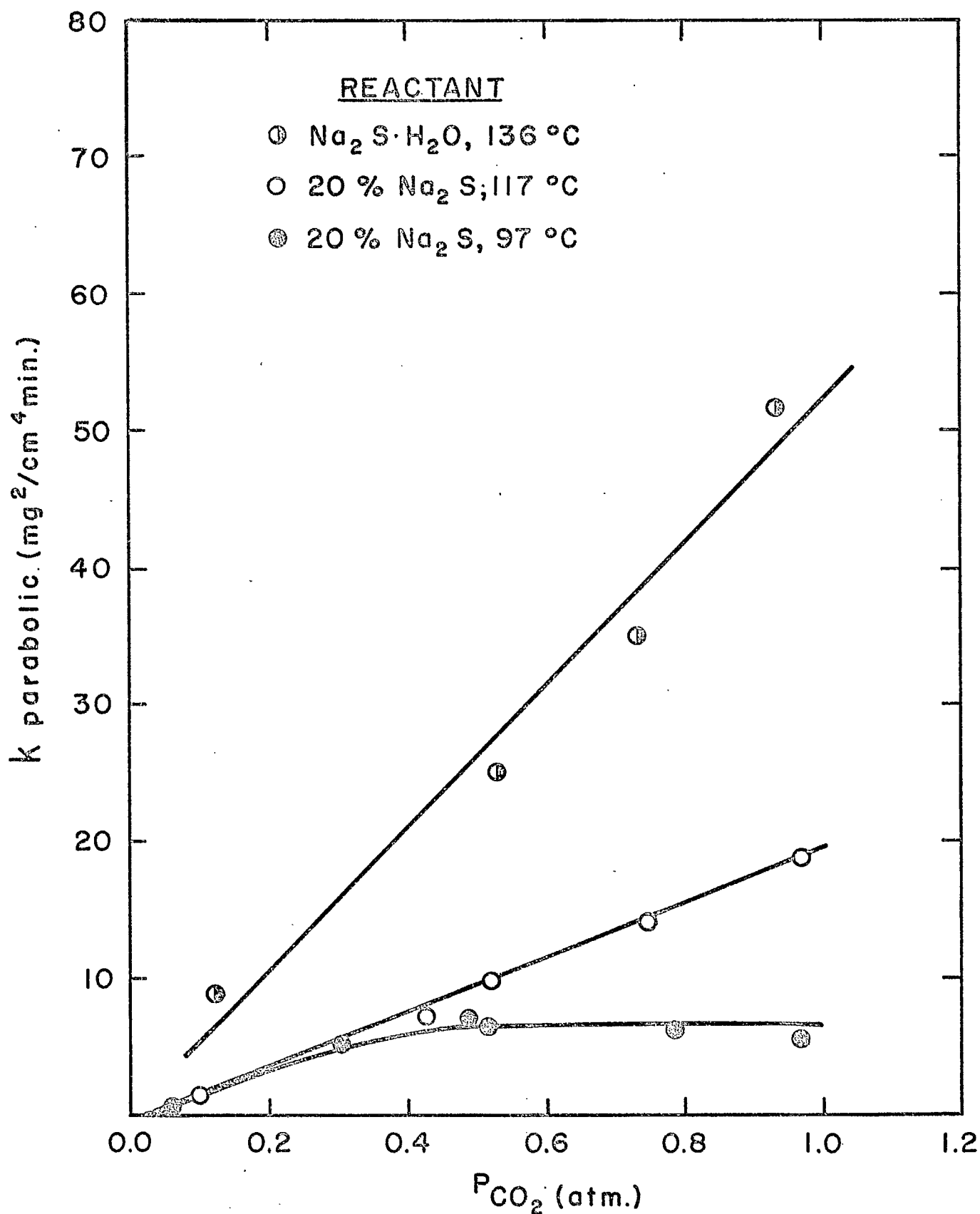|			Linear Rate ($mg/cm^2 \cdot min$)	
II	61	0.17	0.122	2.1
	61	0.52	0.116	4.7
	61	0.90	0.156	5.5
	61	0.97	0.191	8.3

Figure 3: Influence of the Partial Pressure of CO_2 on the Rate of

Carbonation of $Na_2S \cdot H_2O$ and Pelleted 20% Na_2S Smelt.

