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RECYCLING OF WASTE SULFITE LIQUORS
FOR CANADIAN INTERNATIONAL PAPER CO.

HAWKESBURY, ONTARIO

by

R.C. Kerby and T.R. Ingraham
EXTRACTION METALLURGY DIVISION

Mines Branch Research Program
on Environmental Improvement

Mines Branch Investigation Report IR 71-67

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

SUMMARY

The rates of carbonation of synthetic smelts were studied in H_2O-CO_2 gas mixtures using pellets and powders prepared from reagent grade Na_2S and Na_2CO_3 . The reaction rates were rapid initially, but as it formed, the coating of Na_2CO_3 became increasingly protective to the Na_2S . This problem could be avoided and the reactions run to completion by using fine powders at $130^\circ C$.

This work showed that it would be relatively simple to recover the waste sulphite components in liquors and to convert them to reusable products by following the procedures outlined in this report.

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INTRODUCTION

The Canadian pulp and paper industry has been identified by the Honourable J. Davis, Minister of Environment Canada, as one of the major polluters of Canadian waterways⁽¹⁾. In recent environmental legislation, provision has been made to provide Federal Government assistance to the industry in overcoming its problems⁽²⁾.

On February 17, 1971, Mr. F. Hurtubise, Mr. Roy and Mr. Tambler of Canadian International Paper Co., and Mr. Gravelle, a consultant, visited the Mines Branch in Ottawa to discuss a request for assistance in developing a process for recovering sodium sulfite from waste sulfite liquors. The initial proposal involved an adaptation of a process patented by Edwin W. Arnold for the Copeland Process Corporation, Oak Brook, Illinois⁽³⁾. The Copeland process is for use with Kraft liquors, and the proposal was to develop a second stage in which the Na_2S that had been recovered from the liquors would be converted to Na_2SO_3 . It was suggested that a scheme proposed by Battelle Memorial Institute⁽⁴⁾ might be used. The scheme involved roasting Na_2S at elevated temperatures in the presence of steam and CO_2 to form Na_2CO_3 . In the last stage, Na_2SO_3 would be recovered by treating the Na_2CO_3 with an aqueous solution of sulfurous acid.

Before making any commitments, Dr. K.W. Downes, Chief, Extraction Metallurgy Division, suggested that a preliminary examination of the present state of the art should be made. Accordingly, the writers visited the CIP Research Laboratories in

Hawkesbury on March 23, 1971 and reported⁽⁵⁾ that there was indeed an opportunity for the application of metallurgical techniques in the solution of this problem. Accordingly, a literature review was begun, and preliminary results indicated that because of unfavourable thermodynamics, it was unlikely that the Battelle scheme could be developed satisfactorily. It was noted, however, that a recent Japanese process⁽⁶⁾ might be applied in the solution of the CIP problem. This was discussed with Mr. Hurtubise by telephone⁽⁷⁾ and a request was made by Mr. Hurtubise for small-scale test work that would establish whether or not, and if so - under what conditions, the Japanese process could be used.

The Japanese process involves the treatment of sodium sulfide smelts (the fused residue remaining after the pyrolysis of the organic material in waste liquors) with CO_2 and dry steam at much lower temperatures than those suggested by Battelle Memorial Institute. The Japanese experiments showed only 90% conversion to Na_2CO_3 and the rates of the conversion were not well specified. For the process to be applicable, it would be necessary to increase the conversion, or suggest means for coping with a deleterious residue of 10% unconverted Na_2S , and also to determine reaction rates and conditions so that suggestions of appropriate apparatus could be made.

This report covers an examination of the conversion of the Na_2S in smelts to Na_2CO_3 and reports on reaction rates and

the nature of the conversion process. Knowledge of the rates and nature of the process will make it possible to suggest the type of equipment most suitable for implementation.

EXPERIMENTAL

Preparation of Materials

Synthetic smelts were prepared from reagent grade anhydrous sodium sulfide and sodium carbonate. Various ratios of the sulfide to the carbonate were used and the melt was heated to 900°C before cooling and crushing. An argon atmosphere was used to protect the sulfide from oxidation and hydration on cooling.

