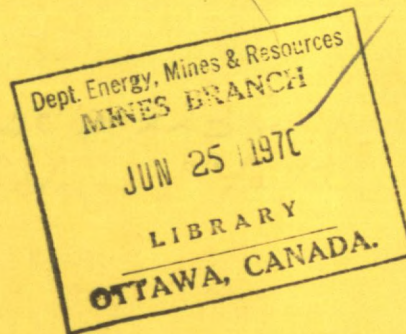




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*THE EXTRACTION OF STRONTIUM FROM
THE MINERAL CELESTITE*



SUTARNO, R.H. LAKE AND W.S. BOWMAN

MINERAL SCIENCES DIVISION

APRIL 1970

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Queen's Printer for Canada
Ottawa, 1970

Mines Branch Research Report R 223

THE EXTRACTION OF STRONTIUM FROM
THE MINERAL CELESTITE

by

Sutarno*, R.H. Lake** and W.S. Bowman**

ABSTRACT

Two potential industrial methods of extracting strontium from the mineral celestite were investigated. These are (i) the direct carbonation method and (ii) the solid-state reduction method. Comparison between the two methods from the technical point of view is discussed. Reduction of synthetic strontium sulphate with various reducing agents was also studied in order to reach an understanding of the mechanism of the above processes.

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Direction des mines

Rapport de recherche R 223

L'EXTRACTION DU STRONTIUM DE LA CÉLESTINE

par

Sutarno*, R.H. Lake** et W.S. Bowman**

Résumé

Les auteurs ont examiné deux méthodes d'extraction du strontium de la célestine qui offrent des possibilités du point de vue industriel. Ce sont: (i) la carbonatation directe, et (ii) la réduction à l'état solide. Le rapport établit une comparaison technique entre les deux méthodes. Les auteurs ont également étudié la réduction du sulfate de strontium synthétique à l'aide de divers agents réducteurs, afin de mieux saisir le mécanisme des deux procédés cités.

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CONTENTS

	<u>Page</u>
Abstract	i
Résumé	ii
Lists of Figures and Tables	iv, v
Introduction	1
A. Materials	2
B. The Direct Carbonation Process	2
(i) Theoretical Considerations	2
(ii) Experimental Procedure	5
(iii) Results and Discussion	7
C. The Reduction Method	13
(i) Thermoanalytical Studies of the Reduction of SrSO_4	13
(a) Experimental Procedure	13
(b) Results and Discussion	14
Reduction of Strontium Sulphate by Hydrogen	16
Reduction of Strontium Sulphate with Carbon	20
(ii) The Conversion of Celestite to Strontium Carbonate by the Reduction Method	26
(a) Experimental Procedure	27
(b) Results and Discussion	27
Discussion of the Comparison Between the Two Processes	30
Acknowledgements	31
References	32

FIGURES

<u>No.</u>		<u>Page</u>
1	Theoretical Quantity of Carbonating Agent Required to Completely Convert Strontium Sulphate into Strontium Carbonate at Various pH Values	6
2	Flow Diagram of Strontium Extraction from Celestite by Direct Carbonation	8
3	Equilibrium Diagram for the SrO-SrS-SrSO ₄ System under Various SO ₂ and O ₂ Partial Pressures	15
4	Thermogram of Reduction of SrSO ₄ to SrS by Hydrogen	17
5	Thermogram of Re-Oxidation of SrS to SrSO ₄ in Oxygen Atmosphere	18
6	Thermograms of Reduction of SrSO ₄ and BaSO ₄ in N ₂ /H ₂ Atmosphere, Followed by N ₂ Atmosphere	19
7	Thermogram of (SrSO ₄ + 4C) Mixture Heated in Argon	21
8	Thermogram of SrSO ₄ Heated in a 100% Carbon Monoxide Atmosphere	22
9	Thermograms of Decomposition of SrCO ₃ in Air and CO ₂ Atmospheres	24
10	Thermogram of N ₂ /H ₂ Reduction of SrSO ₄ , Followed by Carbonation of Product in a 100% CO ₂ Atmosphere	25
11	Flow Diagram of Strontium Extraction from Celestite by Reduction Process	28

TABLES

<u>No.</u>		<u>Page</u>
I	Semi-Quantitative Spectrographic and Wet Chemical Analyses of the Celestite Mineral Sample Used in this work ..	3
II	Conversion of Celestite Powder to Carbonate by Direct Carbonation Under Various Conditions	9
III	Semi-Quantitative Spectrographic Analysis of Strontium Carbonate Prepared from Celestite by the Carbonation Method Compared with Reagent Grade SrCO_3	11
IV	Efficiency of Recovery of Strontium from Mineral Celestite by Direct Carbonation	12
V	Extraction of Strontium from Celestite by the Reduction Method	29

INTRODUCTION

Until recently, strontium was one of the less important elements from the production-volume point of view. This situation has been changed, however, by the recent discovery of two major uses for strontium. Firstly, it is suitable for use as an absorber in the front screens of colour-television tubes to reduce the intensity of X-ray radiation emitted by the tube and secondly, it is one of the basic raw materials used in the manufacture of ceramic permanent magnets.

One of the main sources in nature of the element strontium is the mineral celestite (strontium sulphate). There are at least two possible economically feasible methods of extracting the strontium from celestite. The first method involves the direct conversion of strontium sulphate into strontium carbonate in an aqueous slurry. The crude strontium carbonate thus obtained is then purified by chemical methods. The second method, similar to that used for the extraction of barium from barite (BaSO_4), is by reducing the strontium sulphate to strontium sulphide and then leaching this sulphide. The reduction results from a solid-state reaction at high temperatures. Coal is usually used as the reducing agent. Because of the general insolubility in water of metal sulphides, this process, if water is used as the leaching medium, has a built-in purification action.

It was the purpose of this work to investigate the relative merits of these two processes for the extraction of strontium from celestite, particularly to yield a product having a degree of purity acceptable to the ceramic permanent-magnet industry.

A. Materials

A sample of celestite ore originating from Cape Breton Island, Nova Scotia, was provided by Magnetics International, Ltd., of Prescott, Ontario. This ore was ground to pass a 100-mesh screen and then analysed both chemically and spectrographically. The results of these analyses are given in Table I. Based on the results of these analyses, it was decided that no primary treatment was required to increase the strontium content of the powder and that the crushed material could be employed "as is".

To study the mechanism of the reduction process of strontium sulphate, a synthetic strontium sulphate was prepared by precipitation from strontium nitrate solution. All other reagents used were normal "reagent-grade" chemicals.

B. The Direct Carbonation Process

(i) Theoretical Considerations

The driving force for the conversion of strontium sulphate into the carbonate is the difference between the solubilities of strontium sulphate and strontium carbonate in water.

At room temperature, the solubility product of strontium sulphate, S_{SrSO_4} , is 2.8×10^{-7} , while that of strontium carbonate, S_{SrCO_3} , is 9.4×10^{-10} (1) *.

At equilibrium, the following conditions must be satisfied:

$$S_{\text{SrSO}_4} = [\text{Sr}^{++}][\text{SO}_4^{--}] = 2.8 \times 10^{-7}$$

$$S_{\text{SrCO}_3} = [\text{Sr}^{++}][\text{CO}_3^{--}] = 9.4 \times 10^{-10}$$

$$\text{whence } [\text{SO}_4^{--}] = 2.98 \times 10^2 [\text{CO}_3^{--}] \quad [\text{Eq. 1}]$$

The quantity, $[\text{SO}_4^{--}]$, has a maximum value equal to C, the mole content

*For references, see page 32.

TABLE I

Semi-Quantitative Spectrographic and Wet Chemical Analyses
of the Celestite Mineral Sample Used in this Work

(Contents are given in wt %)

Element	Spec. Analysis (%)	Wet Chem. Anal. (%)	Element	Spec. Analysis (%)	Wet Chem. Anal. (%)	Element	Spec. Analysis (%)	Wet Chem. Anal. (%)
Ba	> 0.5	1.22	Sn	N.D.	-	Mn	0.02	-
Si	0.6	2.70	Cr	N.D.	-	Zr	N.D.	-
Sb	N.D.	-	Fe	0.1	0.65	Cu	0.01	-
Mg	0.1	0.04	Bi	N.D.	-	Ag	0.001	-
As	N.D.	-	Al	0.2	0.17	Na	N.D.	-
Mo	N.D.	-	V	N.D.	-	Zn	N.D.	-
W	N.D.	-	Ca	1.0	0.63	Ti	N.D.	-
Pb	0.1	-	In	N.D.	-	Sr	PC	42.04
Ni	N.D.	-	Co	N.D.	-			

N.D. = none detected.

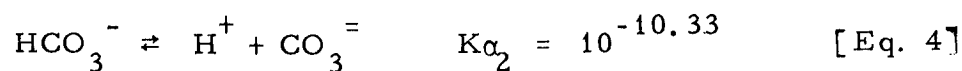
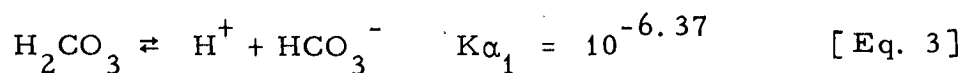
PC = principal constituent.

