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RESEARCH AND DEVELOPMENT BRANCH

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"RECOVERY OF POTASH AND ALUMINA FROM ALUNITE"
PART I.

'Recovery of Potash'

by

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This document consists of 9 pages,
and an Appendix.

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ABSTRACT

Three samples of alunite containing various amounts of silica were subjected to heat treatment and the residues extracted with water to recover potassium sulphate.

High recoveries were obtained from a sample containing only a small percentage of silica while low recoveries were obtained from the sample with a high silica content.

When mixtures of alunite and limestone were heated, improved extraction of potash was generally obtained, while the temperature required was lower than that for alunite alone.

The lowering of the temperature however, does not seem sufficient to enable an economic process to be developed from South Australian alunite deposits.

1. INTRODUCTION.

The mineral alunite which is considered to be a hydrous basic sulphate (Bowley 1921) may be represented by the ideal formula $K_2Al_6(OH)_{12}(SO_4)_4$. Examination of this formula indicates alunite as a potential source of potassium sulphate, potash alum, aluminium sulphate, aluminium metal and sulphuric acid. Several of these products can be obtained much more economically from other sources. For example, alunite cannot compete with bauxite as a source of aluminium metal (Knickerbocker and Koster 1936).

Production of alum from alunite is an industry which dates back to very early times. The method of extraction carried out at La Tolfa, Italy was introduced into Europe in the middle of the thirteenth century (Thorpe 1912). The recovery of alum is low and unless large, easily-mined deposits of alunite are available the method cannot be considered. Recovery of aluminium sulphate is also too costly because the alunite must first be heated to remove sulphur trioxide and the residue treated with concentrated sulphuric acid to dissolve residual alumina.

Methods for extraction of potassium sulphate reported in the literature all require heating the mineral to approximately 900°C to remove most of the sulphur trioxide as for the recovery of alumina. This treatment gives a residue containing water soluble potassium sulphate and water insoluble alumina (Bayliss, Cowley, Farrant and Miles 1948). Potassium sulphate may be recovered by crystallisation of an aqueous leach liquor.

Deposits of alunite of a reasonable size occur on Yorke Peninsula in the Hundred of Ramsay and Curramulka. Much smaller occurrences are found at Carrickalinga Head, Rapid Bay, Warnertown and Sheoak Flat Wells. In a report on the economic possibilities of alunite treatment (Hosking and Weir 1941) the authors make the following statement - "The deposits from the Hundred of Ramsay and Curramulka and the vicinities are worth further investigations." However the results of work shown in this present report appear to be the first chemical investigations made on these deposits.

This report concerns a new approach to the problem of the recovery of potassium sulphate, namely heating a mixture of alunite and limestone, followed by water leaching of the residue. It is well known that when a mixture of two or more compounds in the solid state is heated it is often found that one or more of the components decomposes at a much lower temperature than if heated alone (Cohn 1948). It was thought possible that the reaction of limestone and alunite might proceed at temperatures lower than 900°C and thus enable potassium sulphate to be recovered without the effect of side reactions enhanced by siliceous impurities which are present in most alunites. Thermodynamic considerations of the reaction which are shown in the appendix of this report indicate that the reaction should proceed at low temperatures.

2. RAW MATERIALS.

2.1 Alunite samples

Three samples of alunite were examined.

Sample Al.2 was obtained from the cliffs near Port Vincent, Hundred of Ramsay.

Sample Al.3 was taken from a large nodule in the clay at Carrickalinga Head, Hundred of Myponga.

Sample Al.4 is a representative sample from the Hundred of Ramsay.

Table 1 shows the results of the chemical analysis of each of these samples.

TABLE 1.
CHEMICAL ANALYSIS OF ALUNITE SAMPLES

SAMPLE NO.	K_2O (%)	Na_2O (%)	Al_2O_3 (%)	Fe_2O_3 (%)	SiO_2 (%)	Cl^- (%)	$SO_3^=$ (%)	H_2O below 100°C (%)	H_2O above 100°C (%)
Al.2	7.21	3.04	34.88	trace	11.84	0.20	29.0	1.12	14.02
Al.3	10.1	2.68	34.58	0.48	0.14	1.64	36.3	0.74	17.31
Al.4	5.95	0.83	24.60	1.92	35.40	0.67	19.1	0.92	11.0
Theoretical (Pure alunite)	11.3	nil	37.0	nil	nil	nil	38.5	nil	13.2

Al.3 is a fairly pure potash alunite, while Al.4 has a very high proportion of silica which was shown by X-ray diffractograph examination to be in the form of quartz.

All samples tested were ground to 60 per cent. minus 200 mesh (Tyler Screen).

2.2 Limestone

A sample of Angaston marble crushed to 60 per cent. minus 200 mesh (Tyler Screen) was used. The chemical analysis is shown in Table 2.

TABLE 2.
CHEMICAL ANALYSIS OF LIMESTONE

Radical	Found (%)	Pure Limestone (%)
CaO	54.4	56
MgO	0.87	nil
Fe_2O_3	1.01	nil
CO_2	43.2	44
H_2O	0.26	nil

3. EQUIPMENT.

3.1 Furnace

Samples were heated in an automatically controlled "Glo-Bar" furnace, the temperature being recorded continuously on a Kent Recorder. Temperatures up to 1200°C were readily obtained but most experiments were carried out in the range 300 - 1000°C with a variation of ± 5°C.

3.2 Sample Containers

Reaction mixtures were heated in 3 inch porcelain dishes.

3.3 Leaching Apparatus

A water-bath, maintained at 50°C with a "Circotherm" constant temperature unit was used. Leaching was carried out in 250 millilitre flat bottomed flasks fitted with a mechanical stirrer.

4. EXPERIMENTAL PROCEDURE.

4.1 Heat Treatment of Alunite Samples

Weighed samples of alunite were heated in porcelain dishes in the furnace. Samples were spread evenly in the dishes to ensure that maximum area was available for reaction. At the completion of each experiment the dish was removed from the furnace and allowed to cool to room temperature. The product was weighed, and then crushed using a mortar and pestle.

4.2 Heat Treatment of Alunite-Limestone Mixtures

Weighed alunite samples were mixed thoroughly with enough limestone to react with the sulphate combined as aluminium sulphate in the alunite. The reactants were heated to temperatures of 1000°C. The product was removed from the furnace after each experiment, cooled, weighed and then crushed.

The amount of limestone was varied to give an indication of the minimum quantity required for optimum recovery of potash.

4.3 Extraction of Potash from Residues

The crushed residues were placed in flat bottomed flasks, a fixed volume of distilled water was added, and the contents were stirred for a fixed time in the constant temperature water-bath. This procedure was used in all experiments to ensure uniform leaching conditions.

The leached samples were filtered through a Buchner filter, washed thoroughly with distilled water and the filtrate and washings were diluted to a standard volume and assayed for potash.