Anhydrous reagent grade sodium sulfide and a variety of its hydrates were studied to determine the nature of the carbonation reaction. The hydrates were obtained by dehydrating reagent grade $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ under partial vacuum and with controlled heating. Anhydrous Na_2S was prepared by heating $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ to 700°C under an atmosphere containing 80% N_2 and 20% H_2 .

Apparatus and Method

The rates of reaction were followed by two methods; the first being weight change, and the second, evolution of hydrogen sulfide. A Cahn electrobalance was used for observing the weight change and thermal conductivity cells were used for observing the change in gas composition. Back-up chemical analyses of the gases were made using an iodometric titration technique.

Two forms of sample were used; a finely powdered material was studied in a small fluid bed in which 40-50 g could be used, and compressed cylindrical pellets were used on the thermogravimetric balance. Some powdered samples were also studied by the TGA method. The pellets were 0.5 in. in diameter, 0.04 in. in height, and were prepared at 100,000 psi from minus 48-mesh powder.

Results

Sodium sulfide is very hygroscopic. Because of the possible exposure to moisture of smelts containing Na_2S , the initial experiments in the project were done to assess the stability of the various hydrates of Na_2S . Reagent grade $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was heated at reduced pressure on the thermogravimetric balance and its stagewise dehydration was observed. The results are shown in Figure 1. The range of stability of the hydrates is shown in Table I.

The results shown in Figure 1 were obtained by continuously weighing a sample of hydrated sodium sulfide while it was kept at a reduced pressure, first at 25°C and then under a programmed increase in temperature. The experiment was repeated with $\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$ at atmospheric pressure in a mixture of 80% N_2 and 20% H_2 . The results show that the nona-, penta-, di- and monohydrates are the stable species at various temperatures below 600°C . The dihydrate was observed only when the dehydration was done at atmospheric pressure. The most important points to note are:

1. $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ begins to decompose at an appreciable rate to the pentahydrate, at room temperature, when a stabilizing partial pressure of water is absent.
2. The dihydrate is the stable form of sodium sulfide under the conditions of reaction likely to be used.
3. On gentle heating the pentahydrate may be converted to the monohydrate.
4. The partial pressure of water vapor over the monohydrate is low, and it is stable at temperatures up to 600°C in the absence of a stabilizing partial pressure of water.

TABLE I

Sodium Sulfide Hydrates

<u>Stable Hydrates</u>	<u>Temperature Range ($^\circ\text{C}$)</u>	<u>Gaseous Pressure (Atm)</u>	<u>Gas</u>
$\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$	20 - 40	1.0	N_2
$\text{Na}_2\text{S}\cdot 5\text{H}_2\text{O}$	40 - 70	1.0	N_2
	20 - 40	0.001	N_2
$\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$	130 - 170	1.0	N_2
$\text{Na}_2\text{S}\cdot \text{H}_2\text{O}$	200 - 620	1.0	$\text{N}_2 + \text{H}_2$
	95 - 250	0.001	N_2
Na_2S	700 - 740	1.0	$\text{N}_2 + \text{H}_2$