Note: The theoretical Sr content of SrSO_4 is 47.70% by weight.

of the original strontium sulphate per unit volume of water. This maximum value occurs at the end of conversion. Hence, in order to complete the conversion, there must be an excess of carbonate reagent such that

$$[\text{CO}_3^{=}] = \frac{C}{2.98 \times 10^2} \quad [\text{Eq. 2}]$$

In order to calculate the excess of carbonate in terms of the amount of carbonating agent, the following equilibria must be considered:



At the end of the conversion, the excess of carbonating agent per unit volume, E, will satisfy the equation:

$$E = [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{=}] \quad [\text{Eq. 5}]$$

From [Eq. 3] and [Eq. 4] we get

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K\alpha_1} \quad [\text{Eq. 6}]$$

$$[\text{HCO}_3^-] = \frac{[\text{H}^+][\text{CO}_3^{=}]}{K\alpha_2} \quad [\text{Eq. 7}]$$

Substituting [Eq. 6] and [Eq. 7] into [Eq. 5], we get

$$\begin{aligned} E &= \frac{[\text{H}^+][\text{HCO}_3^-]}{K\alpha_1} + [\text{HCO}_3^-] + [\text{CO}_3^{=}] \\ &= [\text{HCO}_3^-] \left\{ \frac{[\text{H}^+]}{K\alpha_1} + 1 \right\} + [\text{CO}_3^{=}] \\ &= \frac{[\text{H}^+][\text{CO}_3^{=}]}{K\alpha_2} \left\{ \frac{[\text{H}^+]}{K\alpha_1} + 1 \right\} + [\text{CO}_3^{=}] \end{aligned}$$

$$\begin{aligned}
 &= [\text{CO}_3^{=}] \left\{ \frac{[\text{H}^+]}{K\alpha_2} \left(\frac{[\text{H}^+]}{K\alpha_1} + 1 \right) + 1 \right\} \\
 &= [\text{CO}_3^{=}] \left\{ \frac{[\text{H}^+]^2}{K\alpha_1 K\alpha_2} + \frac{[\text{H}^+]}{K\alpha_2} + 1 \right\} \quad [\text{Eq. 8}]
 \end{aligned}$$

Substituting [Eq. 2] into [Eq. 8], we get

$$E = 0.0034C \{ 10^{16.7} [\text{H}^+]^2 + 10^{10.33} [\text{H}^+] + 1 \} \quad [\text{Eq. 9}]$$

The total amount of carbonating agent required for complete conversion is $C + E$, and the amount per mole of strontium sulphate is given by

$$\frac{C + E}{C} = 1 + \frac{E}{C} = 1.0034 + 0.0034 \{ 10^{16.7} [\text{H}^+]^2 + 10^{10.33} [\text{H}^+] \} \quad [\text{Eq. 10}]$$

This value is plotted as a function of pH in Figure 1.

(ii) Experimental Procedure

The detailed procedure used for the extraction is illustrated in Figure 2. The celestite mineral was ground to pass a 100-mesh screen. Some of this powder was further ground in a ball mill for 48 hr. (In further discussions, the former powder will be referred to as "coarse" and the latter as "fine" powder).

About 25g of these powders were slurried in water. A sufficient amount of sodium carbonate was added to the slurry. (Ammonium bicarbonate may also be used, but pH adjustment is necessary; this could be achieved by adding an excess of ammonium hydroxide). The mixture was digested for periods ranging from 3 to 48 hr. at either room temperature, 50°C, or 100°C. The slurry was then filtered and washed. The filtrate, consisting mainly of a solution of sodium sulphate and some sodium carbonate can be treated with sulphuric acid and the sodium sulphate can be recovered as a by-product.

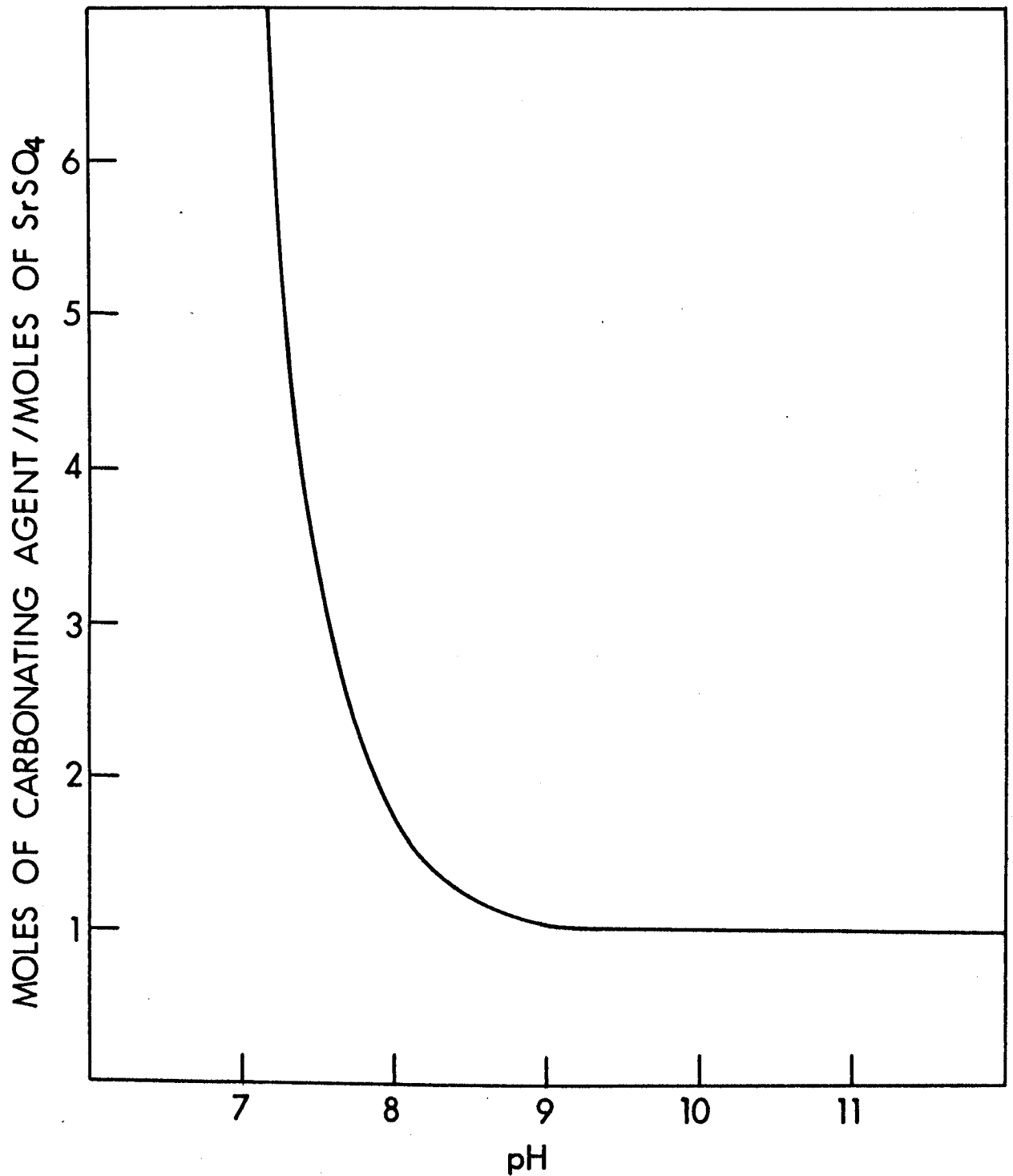


Figure 1. Theoretical Quantity of Carbonating Agent Required to Convert Strontium Sulphate Into Strontium Carbonate Completely at Various pH Values.

The precipitate (crude strontium carbonate) was analysed for its carbonate content(1) , to determine the degree of conversion. The purification of this strontium carbonate is carried out by the dissolution of the precipitate in a hot 5% HCl solution and by the neutralization of this solution with ammonium or sodium hydroxide to precipitate the iron-group impurities. The slurry was then filtered. The precipitate, containing the impurities, was discarded; the filtrate, strontium chloride solution, can either be crystallized or can be precipitated as the carbonate by the addition of either ammonium bicarbonate or sodium carbonate.

(iii) Results and Discussion

Both the chemical and spectrographic analyses showed that the sample of the mineral celestite was remarkably pure. The strontium content was found to be equivalent to 88.13% SrSO_4 , see Table I . This concentration was found to be slightly richer than that reported by Stone(2) for this deposit. The only impurities present at a substantial concentration were Si, Ba, Fe, Al and Ca. All of these impurities, with the exception of Ca, would be removable by the process described. Calcium can be removed by re-conversion of the strontium carbonate into strontium sulphate and a repeat of the procedure of conversion to strontium carbonate.

Table II shows that the conversion factor depends very strongly on pH and on particle size. The strong dependence of the conversion factor on the particle size of the celestite powder suggests that the factor controlling the rate of conversion is the dissolution rate of the strontium sulphate. This rate is a function of the concentration gradient of the strontium ions between a location near to the surface of the celestite particles and the bulk solution. If this assumption is correct, then rapid agitation of the slurry during the digestion should improve the conversion factor. Conversion factors of 95% or better can be achieved by this means, see Table II .

The impurities can be grouped into two categories. Firstly, there are the impurities insoluble in 5% HCl (mainly silica), and secondly, the iron-group impurities.

