Open File Envelope
No. 3081

SADME/AMDEL MINERAL RESEARCH ASSISTANCE TO INDUSTRY

REPORTS ON VARIOUS UNRELATED PROGRAMMES CARRIED OUT OVER THE PERIOD 1977 TO 1983

Submitted by
Amdel Ltd
1983

Enquiries: Customer Services Branch
Minerals and Energy Resources
7th Floor
101 Grenfell Street, Adelaide 5000

Telephone: (08) 8463 3000
Facsimile: (08) 8204 1880

Government of South Australia
Primary Industries and Resources SA

CONTENTS ENVELOPE 3081 DM 394/77 and DM 512/78

TENEMENT: NIL

TENEMENT HOLDER: The Australian Minerals Development Laboratories

REPORTS:

PLans;

REPORTS:

PLANS:

REPORTS:

amdel
The Australian Mineral Development Laboratories
Flemington Street, Frewville, South Australia 5063
Phone Adelaide 79 1662, telex AA 82520

Winner of Award for Outstanding Export Achievement, 1975
Pilot Plant: Osman Place, Thebarton, Sth. Aust.
Phone Adelaide 43 8053
Branch Offices: Perth and Sydney
Associated with: Professional Consultants Australia Pty. Ltd.
Please address all correspondence to Frewville.
In reply quote:

MD 1/31/0

2 November 1977

S.A. Department of Mines
P.O. Box 151
EASTWOOD SA 5063

Attention: Mr R. Wildy

REPORT MD 915/78

YOUR REFERENCE:	Application dated 9 August 1977.
SUBJECT:	An assessment of seven clays for possible pottery use.
MATERIAL:	Seven pottery clays.
DATE RECEIVED:	13 September 1977.
INFORMATION REQUIRED:	Firing Tests.

Investigation and Report by: Dr William G. Spencer and G. Beer.

Manager, Materials Division: Dr Graham L.F. Powell.

for Brian S. Hickman
Acting Managing Director

1. INTRODUCTION

Seven samples were submitted which the applicant had marked 1 to 7 respectively. Firing tests and comments on the potential use as pottery clay were required. Mines Department sample numbers are A2696/77 to A2702/77.

2. PROCEDURE

The samples received were moist as the client had worked them to a suitable plasticity. Extrusion of the samples, as received, were to be done but in some cases the samples required to be dried slightly. Samples were extruded using a Boulton laboratory de-airing extruder, producing a cylindrical column of diameter about 25 millimetres. Extrusion properties were noted and moisture contents determined by moisture balance. Specimens for firing were obtained by wire-cutting the extruded column. Green specimens were dried under moderate (40°C) and severe (105°C) conditions and their shrinkage and behaviour determined.

Specimens for firing were air-dried for a period of days, and then oven dried at 105°C for twelve hours. They were then fired in oil-fuelled Major kiln over the temperature range 900°C, 1000-1300°C in 50°C intervals with a 30 minute soak at each temperature. Samples fired at 1350°C were fired in a gas-fired Major furnace and soaked for 30 minutes. All specimens were removed from the furnace to a holding kiln at 600°C. After all specimens had been fired, the holding kiln was switched off and the samples allowed to cool overnight to room temperature.

Shrinkages for dried and fired specimens were determined by measurement with a travelling microscope of the spacing of a set of marks inscribed immediately after extrusion with a pair of knife edges set 20 millimetres apart. Water absorption properties of the fired specimens were determined by weighing specimens dry and after soaking for 24 hours in water with removal of surface water. The general quality of the specimens was determined by visual inspection. Colours were assessed using a Munsell Rock Color Chart.

3. RESULTS

Sample 1(CE 5167)

The sample was extruded at a moisture content of 25.2%. It produced a smooth, soft-shelled column of low to moderate plasticity. The extrusion rate was quick and the column wire-cut cleanly.

Drying at 40°C and 105°C was satisfactory and the drying shrinkage was about 6.7%.

On firing the light brown material changed to a pinkish orange at the range 900-1050°C. At 1100°C the colour becomes darker; successive specimens go from brown to finally become grey at 1350°C. Firing to 1050°C is necessary to produce a hard product and after this temperature the water absorption is reduced significantly. Shrinkage is minimal after 1150°C and bloating starts at 1300°C. All temperatures produced cracking which is slight, to 1300°C.

The samples fired to a dense stoneware body at about 1200°C with a shrinkage of 14.6%. Slight firing cracks were evident.

Sample 2 (CE 5168)

The sample was extruded at a moisture content of 28.2%. It produced a smooth, hard-shelled column of low to moderate plasticity. The extrusion rate was slow and the column wire cut cleanly.

Drying at 40°C specimen was 5.6% while the 105°C specimens was 5.0%.

On firing the light grey material to a pale pink in the range 900-1050° from 1100°C it changed to an off white becoming greyer as the temperature increased to 1350°C where it was grey. The fired specimens produced high water absorptions up to 1250°C and the shrinkage increases markedly after 1150°C, the temperature where the specimen fires hard. Cracking develops in the specimens at 1050°C and efflorescence shows at 1100°C. Cracking and the efflorescence becomes more marked at 1200°C and 1250°C. Bloating has occurred at 1350°C.

The sample does not fire to a dense stoneware body below 1350°C.

Sample 3 (CE 5169)

The sample was extruded at a moisture content of 25.4%. It produced a smooth, soft-shelled column of low to moderate plasticity. The extrusion rate was slow and the column wire cut cleanly.

Drying at 40°C and 105°C was satisfactory and the drying shrinkage was about 6.4%.

On firing the light grey material changed to a pale pink in the range 900-1100°C. The fired specimen at 1150° is a'dirty white' and increasing temperature gradually changes the colour to grey. At 1100°C the fired products are hard with a shrinkage of 9.5% and the water absorption was markedly reduced. Fired specimen at 1350°C sees a lowering of the shrinkage to bloating and a minimal water absorption. Efflorescence occurs over a range of 1000-1200°C. Cracking has occurred over the 1150-1250° but is slight. Flecking by black particles of the 1350°C sample is more clearly seen.

The material does not fire to a dense stoneware body below 1350°C.

Sample 4 (CE 5170)

The sample was extruded at a moisture content of 25.8%. It produced a smooth, soft-shelled column of low plasticity. The extrusion rate was slow and the column wire cut cleanly.

Drying at 40° and 1050°C was satisfactory and the drying shrinkage was about 5.7%.

On firing the brownish grey material changed to light pink gradually over the range 900°-1100°C. Above 1100° the colour changes from greyish pink to a grey finally at 1350°C. The specimens fire hard at 1150°C where there is a marked reduction in the water absorption. At the higher temperatures the fired product is still shrinking, 13.4% at 1350°C. Water absorption at this temperature is minimal, 0.1%,after decreasing consistently from 1050°C. Efflorescence occurred over the range 1000°-1150°C. Vitrification begins at 1350°C. Flecking by black particles of the 1350°C product is very clear.

The material does not fire to a dense stoneware body below 1350°C.

Sample 6 (CE 5172)

The sample was extruded at a moisture content of 21.1%. It produced a smooth, hard shelled column of moderate plasticity. The extrusion rate was slow and the column wire cut cleanly.

Drying at 40° and 105°C was satisfactory and produced a drying shrinkage of about 6.3%.

On firing the light grey material changed to pale pink gradually over the range 900-1050°C. At 1100°C the colour was an orange-pink and at higher temperatures the colour gradually changed to grey from a brownish olive colour. At 1050°C the fired specimens were hard with a shrinkage of 8.1%. Water absorption is very minimal at 1200°C, 0.2%. At 1300°C bloating begins. Efflorescence is present over the range 1000-1050°C. Vitrification begins at 1200°C and the 1350°C sample is cracked. From 1200°C, where the colours become darker, flecking is more noticeable and is produced by black particles.

The material fires to a dense stoneware body at about 1200°C. Above 1250°C bloating commences.

Sample 7 (CE 5173)

The sample was extruded at a moisture content of 27.0%. It produced a smooth,soft shelled column of low to moderate plasticity. The extrusion rate was slow and the column wire cut cleanly.

Drying at 40° and 105°C was satisfactory and the drying shrinkage produced was about 6.6%.

On firing the light grey material changed to an off white colour over the range 900° - 1100°C. From 1150°C and above, the colour of the fired products change gradually from greyish white to a grey at 1350°C. The material fires hard at 1100°C. Bloating begins to occur at 1350°C where the shrinkage is 14.1%. Efflorescence is present over the range 1000° - 1150°C.

The material does not fire to a dense stoneware body below 1300°C.

4. DISCUSSION

A stoneware body is required to be vitrified after firing to about 1200°C. A water absorption of 0.5% or less would be satisfactory. Using this criteria samples 1 (A2696/77) and 6 (A2701/77) are suitable. The other samples contain too little fluxes to produce satisfactory degrees of vitrification below 1350°C (below 1300°C for No. 7 (A2702/77)).

Of the two possible stoneware blends, sample 6 shows advantages in respect of its lesser tendency to crack and its paler colour which would aid its differentiation from earthenware in the green, dry and biscuit states. The flecking is a disadvantage. Plasticity appears adequate but throwing tests have not been done.

dk:4.

TABLE 1 : DRYING AND FIRING PROPERTIES

Sample No. 1 (CE5167)

Temperature °C	% Total Shrinkage	% Absorption	Relative Hardness	Munsell Colour	Comments
40	6.9	-	-	Moderate orange pink 5 YR 8/4	Satisfactory
105	6.4	-	-	Moderate orange pink 5 YR 8/4	Satisfactory
900	7.8	20.4	Moderate	Moderate reddish orange 10 R 6/6	Satisfactory
1000	9.1	18.3	Moderate	Moderate reddish pink 10R 7/5	Slight cracking internally
1050	10.5	14.3	Hard	Moderate reddish pink 10 R 7/5	Slight cracking internally
1100	13.3	6.9	Hard	Moderate light brown 5 YR 7/4	Slight cracking internally
1150	14.5	2.6	Hard	Light brown 5 YR 6/4	Slight cracking internally
1200	14.6	0.6	Hard	Pale brown 5 YR 5/2	Slight cracking internally
1250	14.5	0.3	Hard	Moderate brownish grey 5 YR 5/2	Slight cracking internally
1300	14.4	0.3	Hard	Moderate olive grey 5 Y 5/1	Slight cracking internally
1350	12.2	0.4	Hard	Light olive grey 5 Y 6/1	Cracking internally and externally, bloated, blotchy colour

TABLE 2 : DRYING AND FIRING PROPERTIES

Sample No. 2 (CE 5168)

Temperature °C	% Total Shrinkage	% Absorption	Relative Hardness	Munsell Colour	Comments
40	5.6	-	-	Very pale orange 10 YR 8/2	Slight external cracking
105	5.0	-	-	Very pale orange 10 YR 8/2	Cracking externally
900	6.4	32.3	Moderate	Greyish orange pink 5 YR 7/2	Satisfactory
1000	7.3	30.8	Moderate	Greyish orange pink 5 YR 7/2	Satisfactory
1050	7.2	30.5	Moderate	Greyish orange pink 5 YR 7/2	Slight cracking internally and externally in latitudinal direction
1100	8.3	28.6	Moderate	Pinkish grey 5 YR 8/1	Slight cracking internally and latitudinal cracking externally. Slight efflorescence
1150	10.5	22.1	Hard	White N 9	Cracking externally (latitudinal) and internally, efflorescence
1200	12.8	15.1	Hard	White N 9	Heavier cracking, efflorescence
1250	15.8	8.9	Hard	Yellowish grey 5 Y 8/1	Heavier cracking, efflorescence
1300	21.9	5.2	Hard	Yellowish grey 5 Y 8/1	Internal and external cracks
1350	18.3	0.8	Hard	Light grey N 7	Bloated and vitrified

TABLE 3 : DRYING AND FIRING PROPERTIES

Sample No. 3 (CE5169)

Temperature °C	% Total Shrinkage	% Absorption	Relative Hardness	Munsell Colour	Comments
40	6.6	-	-	White N 9	Satisfactory
105	6.2	-	-	White N 9	Satisfactory
900	7.3	23.2	Moderate	Greyish orange pink 10 R 8/2	Satisfactory
1000	7.6	21.9	Moderate	Greyish orange pink 10 R 8/2	Slight efflorescence
1050	7.9	21.7	Moderate	Greyish orange pink 10 R 8/2	Slight efflorescence
1100	9.5	17.4	Hard	Greyish pink 5 R 8/2	Efflorescence
1150	11.2	12.2	Hard	Pinkish grey 5 YR 8/1	Efflorescence with slight external, internal cracking
1200	12.3	9.1	Hard	Very pale orange 10 YR 8/2	Efflorescence, slight external cracking
1250	12.7	5.7	Hard	Yellowish grey 5 Y 8/1	Slight internal external cracking
1300	13.7	3.1	Hard	Light olive grey 5 Y 6/1	Partly vitrified
1350	13.3	0.1	Hard	Very light grey N 8	Flecked, partly vitrified

TABLE 4 : DRYING AND FIRING PROPERTIES

Sample No. 4 (CE 5170)

Temperature °C	% Total Shrinkage	% Absorption	Relative Hardness	Munsell Colour	Comments
40	5.8	-	-	Pinkish grey 5 YR 8/1	Satisfactory
105	5.5	-	-	Pinkish grey 5 YR 8/1	Satisfactory
900	5.9	-	Moderate	Greyish orange pink 10 R 8/2	Satisfactory
1000	6.6	24.9	Moderate	Greyish orange pink 10 R 8/2	Slight efflorescence
1050	7.0	23.6	Moderate	Greyish orange pink 10 R 8/2	Slight efflorescence
1100	7.9	20.9	Moderate	Greyish orange pink 10 R 8/2	Slight efflorescence
1150	9.6	16.8	Hard	Greyish pink 5 R 8/2	Efflorescence
1200	10.5	12.5	Hard	Very pale orange 10 YR 8/2	Satisfactory
1250	11.9	9.7	Hard	Yellowish grey 5 Y 7/2	Satisfactory
1300	13.1	4.0	Hard	Yellowish olive grey 5 Y 6/2	Satisfactory
1350	13.4	0.1	Hard	Light grey N 7	Flecked partly vitrified

TABLE 5 : DRYING AND FIRING PROPERTIES

Sample No. 5 (CE5171)

Temperature °C	% Total Shrinkage	% Absorption	Relative Hardness	Munsell Colour	Comments
40	6.8	-	-	White N 9	Satisfactory
105	6.4	-	-	White N 9	Satisfactory
900	7.1	29.9	Moderate	Pinkish grey 5 YR 8/1	Satisfactory
1000	7.7	28.5	Moderate	Pinkish grey 5 YR 8/1	Slight external cracking and efflorescence
1050	7.8	28.0	Moderate	Pinkish grey 5 YR 8/1	Slight external cracking and efflorescence
1100	9.8	23.0	Hard	Light pinkish grey 5 YR 9/1	Efflorescence and slight external cracking
1150	12.6	15.9	Hard	White N 9	Efflorescence and slight external cracking
1200	13.8	11.8	Hard	Light yellowish grey 5 Y 9/1	Efflorescence, slight external cracking
1250	14.6	8.4	Hard	Yellowish grey 5 Y 8/1	Slight external cracking
1300	15.6	5.8	Hard	Yellowish grey 5 Y 8/1	Slight external cracking
1350	16.7	0.5	Hard	Very light grey N 8	Partly vitrified

TABLE 6 : DRYING AND FIRING PROPERTIES

Sample No. 6 (CE5172)