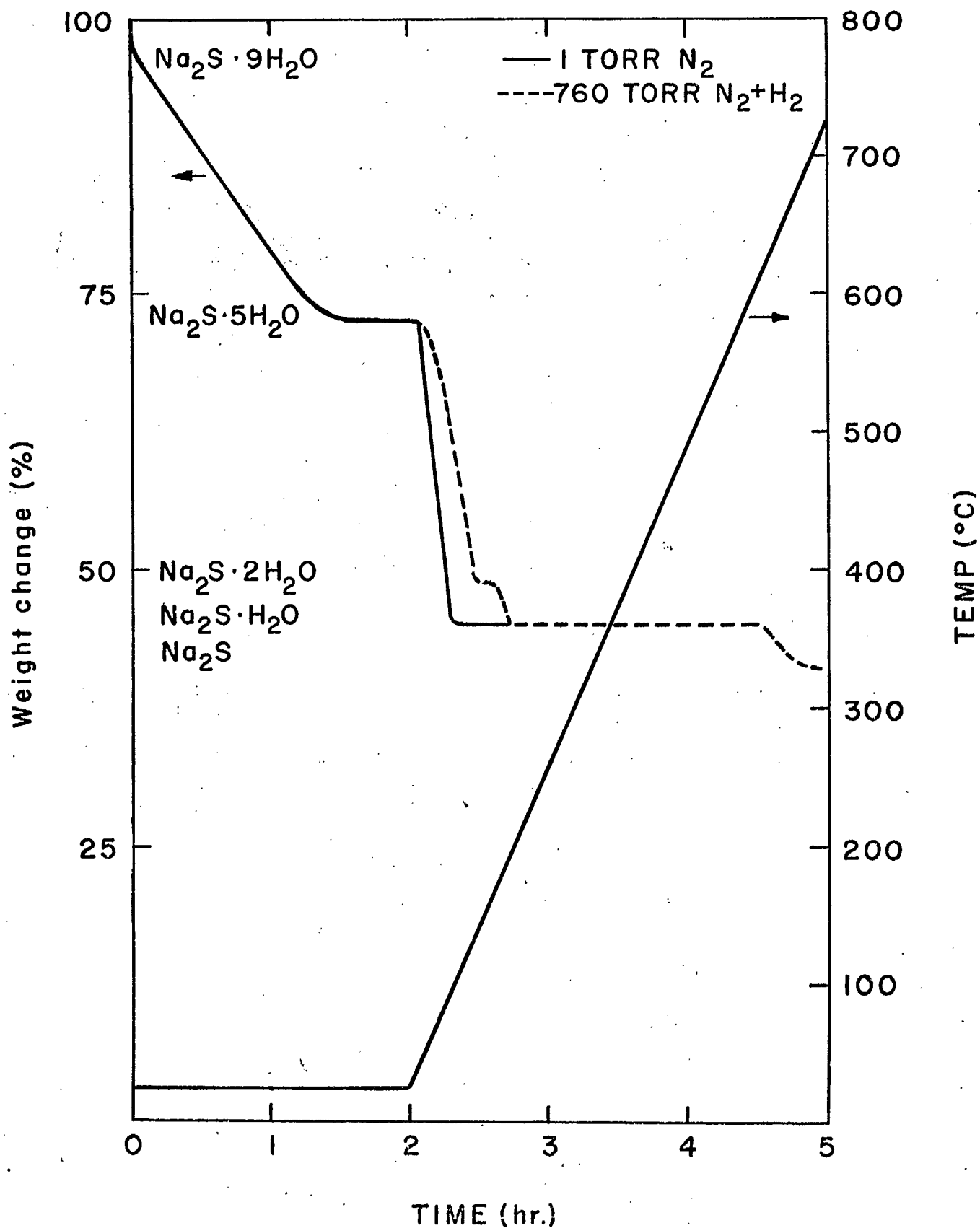
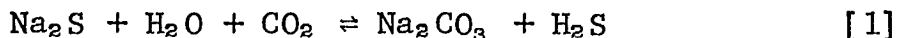


FIG. 1 Dehydration of Na₂S·9H₂O, as determined by Thermogravimetric Analysis

The wide range of temperature over which the monohydrate is stable indicates that the structure of the monohydrate probably includes a molecule of water within the lattice, rather than merely associated with it.

When sodium sulfide is converted to sodium carbonate with gaseous carbonic acid (equimolar $\text{CO}_2 + \text{H}_2\text{O}$), the reaction may be represented by the equation:



When excess water vapor is present, the sulfide may be present as a hydrate (mono-, di- or penta-) and the carbonate product may be hydrated. The carbonate is anhydrous at temperatures above 108°C , but at lower temperatures it may contain one molecule of water. In a series of experiments with powdered material, the rate of carbonation was studied for Na_2S , $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ and $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$. The conditions and results are shown in Table II.

The results shown in Table II were obtained by continuously weighing powdered samples of the material on a thermogravimetric balance. The results show that the conversion of Na_2S and $\text{Na}_2\text{S}\cdot 2\text{H}_2\text{O}$ followed linear kinetics for the first 0.1% of the reaction. Afterwards, the reaction rate became very slow and carbonation ceased when less than 1% had been converted. Alternatively, $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ followed linear kinetics until about 8% of the sample had been converted, then the reaction rate decreased noticeably. Chemical and X-ray diffraction analysis indicated that

the reaction product was predominately sodium carbonate, with less than 1% sodium sulfite.