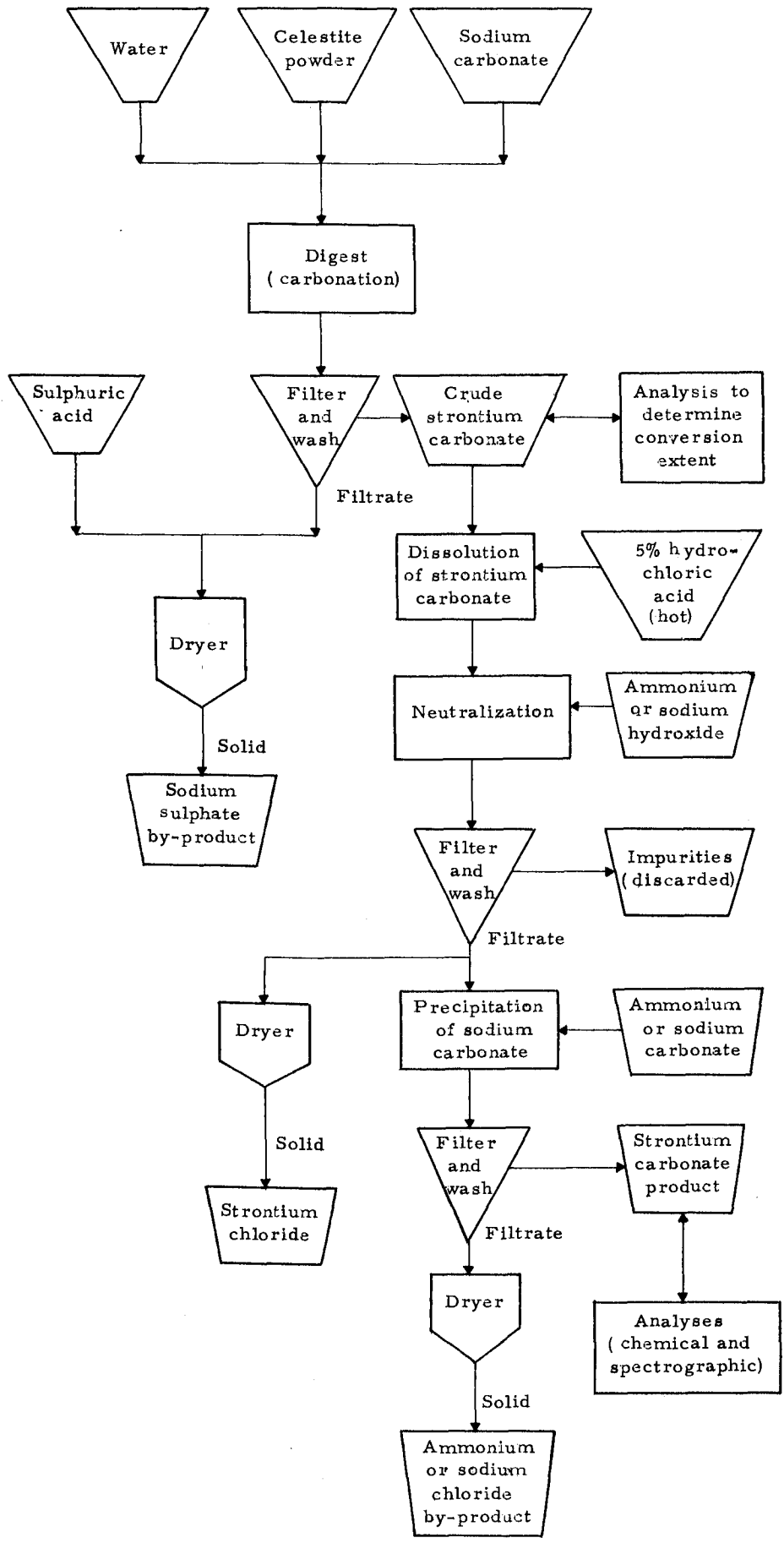


Figure 2. Flow Diagram of Strontium Extraction from Celestite by Direct Carbonation.

TABLE II

Conversion of Celestite Powder to Carbonate by Direct Carbonation
Under Various Conditions

No.	Particle Size ⁽¹⁾	ml H ₂ O per g of Sample	Carbonate Used		Digestion			Carbonate in the Product %	Conversion ⁽²⁾ (%)
			Na ₂ CO ₃ or NH ₄ HCO ₃	Excess (mol %)	Temp. (°C)	pH	Time (hr)		
1	F	20	Na ₂ CO ₃	20	80	11.0	3	84.8	96.2
2	F	20	"	20	80	11.0	48	85.0	96.4
3	F	20	"	25	RT	11.0	3	83.5	94.7
4	F	20	"	20	RT	11.0	3	88.2	-
5	F	20	"	20	RT	11.0	3	92.3	-
6	C	20	"	20	RT	11.0	3	40.0	45.4
7	C	20	"	20	RT	11.0	16	47.8	54.2
8	F	20	NH ₄ HCO ₃	20	RT	8.0	3	10.0	11.3
9	F	20	"	50	RT	8.0	16	16.0	18.2
10	F	20	"	100	RT	10.3	3	82.9	94.1

NOTES

- (1) F = fine, powder milled for 48 hr.; C = coarse powder (-100 mesh)
 (2) Conversion was calculated based on the original % strontium sulphate in the ore (88.13%). Samples #4 and #5 were washed with 5% HCl once and twice, respectively, before conversion. Therefore, the % conversion cannot be calculated for these samples.

The iron-group impurities were removed by neutralization of the chloride solution, which resulted in the separation of a colloidal precipitate. During this process, there is the possibility of the formation of strontium hydroxide which is relatively insoluble in water. Elevating the temperature during the neutralization will both increase the solubility of strontium hydroxide and transform the colloidal iron hydroxide precipitate into a form easier to filter.

Table III shows the spectrographic analyses of the strontium carbonate product, and the insoluble and iron-group impurities in comparison with a "reagent-grade" strontium carbonate. Table IV shows the efficiency of the recovery.

It is shown in Table III that the purity of the product obtained is comparable with that of "reagent-grade" strontium carbonate. In addition, the barium and calcium contents were analysed by the atomic-absorption method and found to be 0.24% and 0.66%, respectively. During the process, the barium content thus decreases from 1.22% to 0.24%. The calcium content, however, remains unchanged. Fortunately for the ferrite industry, which, presumably, will be one of the largest users of the strontium carbonate, these levels of barium and calcium are acceptable(3, 4). For other uses, where a very low calcium content is required, a reversion to sulphate and then back to carbonate must be carried out. After such a second cycle, it was found that the calcium content was down to 0.17%. The cost, however, of completely removing calcium would be prohibitive for the industrial use of this strontium carbonate as a major raw material.

Table III shows that the insoluble impurities consist mainly of silica, and that some loss of strontium does occur during the removal of the iron-group impurities. Boiling the slurry during the removal of these impurities, however, seems to improve the recovery of strontium, see Table IV. Because of the gelatinous nature of the precipitate of the iron-group impurities, which makes it difficult to filter, it may be desirable economically to remove these impurities as much as possible before the extraction process by pre-washing the powder with dilute sulphuric acid.

TABLE III

Semi-Quantitative Spectrographic Analysis of SrCO₃ Prepared from Celestite
by the Carbonation Method Compared With Reagent Grade SrCO₃

Element	SrCO ₃		Iron group* Impurities (%)	Other Impurities (%)	Element	SrCO ₃		Iron group Impurities (%)	Other Impurities (%)
	Reagent Grade (%)	Prepared in this Work (%)				Reagent Grade (%)	Prepared in this Work (%)		
B	N. D.	N. D.	N. D.	N. D.	Bi	N. D.	N. D.	N. D.	N. D.
Sb	N. D.	N. D.	N. D.	N. D.	Al	N. D.	N. D.	P. C.	P. C.
Mg	N. D.	N. D.	N. D.	0.1	V	N. D.	N. D.	N. D.	0.0309
As	N. D.	N. D.	N. D.	N. D.	Ca	0.07	0.4	0.07	N. D.
Mo	N. D.	N. D.	N. D.	N. D.	In	N. D.	N. D.	N. D.	N. D.
W	N. D.	N. D.	N. D.	N. D.	Zr	N. D.	N. D.	N. D.	0.01
Pb	N. D.	N. D.	0.3	N. D.	Cu	N. D.	N. D.	0.05	0.008
Sn	N. D.	N. D.	N. D.	N. D.	Ag	N. D.	N. D.	N. D.	N. D.
Cr	N. D.	N. D.	N. D.	N. D.	Na	N. S.	N. D.	N. D.	N. D.
Si	0.03	N. D.	P. C.	P. C.	Zn	N. D.	N. D.	0.5	0.09
Mn	N. D.	0.01	0.04	N. D.	Ti	N. D.	N. D.	0.01	N. D.
Nb	N. D.	N. D.	N. D.	N. D.	Ni	N. D.	N. D.	0.01	N. D.
Ta	N. D.	N. D.	N. D.	N. D.	Co	N. D.	N. D.	N. D.	N. D.
Fe	N. D.	N. D.	P. C.	0.4	Sr	P. C.	P. C.	0.9	0.25

*Iron-group impurities are the impurities which are soluble in 5% HCl. Other impurities are the insoluble impurities (residue). These two groups of impurities were separated for the purpose of this analysis only.

TABLE IV
Efficiency of Recovery of Strontium from
Mineral Celestite by Direct Carbonation⁽¹⁾

No.	Stirring During Digestion	Neutralization Temp. (°C)	SrCO ₃	
			% of Original Sample	% Sr ⁽²⁾ Recovered
11	Moderate	RT	54.5	76.9
12	"	RT	57.5	81.1
13	"	RT	55.5	78.4
14	"	RT	54.9	77.5
15	"	RT	55.4	78.2
16	"	RT	54.5	76.9
17	"	RT	56.8	80.2
18	"	RT	55.7	78.6
19	"	RT	58.1	82.0
20	"	100	60.4	85.3
21	Rapid	100	62.9	88.8
22	"	100	62.8	88.6
23	"	100	64.7	91.3
24	"	100	66.0	93.1
25	"	100	66.0	93.2

(1) "Fine" powder was used for this experiment.

(2) Based on the original sample containing 88.13% SrSO₄
 which is equivalent to 70.83% SrCO₃.

Table IV shows that, by this method, over 90% of the strontium present in the ore (based on the analysis of the original ore) can be recovered. Since the process is strongly affected by such variables as particle size and agitation that generally have a strong relation to the type of process equipment used, very little benefit could be derived from the exact calculation of the yield from a laboratory-scale experiment. The purpose of this work has been to demonstrate the technical feasibility of this process for industrial use. For further steps and an economic assessment of the process, one must carry out the experiments on a pilot-plant scale. This is beyond the mandate of the Mineral Sciences Division in this instance.

C. The Reduction Method

The second method of extracting strontium from the mineral celestite is by reduction of the strontium sulphate to strontium sulphide. This method has been employed successfully in the extraction of barium from barite (BaSO_4). The basis of the method is the unusual solubility of the sulphide in neutral or weakly-basic aqueous solutions. The strontium sulphide produced by this reduction is then leached and the strontium is precipitated from the leach solution in the form of carbonate. The most common reducing agent that has been used for this process is coal.

In order to understand the mechanism of the reduction process, a synthetic strontium sulphate was prepared and the reduction mechanism was studied using X-ray diffraction and the various techniques of thermoanalysis (thermogravimetric analysis, TGA, and differential thermal analysis, DTA). The results obtained with this pure, synthetic SrSO_4 were then applied to the reduction of the mineral celestite itself.

(i) Thermoanalytical Studies of the Reduction of SrSO_4

(a) Experimental Procedures

The materials used in this work were reagent-grade strontium nitrate, sulphuric acid, charcoal (decolorizing powder), other analytical reagents and various high-purity gases. No further purification was performed on any of these reagents.