5. RESULTS.

5.1 Heat Treatment of Alunite Samples and Extraction of Potash

5.1.1 : Heat treatment -

25 grams of each of the samples A1.2, A1.3, and A1.4 was heated at temperatures in the range 300 - 1000°C. The residues were weighed to determine loss of water and sulphur trioxide. Table 3 shows temperature, heating time and loss of weight.

5.1.2 : Extraction of potash -

The crushed residues were leached at 50°C for one hour with distilled water (150 millilitres): Extraction of potash (K_2O) is shown in Table 3 and also represented graphically in Figures 1, 2, and 3.

TABLE 3.
ALUNITE HEATED ALONE.
LOSS IN WEIGHT AND EXTRACTION OF POTASH ON HEATING 25 GRAM SAMPLE.

Temperature (°C).	Time (hr)	Loss in weight (g)			K_2O Extracted(%)		
		Al.3	Al.2	Al.4	Al.3	Al.2	Al.4
300	1	n.d.	0.5	n.d.	n.d.	0.5	n.d.
300	2	n.d.	0.5	n.d.	n.d.	0.7	n.d.
400	1	1.6	0.7	1.4	16	5	20
400	2	2.1	1.0	1.4	21	10	32
500	1	3.4	2.3	2.7	31	16	38
500	2	4.3	3.5	2.9	40	30	39
600	1	4.6	3.9	3.4	42	36	48
600	2	4.7	4.1	3.6	62	57	48
700	1	5.7	5.1	5.7	63	65	65
700	2	8.1	6.6	5.8	82	79	66
800	1	9.0	7.8	6.3	94	90	54
800	2	10.0	8.9	6.4	96	91	54
900	1	10.3	9.1	6.6	95	76	42
900	2	10.3	9.5	6.9	96	72	32
1000	1	10.5	n.d.	n.d.	92	n.d.	n.d.
1000	2	10.6	n.d.	n.d.	93	n.d.	n.d.

n.d. = not determined

5.2 Heat Treatment of Alunite-Limestone Mixtures and Extraction of Potash

5.2.1 : Reaction with theoretical weight of limestone -

Alunite samples were mixed thoroughly with an amount of limestone sufficient to react with the aluminium sulphate content in each case. The weight of limestone required to react with a 25 gram sample of alunite is as follows :

Al.3 - 8.5 gram limestone
Al.2 - 6.4 " "
Al.4 - 5.3 " "

Temperature, heating time, and loss of weight are shown in Table 4.

Residues were treated using the procedure in Section 5.1.2, and extraction of potash is shown in Table 4. These results are also represented graphically in Figures 4, 5 and 6.

TABLE 4.

HEATING ALUNITE MIXED WITH THE THEORETICAL WEIGHT OF LIMESTONE.

LOSS IN WEIGHT AND EXTRACTION OF POTASH.

Al.3 (25 g) : limestone (8.5 g)
Al.2 (25 g) : limestone (6.4 g)
Al.4 (25 g) : limestone (5.3 g)

Temperature (°C).	Time (hr)	Loss in weight (g)			K_2O Extracted (%)		
		Al.3	Al.2	Al.4	Al.3	Al.2	Al.4
300	1	0.3	n.d.	n.d.	2	n.d.	n.d.
300	2	0.3	n.d.	n.d.	4	n.d.	n.d.
400	1	0.9	n.d.	1.4	16	n.d.	30
400	2	1.9	n.d.	1.4	25	n.d.	31
500	1	4.3	2.9	2.7	54	37	58
500	2	5.1	4.3	2.9	74	47	69
600	1	6.9	5.0	3.4	88	57	62
600	2	7.0	5.8	3.6	93	69	60
650	1	7.4	n.d.	n.d.	92	n.d.	n.d.
650	2	7.7	n.d.	n.d.	94	n.d.	n.d.
700	1	7.7	6.4	5.2	96	86	55
700	2	7.8	7.2	5.6	98	97	46
800	1	8.0	7.6	6.3	100	92	46
800	2	8.1	7.6	6.4	98	86	44
900	1	8.1	7.8	6.8	90	81	41
900	2	8.2	8.0	6.9	90	72	44
1000	1	8.7	n.d.	n.d.	86	n.d.	n.d.
1000	2	8.8	n.d.	n.d.	84	n.d.	n.d.

n.d. = not determined

5.2.2 : Identification of reaction products –

Mixtures of Al.3 (25 grams) and limestone (8.5 grams) were heated at 550°C for four and five hours respectively.

At the completion of each test the residues were crushed and submitted for X-ray diffractograph examination. In each case a strong pattern of $CaSO_4$ - anhydrite was obtained.

Chemical analysis for CO_2 in the residues showed that only one per cent. carbonate was present.

5.2.3 : Treatment of larger sample of Al.3 -

Al.3 (100 grams) and limestone (34 grams) were mixed and heated at 600°C for two hours. The residue was leached with 600 millilitres of distilled water at 50°C for one hour, and then filtered and washed with water. The leach liquor and washings were made to 1000 millilitres.

The liquor was placed in a large evaporating dish and evaporated to dryness. A white crystalline product (23.7 grams) was obtained which had the following composition:

K_2O	40.1%
Na_2O	8.82%
CaO	2.97%
$SO_4^=$	48.4%

These figures represent an overall recovery of 95 per cent. potash in a product containing 74.2 per cent. potassium sulphate, 20.2 per cent. sodium sulphate and 7.2 per cent. calcium sulphate.

5.2.4 : Effect of variation in amounts of limestone -

Samples of Al.2 and Al.3 (25 grams) were mixed with various weights of limestone. The mixtures were heated for two hours at the required temperature and treated as described in Section 4. Extraction of potash is shown graphically in Figures 7 and 8. Under the conditions employed the optimum extraction of potash was obtained when three-quarters of the theoretical weight of limestone was added.

6. DISCUSSION.

6.1 Heat Treatment of Alunite

A maximum recovery of 96 per cent. of the potash was obtained from Al.3 after heating at 800°C for two hours. The maximum recovery of potash from Al.2 was 91 per cent. after heating at 800°C for two hours. Sample Al.4 which has a much higher silica content gave a maximum recovery of

66 per cent. K_2O after two hours' heating at 700°C. In each case as the temperature was increased above 800°C, the potash recovery was lower.

These results support those of Bayliss et al (1948) who found that alunites containing large amounts of silica gave poor recovery of potash. These authors propose the formation of alumino-silicates which bind the potassium in a water insoluble form.

6.2 Heating Alunite-Limestone Mixtures

6.2.1 : Reaction with theoretical weight of limestone -

X-ray diffractograph examination of alunite (Sample Al.3) after treatment with the theoretical weight of limestone showed the presence of anhydrite and chemical analysis of this residue indicated that at 550°C all the carbon dioxide from the limestone had been evolved. On the basis of these results, the equation used in thermodynamic calculations (see Appendix) was derived.