Table 4

Effect of the Partial Pressure of H_2O on the Rate of Carbonation

Of Sodium Sulfide

Gas Flow Rate: 50 ml/min

Gas Composition: CO_2 = 0.520 atm, remainder N_2 and H_2O

I: Sodium sulphide monohydrate ($Na_2S \cdot H_2O$)

II: Smelt (20 mole % Na_2S, 80 mole % Na_2CO_3)

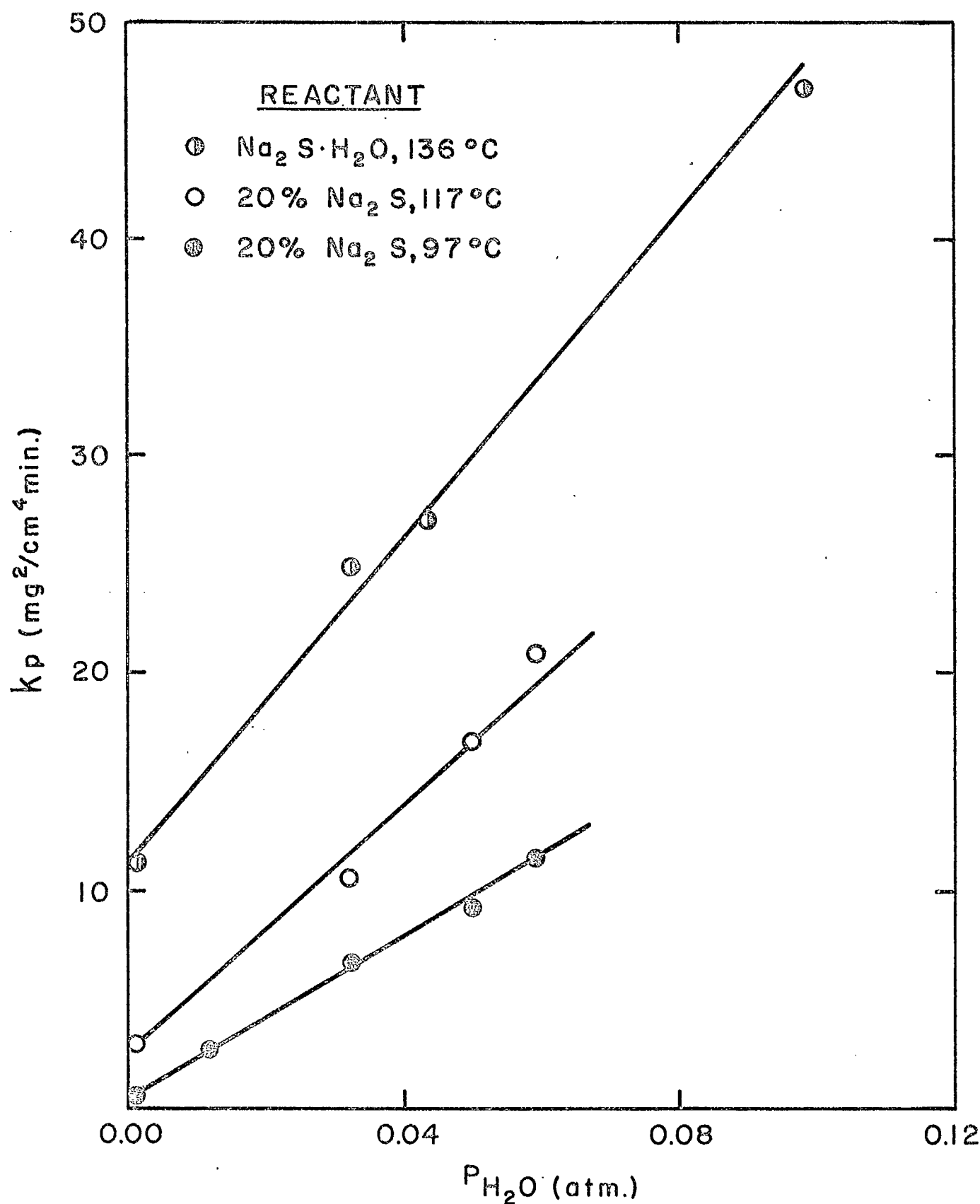| Composition	Temperature (°C)	P_{H_2O} (atm)	Parabolic Rate ($mg^2/cm^4 \cdot min$)	Logarithmic Rate (mg/cm^2 (log min))
I	136	0.001	11.1	8.5
	136	0.032	25.0	13.1
	136	0.043	27.2	7.7
	136	0.098	47.0	14.2
II	117	0.001	3.04	2.28
	117	0.032	10.0	2.13
	117	0.050	16.8	2.80
	117	0.059	20.8	2.24
II	97	0.001	0.54	1.28
	97	0.012	2.88	2.01
	97	0.032	6.8	1.71
	97	0.050	9.2	2.48
	97	0.059	11.2	1.92
			Linear Rate ($mg/cm^2 \cdot min$)	
	61	0.001	0.11	0.46
	61	0.014	0.13	0.61
	61	0.032	0.12	4.7
	61	0.045	0.36	4.8
	61	0.057	0.70	2.9