Strontium sulphate and carbonate were prepared by precipitation from strontium nitrate solution, washed and dried at about 300°C. For solid-state reduction, strontium sulphate powder was mixed manually with the charcoal powder in the desired proportions.

Thermogravimetric analysis (TGA) was used extensively to follow the reactions under various atmospheric conditions. Both the heating rate (6 deg C per min) and the gas-flow rate were controlled to ensure the replication of the experiments. The sample weights used, expressed as strontium sulphate, were maintained approximately constant. On some occasions, differential thermal analysis (DTA) also was used to assist in interpreting the TGA results. The heating rate for the DTA experiments was 12 deg C per min; the sample weights were again maintained approximately constant, and α -alumina was used as the reference material. X-ray diffraction (XRD) was used to identify the crystalline phases present in the products; however, in some cases, wet chemical analysis also was employed for this purpose. Semi-quantitative spectrographic analysis was used to check the purities of both the reagents and products.

The thermogram (TGA result) of strontium sulphate alone showed that no appreciable weight-loss occurs over the temperature range used throughout these experiments.

(b) Results and Discussion

The calculated equilibrium diagram for the $\text{SrS-SrSO}_4\text{-SrO}$ system, under various atmospheric conditions and at the temperatures used in these experiments, is illustrated in Figure 3 (5). From this diagram it can be seen that it would be difficult to avoid the formation of SrO which, in the presence of carbon dioxide, would form the water-insoluble strontium carbonate. The formation of strontium carbonate at this stage is, of course, undesirable since it will diminish the efficiency of the water-leaching stage of the process.

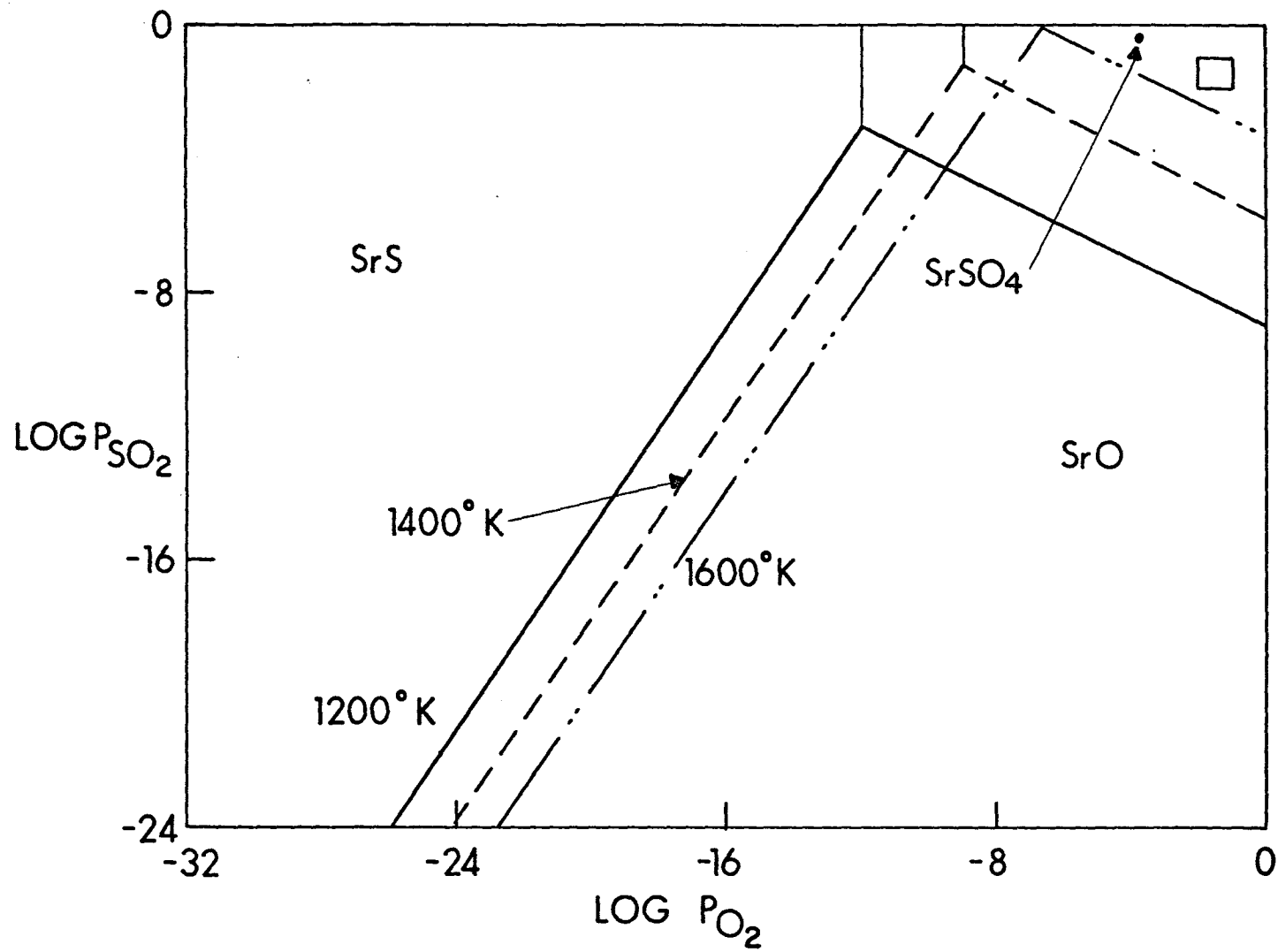
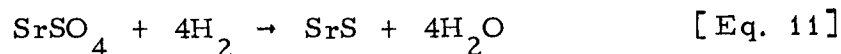
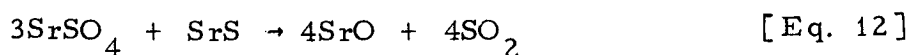


Figure 3. Equilibrium Diagram for the SrO-SrS-SrSO₄ System under Various SO₂ and O₂ Partial Pressures (5)⁴.

Reduction of Strontium Sulphate by Hydrogen



The thermogram* of this reaction is illustrated in Figure 4. A mixture of 75% N₂ and 25% H₂ (by volume) was used during the heating period, and pure N₂ was used during the soaking and cooling periods. It can be seen that the weight loss started at about 800°C and was completed at about 1100°C. It should be noted that the final weight of the sample was slightly less than corresponds to the weight of SrS equivalent to the starting amount of SrSO₄. The XRD pattern of this reduction product, however, showed only SrS lines(5). The colour of this SrS was white, unlike the grey or tan colour previously reported(6, 7). This discrepancy of the weight was also observed after the re-oxidation of this sample to SrSO₄ in pure oxygen (Figure 5). For this reason it was suspected that there was a small amount of SrO formed, according the following reaction:



The occurrence of the above reaction is shown in the thermogram given as Figure 6. Strontium sulphate was heated in a (75% N₂ + 25% H₂) atmosphere to 950°C. The atmosphere was then changed to pure nitrogen and the heating was continued up to 1400°C, followed by cooling in nitrogen at the natural rate of the furnace. The weight loss stopped temporarily at the moment the hydrogen flow was stopped. The sample then started to loose weight again at 1050°C and the reaction was complete at about 1300°C. The XRD of the final product showed strong SrO lines(8).

A similar TGA run was also made for BaSO₄. It can be seen from Figure 6 that a similar series of reactions occurred in this instance. The

*The heat-treatment program used in the thermogravimetric (TGA) experiments is shown on each thermogram as the temperature profile.

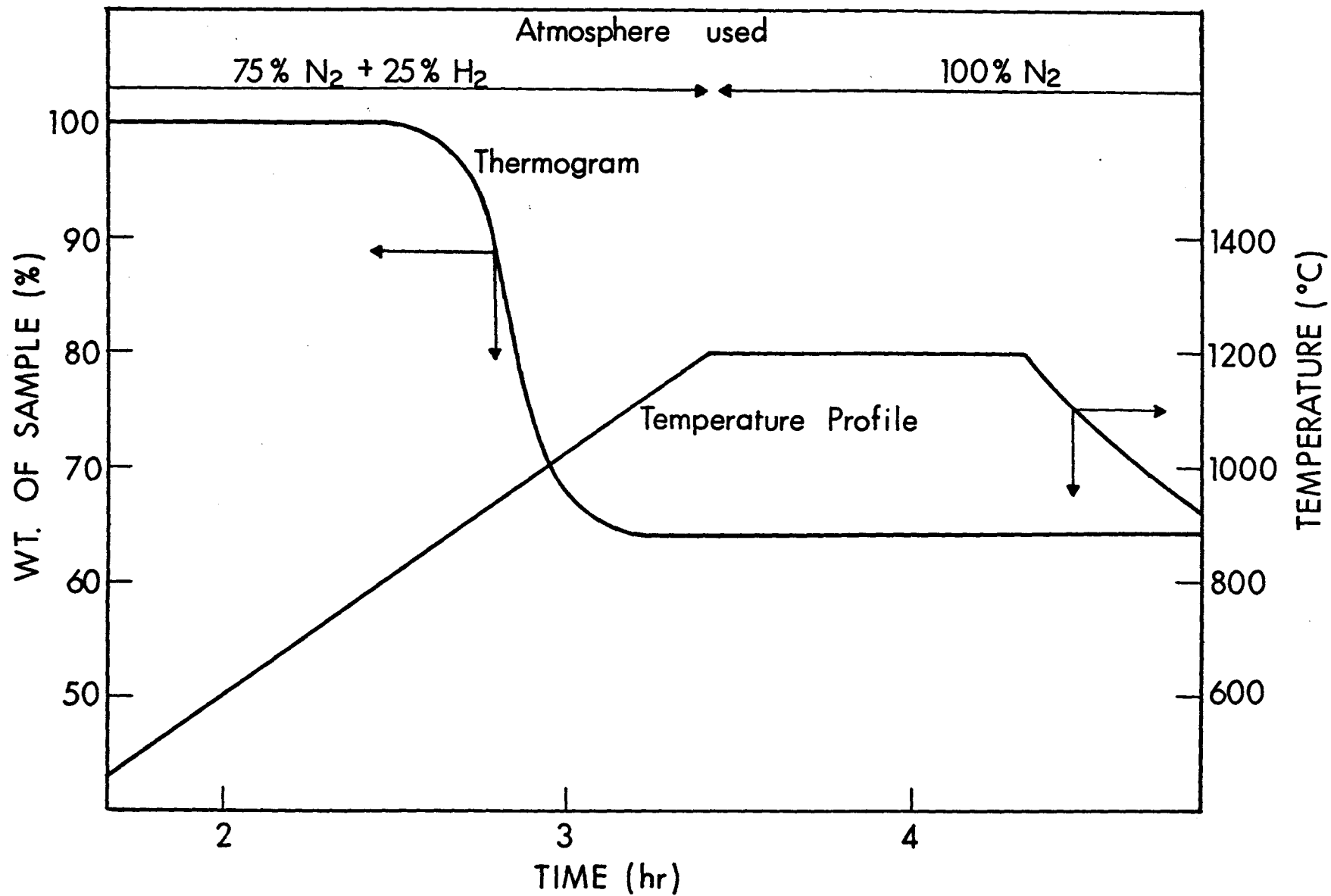


Figure 4. Thermogram of Reduction of SrSO₄ to SrS by Hydrogen.