The thermodynamic calculations which are shown graphically in Figure 9 indicate that the reaction could occur at temperatures above 117°C. Examination of results obtained with sample Al.3 (a reasonably pure potash alunite) showed that after two hours' heating at 300°C, four per cent. of the potash was recovered. This result is in reasonable agreement since thermodynamic values for alunite refer to the pure mineral. Thermodynamic calculations are based on equilibrium conditions and it is likely that if the reaction mixture were heated at low temperatures for an extremely long time, good recoveries of potash could be obtained. This would probably be uneconomic.

Theoretical recovery of potash was obtained after two hours' heating of sample Al.3 at 800°C while sample Al.2 gave 97 per cent. recovery at 700°C. after two hours. A maximum recovery of 69 per cent. K_2O was obtained with sample Al.4 (after heating for two hours at 500°C). Recovery fell sharply after the maximum in each series of experiments. These results showed that the addition of limestone improved the potash recovery. Examination of graphs showing the amount of potash extracted, indicates that at all temperatures, the recovery of potash was higher for the alunite-limestone mixture than for the mineral alone.

Recovery was low in sample Al.4 which contains a large proportion of silica. The formation of insoluble potassium salts with aluminium and silica seems the most probable explanation for this low recovery.

6.2.2 : The effect of variation in amount of limestone -

Figures 7 and 8 show that a slightly higher extraction of potash resulted when three-quarters of the theoretical weight of limestone was added to Al.3, but there was no significant difference in extraction for sample Al.2. No explanation can be offered for this behaviour.

7. CONCLUSIONS.

Any considerations of the costs for recovery of potash from alunite must be based on the results obtained from the treatment of sample Al.4. This sample is a representative one from the Hundred of Ramsay, Yorke Peninsula, and this deposit appears to be the largest and most readily accessible in South Australia.

The following observations can be made :

(a) By heating sample Al.4 alone, the maximum recovery was 66 per cent. after two hours' heating at 700°C.

(b) A slightly higher recovery (69 per cent.) was obtained when this sample was mixed with limestone and heated at 500°C. for two hours.

Although addition of limestone before heating has been shown to improve the recovery of potash, it seems unlikely that a process for the recovery of potash from the Hundred of Ramsay alunite deposits would be economical.

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APPENDIX

A Thermodynamic Study of the System Alunite-Limestone.

The reaction can be considered ideally as :-

$$\underset{\text{(alunite)}}{K_2SO_4\ Al_2(SO_4)_3\ \ 4Al(OH)_3} + 3CaCO_3 \rightleftharpoons K_2SO_4 + 3Al_2O_3 + 3CaSO_4 + 3CO_2 + 6H_2O$$

The free energy change for this reaction can be calculated from the following equation.

$$\Delta G_T = \Delta H_{298} + \int_{298}^{T} \Delta Cp\, dT - T\Delta S_{298} - T\int_{298}^{T} \Delta \frac{Cp}{T}\, dT$$

Evaluation of the terms in this expression for the reaction under consideration, is shown below.

Numerical values of terms for alunite were taken from a paper by K.K. Kelley (1954) while all other values were obtained from a publication by Kubaschewski and Evans (1955).

(1) Heat capacity data (Cp values)

	Substance	Cp
Reactants	alunite	$231.0 + 78.6 \times 10^{-3}T - 67.83 \times 10^{5}T^{-2}$
	$3\ CaCO_3$	$74.94 + 15.72 \times 10^{-3}T - 18.60 \times 10^{5}T^{-2}$

$\therefore \Delta Cp$ reactants $305.94 + 94.32 \times 10^{-3}T - 86.43 \times 10^{5}T^{-2}$

Products	K_2SO_4	$28.77 + 23.80 \times 10^{-3}T - 4.26 \times 10^{5}T^{-2}$
	$3\ Al_2O_3$	$82.29 + 9.18 \times 10^{-3}T - 25.41 \times 10^{5}T^{-2}$
	$3\ CaSO_4$	$50.34 + 70.80 \times 10^{-3}T$
	$3\ CO_2$	$31.65 + 6.48 \times 10^{-3}T - 6.12 \times 10^{5}T^{-2}$
	$6\ H_2O$	$43.02 + 15.36 \times 10^{-3}T + 0.48 \times 10^{5}T^{-2}$

$\therefore \Delta Cp$ products $= 236.07 + 125.62 \times 10^{-3}T - 35.31 \times 10^{5}T^{-2}$

ΔCp (reaction) $= -69.87 + 31.30 \times 10^{-3}T + 51.2 \times 10^{5}T^{-2}$

(2) Entropy Values at 298°K

$$\text{Alunite} + 3CaCO_3 \longrightarrow K_2SO_4 + 3Al_2O_3 + 3CaSO_4 + 3CO_2 + 6H_2O$$

$$S_{298} = 152.2 + 3 \times 22.2 \longrightarrow 42.0 + 3 \times 12.2 + 3 \times 25.5 + 3 \times 51.1 + 6 \times 45.13$$

$\Delta S_{298} = + 360.4$ cals/deg/mole

(3) Calculation of Enthalpy Change at 298°K

$$\text{Alunite} + 3CaCO_3 \longrightarrow K_2SO_4 + 3Al_2O_3 + 3CaSO_4 + 3CO_2 + 6H_2O$$

$$H_{298} = -2471 - 3 \times 288.4 \longrightarrow -342.6 - 3 \times 400 - 3 \times 342 - 3 \times 94.1 - 6 \times 57.8$$

ΔH_{298} reaction $= \Delta H$ products $- \Delta H$ reactants

$\therefore\ \Delta H_{298} = + 138.5$ K cals/mole

(4) Integration of Heat Capacity Data and Evaluation of Constants

$$\Delta Cp = -69.87 + 31.30 \times 10^{-3}T + 51.12 \times 10^{5}T^{-2}$$

Integration gives :-

$$\int_{0}^{T} \Delta Cp \; dT = -69.87T + 15.65 \times 10^{-3}T^{2} - 51.12 \times 10^{5}T^{-1} + \text{const (a)}$$

and $$\int_{0}^{298} \Delta Cp \; dT = -69.87 \times 298 + 15.65 \times 10^{-3} \times 298^{2} - 51.15 \times 10^{5} \times \frac{1}{298} + \text{const (a)}$$

$$= -36,587 + \text{const (a)}$$

whence $$\int_{298}^{T} \Delta Cp \; dT = -69.87T + 15.65 \times 10^{-3}T^{2} - 51.15 \times 10^{5}T^{-1} + 36,587$$