Temperature °C	% Total Shrinkage	% Absorption	Relative Hardness	Munsell Colour	Comments
40	6.4	-	-	Yellowish grey 5 Y 8/1	Satisfactory
105	6.1	-	-	Light yellowish grey 5 Y 9/1	Satisfactory
900	5.7	18.7	Moderate	Greyish orange pink 10 R 8/2	Satisfactory
1000	6.3	17.6	Moderate	Greyish orange pink 10 R 8/2	Very slight efflorescence
1050	8.1	13.6	Hard	Light greyish orange pink 10 R 9/2	Slight efflorescence
1100	11.2	6.8	Hard	Very pale orange 10 YR 8/2	Satisfactory
1150	12.5	2.8	Hard	Light yellowish grey 5 Y 8/2	Satisfactory
1200	13.2	0.2	Hard	Yellowish grey 5 Y 7/2	Satisfactory
1250	13.3	0.2	Hard	Yellowish grey 5 Y 7/2	Partly vitrified
1300	12.3	0.3	Hard	Pale yellowish olive 10 Y 7/2	Partly vitrified, bloating
1350	11.3	0.5	Hard	Very light grey N 8	Bloating, cracked externally vitrified

TABLE 7 : DRYING AND FIRING PROPERTIES

Sample No. 7 (CE 5173)

Temperature °C	% Total Shrinkage	% Absorption	Relative Hardness	Munsell Colour	Comments
40	6.7	-	-	Very light grey N 8	Satisfactory
105	6.5	-	-	Very light grey N 8	Satisfactory
900	7.0	23.1	Moderate	Pinkish grey 5 YR 8/1	Satisfactory
1000	7.8	22.8	Moderate	Pinkish grey 5 YR 8/1	Satisfactory, slight efflorescence
1050	7.8	21.4	Moderate	Light pinkish grey 5 YR 10/1	Efflorescence
1100	10.9	14.0	Hard	Very pale orange 10 YR 9/2	Efflorescence
1150	12.7	9.6	Hard	Very pale orange 10 YR 8/2	Efflorescence
1200	13.6	6.7	Hard	Yellowish grey 5 Y 8/1	Satisfactory
1250	13.9	3.7	Hard	Yellowish olive grey 5 Y 7/1	Satisfactory
1300	14.3	0.7	Hard	Yellowish olive grey 5 Y 6/2	Satisfactory
1350	14.1	0.1	Hard	Yellowish olive grey 5 Y 6/2	Satisfactory

DM 394/77
Env. 3081

021

amdel
The Australian Mineral Development Laboratories
Flemington Street, Frewville, South Australia 5063
Phone Adelaide 79 1662, telex AA 82520

EXPORT AWARD
Winner of Award for Outstanding Export Achievement, 1975

Pilot Plant: Osman Place, Thebarton, Sth. Aust.
Phone Adelaide 43 8053
Branch Offices: Perth ~~and Sydney~~
Associated with: Professional Consultants Australia Pty. Ltd.

Please address all correspondence to Frewville.
In reply quote: OD 1/31/33/0-3/0/0

7 March 1978

Mr W.A. Sloan
Manager
Sloans Sand Depot Pty Ltd
539 Churchill Road
KILBURN SA 5084

REPORT: OD 2912/78 - PART 1

YOUR REFERENCE:	Letter SR 5/6/66/3, II RLW:JS dated 21 February 1978, application dated 16 February 1978
MATERIAL:	Foundry sand
LOCALITY:	Angle Vale
IDENTIFICATION:	4/5, 5/6, 6/7, 8/9 +100
DATE RECEIVED:	16 February 1978
WORK REQUIRED:	Clay determination, sizing, assays

Investigation and Report by:	I.W. McPheat and S.T. Dilley
Manager, Operations Division:	R.E. Wilmshurst

G. A. Dunlop

for R.E. Wilmshurst,
Acting Managing Director

cc. The Director-General
Department of Mines and
Energy
191 Greenhill Road
PARKSIDE SA 5063

rp

TESTING OF FOUNDRY SAND SAMPLES

1. MATERIALS TESTED

The following samples of foundry sand were received:

Sample	Moisture Content %	Dry Weight kg
4/5	4.0	2.5
5/6	17.3	1.9
6/7	1.0	1.4
8/9	4.2	2.8
+100	19.0	1.5

The samples were oven dried and subsampled for sizing, assay and microscopic examination.

2. SIZINGS AND CLAY DETERMINATIONS

Clay determinations and sieve analyses for determination of fineness were determined on 50 g subsamples using standard AFS procedures. The clay contents and grain fineness numbers are listed below. Sizing data are given in Table 1.

Sample	AFS Clay Content	AFS Grain Fineness No.
4/5	0.4	51
5/6	0.3	54
6/7	0.2	63
8/9	<0.1	89
+100	0.3	114

3. WORK IN PROGRESS

Chemical analysis and microscopic examination to assess grain structure are in progress. It is expected that the results of this work will be reported within two weeks.

TABLE 1: SIZING OF FOUNDRY SANDS

Screen Aperture		Weight Retained, %				
Mesh BSS	µm	4/5	5/6	6/7	8/9	+100
10	1680	2.2	-	-	-	-
18	850	4.8	0.1	0.2	0.1	-
25	600	4.2	0.5	0.6	0.2	-
36	420	6.6	4.1	2.6	0.4	0.1
52	300	19.4	28.1	14.8	2.6	0.1
72	210	34.3	36.7	29.0	9.6	1.6
100	150	21.5	25.4	39.3	36.4	16.5
150	105	5.3	4.7	12.2	39.4	49.8
200	75	0.8	0.1	0.8	9.0	23.0
300	53	0.4	-	0.3	1.8	6.1
-300		0.1	-	-	0.5	2.5
Clay content		0.4	0.3	0.2	<0.1	0.3
		100.0	100.0	100.0	100.0	100.0

DM 394/77
Env. 3081

024

amdel
The Australian Mineral Development Laboratories
Flemington Street, Frewville, South Australia 5063
Phone Adelaide 79 1662, telex AA 82520

Winner of Award for Outstanding Export Achievement, 1975

Pilot Plant: Osman Place, Thebarton, Sth. Aust.
Phone Adelaide 43 8053
Branch Offices: Perth ~~and Sydney~~
Associated with: Professional Consultants Australia Pty. Ltd.

Please address all correspondence to Frewville.
In reply quote: OD 1/31/33/0-3/0/0

8 March 1978

Mr W.A. Sloan
Manager
Sloans Sand Depot Pty Ltd
539 Churchill Road
KILBURN SA 5084

REPORT: OD 2912/78 - PART 2

YOUR REFERENCE: Letter SR 5/6/66/3, II RLW:JS dated 21 February 1978, application dated 16 February 1978

MATERIAL: Foundry sand

LOCALITY: Angle Vale

IDENTIFICATION: 4/5, 5/6, 6/7, 8/9, +100

DATE RECEIVED: 16 February 1978

WORK REQUIRED: Optical examination

Investigation and Report by: Dr Brian Steveson

Manager, Geological Services Division: Dr Keith J. Henley

per R.E. Wilmshurst,
Acting Managing Director

cc. The Director-General
Department of Mines and Energy
191 Greenhill Road
PARKSIDE SA 5063

rp

EXAMINATION OF FOUNDRY SAND SAMPLES

Sample 4/5

The sample is a pale brown quartz sand. The sample also contains, however, a small to moderate proportion (probably less than 10%) of somewhat coarser material up to about 3 mm. Some of these large fragments are dark brown and many appear to be angular.

The bulk of the material consists of slightly iron-stained quartz grains which range from round to angular in shape (using Power's scale). The modal shape is probably subround. Few of the grains appear to be fractured and most have their original detrital outline. The grains range in size from 0.1 to about 0.4 mm and the average size is about 0.25 mm.

Heavy minerals appear to be present in trace amounts only and most are opaques (probably iron or titanium oxide). There are traces of ?rutile and tourmaline also. The sample contains neither carbonates nor, apparently feldspar.

Sample 5/6

This is a reddish-brown sand, slightly more darkly-coloured than 4/5; the sample is apparently well-sorted and there are non of the large fragments described in the sample above.

The quartz grains are generally subround but there is a range from notably well-rounded grains to subangular. The grains are commonly relatively smooth-sided and there are fewer distinctly angular grains than are present in 4/5. The sand is well-sorted and the grains commonly range from 0.15 mm to about 0.6 mm. The average size is about 0.25 mm. The grains show considerable iron staining.

Heavy minerals are present only to a very small extent and probably represent less than 0.1 weight percent of the sample. As far as can be determined from the grain mounts most of the heavy minerals are likely to be opaque iron or titanium oxides. Photomicrographs of grain mounts of this sample are shown in the plate.

Sample 6/7

This is a pale, buff-coloured sand which appears to be well-sorted. The sand contains a few black specks, possibly of carbonaceous material.

The quartz grains are generally subangular to round in shape and most are subrounded, and in general, the grains have smoother outlines than those in the two samples described above. There are a few grains as much as 0.5 mm in diameter but most of the grains range from 0.1 to 0.2 mm and therefore the sample shows excellent sorting. Iron-staining of grain surfaces is commonly observed but is probably not as intense as in sample 5/6.

Heavy minerals are a little more abundant than in other samples and most are opaque in transmitted light. It is likely that the heavy minerals comprise of the order of about 1% of the sample. Rare grains of tourmaline and rutile were identified. As far as can be determined in the grain mount the sample contains neither feldspar nor carbonate minerals.

Sample 8/9

This sample is similar in macroscopic appearance to sample 6/7 in terms of colour and the presence of small black specks. In addition, however, this sample contains rare large fragments exceptionally up to about 1 cm in size.

The bulk of the sample consists of quartz grains, characteristically subangular to subround in shape and notably a little more angular than those in 6/7. The sample shows excellent sorting and the grains have an average size of approximately 0.15 to 0.2 mm. The quartz grains show a similar amount of staining to those in sample 6/7.

Heavy minerals are present in trace amounts only and there are only one or two grains of opaque material in the temporary grain mount. Also present are a few patches of clay material and these form pale brown aggregates, similar in size to most of the quartz grains. As far as can be determined, clay probably does not contribute more than 1% to the total volume of the sample.

Carbonate minerals were not identified in the sample.

Sample +100

This is a fine-grained sand with a buff colour similar to that of 8/9.

The sample consists of well-sorted quartz grains which have an average size of approximately 0.1 mm. The quartz grains range considerably in their degree of roundness but most tend to be subround to subangular in shape. The grains appear to be a little freer of iron-staining.

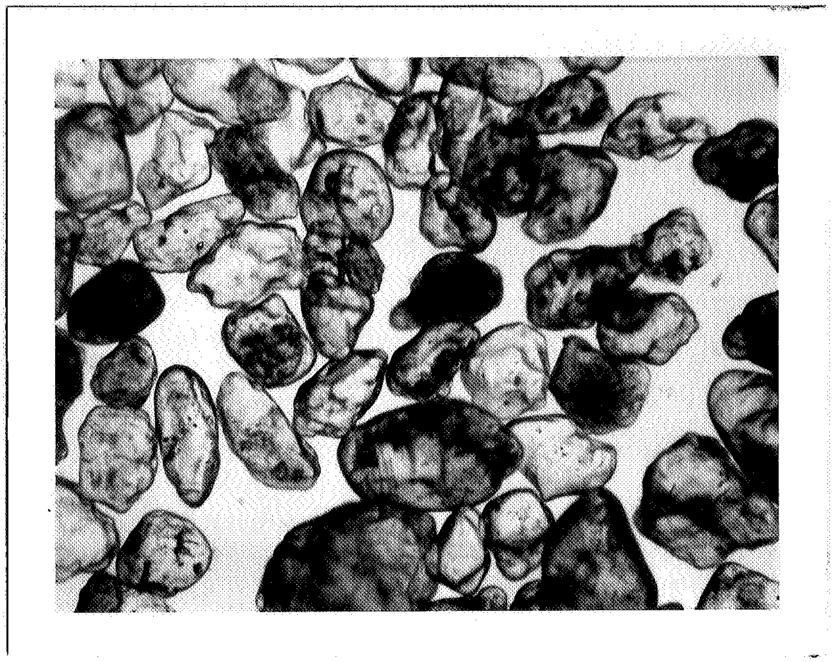
This sand contains a greater abundance of detrital heavy minerals than do the others in this group and grains of rutile, opaques and tourmaline were identified. Most of the heavy minerals are similar in size to the quartz grains and they are generally angular. Some of the tourmaline grains show subhedral outlines.

The sample does not contain any carbonate minerals.

PLATE (Sample 5/6)

Both photomicrographs were taken in plane polarised light; the width of the field is 1.25 mm. The upper field (a) shows a rounded grain which is relatively large among sub-rounded, smaller grains. The lower field (b) is more typical and contains numerous sub-round grains which have clearly been well-sorted. The extent of iron-staining can clearly be assessed from the photographs.

a.



b.

DM 394/77
Env 3081. 7

amdel
The Australian Mineral Development Laboratories
Flemington Street, Frewville, South Australia 5063
Phone Adelaide 79 1662, telex AA 82520

EXPORT AWARD
Winner of Award for Outstanding Export Achievement, 1975

Pilot Plant: Osman Place, Thebarton, Sth. Aust.
Phone Adelaide 43 8053
Branch Offices: Perth ~~and Sydney~~
Associated with: Professional Consultants Australia Pty. Ltd.

Please address all correspondence to Frewville.
In reply quote: OD1/31/33/0-3/0/0

19 June 1978

Mr W.A. Sloan,
Manager,
Sloans Sand Depot Pty. Ltd.,
539 Churchill Road,
KILBURN. SA 5084

REPORT: OD2912/78 - PART 3 (FINAL)

YOUR REFERENCE:	Letter SR 5/6/66/3, II RLW:IS dated 21 February 1978, application dated 16 February 1978.
MATERIAL:	Foundry sand
LOCALITY:	Angle Vale
IDENTIFICATION:	4/5, 5/6, 6/7, 8/9, +100
DATE RECEIVED:	16 February 1978
WORK REQUIRED:	Silicate analyses

Investigation and Report by:	I.W. McPheat
Manager, Operations Division:	R.E. Wilmshurst

IW McPheat
for R.E. Wilmshurst
Acting Managing Director

cc The Director-General,
Department of Mines and Energy,
191 Greenhill Road,
PARKSIDE. SA 5063

cah

EXAMINATION OF FOUNDRY SAND SAMPLES

We attach our analytical report for silicate analyses for the five samples of foundry sand. A copy of this report was sent to Mr Bromley on 23 May 1978.