Figure 4: Influence of the Partial Pressure of H_2O on the Rate of Carbonation of $Na_2S \cdot H_2O$ and Pelleted 20% Na_2S Smelt.

CO_2 and H_2O to the reaction interface is an important step in the reaction mechanism. This is particularly evident for temperatures above 80°C, at which initial parabolic-type reaction kinetics were found. However, the rate-controlling step of the reaction mechanism apparently shifts toward chemical control at the reaction interface as the partial pressures of CO_2 and H_2O are increased. This is shown by the increase in activation energies and the decrease in the effect of CO_2, and probably H_2O, on the reaction rate as their partial pressures are increased. The logarithmic rate that was observed as the reaction progressed could indicate that the diffusion of CO_2 and H_2O through the reaction products is hindered in some way or that the chemisorption of the reacting gases is the rate-determining step[6].

Effect of Gas Flow Velocity on the Rate of Carbonation

The carbonation rate of a 20% Na_2S smelt increased with increasing gas flow velocity over the pellets (Table 5), but the effect became less pronounced as the gas flow velocity was increased or the temperature decreased. Increasing the gas flow velocity had two effects: it increased the supply of CO_2 and H_2O to the reacting pellet, and it increased the rate of removal of the product gas (H_2S) from the surface of the pellet. Both effects could increase the rate of carbonation. Several empirical tests indicated that the rate of

carbonation was reduced as the partial pressure of H_2S in the
reactant gas flow was increased.

Table 5

Temperature (°C)	Measured Flow Rate (ml/min)	Flow Rate Past Sample (cm/min)	Parabolic Rate ($mg^2/cm^4 \cdot min$)
117	50	5.2	10.0
117	78	8.2	14.4
108	50	5.1	8.2
108	75	7.6	10.6
98	50	4.9	6.9
98	80	7.9	9.4

The Solid-State Carbonation Process

A flow-sheet of the solid-state carbonation process
for the removal of sodium sulfite from waste sulfite pulp
liquors is shown in Figure 5. The waste sulfite liquor is
first evaporated to between 50 and 60% solids and is then burned
to yield a smelt consisting primarily of sodium carbonate with some
(10 wt %) sodium sulfide present. The smelt is cooled, crushed,
and then carbonated in a suitable reactor such as a rotary
kiln or a fluidized bed. The carbonated smelt is dissolved
to form a concentrated aqueous solution and sulfited, using
SO_2 formed from the oxidation of the carbonation product gas
H_2S. Additional SO_2 is recovered from the pyrolysis step by
passing the combustion gases through the sulfitation process.
Part of the waste gas from the sulfitation step, which contains
appreciable amounts of CO_2 and H_2O is used in the carbonation

step, while the remainder is vented to the atmosphere. This step has the additional advantage that only "clean" combustion gases are vented. The resulting sodium sulfite solution is returned to the pulping circuit.