Now $$\int_{0}^{T} \Delta \frac{Cp \; dT}{T} = -69.87 \ln T + 31.30 \times 10^{-3}T - 25.56 \times 10^{5}T^{-2} + \text{const (b)}$$

$$\therefore \int_{0}^{298} \Delta \frac{Cp \; dT}{T} = -417.6 + \text{const (b)}$$

i.e., $$\int_{298}^{T} \Delta \frac{Cp \; dT}{T} = -69.87 \ln T + 31.30 \times 10^{-3}T - 25.56 \times 10^{-5} \times T^{-2} + 417.6$$

(5) Substitution of Values in ΔG_T equation

$$\Delta G_T = 138.500 - 69.87T + 15.65 \times 10^{-3}T^{2} - 51.12 \times 10^{5}T^{-1} + 36.587$$

$$- T \times 360.4 + 69.87T \ln T - 31.30 \times 10^{-3}T^{2} + 25.56 \times 10^{5}T^{-1} - 417.6\,T$$

Simplification gives

$$\Delta G_T = 175,087 - 847.9T - 15.65 \times 10^{-3}T^{2} + 2.303 \times 69.87 \times T \log T - 25.56 \times 10^{5}T^{-1}$$

Free energy changes calculated from the above dquation are plotted graphically (Figure 9), from which it is seen that $\Delta G_T = 0$ at T = 398°K.

Thus it can be assumed that the alunite limestone reaction could occur at temperatures above 117°C, i.e., when ΔG_T is negative. An inspection of Figure 3, shows that at 200°C there is no visible reaction between Carrickalinga alunite and limestone. However, appreciable reaction occurs at 300°C. The thermodynamic calculations are of course, determined for ideal conditions e.g., the values for alunite refer to pure alunite. The sample from Carrickalinga is not an ideal alunite and therefore the thermodynamic functions used in these calculations can be considered as only approximate.

It is probable that if the heating time were very long some reaction would be detected at temperatures below 200°C. The fact that some reaction occurs at 300°C after one hour indicates that experimental results for the alunite-limestone reaction are in agreement with the thermodynamic calculations.

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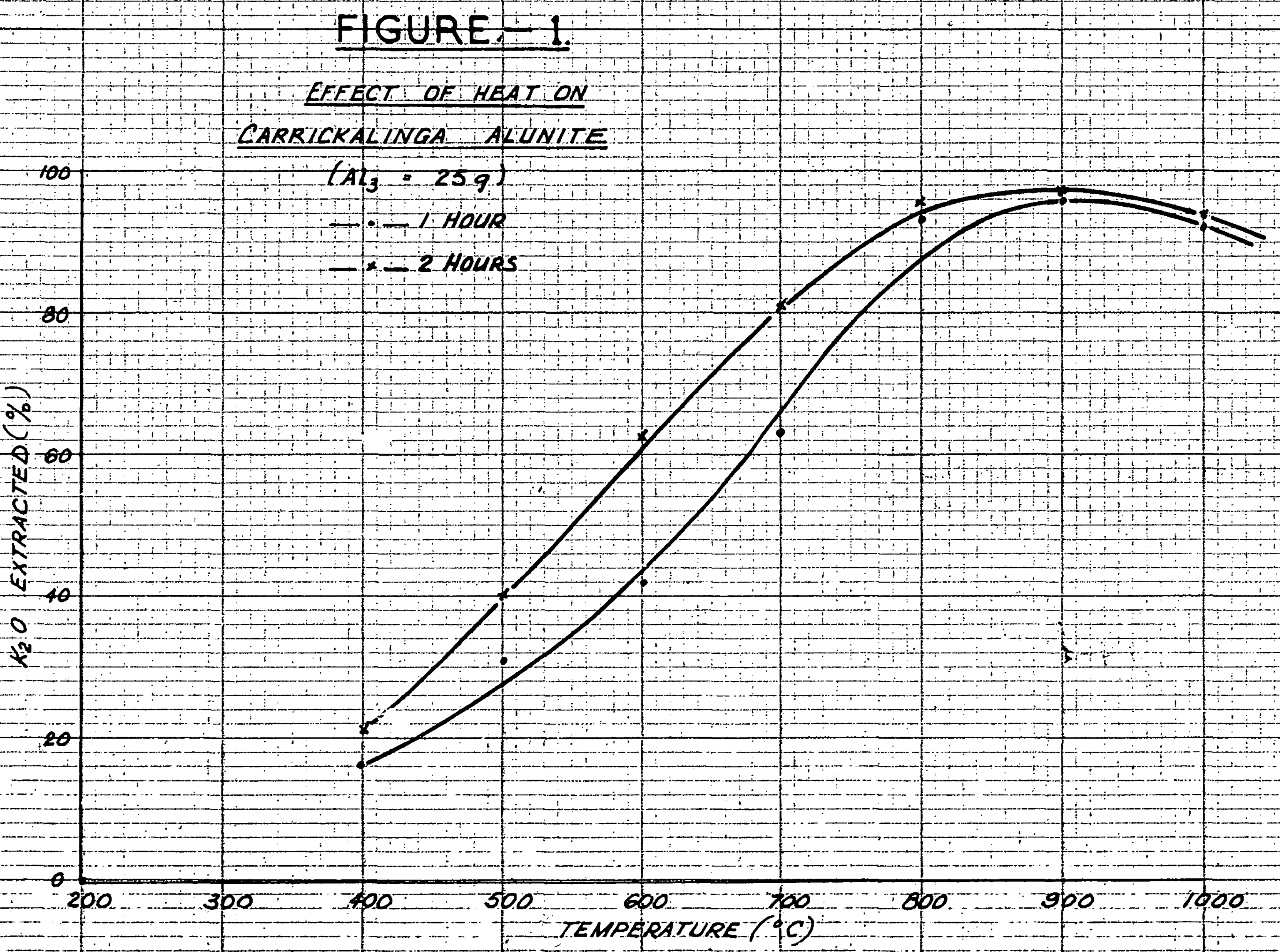