AMDEL ANALYTICAL SERVICE (NATA CERTIFICATE)

SILICATE ANALYSES : CODE H3

JOB NUMBER AN 2997/78

ANALYSIS PERCENT

4/5		5/6		6/7		8/9	
SI02	98.20	SI02	98.19	SI02	98.29	SI02	97.78
TI02	.21	TI02	.07	TI02	.11	TI02	.17
AL203	.47	AL203	.47	AL203	.50	AL203	.67
FE203	.26	FE203	.16	FE203	.17	FE203	.18
MNO	<.01	MNO	<.01	MNO	<.01	MNO	<.01
MGO	.03	MGO	.05	MGO	.03	MGO	.05
CAO	.03	CAO	.06	CAO	.04	CAO	.05
NA20	.09	NA20	.08	NA20	.10	NA20	.16
K20	.04	K20	.06	K20	.11	K20	.14
P205	.01	P205	.01	P205	.01	P205	.01
LOI	.34	LOI	.41	LOI	.33	LOI	.26
TOTAL	99.68	TOTAL	99.55	TOTAL	99.69	TOTAL	99.47
H20+		H20+		H20+		H20+	
H20-		H20-		H20-		H20-	
C02		C02		C02		C02	
S03		S03		S03		S03	

AMDEL ANALYTICAL SERVICE (NATA CERTIFICATE)

SILICATE ANALYSES : CODE H3

JOB NUMBER AN 2997/78

ANALYSIS PERCENT

	+100
SiO_2	96.84
TiO_2	.25
Al_2O_3	1.15
Fe_2O_3	.25
MNO	<.01
MGO	.07
CAO	.10
Na_2O	.26
K_2O	.29
P_2O_5	<.01
LOI	.35
TOTAL	99.56
H_2O+	
H_2O-	
CO_2	
SO_3	

030

amdel
The Australian Mineral Development Laboratories
Flemington Street, Frewville, South Australia 5063
Phone Adelaide 79 1662, telex AA 82520

Winner of Award for Outstanding Export Achievement, 1975

Pilot Plant: Osman Place, Thebarton, Sth. Aust.
Phone Adelaide 43 8053
Branch Offices: Perth ~~and Sydney~~
Associated with: Professional Consultants Australia Pty. Ltd.
Please address all correspondence to Frewville.
In reply quote: OD 1/1/227

11 October 1978

Director-General
Department of Mines and Energy
PO Box 151
EASTWOOD SA 5063

Attention: Mr R.L. Wildy

COMMENTS ON THE USE OF A TOP BLOWN ROTARY CONVERTER IN SOUTH AUSTRALIA

Investigation and Report by: J.R. Tuffley

Manager, Operations Division: R.E. Wilmshurst

J W McPheat
for Norton Jackson,
Managing Director

rp

1. INTRODUCTION

Since 1970, Amdel has examined various possibilities for treating all copper sulphide concentrates from South Australian mines at some central facility. These have included a feasibility study of establishing a central copper smelter (Report No. 695, 1970); determination of the most suitable hydrometallurgical process (Report No. 1008, 1974); and testing of concentrates from Kanmantoo and Mount Gunson by this process (Report No. 1099, 1976).

In this context, Amdel has been requested to comment on the use of a top blown rotary converter (TBRC), developed by the Dravo Corporation, Pittsburgh, for use in a central copper smelter in South Australia. To this end the SADME supplied Amdel with the following literature:

1. DANIELE, R.A., and JAQUAY, L.H. (1972). TBRC - A new smelting technique. AIME Annual Meeting, San Francisco.

2. DANIELE, R.A., and JAQUAY, L.H. (1974). Full scale TBRC smelting tests on copper concentrate. AIME Annual Meeting, Dallas.

3. Dravo Corporation publicity pamphlet - TBRC smelter process for copper.

2. TECHNICAL CONSIDERATIONS

The TBRC (or Kaldo furnace) has been used successfully in the steel and nickel smelting industries. From the South Australian viewpoint, it is important to establish the extent to which this unit has been used successfully in copper smelting operations similar to the one that may be envisaged for this State.

Daniele and Jaquay (1972) discussed the following process applications for the TBRC in copper smelting:

1. Smelting and refining of cement copper.
   No sulphides are present during this operation.

2. Smelting and refining of white metal (Cu_2S).
   In this process, high grade scrap copper or recycling granulated copper may be added to control the rise in temperature.

3. Smelting of matte.
   The use of two units is favoured, one for slag and white metal formation and the other for white metal conversion as described in "2" above.

4. Smelting of concentrates.
   Normally two units are required as described in "3".

In 1976, Morris and Wallden* reviewed the progress of the TBRC to that date. The actual paper is not available in Adelaide, but the Mining Annual Review, 1977, published a summary which is reproduced in full below:

> *In the paper the development of the Kaldo furnace in the steel industry is traced and its application as a top blown rotary converter in the non-ferrous industry is described. Its use by INCO for the production of nickel from sulphide concentrates is well known but in the copper industry the first commercial scale application occurred in the secondary processing plant of La Metallo-Chimique in Belgium. At this plant successful techniques have been developed for all the operations of smelting, copper upgrading and slag treatment. These methods are covered by patents, (including US patent No. 3,682,623) and the aspect of interest and importance to the industry is the marked degree of flexibility possible with such a furnace. As described later, Boliden have also highlighted its flexibility by adapting its use to the processing of copper rich oxidised converter slags and also to the treatment of pelletised lead-rich by-products.*
>
> *Within the primary copper industry 2-25 ton Kaldo furnaces were installed at the Tennant Creek smelter for converting copper matte, containing 0.2% bismuth. As bismuth is a most undesirable impurity in copper and cannot be readily removed by conventional converting, tests were conducted initially using a small scale TBRC with good results. Amongst the problems encountered was the accurate determination of the weight of charge, which made flux requirements difficult to assess. Clean separation of slag and matte was also difficult and any residual slag present made blowing to copper inefficient. Excessive mouth build up was reduced by the installation of impact hammer devices but this entailed downtime and increased labour usage. The furnace mechanism, etc., had to withstand a rotation rate of 40 rpm at high temperature.*
>
> *The paper concludes that technically bismuth can be eliminated from high grade matte to less than 0.04%, but only at the cost of extended blowing times and high fuel and refractory usage. For successful operation a means of clean slag/matte separation is essential, as is increased oxygen efficiency during the copper blow. The authors quote as favourable factors low gas volumes, compact equipment and high energy efficiency. There still remain some problems but the use of the TBRC for qualified processes is considered probable. However, it was concluded that it may be a long time before the problems encountered have been overcome and the process can be used for primary treatment of copper concentrate on a large scale. It is therefore interesting, in this respect, to read that Afton Mines Ltd are installing at their operations in Western Canada a TBRC to treat the high grade concentrates that will be produced there.*

This paper shows that the process has been used successfully for copper upgrading and slag treatment, but indicates that there are significant problems in its use for full scale primary treatment of copper sulphide concentrates. At first sight, the installation of the TBRC by Afton Mines Ltd at Kamloops, British Columbia, appears to refute this. However, the Dravo Corporation pamphlet states that the Afton orebody is principally native copper, with some bornite, chalcocite

---

*MORRIS, C.W., and WALLDEN, S.J. (1976). The development of the Kaldo furnace smelting technique and its application to TBRC copper smelting and refining. Extractive Metallurgy of Copper, AIME Symposium, pp 427-438.

and chalcopyrite in the deeper deposits. Hence, the TBRC is being used for what is essentially a metal melting and refining operation.

As a result, it appears that the TBRC is not as yet a proven unit for handling the type of copper smelting operation required in South Australia. However, the development of this and other types of copper smelting units should be followed in the technical literature.

3. ECONOMIC CONSIDERATIONS

While a complete feasibility study is beyond the scope of this report, some inferences can be drawn from other feasibility studies, taking into account the level of production that can be expected in South Australia.

3.1 South Australian Production Capacity

From information supplied by the Department of Mines and Energy, and from information contained in Amdel Report No. 1099, it appears that the State's production capacity of copper sulphide concentrates is as follows:

Kanmantoo:	45,000 tonnes/a concentrates containing 23% Cu, 1.8 g/tonne Au and 50 g/tonne Ag
Mount Gunson:	30,000 tonnes/a concentrates containing 45% Cu, 1.8% Pb, and 9% Zn

In addition, if the copper smelter at Port Kembla were to close, an additional 100,000 tonnes/a concentrates containing 25% Cu may become available. Total capacity is, therefore, 70 tonnes Cu/day from South Australia, with a possible total of 150 tonnes Cu/day if the smelter at Port Kembla closes. (These figures take no account of the possibility of copper production at Roxby Downs as this would be a major copper smelting venture in its own right).

3.2 Other Feasibility Studies

In Amdel Report No. 695, it was shown using 1970 costs that a conventional smelter would be uneconomic if it smelted less than 100 tonnes Cu/day assuming a copper price of $1200/tonne. This figure approximates the current copper price, but wages and all other costs have more than doubled since 1970, or even trebled in many instances. On this basis, the minimum economic size of a conventional smelter may well be in the range of 250 to 300 tonnes Cu/day.

Figures derived by the Dravo Corporation indicate that the operating costs for TBRC process would be about 65% of those for the conventional smelting process, but even that may not be sufficient to reduce the minimum economic size of smelter to within the scope of South Australia production.

In addition, these operating costs were derived for a smelter capacity of 1000 short tons Cu/day. For the size of smelter required in South Australia, operating costs would rise for both types of smelter as the economy of scale is lost. In the TBRC process the rise in the cost of oxygen production, which is used in this process only, would probably cause the operating costs for this process to rise proportionally to a greater extent than the costs for the conventional process. Hence some of the cost advantage would be lost.

4. CONCLUSIONS

The following conclusions have been drawn from this brief survey:

1. The use of the TBRC for primary smelting of copper sulphide concentrates has yet to be proven on a commercial scale.
2. The minimum economic size for a greenfield copper smelter is likely to be in excess of the size required in South Australia.

amdel
The Australian Mineral Development Laboratories
Flemington Street, Frewville, South Australia 5063
Phone Adelaide 79 1662, telex AA 82520

036

EXPORT AWARD
Winner of Award for Outstanding Export Achievement, 1975
Pilot Plant: Osman Place, Thebarton, Sth. Aust.
Phone Adelaide 43 8053
Branch Offices: Perth ~~and Sydney~~
Associated with: Professional Consultants Australia Pty. Ltd.
Please address all correspondence to Frewville.
In reply quote:

OD1/31/31/0

19 October 1978

The Director-General,
Department of Mines and Energy
191 Greenhill Road,
PARKSIDE. S.A. 5063

Attention: Mr. R.L. Wildy

REPORT: OD2267/77

YOUR REFERENCE:	DM507/76
MATERIAL:	Baryte
LOCALITY:	Mt. Frome S.A.
DATE RECEIVED:	17 January 1977
WORK REQUIRED:	Preliminary Separation study

Investigation and Report by:	K.Y. Wong
Manager, Operations Division:	R.E. Wilmshurst

R Wilmshurst

for Norton Jackson,
Managing Director

sjs

1. INTRODUCTION

Jarvis Industries Pty. Ltd. of South Australia was concerned with the difficulty of separating silica from the Mt. Frome baryte in order to meet the marketing specifications. Amdel was commissioned by the South Australian Department of Mines and Energy to conduct a preliminary investigation into this beneficiation problem. The proposed test programme and cost estimate were outlined in a letter from Amdel to SADM dated 23 December 1976 and these were approved by SADM dated 13 January 1977.

2. ON-SITE PLANT STUDY

A visit to Jarvis Industries at Beverley S.A. was made on 14 January 1977 for inspection of the processing plant. The Mt. Frome baryte was not treated during that day and consequently the plant performance and the associated operating problems could not be observed in detail. However, it was possible to see the same processing equipment in operation and to see the general layout of the plant. The dry grinding/separation section of the plant consisted of a pendulum type roller mill incorporated a double cone whizzer classifier with a silica grit trap. The roller mill was claimed to crush feed materials from minus 12.7 mm to minus 0.045 mm. Product materials ranging from 0.50 mm to 100% passing 0.045 mm could be obtained from the cone separator. Because of the high silica content of the Mt. Frome baryte and in order to achieve mineral liberation by finer grinding, the normal rate of through-put of the Jarvis Plant could not be maintained without over loading the system. The silica trap normally worked quite efficiently and effectively for processing other industrial minerals. However, in the case of processing Mt. Frome baryte, this trap was over loaded and thus decreased in separation efficiency.

In view of the treatment problems associated with the Mt. Frome baryte, it was agreed that another visit to Jarvis Plant would be made to observe milling performance of the next batch of material. However, it was understood that Jarvis Industries has discontinued processing the Mt. Frome baryte since the date of the first plant visit.

3. LABORATORY STUDY

A preliminary laboratory beneficiation study was conducted on a Mt. Frome baryte sample which was secured from Jarvis Industries after the plant visit. A summary of the test work and results are presented in this report.

3.1 Sample Received for Investigation and Preparation

A 455kg sample of Mt. Frome baryte was received from Jarvis Industries for investigation. The submitted sample was all minus 101.5 mm material and the whole of sample was stage jaw-crushed to minus 6.35 mm.

3.2 Screening Test and Specific Gravity Determination

One quarter of the minus 6.35 mm crushed material was riffled out for screening test. A sub-sample of each of the screened fraction was prepared for specific gravity determination using a air comparison pycometer. The results obtained are tabulated as follows:

Size Fraction mm		Weight %	S.G.
-6.35	+3.17	25.2	3.71
-3.17	+1.00	28.2	3.88
-1.00	+0.71	6.7	3.84
-0.71	+0.50	5.2	3.90
-0.50	+0.355	4.8	3.89
-0.355	+0.25	3.8	3.88
-0.25	+0.18	3.8	3.77
-0.18	+0.125	3.4	3.79
-0.125	+0.090	3.3	3.82
-0.090	+0.063	3.0	4.05
-0.063	+0.045	7.3	4.08
-0.045		5.3	4.15
		100.0	

3.3 Head Assay and Specific Gravity Determination

A representative head sample of the minus 6.35 mm crushed material was riffled out and prepared for head assay. In addition, a sub-sample of the minus 0.045 mm fraction of the screened product obtained in Section 3.2 above was prepared for head assay. Specific gravity was determined similarly on these two head samples. The results obtained are as follows:

Sample		Assay			S.G.
		$BaSO_4$, %	$SrSO_4$, %	SiO_2,%	
Head	(-6.35 mm)	75.6	1.31	21.2	3.86
Fraction	(-0.045mm)	87.9	1.49	9.8	4.15

3.4 Air Separation Test

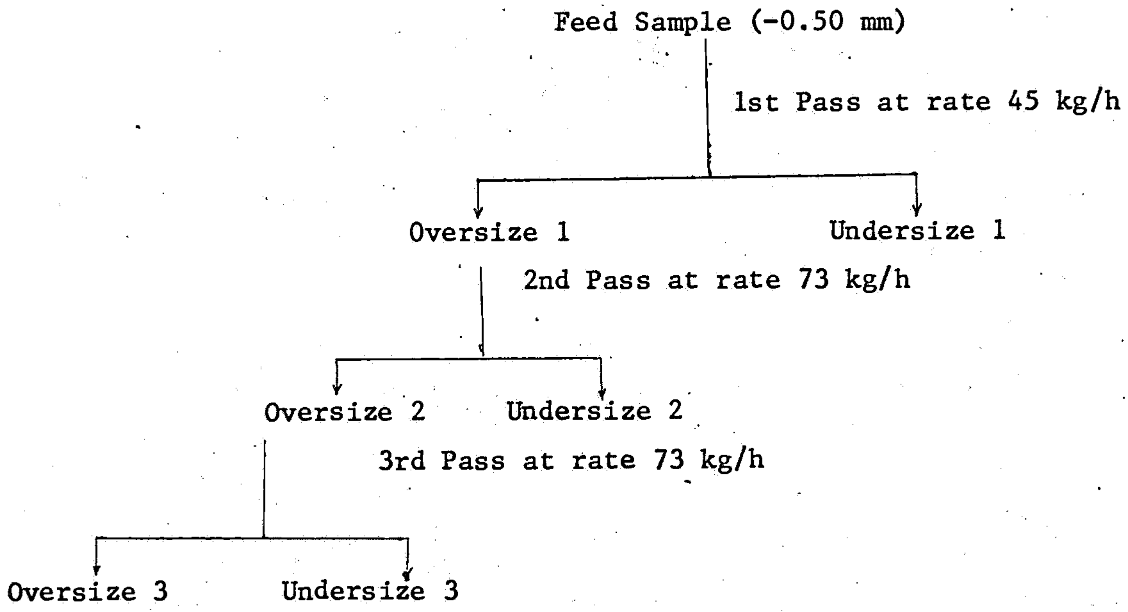
Initially, a scouting test was carried out on the Mt. Frome baryte using the Raymond air separator. The Raymond test result was poor and further tests were conducted using the Gayco air separator which gave some encouraging results.