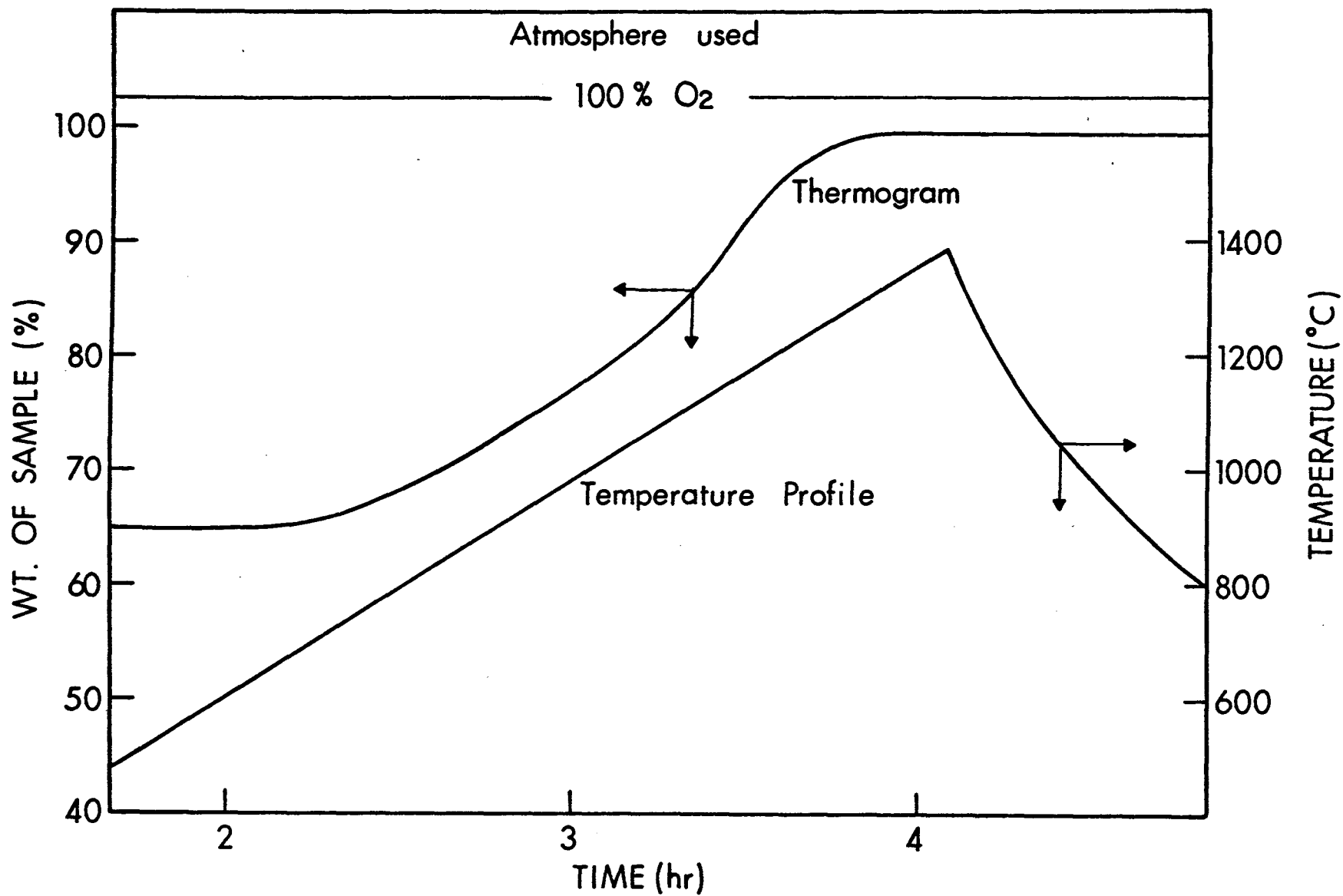


Figure 5. Thermogram of Re-Oxidation of SrS to SrSO₄ in Oxygen Atmosphere.

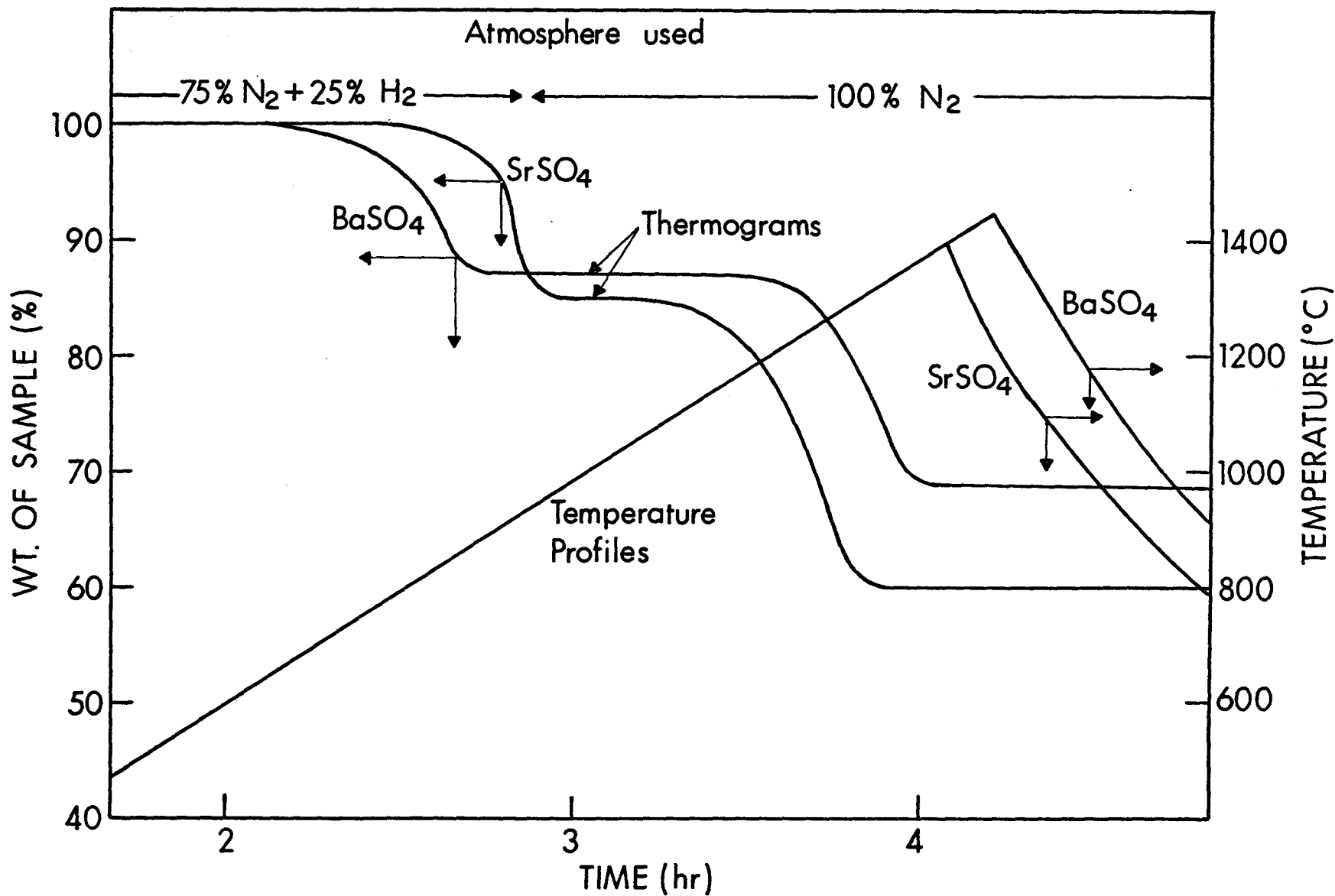


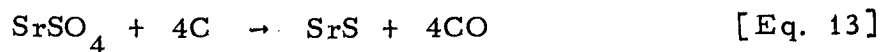
Figure 6. Thermograms of Reduction of SrSO₄ and BaSO₄ in N₂/H₂ Atmosphere, followed by N₂ Atmosphere.

difference between the two cases is that the reduction of barium sulphate (the first step of the weight loss) occurred at a lower temperature than was observed for strontium sulphate, and the formation of BaO occurred at a slightly higher temperature than that of SrO. The flat region of the thermogram, where BaSO_4 and BaS are co-existing without reacting with one another, is thus wider than for the SrSO_4/SrS case. This results in the completion of the reduction of BaSO_4 to BaS without the formation of any BaO. This reaction forms the basis of the extraction of barium from barite. Unfortunately, the same situation does not hold for the SrSO_4 decomposition. In consequence, there will be always some SrO formed during the reduction of SrSO_4 .