A wealth of engineering and scientific data[2,7,8,9] are available on several aspects of the process, including the evaporation and pyrolysis of the waste sulfite liquors, the oxidation of gaseous H_2S, and the sulfitation of concentrated carbonate solutions. However, only a limited amount of data are available on the solidifying, crushing and solid state carbonation of smelts produced from the pyrolysis of waste sulfite liquors. A thermodynamic analysis indicated that the carbonation of sodium sulfide has an upper temperature limit of approximately 500°C[5], above which sodium carbonate begins to dissociate. The kinetic analysis of the carbonation reaction reported in this paper indicates that the carbonation of $Na_2S \cdot H_2O$, and synthetic smelts containing Na_2S, takes place quickly and efficiently under the proper conditions. Pilot plant tests with smelts prepared by the pyrolysis of waste sulfite pulp liquors have shown that more than 90% conversion to carbonate is possible for retention times of five to ten minutes[10]. Thus the solid-state carbonation of smelts containing sodium sulfide is certainly feasible, although there is not much data available on the engineering aspects
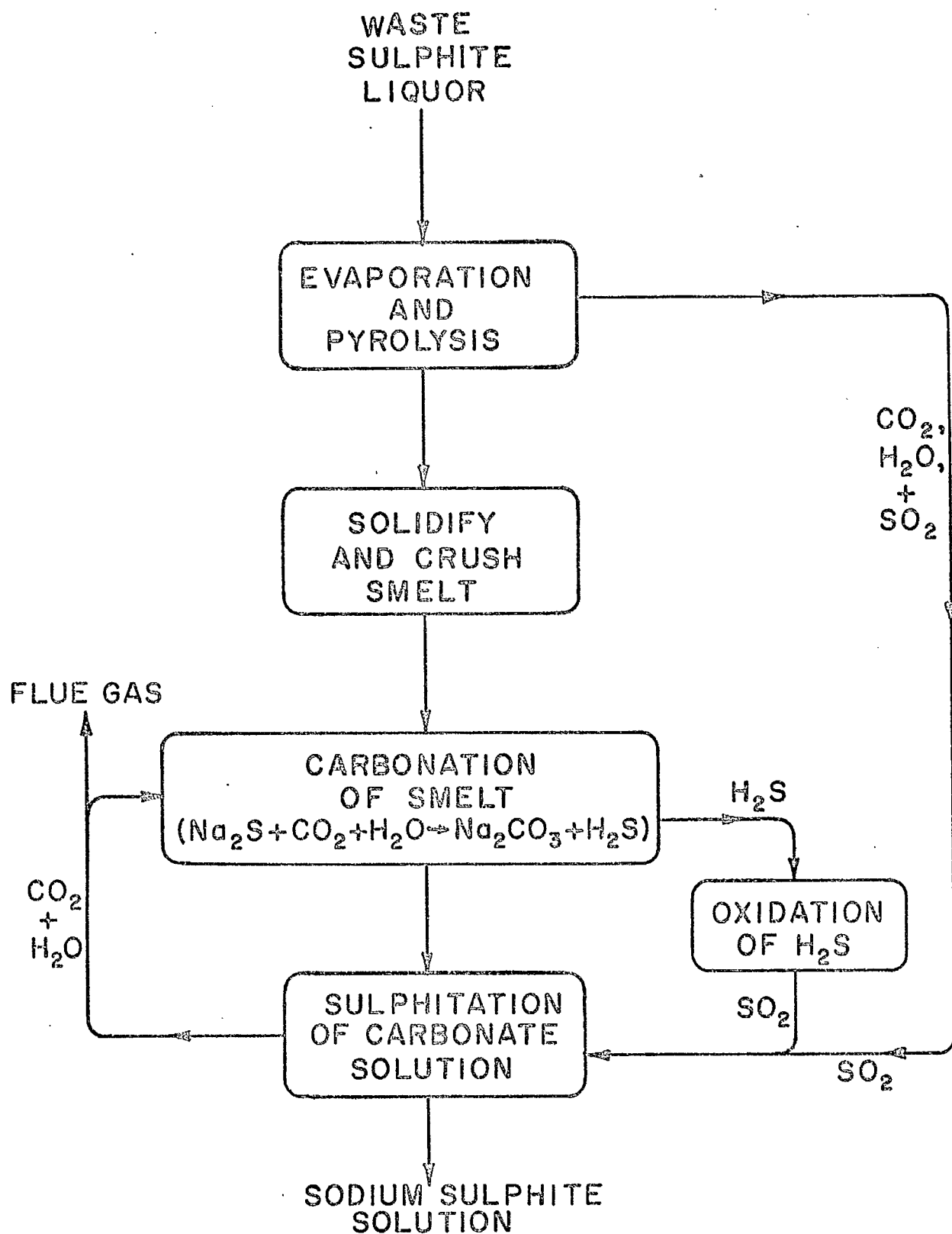
Figure 5: Flow-sheet of Solid-State Carbonation Process for Removal of Sodium Sulfide from Waste Sulfite Pulp Liquors.

of the process.