Raymond Air Separator Test - A 30 inch Raymond double cone air separator was used for investigation. The combined fractions of the minus 0.50 mm materials obtained in Section 3.2 above was used as feed sample. A feed rate of 50 kg per hour was used and the results obtained are as follows:

Product	Wt. %	S.G.
Undersize +0.045 mm	24.1	3.80
-0.045 mm	46.9	4.11
Oversize	29.0	3.83
	100.0	

Gayco Air Separation Test - A 18 inch Gayco centrifugal air separator, Model 44, with adjustable internal air velocity by way of an annular shutter was used for investigation. The feed sample was prepared by stage cone-crushing the minus 6.35 mm material to minus 0.50 mm. A feed rate of 45 kg per hour was used for the first pass using maximum internal air current. The flowsheet used and results obtained are as follows:

Flowsheet



Feed and Product Size Analysis

Size Faction mm	Feed Sample	Cumulative Weight % Passing					
		1st Pass		2nd Pass		3rd Pass	
		O/S1	U/S1	O/S2	U/S2	O/S3	U/S3
0.355	84.5	80.7		80.9		83.2	
0.250	72.0	64 5		63.7		66.7	
0.180	60.6	49.7		48.4		50.6	
0.125	51.3	37.6		35.8		37.3	
0.090	43.4	27.8		25.5		25.9	
0.063	38.1	20.4		18.4		18.1	
0.045	33.5	15.2	100	12.5	96.5	11.4	93.1

Metallurgical Balance

Stage	Test Product	Weight %	Assay % $BaSO_4$	Assay % SiO_2	Recovery % $BaSO_4$	Recovery % SiO_2	Sp. Gr.
1st Pass	Undersize 1	23.15	86.2	8.65	26.45	9.28	4.15
	Oversize 1 (+0.25 mm)	27.28	68.0	31.7	24.59	40.09	
	(+0.090mm)	28.20	70.0	27.5	26.16	35.95	
	(+0.045mm)	9.70	74.8	21.8	9.62	9.81	
	(-0.045mm)	11.67	85.2	9.00	13.18	4.87	
	(Oversize 1)	(76.85)	(72.2)	(25.5)	(73.55)	(90.72)	3.82
	Calc. Head	100.00	75.4	21.6	100.00	100.00	
2nd Pass	Undersize 2	5.46	85.4	9.0	6.36	1.95	4.13
	Oversize 2	94.54	72.6	26.1	93.64	98.05	3.80
	Calc. Oversize 1 Head	100.00	73.3	25.2	100.00	100.00	
3rd Pass	Undersize 3	3.07	83.4	11.2	3.50	1.33	4.10
	Oversize 3	96.93	72.9	26.3	96.50	98.67	3.81
	Calc. Oversize 2 Head	100.00	73.2	25.8	100.00	100.00	
1st + 2nd + 3rd Pass	Undersize 1	23.15	86.2	8.65	26.00	9.47	4.15
	Undersize 2	4.20	85.4	9.0	4.67	1.79	4.13
	Undersize 3	2.23	83.4	11.2	2.42	1.18	4.10
	(Undersize 1+2+3)	(29.58)	(85.9)	(8.98)	(33.09)	(12.44)	(4.14)
	Oversize 3	70.42	72.9	26.3	66.91	87.56	3.81
	Calc. Head	100.00	76.7	21.2	100.00	100.00	

4. DISCUSSION

The Mt. Frome baryte submitted for investigation was low in $BaSO_4$ (75.6%) and high in SiO_2 (21.2%) with a Sp. Gr. of 3.86. There was considerable variation in mineral distribution obtained in particle size reduction by simple crushing/grinding. The minus 0.045 mm fraction of the head material contained 87.9% $Ba\ SO_4$ and 9.8% $Si\ O_2$ with a Sp. Gr. of 4.15 and this was the highest grade material. However, this material would still fall short of the marketing specifications which require baryte of 92% $BaSO_4$ and Sp. Gr. 4.2 for oil drilling purposes. It appeared that the present material could be upgraded by further size reduction but the processing would most likely increase the practical problems in crushing/grinding and separation.

The Gayco air separation test was successful in producing a material close to 100% minus 0.045 mm which was assayed as 85.9% $BaSO_4$ and 8.89% SiO_2 with a Sp. Gr. of 4.14. Recovery of baryte in the three-pass test was only about 33% with a rejection of 88% silica. A cleaning treatment by repassing the undersize products could improve the grade of baryte with further rejection of silica. Based on these results, a continuous plant operation would most likely generate a very high circulating load with a low recovery of final product. Separation efficiency could be maintained by reduction of feed rate.

It is considered that the information obtained in this preliminary investigation could be utilized in the plant operation to establish a set of processing guidelines for Mt. Frome baryte At the same time, attempts should be made in the plant operations to obtain a finer size reduction/separation in the hope of improving the quality of the final baryte product.

The Australian Mineral Development Laboratories

amdel

mington Street, Frewville,
South Australia 5063
Phone Adelaide 79 1662
Telex AA 82520

Please address all
correspondence to
P.O. Box 114 Eastwood
SA 5063
In reply quote:

044

29 April 1981

OD 1/1/249

The Director-General
South Australian Department
of Mines and Energy
191 Greenhill Road
PARKSIDE SA 5063

Attention: Mr R.L. Wildy

WARRAKIMBO MICACEOUS IRON OXIDE

Progress Report No. 2

Investigation and Report by: J.K.W. Ellis

Manager, Operations Division: Bruce E. Ashton

for Norton Jackson,
Managing Director

sh

ilot Plant: Osman Place
Thebarton S.A.,
Telephone 43 8053
Branch Laboratories:
Perth W.A.
Telephone 325 7311
Melbourne Vic.
Telephone 645 3093

1. INTRODUCTION

Warrakimbo Mine is located west of Hawker, South Australia in the Flinders Ranges. On behalf of S.A. Ore Treatment, the South Australian Department of Mines and Energy requested AMDEL to conduct preliminary beneficiation testwork on samples of micaceous iron oxide from Warrakimbo.

Stage I of the testwork comprised a qualitative spectrographic analysis, a quantitative head analysis, and a mineralogical examination, and was reported in Progress Report No. 1, September 1980. It was recommended that further testwork should be carried out to evaluate magnetic separation and flotation of the sample.

2. REVIEW OF PROGRESS

The examinations conducted in Stage 1 of the survey showed that the sample consisted mainly of micaceous hematite with minor amounts of non-opaque gangue, goethite, and sulphide minerals including pyrite and various copper bearing sulphides. Hematite was well liberated in all size ranges, with pyrite well liberated in finer size ranges. Chalcopyrite was observed as liberated grains locked with non-opaque gangue and goethite.

Stage 2 of the testwork covered magnetic separation and flotation at grind sizes of -75 µm, and -212 µm.

Hematite is weakly magnetic and it was found possible to effect separation at high field intensity using a Jones Magnetic Separator. The magnetic portion of the material was preliminarily black in colour (hematite) while the non-magnetic portion was red-brown.

Flotation tests were carried out using conditions appropriate for flotation of chalcopyrite and pyrite. Flotation results were encouraging, with fair recoveries of copper (50-60%) and good recoveries of sulphur (in excess of 90% of sulphur in feed to flotation). Much better flotation results were achieved with feed at 100% -75 microns (200 mesh BSS) than at 100% -212 microns (72 mesh BSS).

During initial flotation tests it was felt that iron oxide slimes might be affecting flotation performance. Preliminary desliming (using a small laboratory cyclone to remove particles of less than c. 10 microns) was found to improve flotation at 212 microns, but not at 75 microns. In each case however, copper recovery to copper concentrate was reduced, due to the removal of 14-15% of the copper in feed, along with the slimes.

Tests in which magnetic separation preceded flotation showed that to some extent, copper recovery was reduced by the removal from the main (magnetic) product, of some 20-30% of the total copper, prior to flotation.

It was concluded that to most effectively process ore at 100% -75 microns, the order of treatment should be flotation - magnetic separation - desliming.

In all tests, the final magnetic product was a high grade micaceous hematite with a low copper and sulphur content.

3. WORK IN HAND

Stage II of the test programme to evaluate the beneficiation of Warrakimbo ore has now been completed.

Further work on this material would be directed towards the establishment of an economic and efficient full scale operation, and would of necessity require:

(a) Tabulation of relevant physical and chemical characteristics of Warrakimbo Micaceous Hematite. and

(b) Market information in order to establish the product specification required and the basic economics of the project.

Metallurgical work should include:

(1) Optimisation of sulphide flotation conditions to maximise extraction of copper and sulphur from the hematite.

(2) As a lesser priority - the evaluation of concentrate cleaning.

(3) Selection of suitable equipment for full scale continuous operation, ideally based on -

(4) Translation of laboratory results to pilot scale continuous operation.

(5) Investigation of potential for up-grading the non-magnetic product (red oxide and gangue).

4. PROCEDURE

4.1 Preparation of Sample for Testwork

A 24 kg sample of micaceous iron oxide ore as received at 100% -6 mm was riffle split to two 12 kg portions of which one was crushed in a rolls crusher to 100% -10 mesh. The crushed product was split to twelve 1 kg portions of which six were riffle split to twelve 500 kg portions.

One portion was stage ground in a 190 mm dia. laboratory rod mill to establish minimum grinding times required to achieve the product sizes required for testwork.

These were:

Material Size	Grinding Time
100% - 212 microns (72 mesh BSS)	1.5 minutes
100% - 75 microns (200 mesh BSS)	5.5 minutes

Three portions of material were ground at each of the above grinding times for flotation and magnetic separation testwork.

4.2 Test Programme

The test programme was arranged to evaluate the potential for beneficiation of the ore by flotation and magnetic separation in order to produce an upgraded specular hematite low in copper, sulphides, and red iron oxides.

The following tests were carried out on ore samples in the two size ranges referred to above.

1. Stage 1 Flotation
   Stage 2 Magnetic separation of flotation tailings
2. Stage 1 Magnetic separation
   Stage 2 Flotation of (major) magnetic fraction
3. Stage 1 Desliming
   Stage 2 Flotation of deslimed feed
   Stage 3 Magnetic separation of flotation tailing

4.3 Test Conditions

4.3.1 Flotation

Flotation tests were carried out using a Denver Laboratory Flotation Machine equipped with a 1 litre glass cell. Conditions were as follows:

pH	8.5
pH Modifier	Na_2CO_3
Impeller speed	1500 r.p.m.
Collector	1% sol. Potassium Amyl Xanthate (PAX)
Frother	Methyl Isobutyl Carbinol (MIBC)

Rougher One Flotation

Slurry in cell, ph to 8.5/Na_2CO_3 soln.

Collector 1 ml PAX, condition for 3 minutes

Frother 2 drops MIBC, float for 5 minutes.

Rougher Two Flotation

pH to 8.5/Na_2CO_3

Collector 1 ml PAX, condition for 2 minutes

Frother 1 drop MIBC, float for 3 minutes

Reagent Usage

Na_2CO_3	∿	1.5 kg/tonne
PAX	∿	0.04 kg/tonne
MIBC	∿	0.01 kg/tonne

4.3.2 Magnetic Separation

Magnetic separation was carried out using a Jones Wet Magnetic Mineral Separator (Laboratory/Pilot Plant Model). This machine has a nominal capacity of 100 kg/hour.

Operating data were:

Pole gap	0.03 inches (0.76 mm)
Water pressure	30 psi
Current	25 amps (maximum setting)
Feed slurry	15% solids in water

Hematite is weakly or feebly magnetic and a high intensity machine such as the Jones Magnetic Separator is required. Little or no separation occurred in experimental tests on Warrakimbo Ore, using a laboratory Davis tube separator.

Each sample was passed through the machine three times at which point the operators were satisfied that no further magnetic material could be extracted from the feed/non-magnetic product.

5. RESULTS AND DISCUSSION

Detailed results of the testwork are shown in:

Table 1: Testwork on -75 micron ore

Table 2: Testwork on -212 micron ore

A comparison of the results obtained from Tests 1, 2 and 3, on the two ore sizes, is shown in Table 3.

5.1 Discussion of Results

The Warrakimbo ore is a relatively high grade hematite ore and all of the test routes followed were successful in producing a specular hematite at 90% Fe_2O_3 grade, or better.

In general, treatment of ore at 100% -75 μm yielded a higher grade product, with lower copper and sulphur content, than at 100% -212 μm.

Recovery of copper to copper concentrates was in each case higher at 75 μm than at 212 μm, although the grade of concentrate produced was in each case lower.

It should be noted that the cleaning of concentrates was not included in this test programme, and would require rougher flotation of a larger amount of feed to prepare sufficient concentrates for cleaning testwork. However, it would be expected that a copper-sulphide concentrate of this type, would be amenable to upgrading by cleaning. This may not be considered a priority issue as the revenue to be expected from copper would only amount to about 2% of the revenue to be expected from the main product, hematite.

5.2 Flotation - Desliming

The sulphide flotation technique employed was successful in floating pyrite and copper bearing sulphides as evidenced by sulphur recoveries, up to 92% in some cases.

During testwork it was felt that the presence of iron oxide slimes may have had deleterious affects on sulphide flotation. A comparison of results of Tests 1 and 3, for both ore sizes shows the effect of desliming (using a small desliming cyclone before flotation.

In each case the slimes contained 14% of the total copper in feed. Recovery of copper to concentrates was slightly worse at -75 μm, and rather better at -212 μm, after desliming. Recovery of sulphur to copper concentrates was virtually unchanged at -75 μm, and much better (83.9% vs 54.1%) at -212 μm.

Hence the effect of desliming feed was beneficial in the -212 μm case, but of no discernible benefit at -75 μm.

It is noted that Na_2CO_3 used here as a pH modifier is also a dispersant for iron oxides and this factor may have had some effect in minimising interference from iron oxide slimes.

Copper recovery to copper-sulphur concentrate was better in each case:

(a) At 75 μm rather than 212 μm

(b) Where flotation preceded magnetic separation

Copper recovery varied from 30 to 58.2%, and sulphur recovery varied from 51 to 92%.

5.3 Magnetic Separation

The following products were separated using the Jones Magnetic Separator:

(a) Feed ore at -212 µm, -75 µm

(b) Flotation Tailings at -212 µm, -75 µm

(c) Tailings from the flotation of deslimed feed at -212 µm, -75 µm

In each case the obvious visual effect was the separation of red-brown iron oxide from the specular black hematite. When separating deslimed material the arisings of non-magnetic material were reduced, however, there was little or no reduction in arisings of magnetic material.

(a) Separation of Feed Ore

	Weight, %	% T. Fe	Dist^{n}. % Fe
Head (Feed 100% -212 µm)	100.0	58.5	100.0
Magnetics	83.1	63.1	89.7
Non-Magnetics	16.9	35.6	10.3
Head (Feed 100% -75 µm)	100.0	56.8	100.0
Magnetics	76.8	65.1	87.9
Non-Magnetics	23.2	29.7	12.1

(b) Separation of Flotation Tailings

Tails from 212 µm Flotation	100.0	59.0	100.0
Magnetics	82.1	62.9	87.5
Non-Magnetics	17.9	41.0	12.5
Tails from 75 µm Flotation	100.0	58.0	100.0
Magnetics	81.8	65.1	91.8
Non-Magnetics	18.2	26.2	8.2

(c) Separation of Tailings
Flotation of Deslimed Hematite

Tailings from 212 µm Flotation	100.0	58.0	100.0
Magnetics	88.8	63.6	97.4
Non-Magnetics	11.2	13.9	2.6
Tailings from 75 µm Flotation	100.0	58.8	100.0
Magnetics	88.8	64.7	97.7
Non-Magnetics	11.2	12.6	2.3

In all cases, the magnetic product was a high grade hematite containing 62-65% Fe, equivalent to 88-93% Fe_2O_3 (excluding possible FeO content in the final product).