Reduction of Strontium Sulphate with Carbon

The TGA results with the mixture of SrSO_4 and carbon exhibited a certain degree of inconsistency in the magnitude of the weight loss observed. It was suspected that this inconsistency was caused by uncontrolled factors, such as the packing of the powder, which will alter the local partial-pressure or concentration of the reducing agent. In order to study this point, several additional TGA experiments were performed.

The thermogram of the mixture of $\text{SrSO}_4 + 4\text{C}$ heated in argon is illustrated in Figure 7. It can be seen that the reaction started at about 850°C . Because of the inert atmosphere, the starting reaction must be a solid-solid reaction between the strontium sulphate and the carbon particles.



The formation of SrSO_3 was never detected; hence, it is assumed that either SrSO_3 was never formed or was formed only as an unstable intermediate product.

At the same time, Figure 8 shows that carbon monoxide is capable of reducing strontium sulphate. In a pure carbon monoxide atmosphere, the reduction starts at about 700°C . Although, in any real industrial process,

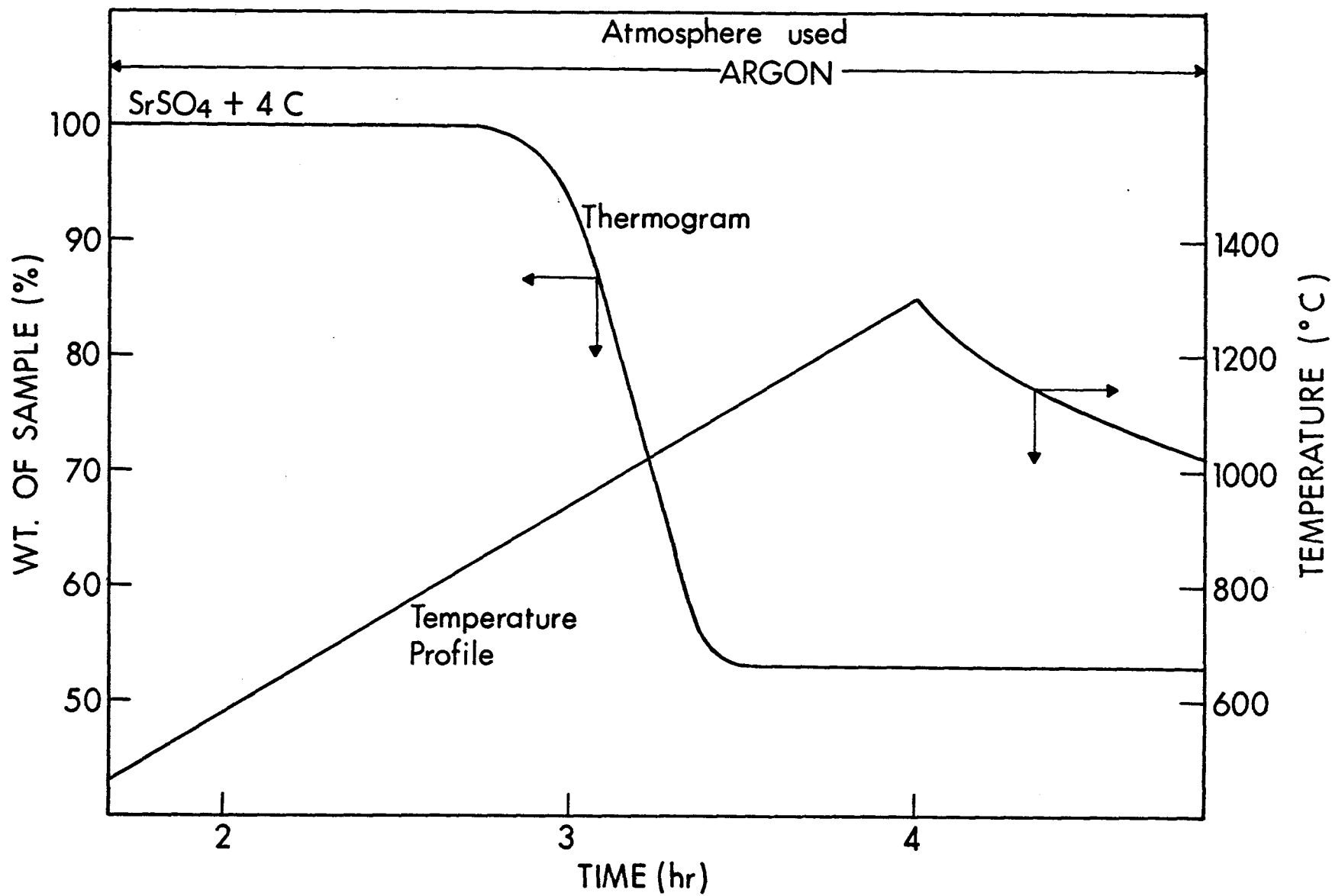


Figure 7. Thermogram of (SrSO₄ + 4C) Mixture Heated in Argon.

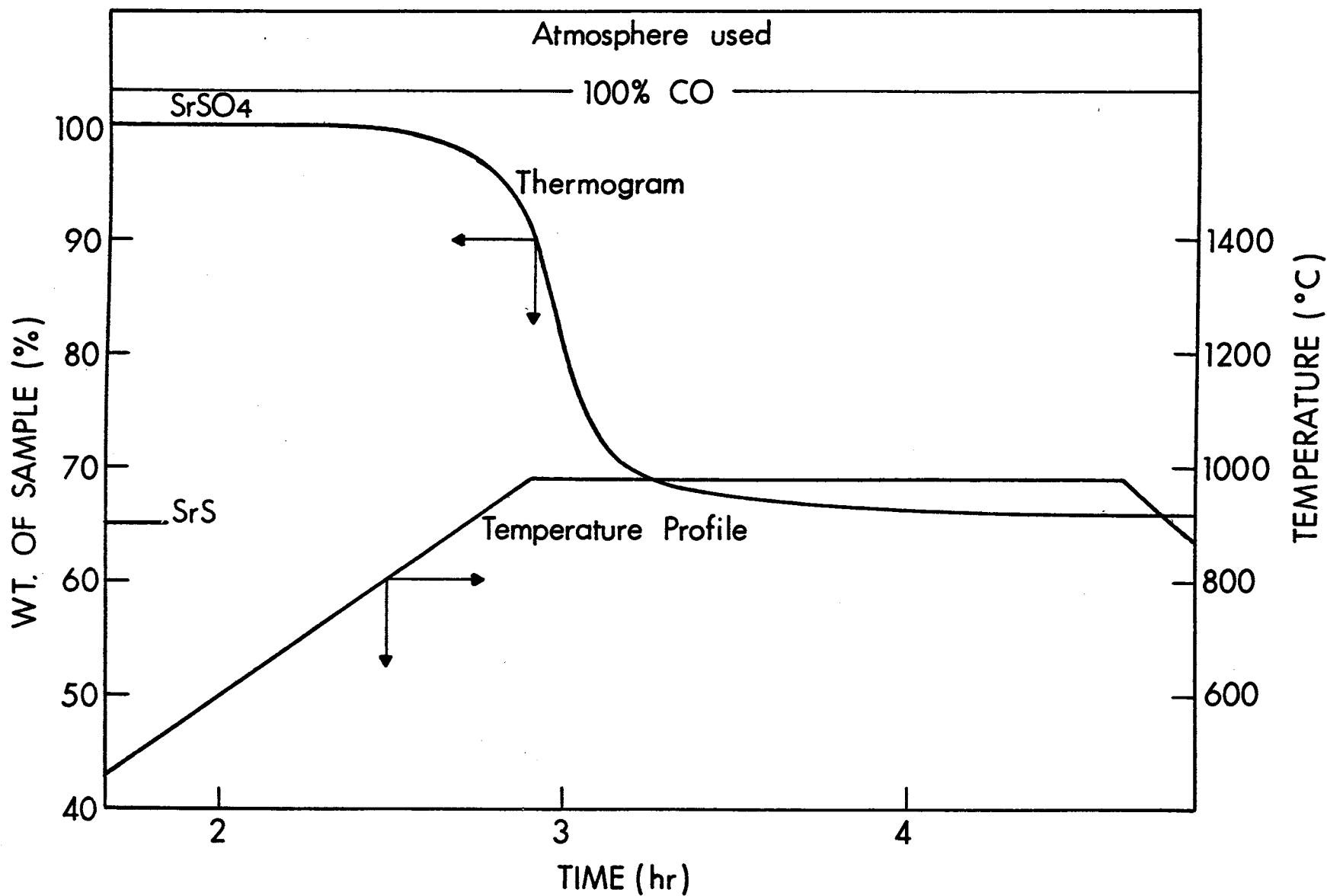


Figure 8. Thermogram of SrSO₄ Heated in a 100% Carbon Monoxide Atmosphere.

the carbon monoxide partial pressure would probably be much lower than 100%, and hence the reduction temperature might be higher than 700°C; nevertheless, it is very probable that the reduction of SrSO₄ by carbon monoxide would occur simultaneously with the reduction by carbon particles thus:

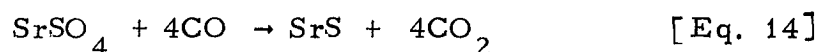
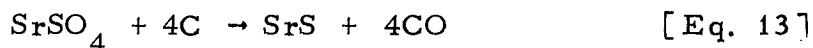


Figure 9 shows the thermogram of the decomposition of strontium carbonate both in air and in CO₂ atmospheres. The decomposition reaction started at 900°C under the air atmosphere and at about 1300°C under a pure CO₂ atmosphere. The carbon dioxide produced by the reaction [Eq. 14] would probably react with the SrO from the reaction [Eq. 12] to produce the insoluble SrCO₃. Figure 10 shows this thermogram of the reduction of strontium sulphate by hydrogen followed by carbonation in a CO₂ atmosphere.