TABLE II

Effect of State of Hydration on the Rate of Carbonation of Sodium Sulfide.

Gas flow rate: 50 ml/min

Gas composition: $\text{CO}_2 = 0.511 \text{ atm}$, $\text{N}_2 = 0.453 \text{ atm}$, $\text{H}_2\text{O} = 0.036 \text{ atm}$

Temperature: 115°C

Mesh size: minus 10

Sample weight: 0.110 gm

Material	Linear Rate mg/min	% conversion by linear kinetics
Na_2S	0.004	0.1
$\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$	2.010	8.0
$\text{Na}_2\text{S} \cdot 2\text{H}_2\text{O}$	0.021	0.1

The most significant point to note is that the rate of carbonation of the dihydrate is five times faster than that for the anhydrous material, and the rate of conversion of the monohydrate is one hundred times faster than that of the dihydrate. It would seem reasonable to conclude that the monohydrate is the preferred material for carbonation. The sodium carbonate layer is partly protective to each of the materials. The rate of reaction on the monohydrate is sufficiently rapid to indicate that it would probably go to completion if a finer powder were used.

To study the actual kinetics of the carbonation of $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$, pelletized samples were prepared and weighed continuously while they were carbonated at various temperatures in the presence of CO_2 and water vapor. The results are shown in Tables III, IV and V.

TABLE III

Influence of the Partial Pressure of Water Vapour on the Carbonation of Sodium Sulfide Monohydrate

Gas flow rate: 50 ml/min

Gas composition: $\text{CO}_2 = (0.526 - x)$ atm, $\text{N}_2 = 0.474$ atm, $\text{H}_2\text{O} = x$ atm

Temperature: 106°C

$P_{\text{H}_2\text{O}}$ (atm)	Linear Rate (mg/cm ² min)	% conversion by linear kinetics
0.076	0.441	5.5
0.049	0.318	4.9
0.026	0.076	2.5
>0.001	0.059	1.2

TABLE IV

Influence of the Partial Pressure of Carbon Dioxide on
the Rate of Carbonation of Sodium Sulfide Monohydrate

Gas flow rate: 50 ml/min

Gas composition: $H_2O = 0.026$ atm, $N_2 = (0.974 - x)$ atm, $CO_2 = x$ atm

Temperature: 132°C

P_{CO_2} (atm)	Linear Rate (mg/cm ² min)	% conversion by linear kinetics
0.928	7.00	22.5
0.710	5.13	18.5
0.533	3.80	25.9
0.204	1.51	4.5
0.121	1.04	3.2

TABLE V

Effect of Temperature on the Rate of Carbonation
of Sodium Sulfide Monohydrate

Gas flow rate: 50 ml/min

Gas composition: $\text{CO}_2 = 0.500 \text{ atm}$, $\text{N}_2 = 0.474 \text{ atm}$, $\text{H}_2\text{O} = 0.026 \text{ atm}$

Temperature (°C)	Linear Rate (mg/cm ² min)	% conversion by linear rate
25	0.86	5.3
27	0.90	10.4
29	1.01	15.3
32	1.10	10.3
36	1.03	3.6
42	0.58	3.1
47	0.47	7.3
52	0.37	8.2
60	0.46	3.2
66	0.56	2.8
78	0.60	3.1
88	0.50	2.6
102	0.07	2.5
108	1.14	14.7
121	2.14	12.8
132	3.80	25.9
143	2.64	10.5
150	2.08	10.0

The results of experiments showing the rate variation with changes in the partial pressure of water are shown in Figure 2. The results were normalized to obtain the rate of migration of the $\text{Na}_2\text{CO}_3 - \text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ interface into the pellet⁽⁸⁾. The rate of migration is $r_0 f$, where r_0 is the equivalent radius and f the fractional penetration for a given geometry. The product $r_0 d_0 f$ is the weight change per unit area that takes place as the interface advances. The results show that the rate of reaction (slope of the curve) decreases in each instance as the layer of product becomes thicker. The uppermost curve represents a conversion of about 6.0% before the rate of reaction becomes slower. The results also show that both the rate of reaction and the amount of conversion increase with an increasing partial pressure of water vapor. The reaction kinetics are not simple. The rate of reaction is controlled in a complex manner by the coating of Na_2CO_3 . The initial reaction rates are essentially linear for the first 50% of the observed amount of reaction. From the initial slopes, a number of correlations have been made for the factors affecting the reaction rate.