5.4 Gold

Gold was present in the samples used in the testwork, but was apparently not evenly distributed. Gold assays were low and the metallurgical balances for gold were generally unsatisfactory.

Gold head grades were:

	Gold g/tonne
-75 µm Head	0.065
-212 µm Head	0.170

In general, gold recovery to copper concentrates was very poor, (0-5%) except in one case (the flotation of deslimed feed at 100% -212 µm). In this test a calculated gold head grade of 0.270 g/tonne occurred and 79.3% of the gold in the head reported to copper concentrates at an overall grade of 5.7 g/tonne gold.

Otherwise, the small 'background' gold occurrance reported equally to magnetic and non-magnetic products at 212 µm, and predominantly to the non-magnetic product at 75 µm.

6. CONCLUSIONS AND RECOMMENDATIONS

The test programme confirmed that the sample of Warrakimbo Ore submitted for examination can be beneficiated by flotation and magnetic separation. Testwork carried out on material at 100% -75 µm and 100%-212 µm showed that at -75 µm, separation of copper and sulphur from the hematite was better than at -212 µm, recoveries of 58% Cu, and 92% S to copper-sulphide concentrates being achieved by normal sulphide flotation methods.

Magnetic separation was effective in separating a high grade hematite (88-94% Fe_2O_3) from non-magnetic gangue and other iron oxides. In tests where desliming preceded flotation and magnetic separation, a proportion of the non-magnetic material was removed as slimes. A proportion of the copper was however also removed, reducing the potential overall copper recovery to concentrates.

6.1 Product Specification

From the analytical data produced within the scope of this investigation, it appears feasible to produce an upgraded Warrakimbo Ore to meet commercial specifications for micaceous iron oxide.

The data below compares an average of the products from tests on 100% -75 µm material, with 'Miox', an Australian micaceous iron oxide.

Warrakimbo	MiOx	Warrakimbo
% Fe	59.4-65.0	65.4
Equiv. to % Fe_2O_3	85-93	93.6
(not allowing for possible FeO content in Warrakimbo oxide)		
% S	0.12	0.02

Other characteristics of MiOx are reported as follows:

SiO_2	3.5%
Al_2O_3	2.4%
FeO	2.0%
CaO	0.5%
MgO	1.0%
Moisture	0.1%
Soluble Chlorides	-
S.G.	4.8%
Oil Absorption (ASTM)	11.0%
pH	7.7%
Total Surface Area	88 m^2/litre
Loss on ignition at 1000°C	0.64%
Ultra Violet Transmission	Zero
Colour	Steel Gray
Acid/Alkali Resistance	Loss in wt.% at normal temp.
HCL (1:3)	1.44
HNO_3 (1:3)	1.35
H_2SO_4 (1:3)	2.48
KOH (10%)	0.31
Na_2CO_3 (10%)	0.44

The hematite produced from Warrakimbo ore (-75 μml had a copper content of 0.16 -0.22% Cu which may affect it's suitability for use in welding rods or protective covering.

6.2 Process Flowsheet

The form of the final process flowsheet will to some extent depend on the desired product specification.

The factors which will need to be determined are:

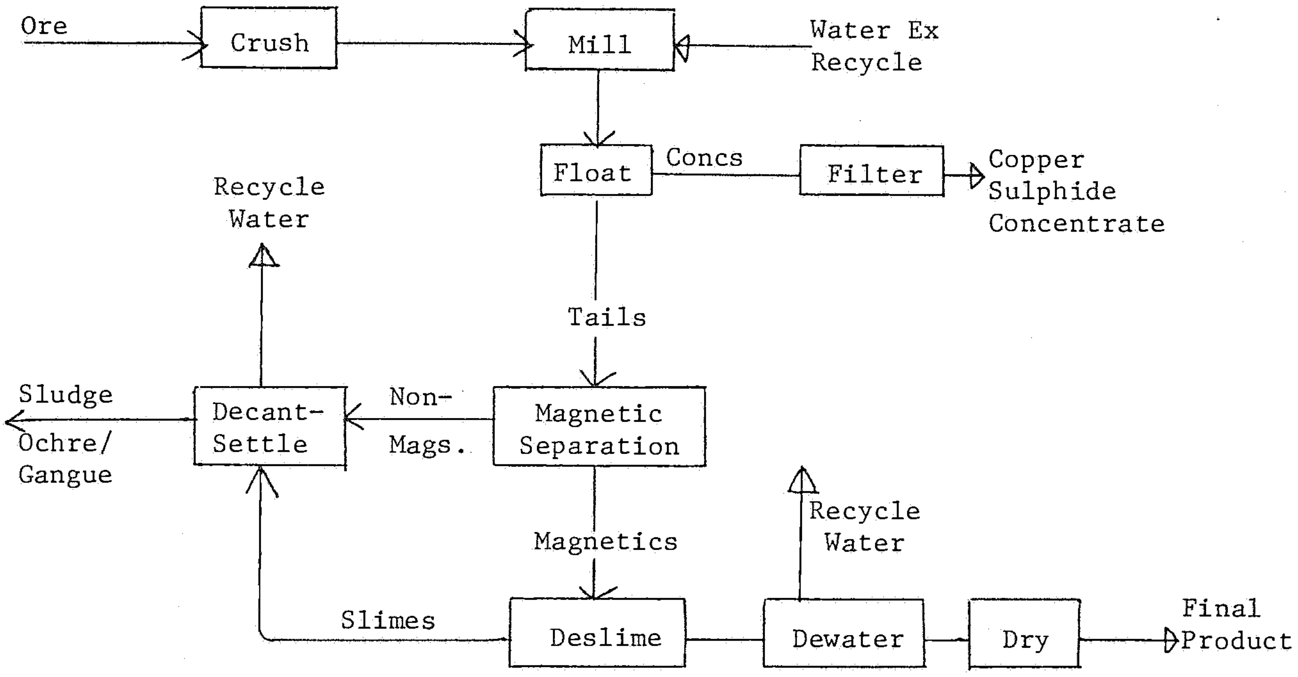
(a) Intended production rate.

(b) The product size range.

(c) The derived and/or allowable physical and chemical characteristics of the product.

From the work completed so far, it is suggested that a suitable flowsheet will take the form shown below:

Provisional Flowsheet for Processing Warrakimbo Iron Oxide Ore



Flotation is included as an initial stage to remove Cu, S, before magnetic separation and desliming. Magnetic separation follows before desliming. This is because the testwork showed the action of desliming and magnetic separation to be similar: both cases the discard product is largely gangue and red oxides. Magnetic separation did not appear to operate more effectively when preceded by desliming.

It is suggested that final product dewatering should incorporate a desliming stage in order to ensure that the final product is of the highest grade possible. Final desliming could be carried out either by cycloning, washing (e.g. passing through a wash thickener, or classification using a spiral classifier. Any adjustment to final product size specification may need to be made at this final stage before the product is dried and bagged for despatch.

Copper-sulphide concentrates will arise at a rate of 2-10% of the weight of ore treated and it is suggested that this concentrate should be systematically sampled and assayed for gold. At best, however, based on results to date, revenue from gold at the level encountered in the sample provided would only be of the order of 0.5% of the revenue from micaceous hematite.

TABLE 1: WARRAKIMBO MICACEOUS IRON OXIDE. FLOTATION/MAGNETIC SEPARATION AT 100% -75 MICRONS.

3081-1

	Product	Weight gm	Weight %	Assay Percent					Metal Content, gm				Recovery Percent			
				Cu	a.s.Fe	T.Fe	S	Au g/t	Cu	T.Fe	S	Au	Cu	T.Fe	S	Au
	Head			0.54	56.7	57.3	0.97	0.065								
1 Flotation followed by Magnetic Separation of Flotation Tailings.	Rougher Conc 1	19.0	4.2	7.15	35.0	40.3	13.9	0.080	1.359	7.656	2.641	0.015	52.7	3.0	59.0	10.2
	Rougher Conc 2	10.0	2.2	1.42	34.2	46.6	14.8	0.080	0.142	4.660	1.480	0.008	5.5	1.8	33.1	5.4
	Combined Concs	29.0	6.4	5.18	-	42.5	14.2	0.080	1.501	12.316	4.121	0.023	58.2	4.8	92.1	15.6
	Tail magnetic fraction	345.2	76.6	0.22	65.0	65.1	0.03	0.035	0.759	224.725	0.103	0.121	29.4	87.4	2.3	82.3
	Tail non-magnetic	76.6	17.0	0.42	26.2	26.2	0.33	0.005	0.321	20.069	0.252	0.003	12.4	7.8	5.6	2.1
	Tails calculated	421.8	93.6	0.26	-	58.0	0.08	0.029	1.080	244.794	0.355	0.124	41.8	95.2	7.9	84.4
	Tails assayed	421.8		0.25	58.2	58.2	0.10	0.080								
	Calculated Head	450.8	100.0	0.57	-	57.0	0.99	0.033	2.581	257.110	4.476	0.147	100.0	100.0	100.0	100.0
2 Magnetic Separation followed by flotation of Magnetic Fraction.	Rougher 1 (magnetic)	7.2	1.5	5.8	53.0	55.9	7.95	0.100	0.418	4.025	0.572	0.007	20.0	1.5	12.3	3.2
	Rougher 2 (magnetic)	9.7	2.1	5.0	52.8	55.8	6.45	0.050	0.485	5.413	0.626	0.005	23.2	2.0	13.5	2.3
	Combined Concs	16.9	3.6	5.3	-	55.8	7.09	0.071	0.903	9.438	1.198	0.012	43.2	3.5	25.8	5.5
	Tail (magnetic)	341.8	73.2	0.16	65.4	65.5	0.01	0.050	0.546	223.879	0.034	0.171	26.1	84.3	0.7	77.4
	Magnetic Fraction to flot^n.	358.7	76.8	0.40	-	65.1	0.34	0.051	1.449	233.317	1.232	0.183	69.4	87.9	26.5	82.8
	Non-magnetic fraction	108.5	23.2	0.59	27.2	29.7	3.15	0.035	0.640	32.225	3.418	0.038	30.6	12.1	73.5	17.2
	Calculated Head	467.2	100.0	0.45	-	56.8	0.99	0.047	2.089	265.542	4.650	0.221	100.0	100.0	100.0	100.0
3 Flotation of Deslimed Feed, followed by Magnetic Separation of Flotation Tailings.	Rougher Conc 1	14.7	3.0	6.15	32.8	45.9	18.6	0.420	0.904	6.747	2.734	0.062	32.9	2.4	59.2	18.5
	Rougher Conc 2	16.8	3.4	3.25	42.8	47.2	8.50	0.250	0.546	7.930	1.428	0.042	19.8	2.8	30.9	12.6
	Combined Concs	31.5	6.4	4.60	-	46.6	13.2	0.330	1.450	14.677	4.162	0.104	52.7	5.2	91.1	31.1
	Tails (magnetic)	382.9	77.8	0.20	64.7	64.7	0.02	0.050	0.766	247.736	0.077	0.191	27.8	88.0	1.7	57.2
	Non-magnetic	48.5	9.8	0.27	12.6	12.6	0.13	0.050	0.131	6.111	0.063	0.024	4.8	2.2	1.4	7.2
	Tails calculated	431.4	87.6	0.21	-	58.8	0.03	0.050	0.897	253.847	0.140	0.215	32.6	90.2	3.1	64.4
	Tails assayed	431.4	87.6	0.23	58.3	58.3	0.03	0.050								
	Slimes	29.5	6.0	1.37	43.4	44.0	1.07	0.050	0.404	12.980	0.316	0.015	14.7	4.6	6.8	4.5
	Deslimed Feed	462.9	94.0	0.51	-	58.0	0.93	0.069	2.347	268.524	4.302	0.319	85.3	95.4	93.2	95.5
	Calculated Head	492.4	100.0	0.56	-	57.2	0.94	0.068	2.751	281.504	4.618	0.334	100.0	100.0	100.0	100.0

3081-2

TABLE 2: WARRAKIMBO MICACEOUS IRON OXIDE. FLOTATION/MAGNETIC SEPARATION AT 100% -212 MICRONS

	Product	Weight gm	Weight %	Assay Percent					Metal Content, gm				Recovery Percent			
				Cu	a.s.Fe	T.Fe	S	Au g/t	Cu	T.Fe	S	Au	Cu	T.Fe	S	Au
	Head			0.54	56.3	57.9	1.13	0.170								
1 Flotation followed by Magnetic Separation of Tailings.	Rougher Conc 1	5.8	1.2	14.5	30.5	39.2	14.7	0.150	0.841	2.274	0.853	0.009	28.9	0.8	25.7	2.6
	Rougher Conc 2	4.8	1.0	6.1	26.6	42.6	19.7	0.260	0.293	2.045	0.946	0.012	10.1	0.8	28.4	3.4
	Combined Concs	10.6	2.2	10.7	-	40.7	17.0	0.198	1.134	4.319	1.799	0.021	39.0	1.6	54.1	6.0
	Tails magnetic	372.2	80.3	0.33	62.6	62.9	0.34	0.035	1.228	234.114	1.265	0.130	42.2	86.1	38.0	37.1
	Tails non-magnetic	81.4	17.5	0.67	40.8	41.0	0.32	0.245	0.545	33.374	0.261	0.199	18.8	12.3	7.9	56.9
	Tails calculated	453.6	97.8	0.39	-	59.0	0.34	0.073	1.773	267.488	1.526	0.329	61.0	98.4	45.9	94.0
	Tails assayed			0.35	57.1	57.4	0.72	0.225								
	Calculated Head	464.2	100.0	0.63	-	58.6	0.72	0.075	2.907	271.807	3.325	0.350	100.0	100.0	100.0	100.0
2 Magnetic Separation followed by flotation of Magnetic Fraction.	Combined Concs (magnetic)	8.4	2.1	9.6	40.5	48.8	15.10	0.310	0.806	4.099	1.268	0.026	30.7	1.7	51.4	5.7
	Tails (magnetic)	326.4	81.0	0.38	63.3	63.5	0.30	0.065	1.240	207.264	0.979	0.212	47.3	88.0	39.7	46.2
	Magnetic fraction to flot^n.	334.8	83.1	0.61	-	63.1	0.67	0.071	2.046	211.363	2.247	0.238	78.0	89.7	91.1	51.9
	Non-magnetic fraction	68.0	16.9	0.85	33.2	35.6	0.32	0.325	0.578	24.208	0.218	0.221	22.0	10.3	8.9	48.1
	Calculated Head	402.8	100.0	0.65	-	58.5	0.61	0.114	2.624	235.571	2.465	0.459	100.0	100.0	100.0	100.0
3 Flotation of Deslimed Feed, followed by Magnetic Separation of Flotation Tailings.	Rougher Conc 1	7.8	1.7	7.6	34.6	46.8	17.2	2.60	0.593	3.650	1.342	0.203	24.0	1.4	33.6	16.6
	Rougher Conc 2	7.2	1.6	7.4	18.9	40.7	27.2	10.7	0.533	2.930	1.958	0.770	21.5	1.1	49.1	62.7
	Rougher Conc 3	2.0	0.4	5.0	28.4	30.2	2.35	-	0.100	0.604	0.047	-	4.0	0.2	1.2	-
	Combined Concs	17.0	3.7	7.2	-	42.3	19.7	5.7	1.226	7.184	3.347	0.973	49.5	2.7	83.9	79.3
	Tails (magnetic)	347.1	76.6	0.22	63.6	63.6	0.04	0.035	0.763	220.756	0.139	0.121	30.8	85.9	3.5	9.9
	Non-magnetic	44.1	9.7	0.31	13.7	13.9	0.36	0.050	0.137	6.130	0.159	0.022	5.5	2.4	4.0	1.8
	Tails calculated	391.2	86.3	0.23	-	58.0	0.08	0.037	0.900	226.886	0.298	0.143	36.4	88.3	7.5	11.7
	Tails assayed		86.3	0.22	58.2	58.3	0.07	0.585								
	Slimes	44.7	9.9	0.78	51.1	51.5	0.77	0.245	0.349	23.021	0.344	0.110	14.1	9.0	8.6	9.0
	Deslimed Feed	408.2	90.1	0.52	-	57.3	0.89	0.273	2.126	234.070	3.645	1.116	85.9	91.0	91.4	91.0
	Calculated Head	452.9	100.0	0.55	-	46.8	0.88	0.270	2.475	257.091	3.989	1.226	100.0	100.0	100.0	100.0