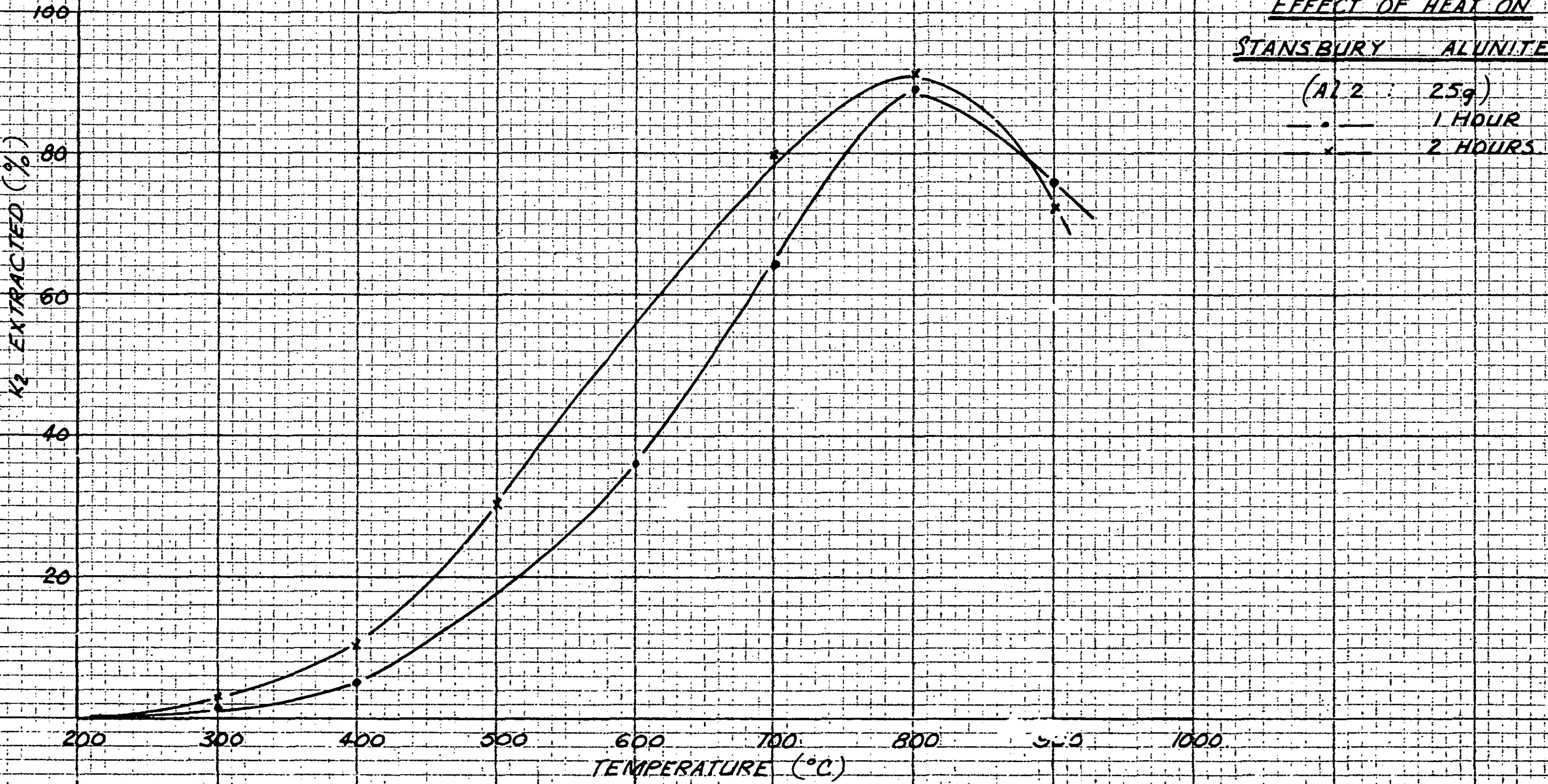
FIGURE — 1.

EFFECT OF HEAT ON CARRICKALINGA ALUNITE

(Al_3 = 25g)

FIGURE 2

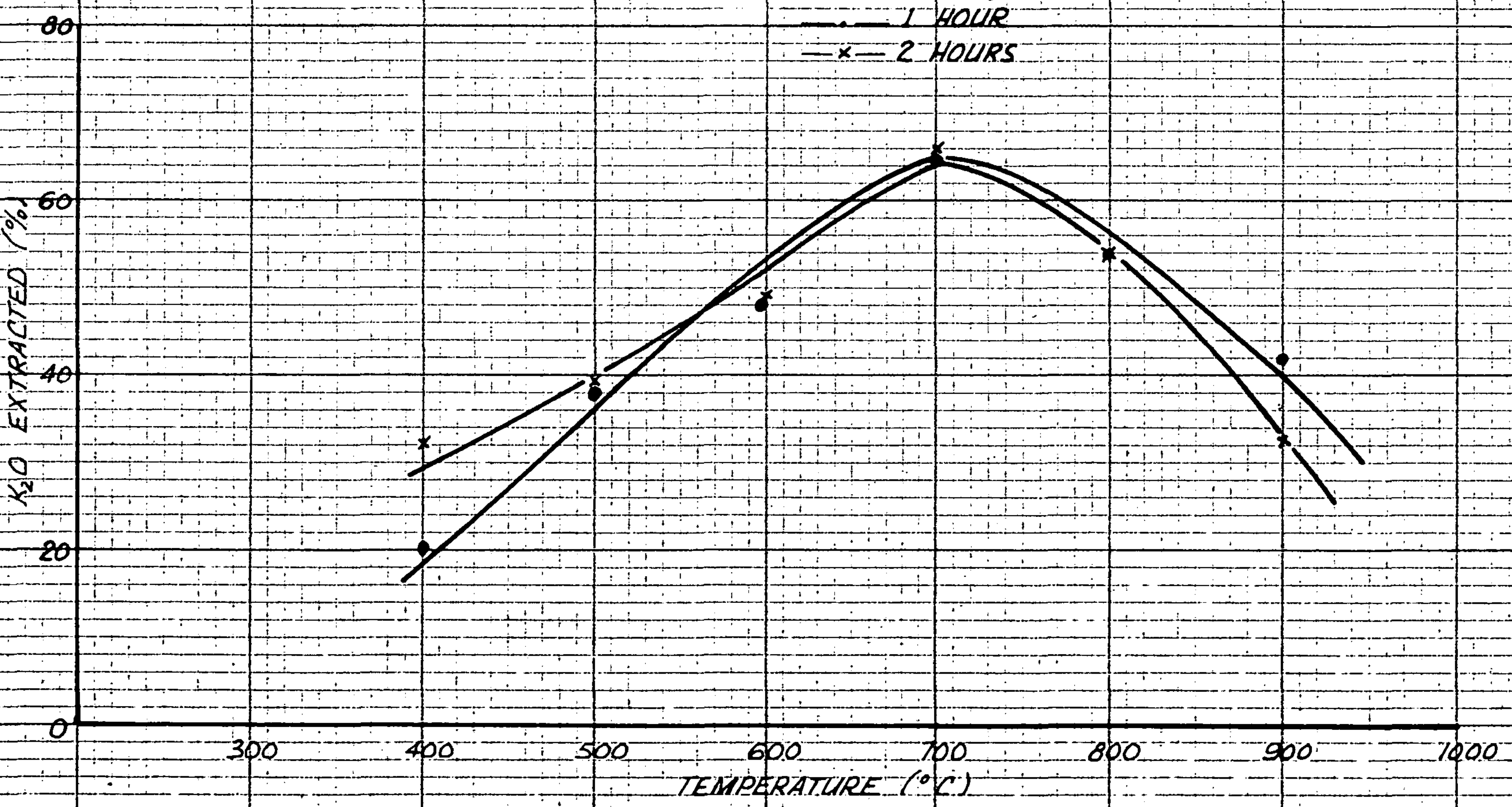
EFFECT OF HEAT ON STANSBURY ALUNITE



RG. 799.