The equilibrium partial pressure of water vapour over $\text{Na}_2\text{S} \cdot \text{H}_2\text{O}$ is unknown, but is now being determined in these laboratories. Initial experiments have indicated that the rate of reaction increases with increasing partial pressures of water vapour, but sufficient data are not yet available to specify the nature of the relationship.

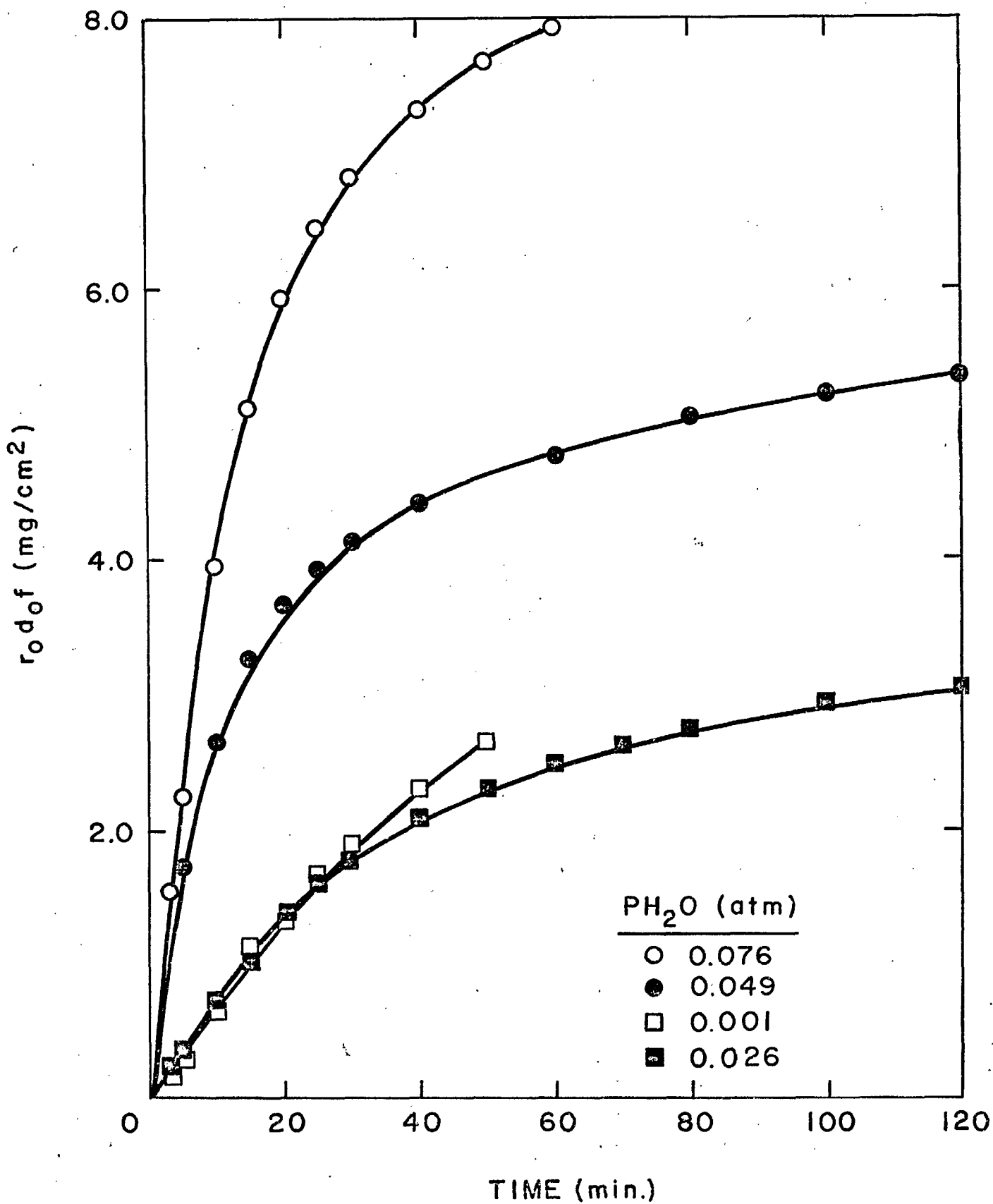


FIG.2 Influence of the partial pressure of water vapour on the carbonation of sodium sulfide monohydrate (Temperature = 106°C)