TABLE 3: COMPARISON OF TEST RESULTS

	1 Flotation-Magsep		2 Magsep-Flotation		3 Deslime-Flotation-Magsep	
Product Micaceous	Size Microns		Size Microns		Size Microns	
Hematite (M.H.)	75	212	75	212	75	212
Recovery %	76.6	80.3	73.2	81.0	77.8	76.6
Percent Total Iron	65.1	62.9	65.5	63.5	64.7	63.6
Equivalent % Fe_2O_3	93.1	89.9	93.6	90.8	92.5	90.9
Percent Copper	0.22	0.33	0.16	0.38	0.20	0.22
Percent Sulphur	0.03	0.34	0.01	0.30	0.02	0.04
Copper Concentrate						
Copper Grade						
Percent T. Cu.	5.18	10.7	5.30	9.6	4.60	7.2
Copper Recovery %	58.2	39.0	43.2	30.7	52.7	49.5
Sulphur Recovery	92.1	54.1	25.8	51.4	91.1	83.9
Percent Sulphur	14.2	17.0	7.1	15.1	13.2	19.7

The Australian Mineral Development Laboratories

emington Street, Frewville
South Australia 5063
Phone Adelaide 79 1662
Telex AA82520

Please address all correspondence to
P.O. Box 114 Eastwood
SA 5063
In reply quote:

amdel

29 July 1983

OD 3/0/0

The Director-General
South Australian Department of Mines and Energy
PO Box 151
EASTWOOD SA 5063

Attention: Mr R.L. Wildy

REPORT: OD 5620/83 - PART 1

YOUR REFERENCE:	Your letter of 30 May 1983 File No. 11-20-1200
MATERIAL:	Calcium carbonate waste ('caustic mud')
LOCALITY:	ex ICI Australia Operations Pty Limited, Osborne, S.A.
WORK REQUIRED:	Optimisation of conditions for purification process

Investigation and Report by: R.J. Allen and B.H.J. Waters

Acting Manager, Operations Division: Ian W. McPheat

I W McPheat

for Brian S. Hickman,
Managing Director

cc. The Managing Director
Piber Contractors Pty Limited
26 Wingfield Road
WINGFIELD SA 5013

Attention: Mr T.L. Nicholls

rp

Head Office:
emington Street, Frewville
South Australia 5063
Telephone (08) 79 1662
Telex: Amdel AA82520
Pilot Plant:
Osman Place
Thebarton, S.A.
Telephone (08) 43 5733
Branch Laboratories:
Melbourne, Vic.
Telephone (03) 645 3093
Perth, W.A.
Telephone (09) 325 7311
Telex: Amdel AA94893
Townsville
Queensland 4814
Telephone (077) 75 1377

CONTENTS

1. INTRODUCTION

Exploratory tests[*] at laboratory bench scale at AMDEL for Piber Pty Limited established conditions whereby a crude waste calcium carbonate ('caustic mud') can be dissolved and reprecipitated in a fine, pure form, having a brightness exceeding 96%. Chemical analysis[†] showed that the product contained at least 98% $CaCO_3$. Its low content of impurities should make the product suitable for many applications in the paper, paint and plastics industries, provided that its particle size can be suitably controlled by modifying the conditions of the precipitation step.

A market survey[§] revealed that currently, only about 2500 tonnes per annum of precipitated calcium carbonate are imported into Australia; this premium grade material commands a price of $400-$600 per tonne, delivered. The remaining calcium carbonate consumed in Australia around 70,000 tonnes per annum which comprises finely-milled local limestone, would be priced in the range $50-$250 per tonne, depending on particle size and purity.

It was recommended that a preliminary estimate of costs be made for purifying the 'caustic mud'; this recommendation was adopted by the South Australian Department of Mines and Energy, who approved $3500 in a letter dated 30 May 1983. Piber Pty Limited approved the expenditure of an additional $3300, for experimental work aimed at optimising the reaction between ammonium chloride and 'caustic mud', and providing additional data required for the process costing.

2. MATERIAL EXAMINED

The 'caustic mud' used for this investigation was part of a sample supplied for earlier experimental work.

The sample, as used for the present experiments was shown to contain 20% moisture. Thermal analysis (Fig. 1) showed two major endothermic DTA peaks, corresponding to loss of moisture (19%) and loss of carbon dioxide (27.5%, equivalent to 63% $CaCO_3$). A third DTA endotherm, at about 440°C, was attributed to loss of combined water from $Ca(OH)_2$ {1.7% H_2O, equivalent to 7% $Ca(OH)_2$}.

From these results, and from previous analyses, the following approximate composition is inferred:

	%
Calcium carbonate, $CaCO_3$	63
Calcium hydroxide, $Ca(OH)_2$	7
Sodium hydroxide, NaOH	3.5[¶]
Silica, SiO_2	1
Iron oxide, Fe_2O_3	0.25
Magnesium, aluminium, potassium	0.5
Moisture, H_2O	$\sim$20
Total	95.3

[¶] Not determined ('typical' value).

---

[*] See AMDEL Service Report No. OD 5043/81, dated 12 May 1981.
[†] See AMDEL Service Report No. OD 5825/81, dated 9 July 1981.
[§] See AMDEL Service Report No. OD 2714/82, dated 2 February 1982.

X-ray diffraction indicated the presence of quartz and a small amount of mica in the residue from leaching the mud with hydrochloric acid.

3. EXPERIMENTAL PROCEDURE AND RESULTS

3.1 Study of the Reaction of the Caustic Mud with Ammonium Chloride

Thermal analysis - simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) - was used to investigate the caustic mud, ammonium chloride, and their interaction in a mixture (NH_4Cl:mud = 1.07:1).

The thermal analysis curves for the caustic mud alone (Fig. 1) show three endothermic DTA peaks accompanied by weight loss. These correspond to loss of moisture (ambient-150°C), decomposition of $Ca(OH)_2$ (400-460°C) decomposition of $CaCO_3$ (640-830°C).

Ammonium chloride, and the mixture with caustic mud, were heated at 5°C per minute to about 370°C in a stream of nitrogen. The detailed conditions are shown in Figs 2 and 3, along with resulting thermal analysis curves.

For ammonium chloride (Fig. 2), there were two major thermal effects:

(1) A sharp endothermic DTA peak at about 190°C, before any significant weight loss had occurred. This corresponds to a physical transition in the crystal structure of the ammonium chloride.

(2) A very large endothermic DTA peak, associated with the volatilisation of the entire sample (200-360°C).

For the mixture (Fig. 3), the following thermal effects were distinguishable:

(1) A broad endothermic DTA peak, 50-110°C, accompanied by weight loss, due to removal of moisture.

(2) The sharp endothermic DTA peak at about 190°C, characteristic of ammonium chloride (phase transition).

(3) The very large endothermic DTA peak, indicating volatilisation of ammonium chloride (200-350°C).

(4) Apparently superimposed on the large endotherm (3), was an exothermic DTA peak, approximately 300°C to 340°C. This can be attributed to the reaction of ammonium chloride with calcium carbonate:

$$2NH_4Cl + CaCO_3 \rightarrow CaCl_2 + 2NH_3\uparrow + H_2O\uparrow + CO_2\uparrow$$

Fig. 4 is a plot of the rate of weight loss for the mixture relative to weight loss for the ammonium chloride, normalised to the same weight of NH_4Cl. It shows that from about 250°C to 310°C the rate of weight loss was greater than that expected for loss of NH_4Cl by volatilisation alone, confirming that NH_4Cl was being consumed in an additional reaction, i.e.

$$NH_4Cl_{(s)} \leftrightarrows NH_4Cl(g) \rightleftarrows NH_3\uparrow + HCl\uparrow \qquad \ldots 1$$

$$2NH_4Cl + CaCO_3 \rightarrow CaCl_2 + 2NH_3\uparrow + H_2O\uparrow + CO_2\uparrow \qquad \ldots 2$$

However, by 310°C, the rate of weight loss had fallen to the expected level, and thereafter the rate was lower than with NH_4Cl alone, possibly because the product $CaCl_2$ reduces the volatility of the ammonium chloride.

Using the Stanton thermobalance, a larger sample of the ammonium chloride/caustic mud mixture (1.50 g) was heated in a stream of nitrogen (150 ml per minute) to 390°C (sample temperature about 350°C) and this temperature held until no further weight loss was recorded. Again, the two distinct weight losses were recorded:

(1) moisture over the temperature range ambient - 120°C

(2) ammonium chloride and reaction products, from about 250°C.

The ammonium chloride was completely consumed after about 80 min. above 250°C.

The results are shown graphically in Fig. 5.

This experiment was repeated, at 490°C (sample temperature about 450°C) instead of 390°C. The results are also included in Fig. 5. The time for complete removal of NH_4Cl was reduced to 45 min. after passing 250°C.

3.2 Study of Process Steps

3.2.1 Conversion of Calcium Carbonate to Chloride and Leaching

Effect of Reaction Time, Temperature

In several series of tests, the caustic mud (1.00 part) was reacted with ammonium chloride (1.07 parts) at temperatures ranging from 320 to 550°C, for times ranging from 1 hour to 4.5 hours.

In each case, the mixture was moistened with water to form a thick paste and ensure uniform mixing. The reaction mixture was transferred to a silica or glass reactor, and heated to the reaction temperature in stages, thus:

Control Temperature	Time (min.)
120°C	45
220°C	30
Reaction Temperature	(variable)

Throughout the experiment, a flow of air (150 ml per minute) was maintained through the reactor, sweeping the volatile products from the reaction mixture through the heated exit tubing to the scrubber, which comprised a bubbler tube containing calcium chloride solution (500 g/*l* $CaCl_2$), or two bubbler tubes containing water and calcium chloride solution, respectively (see Fig. 6).

During the heating, the water was first driven off, and then ammonium chloride plus reaction products. It was observed that ammonium chloride, NH_4Cl, and iron (ferric) chloride, $FeCl_3$, sublimed from the mixture, and condensed just beyond the furnace hot zone. In the first few experiments, this sublimate tended to block the narrow exit tube of the silica reactor. Later, a glass reactor was used, having wider bore exit tubing to the scrubber. Beyond the heating tape, and just before the scrubber, another sublimate, colorless and crystalline, condensed in the tubing. This was presumed to be ammonium carbonate $(NH_4)_2CO_3$.

At the end of the specified reaction, period, the reaction product in the reactor was leached with water to dissolve $CaCl_2$ and NaCl, and the sublimed NH_4Cl plus $FeCl_3$ were recovered separately by scraping the walls of the reactor and the exit tubing. The scrubber solution was used to dissolve any ammonium carbonate deposited before the bubbler tube, and allowed to stand overnight to permit the calcium carbonate to precipitate and settle out.

061

The residue from the water leaching step was collected by filtration, washed with a little more water, dried and weighed. The reaction residue filtered rapidly.

The filtrate and washings, containing $CaCl_2$ (and NaCl) dissolved from the reaction product, were treated with ammonium carbonate, until no more calcium carbonate was precipitated. The precipitate was collected by filtration, washed, dried and weighed.

The results of these experiments are summarised graphically in Fig. 7. Conversions were calculated from the weight of pure $CaCO_3$ precipitated from the leach liquor, as a percentage of (weight of $CaCO_3$ precipitate + weight of leach residue).

The conversion efficiency increased from 63% to 79% as the time of reaction increased from 1 to 4 hours at 350°C. At 370°C, there was a comparable increase, from 57% to 81% for 1.75 to 4.5 hours respectively.

More rapid rates of heating up to 350°C and 370°C appeared to have little effect on the conversion efficiency. At 320°C, the conversion efficiency was considerably lower (47% after 4 hours).

The results for the higher reaction temperatures, 450°C to 550°C, suggested that similar conversions can be achieved using shorter reaction times. For a reaction mixture brought rapidly to a control temperature of 450°C, for a total heating time of 2 hours, the calculated conversion of $CaCO_3$ to $CaCl_2$ was 86%.

Effect of NH_4Cl:Mud Ratio

Increasing the proportion of NH_4Cl:mud from about 1:1 to 1.5:1 did not significantly improve the conversion.

Effect of Second Reaction Stage

The reaction residue from one experiment (74% conversion) was examined using thermal analysis. The TGA trace indicated that the residue still comprised about 82% $CaCO_3$.

A composite of reaction residues from previous experiments was prepared, and mixed with ammonium chloride in the ratio 1:1.07. This mixture was heated rapidly, using a furnace control temperature of 450°C for a total time of one hour. The calculated efficiency of conversion of $CaCO_3$ to $CaCl_2$ was 71%, confirming that the $CaCO_3$ in the reaction residues is still reactive.

3.2.2 Recovery of Calcium Carbonate from the Leach Solution

The addition of excess ammonium carbonate to the leach solution effectively precipitated the dissolved calcium as pure white calcium carbonate:

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + 2NH_4Cl$$

This $CaCO_3$ product was finely divided, but filtered well using a laboratory Buchner funnel.

For the last six experiments, the total recovery of calcium carbonate in the product plus residue averaged 90%. Allowing for some inevitable losses in handling small quantities of these solids, it is clear that after treatment with excess ammonium carbonate, little calcium remained in the leach liquor.

3.2.3 Recovery of Ammonia, Carbon Dioxide

In most experiments, the exhaust gases from the reactor were passed through a bubbler tube containing calcium chloride solution (500 g/*l* $CaCl_2$). Some precipitation of calcium carbonate resulted, but the weight of precipitate was invariably well below that expected if all of the evolved CO_2 had been reprecipitated as $CaCO_3$. Some of the evolved CO_2 undoubtedly recombined with ammonia, NH_3, and condensed on the exit tubing as ammonium carbonate, $(NH_4)_2CO_3$. However, careful washing of the $(NH_4)_2CO_3$ from the tubing using the $CaCl_2$ solution in the bubbler still did not result in the expected quantity of $CaCO_3$ precipitate.

In two experiments, the bubbler tube was filled with water, instead of calcium chloride solution, and when the experiments were finished, the water from the scrubber was submitted for chemical analysis for ammonia and carbonate. The results showed that the scrubber contained 78%-88% of the expected quantities of ammonia and carbon dioxide, assuming that <u>all</u> of the calcium chloride in the leach liquor had been formed by the reaction:

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + H_2O + CO_2$$

The actual efficiencies of carbon dioxide recovery would have been even higher, because, some calcium chloride is also formed without the release of CO_2:

$$Ca(OH)_2 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + H_2O$$

4. DISCUSSION

4.1 Composition of the Caustic Mud

Thermal analysis demonstrated that this sample of caustic mud had a lower content of calcium carbonate - 63%, equivalent to 79% $CaCO_3$ on a dry basis - than the value quoted as typical, viz about 90% $CaCO_3$ on a dry basis.

Countering this, the content of lime was substantially higher than the typical figure - 9.5% $Ca(OH)_2$ (dry basis) versus 3%. The content of free caustic soda, NaOH, has <u>not</u> been determined for this sample; this, too, may be higher than the '<u>typical</u>' value quoted (about 4% on a dry basis).

The quartz and mica would account for the small amounts of silica, potassium, aluminium and magnesium in the mud; presumably these minor impurities, and the iron oxide (0.25% Fe_2O_3) are derived from the lime used in the causticisation step in which the mud is formed at the ICI plant.