The composition of the smelt is of some importance to the process. Depending on the combustion parameters, the sulfur present in the waste sulfite liquors can be recovered either as sodium sulfide in the smelt, or as SO_2 in the combustion gas. When present as sodium sulfide in the smelt, the sulfur is released as H_2S in the carbonation stage and is converted to SO_2 which may be used to regenerate the sodium sulfite solution. When the sulfur is present as SO_2 in the combustion gas, it may be used directly to regenerate the sodium sulfite solution (Figure 5). There are some advantages in keeping the sodium sulfide content of the smelt reasonably low, because the carbonation reaction rate does not depend on the sodium sulfide concentration of the smelt. Several furnaces have been devised which will give low sulfide content smelts[7,11,12]. However, it must be kept in mind that the H_2S concentration in the off gases from the carbonation step must be kept high enough (approximately 15 vol %, ref.10) for oxidation of the H_2S to occur.

It is important that the solidified smelt be prevented from oxidizing or hydrolyzing before it reaches the solid-state carbonation reactor. This could be achieved by using an inert-gas blanket over the smelt when it is cooled and crushed. The degree of crushing would depend somewhat on

the type of reactor used in the solid-state carbonation step.
Fluid-bed reactors, which have good heat distribution and
gas-flow characteristics, would require particle sizes
between 100 and 325 mesh. Rotary kiln-type reactors[10]
would require particle sizes between 48 and 100 mesh. Because
the reaction is exothermic, some of the heat needed to keep
the crushed smelt at 150°C would be supplied by the reaction
itself.

SUMMARY

A study was made of several aspects of the solid-
state carbonation process for recovering sodium sulfite from
waste sulfite pulping liquors. In particular, the kinetics of
the solid-state carbonation step of the process were examined
in detail. On the basis of the studies reported here and
the pilot plant studies of a similar process reported else-
where[10,13], the process appears feasible. It offers several
advantages over other processes being developed. In particular,
the solid-state carbonation step is both fast and relatively
simple to operate. The process has the advantage that it is
continuous, and that both sodium and sulfur are conserved
throughout the process.

The process could now be taken to the pilot plant
stage, with some supporting bench-scale studies on the
carbonation of powdered smelts in a rotary kiln or a fluid-bed

reactor. Most steps of the process use existing technology. The only process step which has not been proven on a large scale is the solid-state carbonation step, and no difficulty should be encountered here. The experimental results indicate that the optimum conditions for the solid-state carbonation step are temperatures between 150 and 200°C, with a CO_2 partial pressure greater than 0.4 atm and a water vapour partial pressure between 0.05 and 0.10 atm. Operating conditions must be such that a good supply of CO_2 and H_2O are provided to the reacting smelt, and the product gas (H_2S) is quickly removed from the carbonation reactor.

REFERENCES

1. Ingraham, T.R., and Kerby, R.C., Extraction Metallurgy Division Internal Report EMV 71-16, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Canada (1971).

2. Collins, T.T., Jr., and Shick, P.E., Paper Trade Journal, vol. 153 (1969), June 30, 30-38; July 21, 54-57; Sept. 1, 36-44; Sept. 24, 48-52; Oct. 13, 72-74; vol. 154, (1970), June 22, 39-49; July 27, 39-42; Oct. 5, 50-53.

3. Kerby, R.C., and Ingraham, T.R., Mines Branch Investigation Report IR 71-67, Department of Energy, Mines and Resources, Ottawa, Canada (1971).

4. Ingraham, T.R., and Marier, P., Can. J. Chem. Eng., $\underline{41}$, 170 (1963).

5. Kaszegi, L., and Rosén, E., Trans. Roy. Inst. Tech., Sweden, Chem. $\underline{27}$, 21 pp (1964).

6. Landsberg, P.T., J. Chem. Phys. $\underline{23}$, 1079 (1955).

7. Rydholm, S.A., "Pulping Processes", Interscience Publishers, New York (1965).

8. Britt, K.W., ed., "Handbook of Pulp and Paper Technology", Reinbold Publishing Corp., New York (1964).

9. Stephenson, J.N., ed., "Pulp and Paper Manufactor", McGraw-Hill Book Co., New York (1950).

10. Nishizawa, A., Fukui, S., and Ono, M., Proc. Symp. Recovery Pulping Chem., 1st, 659(1968).

11. Gauvin, W.H., and Gravel, J.J.O., Tappi, $\underline{43(8)}$, 678 (1960).

12. Harntvedt, E., Tappi, $\underline{53(11)}$, 2147 (1970).

13. Ono, M., Horiguchi, T., Can. Patent 764,865, issued Aug. 8, 1967.