FIGURE — 3

EFFECT OF HEAT ON
STANSBURY ALUNITE
(AC 4 = 25g)



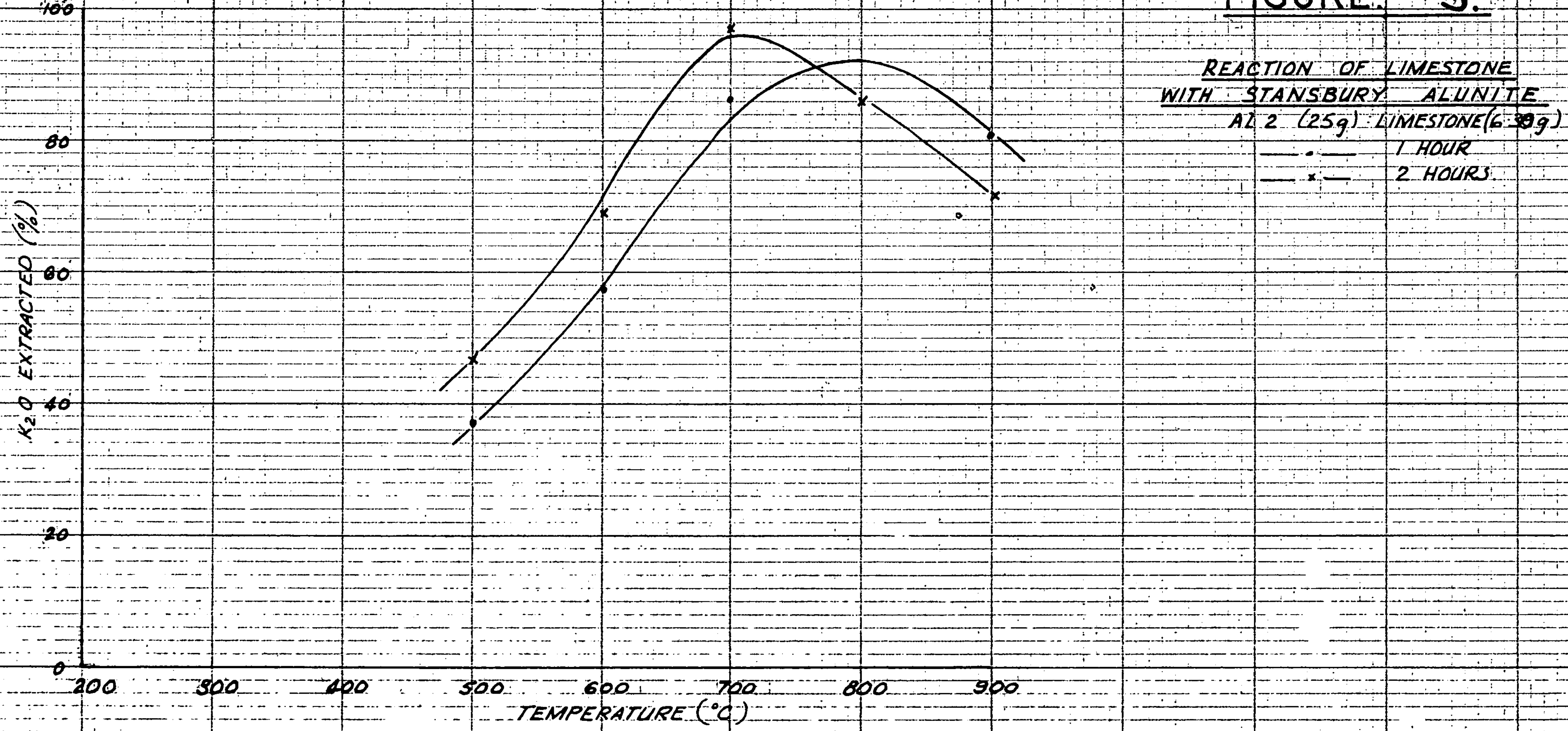
R.G. 863.

FIGURE 4

REACTION OF LIMESTONE WITH CARRICKALINGA ALUNITE AL 3 (25g) : LIMESTONE (8.5g)

R.G. 798.

FIGURE. — 5.



REACTION OF LIMESTONE WITH STANSBURY ALUNITE

RG 800.