4.2 Reaction of the Caustic Mud with Ammonium Chloride, NH_4Cl

The thermal analysis experiments confirmed that some of the NH_4Cl reacts exothermically with the caustic mud, rather than simply volatilising (subliming) from the reaction mixture.

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + 2NH_3 + CO_2 + H_2O$$

$$NH_4Cl(s) \rightarrow NH_4Cl(g) \rightleftarrows NH_3 + HCl$$

Fig. 7 shows that there was a general improvement in conversion as the reaction temperature was increased from 320°C to 550°C and as the time was increased from 1 to 4 hours. At 450°C, 86% conversion to calcium chloride was achieved after 2 hours' reaction. Clearly, from Fig. 7, the reaction would proceed more rapidly at 550°C. However, this temperature is beyond the maximum-useful temperature (500°C) for Pyrex glass-lined equipment, which is probably the most practical way* of conducting the reaction commercially, given the corrosiveness of the ammonium chloride.

It may be possible to accelerate the reaction at 450°C by sweeping away the NH_3 and CO_2 products more rapidly; certainly under the high gas-flow conditions of the thermobalance, (Fig. 5) it required only 45 minutes to entirely consume the ammonium chloride, by sublimation and by reaction with the caustic mud at 450°C. On the other hand, the increased gas-flow would also sweep away the subliming NH_4Cl, which may increase the rate of volatilisation *relative* to the rate of reaction with the mud, thereby reducing the attainable conversion.

4.3 Reprecipitation of Pure Calcium Carbonate, $CaCO_3$

Analysis of the solutions obtained by scrubbing the exhaust gases from the reactor, indicated that the ammonia and carbon dioxide were efficiently absorbed in the scrubber.

$$CaCO_3 + 2NH_4Cl \rightarrow CaCl_2 + H_2O + \underline{NH_3}\uparrow + \underline{CO_2}\uparrow$$

However, when the exhaust gases were passed into an excess of concentrated calcium chloride solution in the scrubber, the carbon dioxide was incompletely precipitated as calcium carbonate, and the precipitate was slow to filter.

$$CaCl_2 + 2NH_3 + CO_2 + H_2O \rightleftarrows CaCO_3\downarrow + 2NH_4Cl$$

This may be explained by the acidity of the scrubber solution, due to hydrolysis of both the calcium chloride and the ammonium chloride:

$$CaCl_2 + 2H_2O \rightleftarrows Ca(OH)_2 + 2Cl^- + \underline{2H}^+$$

$$NH_4Cl + H_2O \rightleftarrows NH_4OH + Cl^- + \underline{H}^+$$

This would in turn mean that the carbon dioxide would be present in the scrubber solution largely in the form of bicarbonate ions, HCO_3^-, rather than carbonate ions CO_3^{2-}:

$$H^+ + CO_3^{2-} \rightleftarrows HCO_3^-$$

Since bicarbonate ions are not precipitated by calcium, precipitation of the carbon dioxide from the exhaust gas is incomplete:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3$$

On the other hand, when the calcium chloride produced in the reaction of NH_4Cl with the mud was dissolved in water and treated with an excess of ammonium carbonate, $(NH_4)_2CO_3$, the dissolved calcium was efficiently reprecipitated as a readily filterable calcium carbonate:

$$CaCl_2 + (NH_4)_2CO_3 \rightarrow CaCO_3\downarrow + 2NH_4Cl$$

In this case, the excess $(NH_4)_2CO_3$ would provide sufficient free carbonate ions, CO_3^{2-}, to precipitate virtually all of the calcium, since the solution here is not so acidic that the carbonate ions, CO_3^{2-}, are converted to bicarbonate, HCO_3^-.

---

*Lead-lined equipment, used for hot NH_4Cl solutions, would not be suitable at such high temperatures.

This suggests that it will be desirable to ensure a small excess of ammonium carbonate at the reprecipitation stage. In the proposed flowsheet of Fig. 8, this is achieved by recirculating some excess ammonia and carbon dioxide; the filtrate from the precipitation stage is degassed using the hot gases from the reactor, thereby augmenting their content of NH_3 and CO_2 before the gases contact the $CaCl_2$ solution in the precipitator.