The effect of the partial pressure of carbon dioxide on the initial rate of carbonation was found to be linear, as shown in Figure 3. If additional experimental work confirms that the reaction rate is also proportional to the partial pressure of water vapour, it will be possible to deduce that Equation 1, as written, is the rate controlling reaction and that the rate for any specified condition can be evaluated from an equation of the form:

$$\text{rate} = A(\exp(-E/RT)) P_{\text{CO}_2} \cdot P_{\text{H}_2\text{O}}$$

The temperature coefficient of the reaction is particularly interesting. Figure 4 shows the results that arise from the competing reactions involved. On the left hand side of the graph in Figure 4, the linear rate constant is plotted against temperature in degrees centigrade for the formation of one mole of $\text{Na}_2\text{CO}_3 \cdot 7\text{H}_2\text{O}$. The graph shows that the reaction rate increases initially, passes through a maximum and then decreases steeply. When the temperature is higher, and the reaction product is $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, the rate constant follows the same sort of behaviour, except that the maximum rate is only about half the value per mole of Na_2CO_3 . When the activation energies for those parts of the curve where the rate is increasing with increasing temperature, are compared for the two compounds, a value of about 6 kcal/mole is obtained for each. The magnitude of the value suggests that the reaction rate may be controlled by the rate of diffusion of a gaseous species.