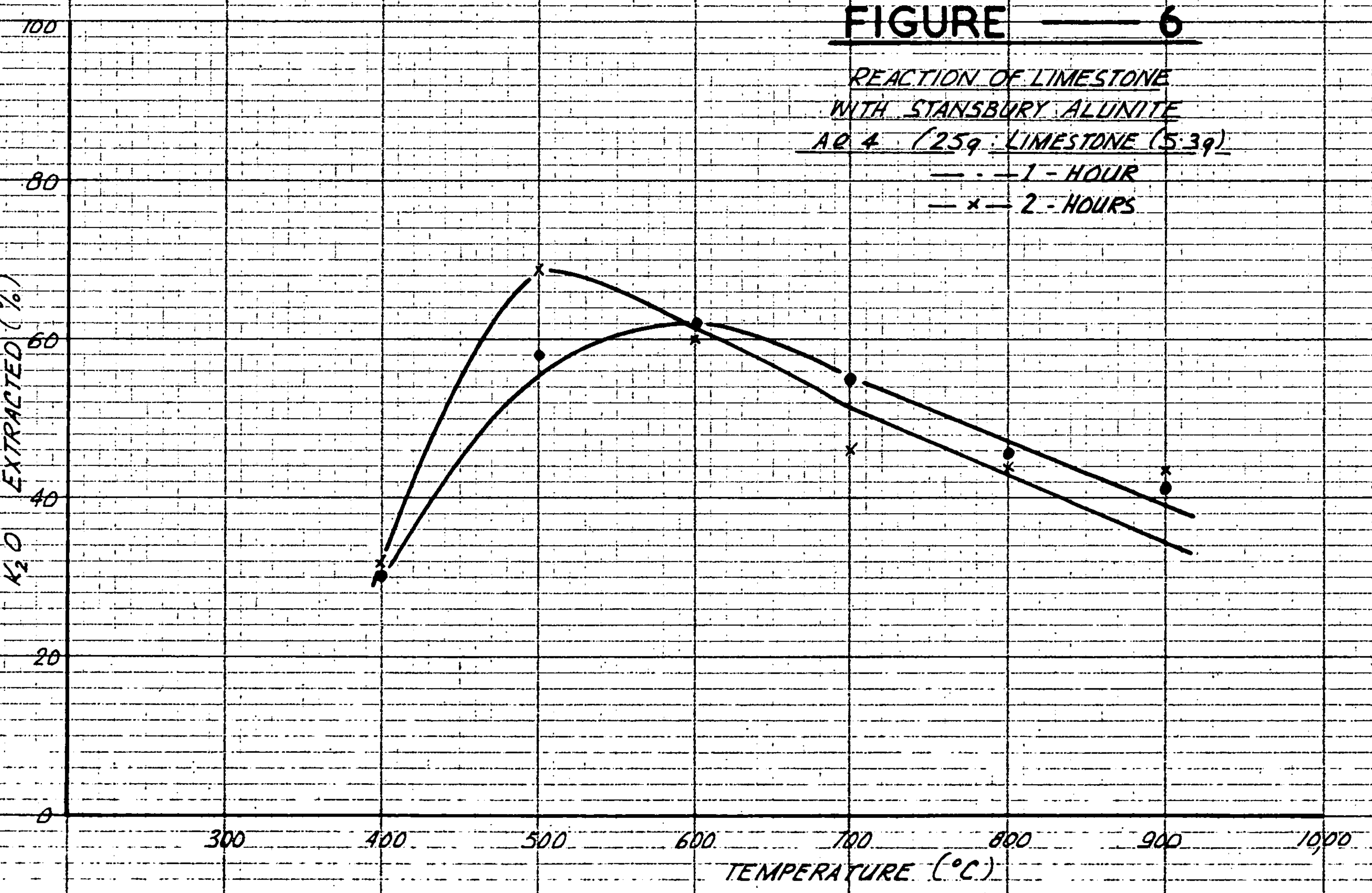


FIGURE — 6

REACTION OF LIMESTONE
WITH STANSBURY ALUNITE
AQ 4 (25g : LIMESTONE (5.3g)

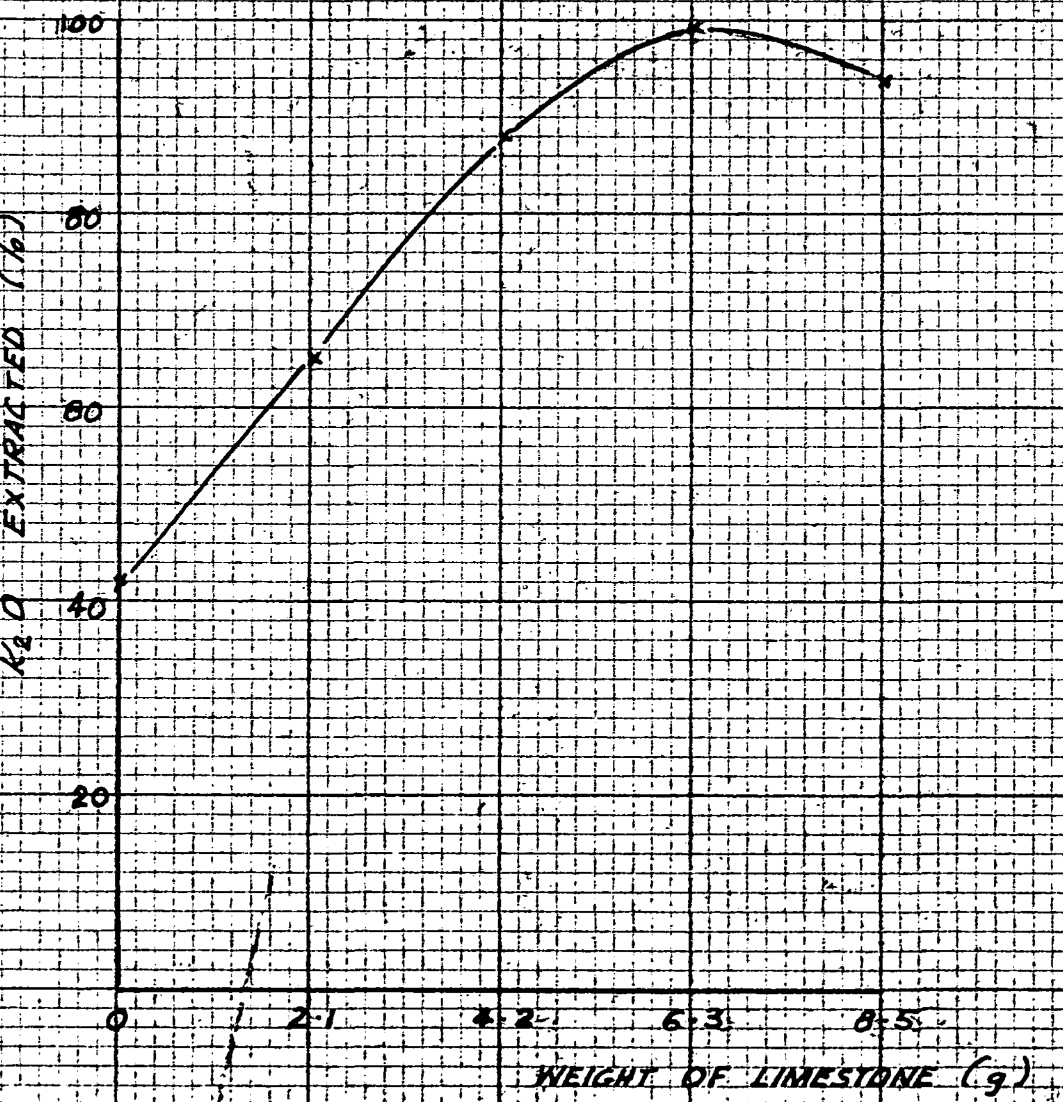


FIGURE — 7.

EFFECT OF LIMESTONE ON CARRIGKALINGA ALUNITE

TEMP 600°C
TIME 2 HOURS
AL 3 25g

RG 801.