Strontium sulphate was heated to 980°C in an atmosphere of 75% N₂ + 25% H₂, soaked for about 40 minutes, and then cooled to about 450°C in the same atmosphere. At this point the weight of the sample was down to about 59% of the original weight of SrSO₄ which is about 3% more than the equivalent weight of SrO, assuming all of the SrSO₄ to be converted to SrO. Since the hydrogen was kept flowing during the soaking and no weight loss occurred at this time, it can be concluded that the sample at this stage consisted of a mixture of SrO and SrS. The sample was then re-heated to 1150°C and soaked for 50 minutes in a CO₂ atmosphere. The weight of the final product was about 85% of the original weight. A stoichiometric calculation of the weight of the sample at various stages shows that the strontium sulphate was reduced to a mixture of strontium sulphide and strontium oxide. In the CO₂ atmosphere, the oxide was converted to strontium carbonate and the strontium sulphide was re-oxidized back to strontium sulphate.

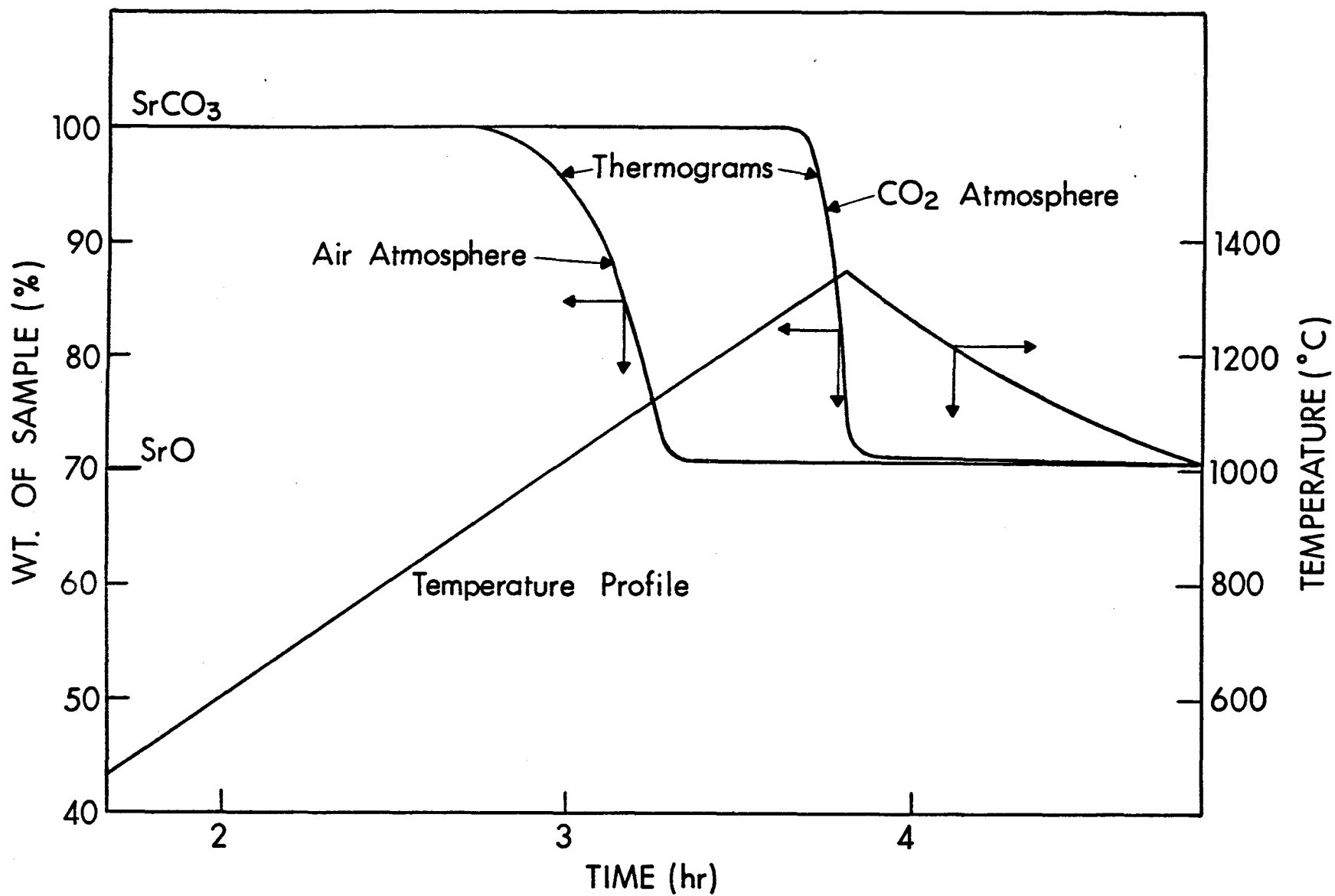


Figure 9. Thermogram of Decomposition of SrCO_3 in Air and CO_2 Atmospheres.

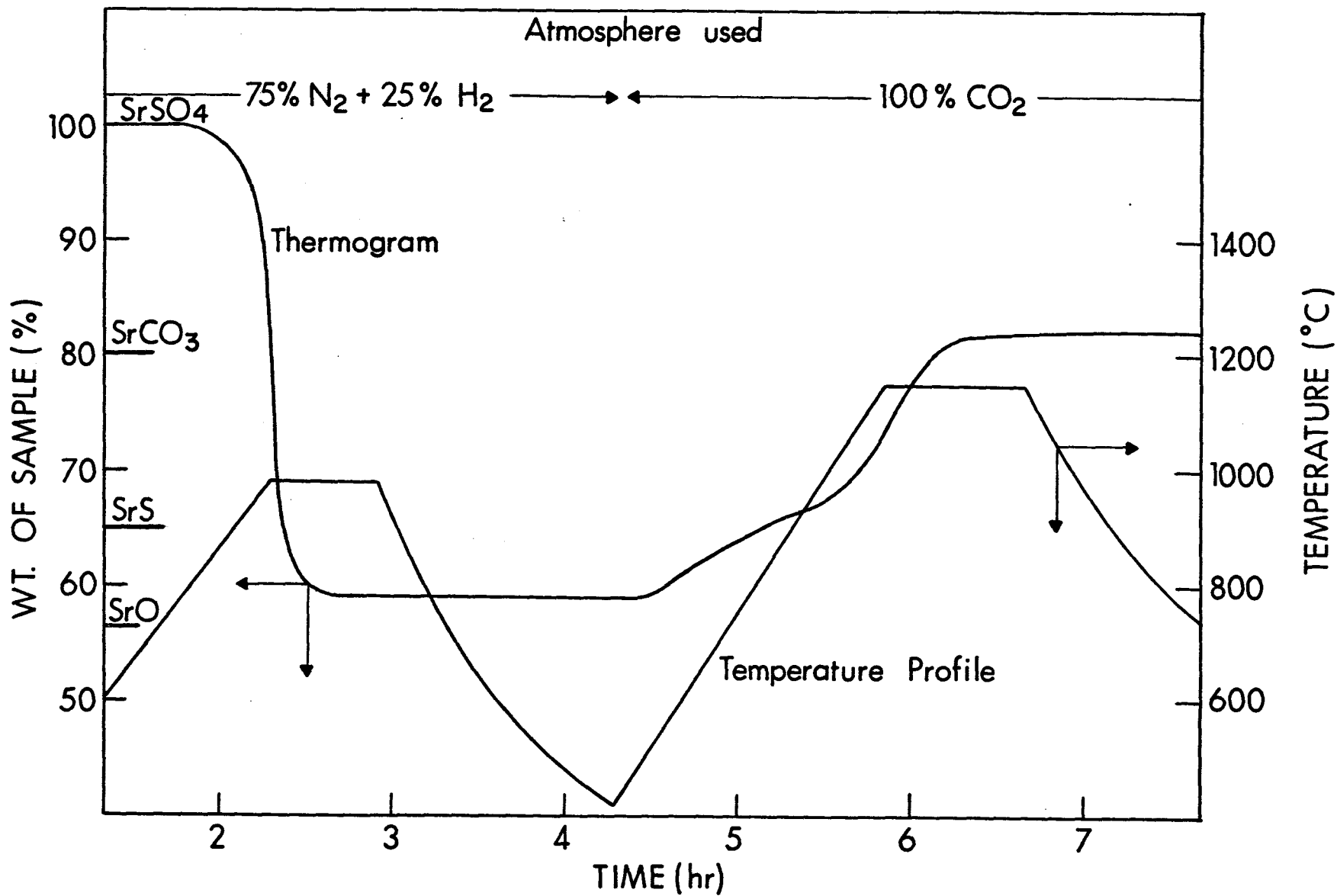


Figure 10. Thermogram of N₂/H₂ Reduction of SrSO₄, Followed by Carbonation of Product in a 100% CO₂ Atmosphere.

From the above discussion, it can be concluded that the cause of the apparently inconsistent results of the TGA run on the mixture of strontium sulphate and carbon lies in the relative kinetics of each of the reactions [Eqs. 12, 13 and 14] at a given temperature, because of the changing local partial pressures of CO and CO₂ due to such factors as packing, the rate of gas flow, and the rate of the removal of reaction products. These variables will have some effect also on the rate of formation of SrO and SrCO₃ and, in consequence, will have some effect on the efficiency of the subsequent leaching.

(ii) The Conversion of Celestite to Strontium Carbonate by the Reduction Method

This method is based on the solubility of strontium sulphide in water. Since, in general, metal sulphides are insoluble in neutral or mildly basic solutions, this method has a feature of built-in purification. Barium and calcium sulphides however, are soluble to an approximately equal extent to strontium sulphide. Thus, if the ore contains high percentages of barium and calcium, further purification would be required to remove these elements.

Another obstacle in this method is the formation of SrO from reaction [Eq. 12] which, in the relatively carbon dioxide-rich atmosphere, will form the insoluble SrCO₃, and consequently will decrease the efficiency of water-leaching. This obstacle can, in theory, be solved in either of two ways:

- (1) By preventing the formation of SrO. Thermodynamically, this can be done by maintaining a low partial pressure of oxygen by using an excess of carbon (Figure 3).
- (2) By utilizing the formation of SrO and subsequent dissolution of SrO in water. The formation of strontium carbonate must be prevented either by employing no excess of carbon (thus risking the possibility of a low efficiency due to the presence of un-reduced SrSO₄) or by calcination at a higher temperature than the decomposition temperature of SrCO₃, see Figure 9. This high calcination temperature, however, may create

some technical problems due to the formation of low-melting-point silicates.