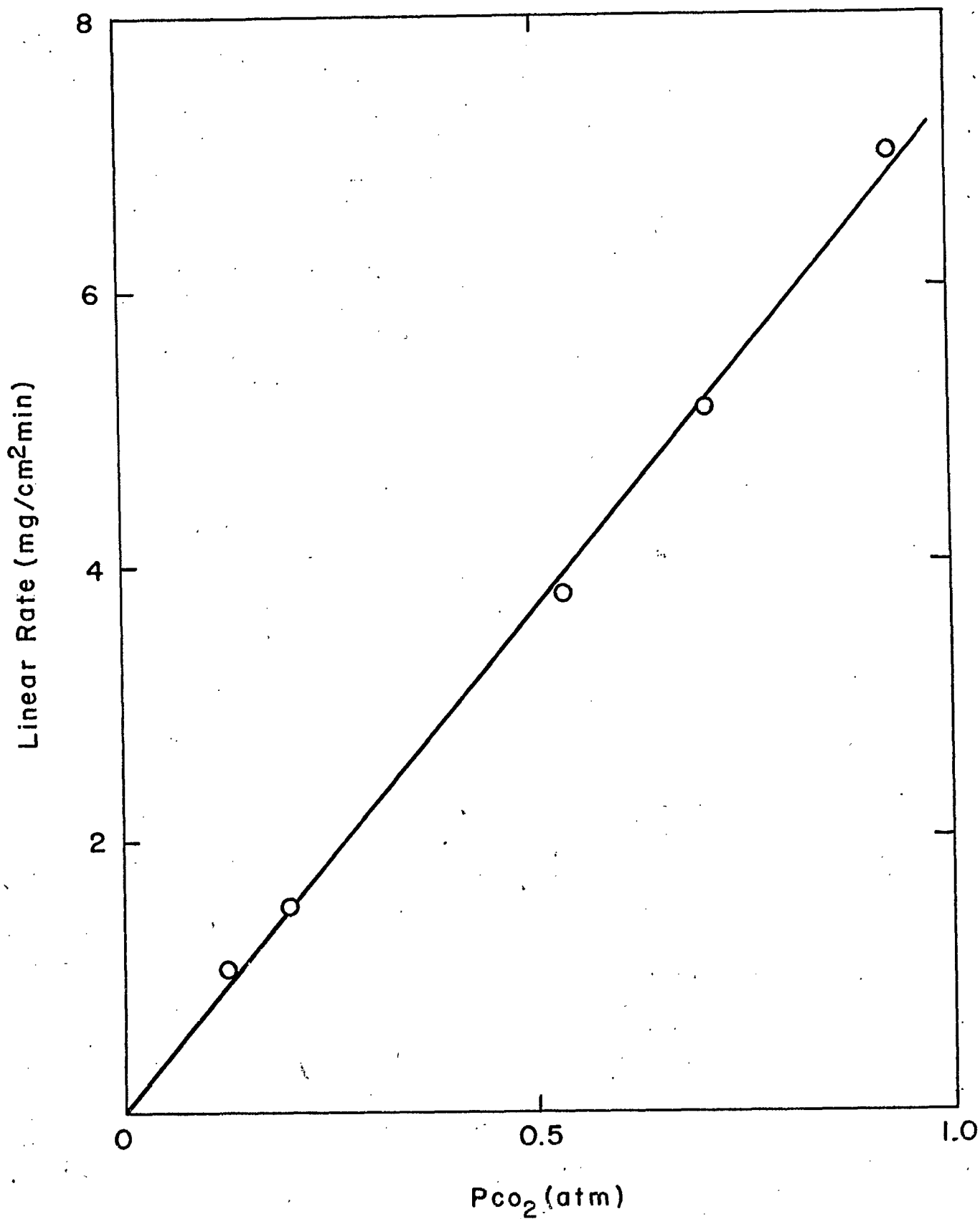


FIG. 3: Influence of the partial pressure of carbon dioxide on the rate of carbonation of sodium sulfide monohydrate (Temperature = 132°C)