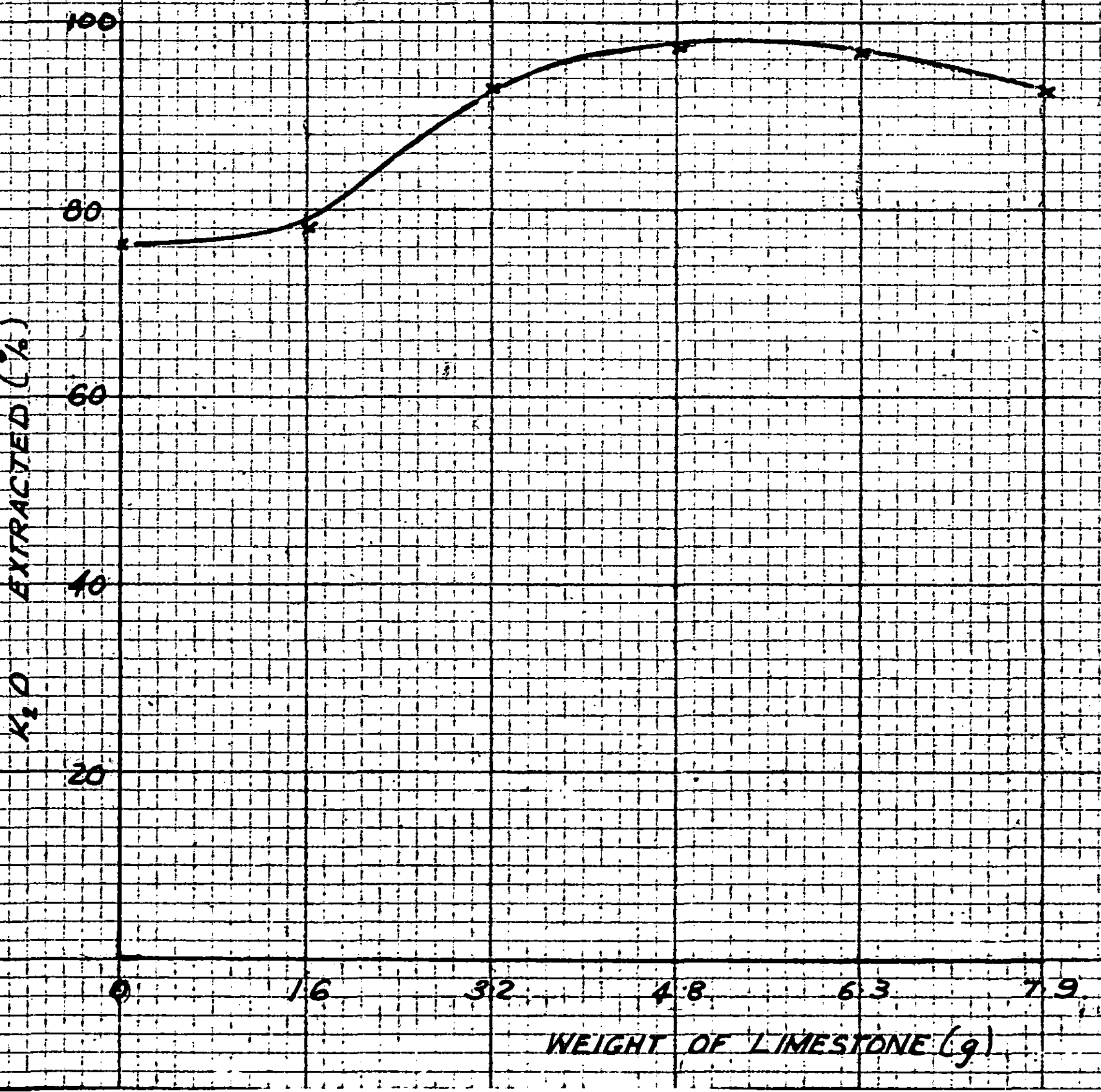


FIGURE-8

EFFECT OF LIMESTONE ON

STANSBURY ALUNITE

TEMP. 700°C
TIME 2 HOURS
A1 2 25g

RG.802

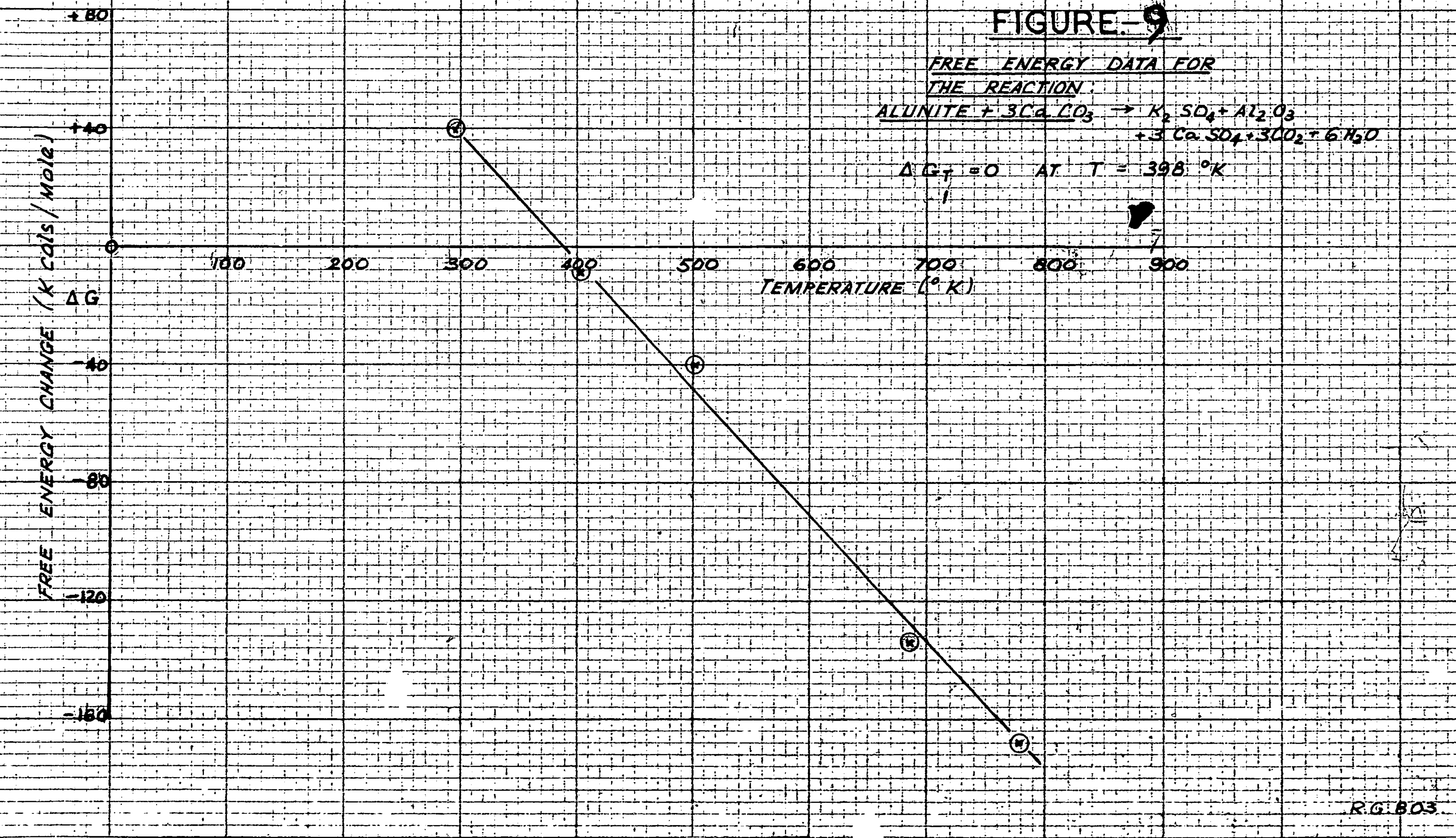


FIGURE-9

FREE ENERGY DATA FOR THE REACTION:

ALUNITE + $3CaCO_3 \rightarrow K_2SO_4 + Al_2O_3 + 3CaSO_4 + 3CO_2 + 6H_2O$

$\Delta G_T = 0$ AT $T = 398$ °K