(a) Experimental Procedure

This experiment utilized the first of the above suggestions, i. e., preventing of the formation of SrO. The experimental procedure is illustrated in Figure 11.

Celestite and carbon powders were mixed in the molecular ratio of 1 SrSO₄:4C (assuming the celestite powder to contain 100% SrSO₄). Since the SrSO₄ content is actually less than 100%, the presence of an excess of carbon is thus assured. The mixture was calcined at various temperatures between 900°C and 1150°C in either a nitrogen or an air atmosphere. The calcined products were leached in water. Strontium carbonate was then precipitated from the sulphide solution by addition of ammonium bicarbonate*. The residue was then leached with hot 5% HCl. The solution from this leaching, containing strontium chloride and the iron-group impurities was then neutralized to separate the impurities. This process of purification was exactly the same as that employed for the purification of the crude strontium carbonate obtained in the direct carbonation described earlier in the report. The strontium carbonate was then precipitated from this neutral solution by the addition of ammonium bicarbonate**.

(b) Results and Discussion

The results of the reduction process at various calcination temperatures are listed in Table V. The best yield observed for the water-leached strontium carbonate was 39%. On the other hand, a total yield (water plus acid-leached strontium carbonate) of 92% was observed with the calcination temperature of 970°C for 2 hr. This indicated that the reduction process was almost complete, but that a water-insoluble strontium compound (presumably the carbonate) was being formed to a large extent.

*In further discussions, this strontium carbonate will be referred to as "water-leached strontium carbonate".

**This strontium carbonate will be referred as the "acid-leached strontium carbonate".

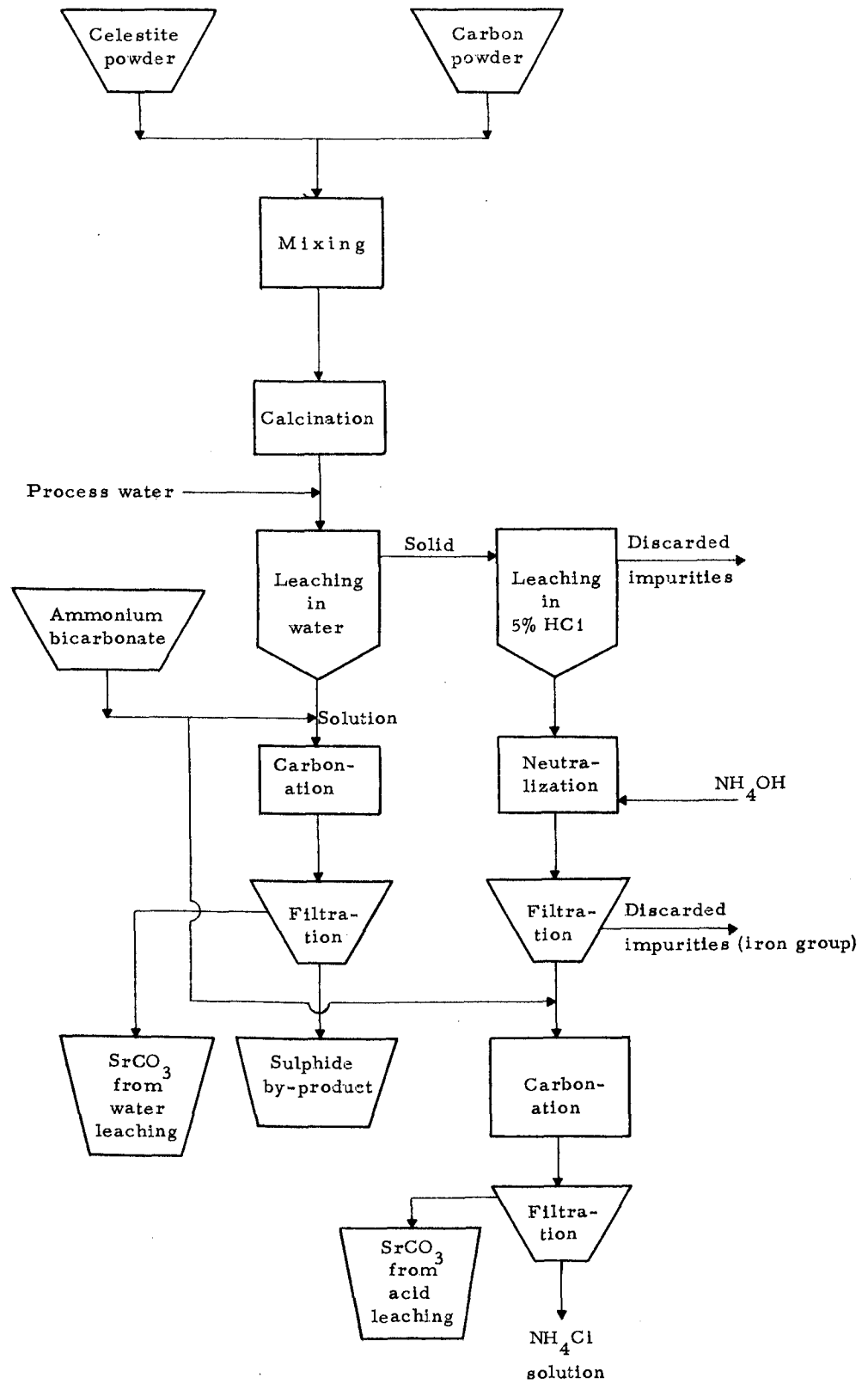


Figure 11. Flow Diagram of Strontium Extraction from Celestite by Reduction Process.

TABLE V

Extraction of Strontium from Celestite by
the Reduction Method

No.	Moles Carbon per Mole Celestite*	Reduction Process			Yield %**	
		Temp. (°C)	Time (hr)	Atmosphere	Water-leached SrCO ₃	Total SrCO ₃
1	4	900	1	N ₂	16	55
2	4	900	1	N ₂	16	65
3	4	950	1	N ₂	14	69
4	4	950	1	N ₂	12	79
5	4	970	2	N ₂	39	89
6	6	970	2	N ₂	29	92
7	4	1000	2	N ₂	24	-
8	4	1000	2	N ₂	23	-
9	4	1100	2	N ₂	32	-
10	4	1150	2	N ₂	31	-
11	4	1100	3.5	Air	35	-
12	4	1100	6	Air	16	-
13	4	1150	6	Air	14	-

*Assuming that the celestite contains 100% SrSO₄.

**Based on the original ore containing 88.13% SrSO₄.

The acid leaching is therefore efficient. However, the use of acid defeats the built-in purification feature of the reduction process. Further purification, i. e. , removal of the iron-group impurities , then becomes necessary.

DISCUSSION OF THE COMPARISON BETWEEN THE TWO PROCESSES

Having discussed the background of both the direct carbonation and the reduction processes for the extraction of strontium from celestite, a number of points of comparison can be drawn:

1. Both processes start from pre-beneficiated ore. Both require comminution to minus 100 mesh, and both will benefit from the removal of iron-group metals. This can be done by pre-washing the crushed ore with dilute sulphuric acid before starting the main extraction process.
2. The direct conversion requires a more expensive reagent (sodium carbonate) than coal in the reduction process. However, the power requirement for the former process is much lower since it is conducted at room temperature; also, the equipment needed is relatively simpler. For a batch process, which might still be economical, the equipment consist of series of stainless steel tanks that will withstand action by dilute (5%) hydrochloric acid. The reduction process will require a kiln that can be operated between 900 and 1000°C in a sulphur dioxide atmosphere. On the other hand, this equipment could be useful for processing barite.
3. The by-products of the direct carbonation process will be in the form of solutions, which can easily be recovered. The by-products of the reduction process consist of both a sulphide solution and sulphur dioxide gas, which, in view of the necessity for pollution control, must be removed from the stack gases.

For the above reasons, the choice between the two methods will depend largely on such economic factors as marketability of the by-products, transportation costs, availability and cost of the reagents; these costs will probably be valid only for a specific set of conditions or for a particular location.

ACKNOWLEDGEMENTS

This work was conducted, as part of the Ferrite Project, under the general direction of Dr. N.F.H. Bright, Head, Physical Chemistry Section, Mineral Sciences Division.

The first stage of comminution of the sample was performed by the Non-ferrous Metals Section, Mineral Processing Division. The chemical analysis of the celestite was performed by Mr. J.C. Hole, Analytical Chemistry Section, Mineral Sciences Division; the spectrographic analysis by Mr. D.P. Palombo, Spectrochemistry Section, Mineral Sciences Division.

The authors would also like to thank Dr. A.H. Webster for his valuable discussions throughout the period of the work and Mr. G.A.C. Wills for his experimental assistance. Both are members of the staff of the Physical Chemistry Section, Mineral Sciences Division.

REFERENCES

1. Arthur I. Vogel, "A Text-Book of Quantitative Inorganic Analysis",
Published by John Wiley and Sons Inc., New York (1963).
2. W. J. D. Stone, "An Integrated Mining and Chemical Plant Complex for
Various Strontium and Barium Products", Can. Min. Met. Bull., 62
[690], 1083-1086 (1969).
3. A. Cochardt, "Recent Ferrite Magnet Developments", J. Appl. Phys.
[3], 1112-1115 (1966).
4. Sutarno, W.S. Bowman and G.E. Alexander, "Ferrites: Part IV.
The Magnetic and Ceramic Properties of Mixed Barium-Strontium
Ferrites", Mines Branch Investigation Report IR 69-49 (1969).
5. R.F. Pilgrim, "Predominance Area Diagrams for the Sr-S-O System
in the Temperature Range 1200-1600°K", Extraction Metallurgy
Division, Internal Report EMT 70-8.
6. H.E. Swanson, N.T. Gilfrich and M.I. Cook, "Standard X-ray Diffraction
Powder Patterns", NBS Circular 539, 7, pp. 52-53 (1957).
7. R.M. Weast "Handbook of Chemistry and Physics", Published by The
Chemical Rubber Co., Cleveland, Ohio, 48th, ed. (1967).
8. H.E. Swanson et. al., "Standard X-ray Diffraction Powder Patterns",
NBS Circular 539, 5, (1955).