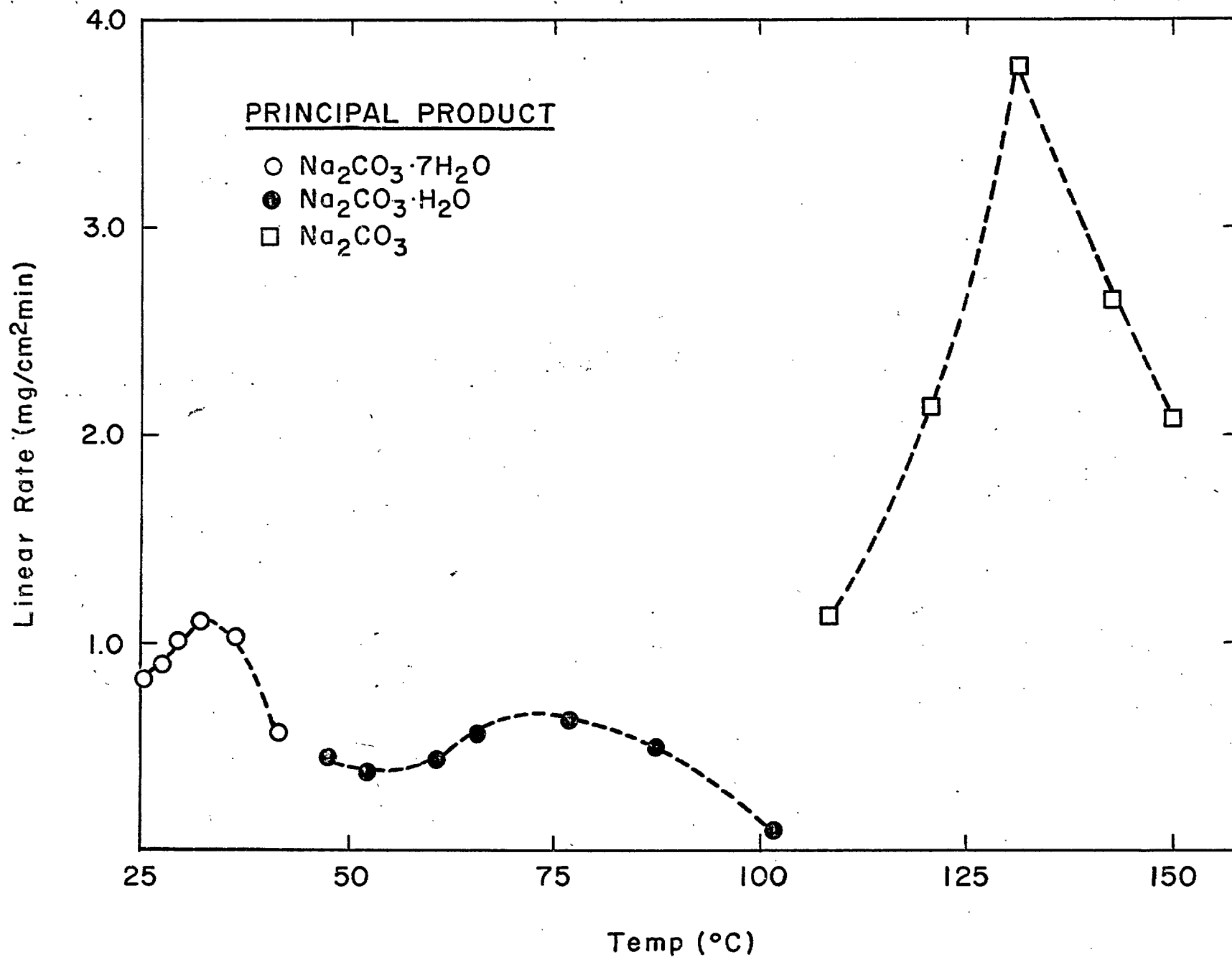


FIG. 4 Effect of temperature on the rate of carbonation of sodium sulfide monohydrate.

At temperatures above 108°C, anhydrous sodium carbonate is the principal product and a maximum in the carbonation rate is observed at 132°C. The activation energy for the increasing rate portion of the curve is 14 kcal/mole, which would suggest that the reaction rate is controlled by the chemical reaction that takes place at the interface between the sulfide and carbonate.

The existence of a maximum rate for each of the compounds is particularly interesting. At 30°C with a partial pressure of 0.026 atm. CO₂ and a partial pressure of water at saturation, the maximum rate of formation of the heptahydrate was 1.1 mg/cm² min, whereas at 73°C under similar conditions the maximum rate of formation of monohydrate was about 0.6 mg/cm² min and at 132°C, the maximum rate was 3.8 mg/cm² min. When these results were examined, there was a tendency to reason that the reaction rate would be even higher if the partial pressure of water were increased, or even if the reaction were done in aqueous solution. The factor that prohibits working in aqueous solution is the low solubility of CO₂ in water. It is not possible to approach sufficiently large partial pressures of CO₂ without placing the system under pressure. Enclosing the system would make it impossible for the liberated H₂S to escape. It is, therefore, most convenient to expect to work at or near temperatures of 130°C with carbon dioxide gas saturated with moisture.

Synthetic smelts were prepared for study by melting together various proportions of $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$ and Na_2CO_3 . During the melting at 900°C , the monohydrate was dehydrated. The composition of the smelts are shown in Table VI.

TABLE VI

Carbonation rates of Sodium Sulfide - Sodium Carbonate Slags

Gas flow rate: 50 ml/min

Gas composition: $\text{CO}_2 = 0.450$ atm, $\text{N}_2 = 0.474$ atm, $\text{H}_2\text{O} = 0.076$ atm

Temperature: 106°C

Composition	Linear Rate (mg/cm ² min)	% composition by linear rate
100% $\text{Na}_2\text{S}\cdot\text{H}_2\text{O}$	0.441	5.5
50% Na_2S - 50% Na_2CO_3	0.132	3.2
20% Na_2S - 80% Na_2CO_3	2.960	50.0
10% Na_2S - 90% Na_2CO_3	0.242	5.0

The preliminary results shown in Table VI indicate that the most rapid rates of carbonation are obtained when the smelt compositions contain about 20% Na_2S . Additional experiments are now being done to elucidate the mechanism that would permit such marked changes in the rate to occur with small changes in smelt composition.

CONCLUSIONS

Smelts containing 20% Na_2S and 80% Na_2CO_3 may be carbonated rapidly and completely to Na_2CO_3 in the presence of water vapour and carbon dioxide at 130°C . The Na_2CO_3 product is protective to the underlying Na_2S and the reaction is most effective when done on finely divided powders. Based on the observations made to date, it would seem most reasonable to do the carbonation in a rotating kiln in which some tumbling and abrading action could be provided.

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