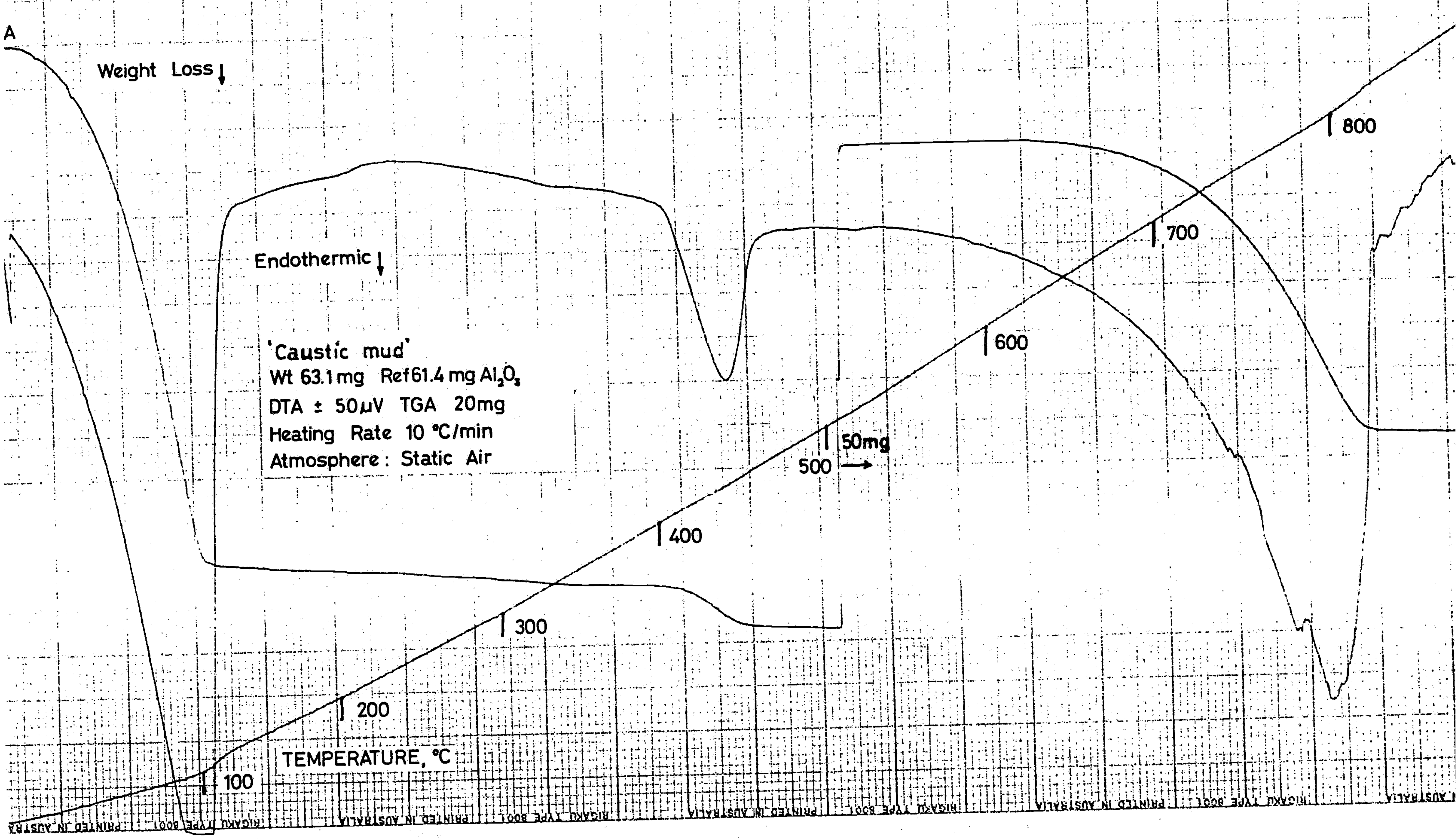


FIG. 1: THERMAL ANALYSIS OF CAUSTIC MUD

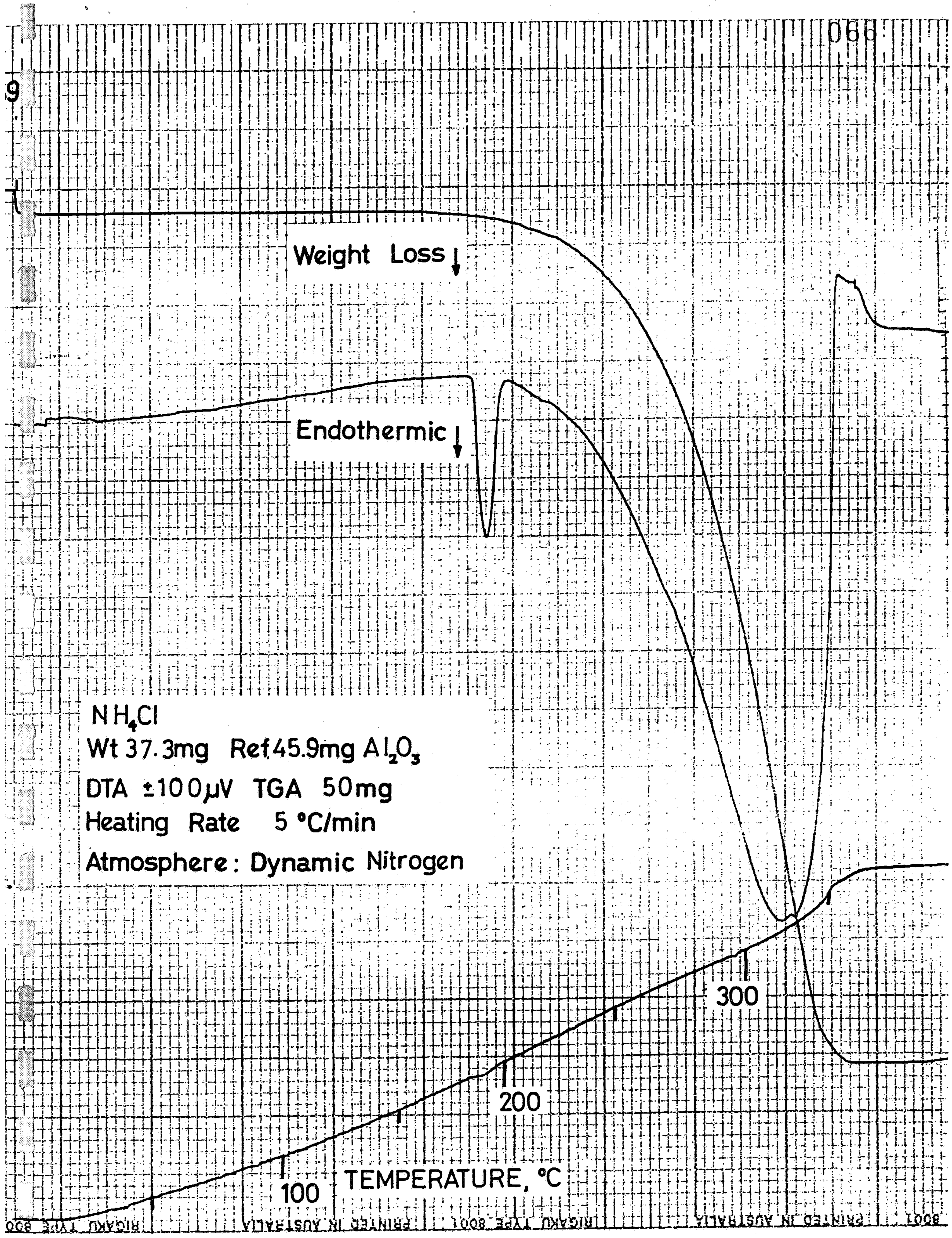


FIG. 2: THERMAL ANALYSIS OF AMMONIUM CHLORIDE

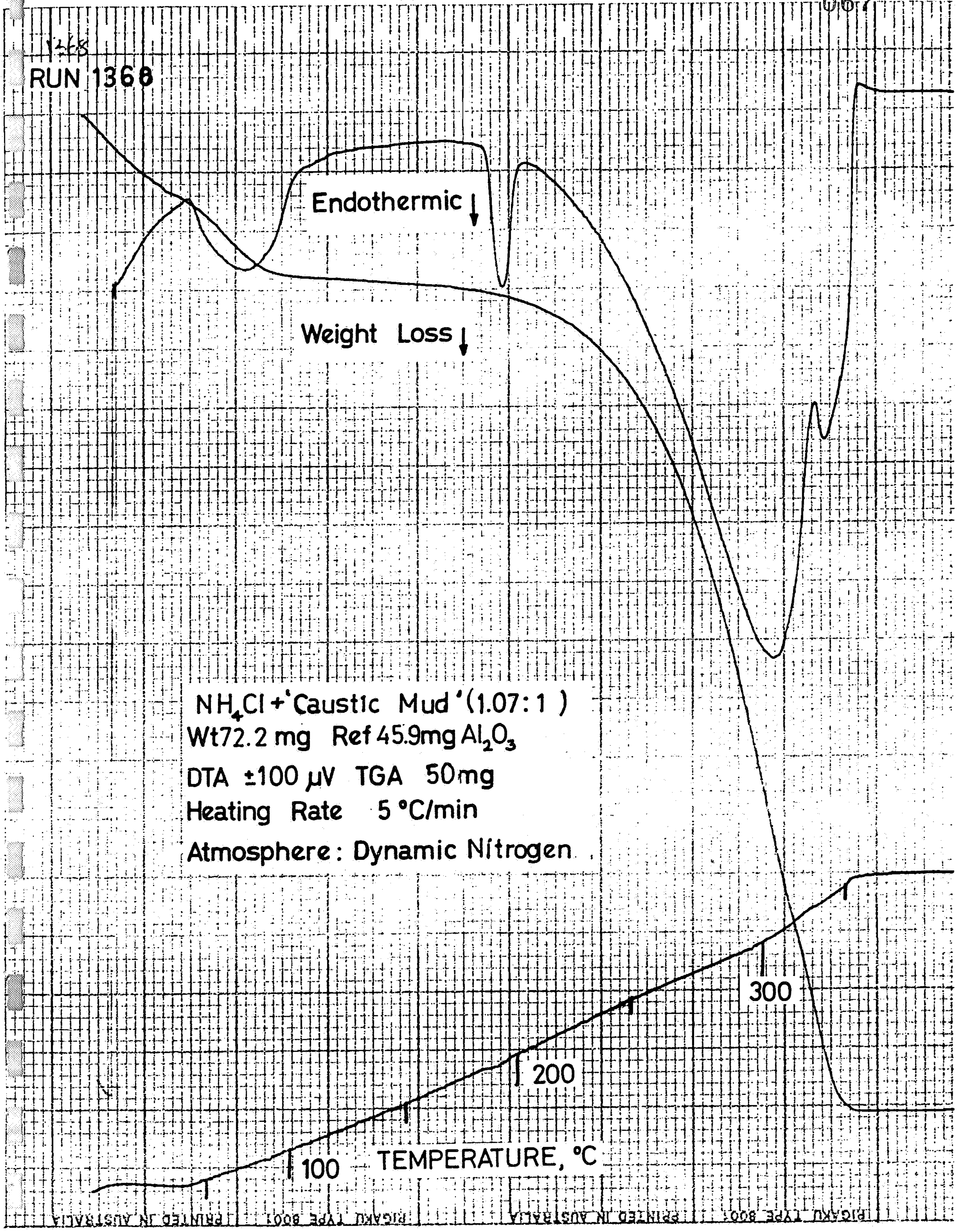


FIG. 3: THERMAL ANALYSIS OF AMMONIUM CHLORIDE/CAUSTIC MUD MIXTURE

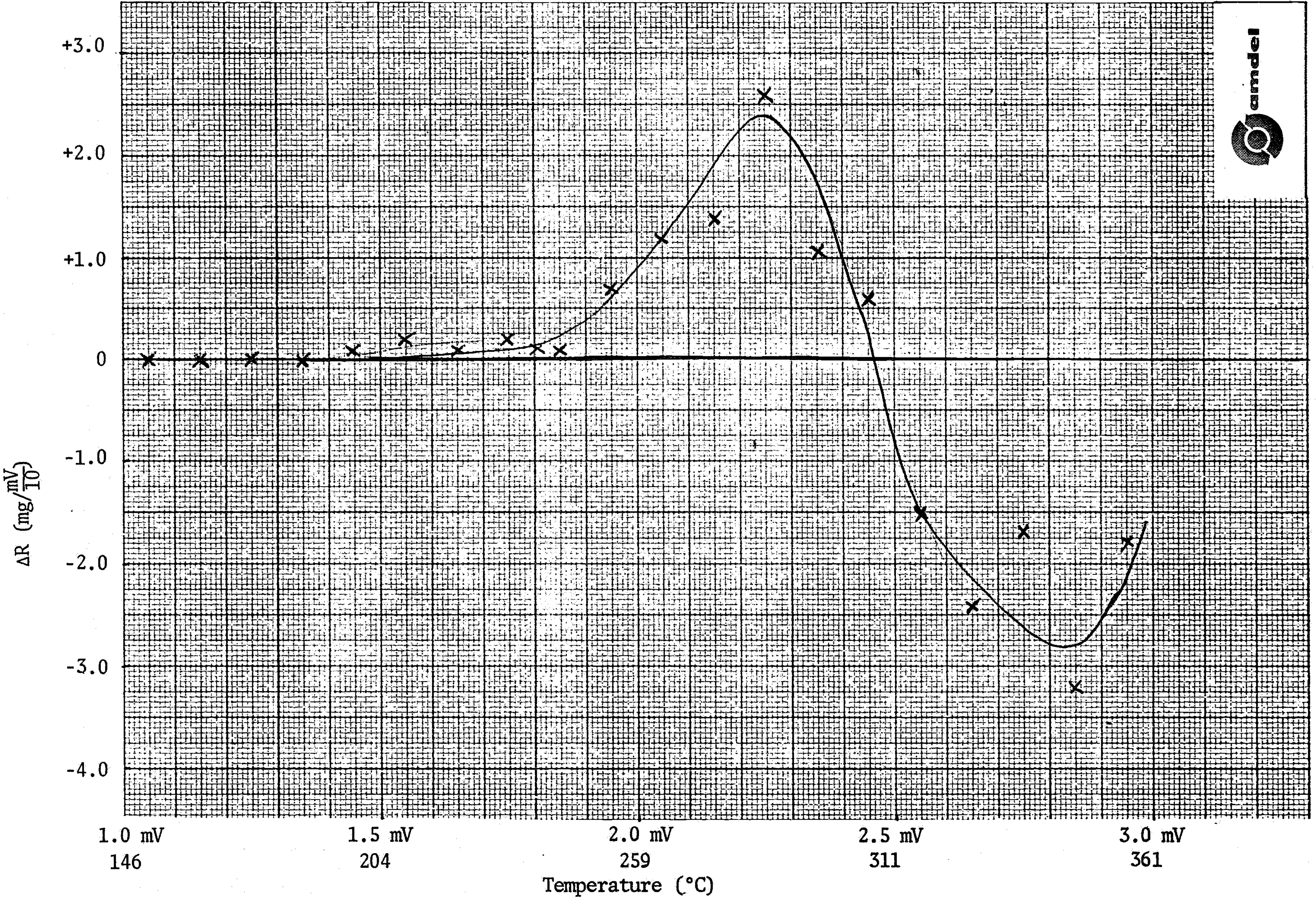


FIG. 4: DIFFERENCE IN RATES OF WEIGHT LOSS - NH_4Cl/MUD VERSUS NH_4Cl ALONE

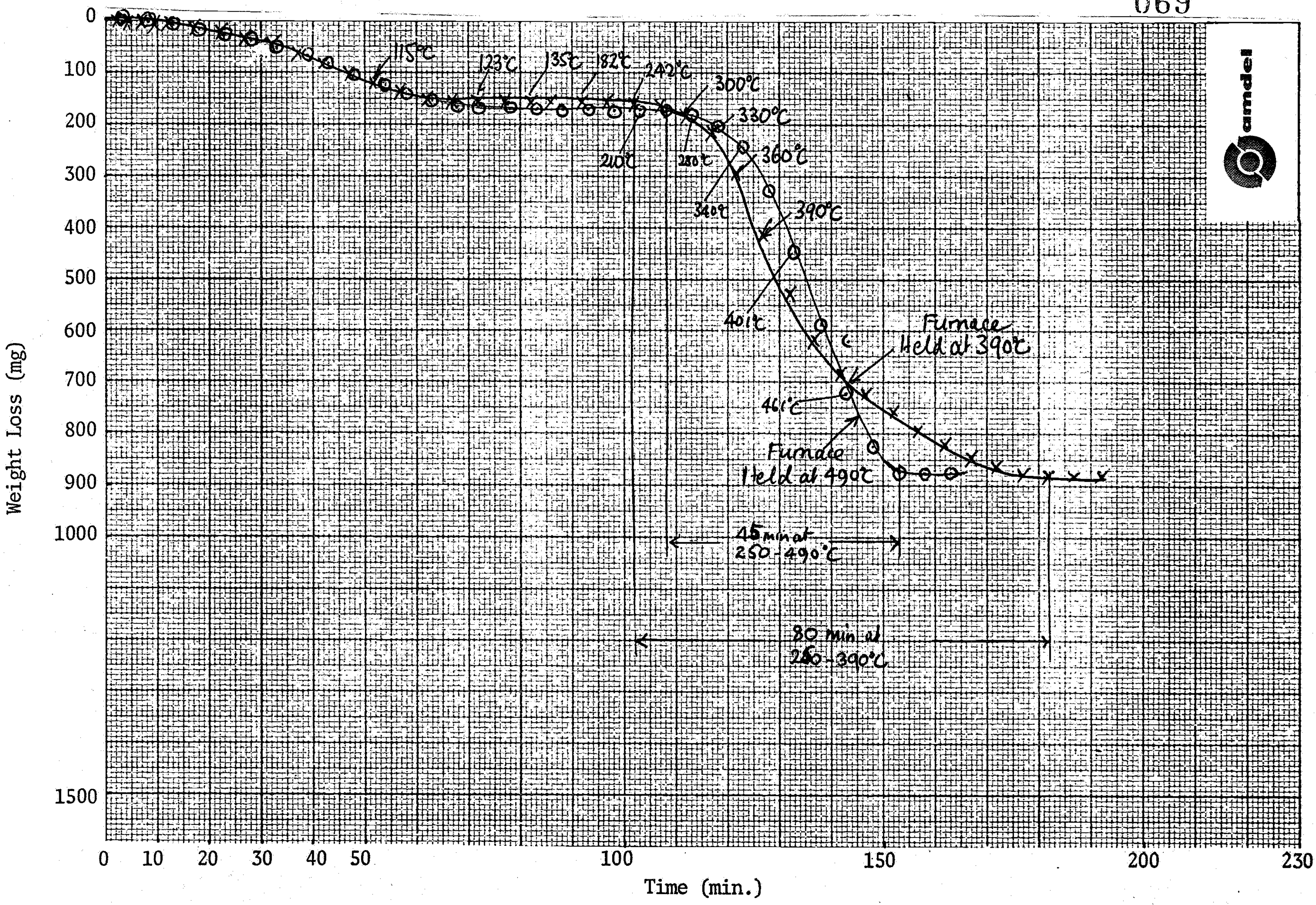


FIG. 5: WEIGHT LOSS CURVES FOR AMMONIUM CHLORIDE/CAUSTIC MUD (1.50 g)

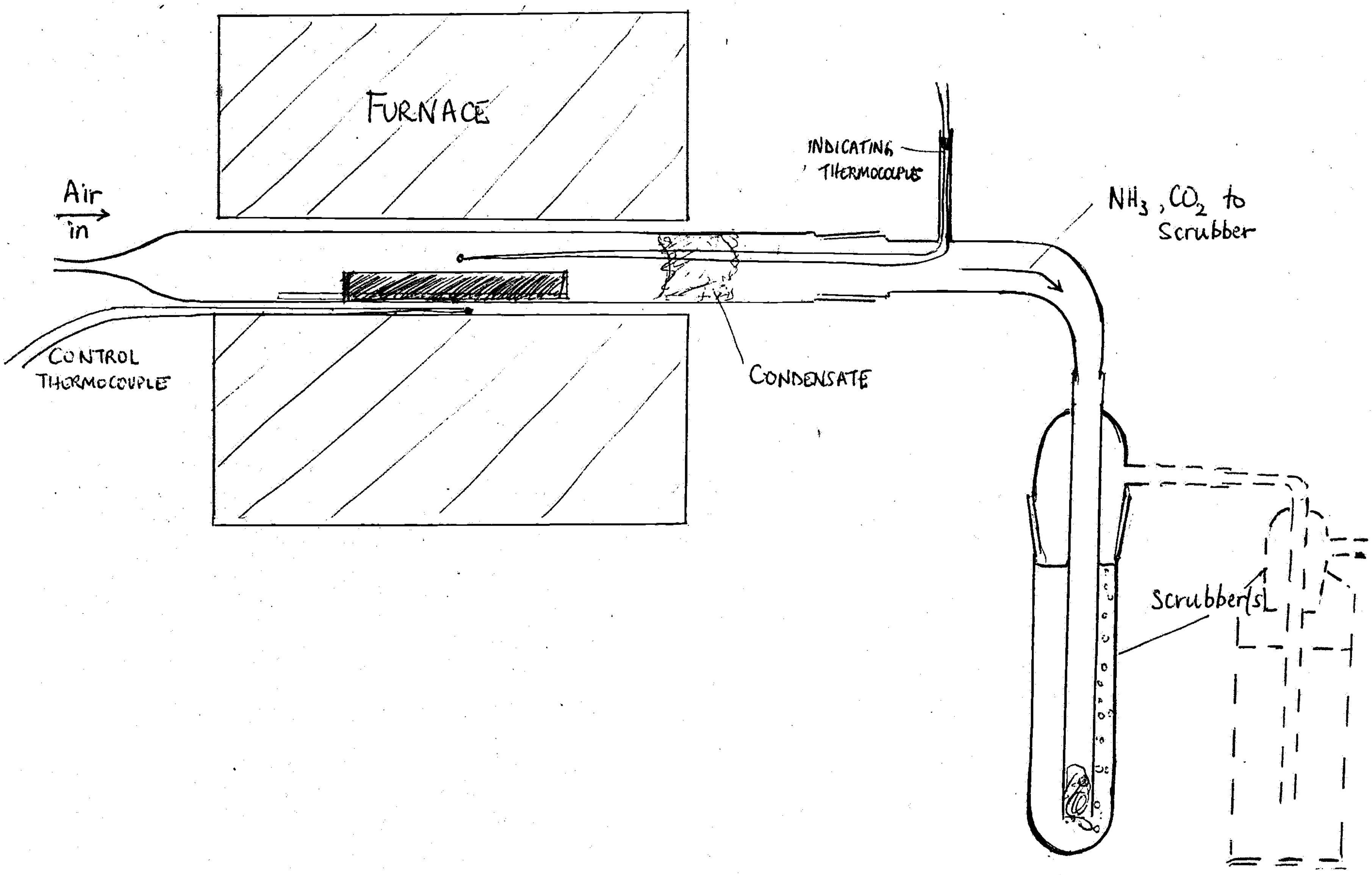


FIG. 6: GLASS REACTOR/SCRUBBER SYSTEM

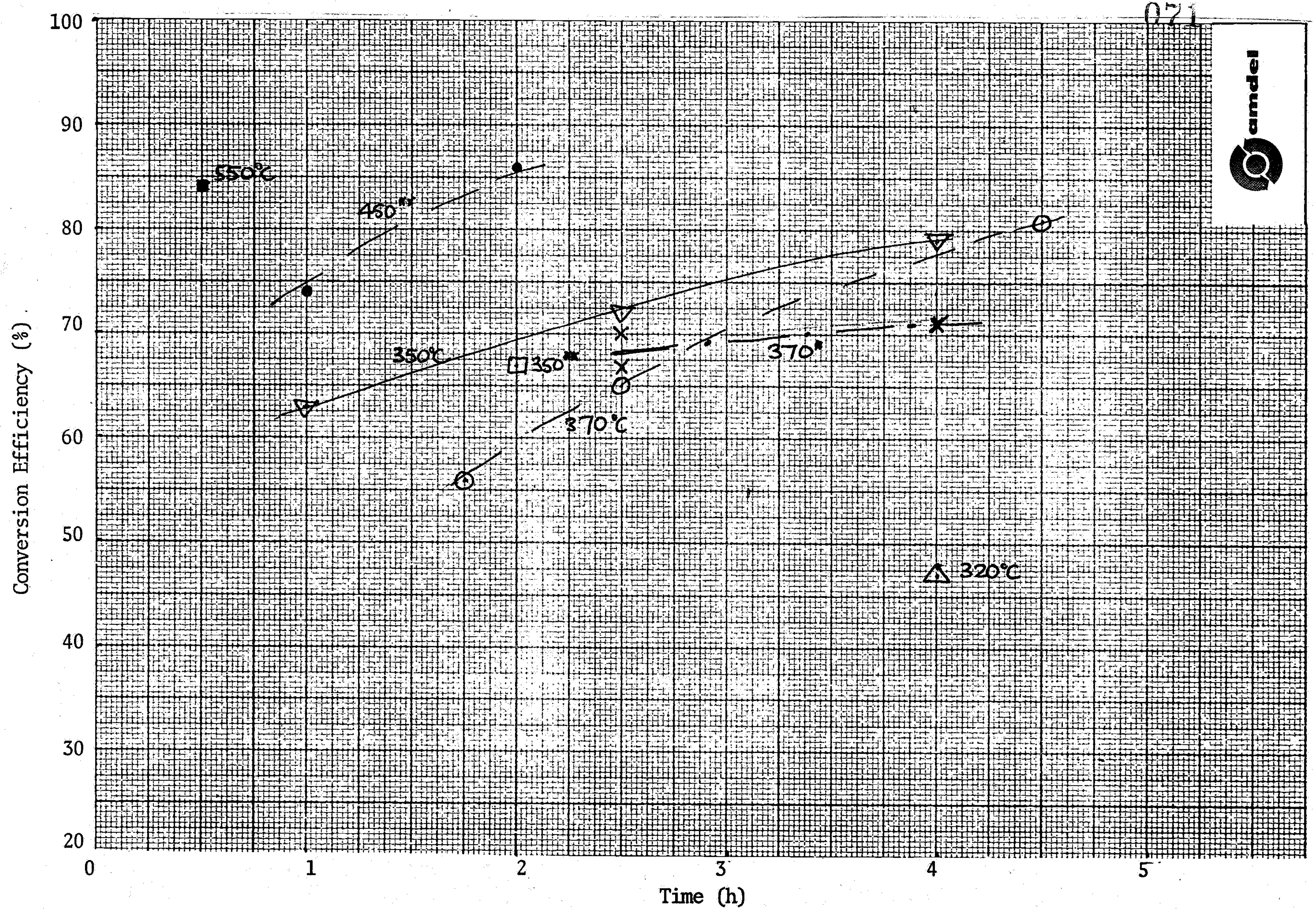


FIG. 7: EFFECT OF REACTION TEMPERATURE AND TIME ON CONVERSION

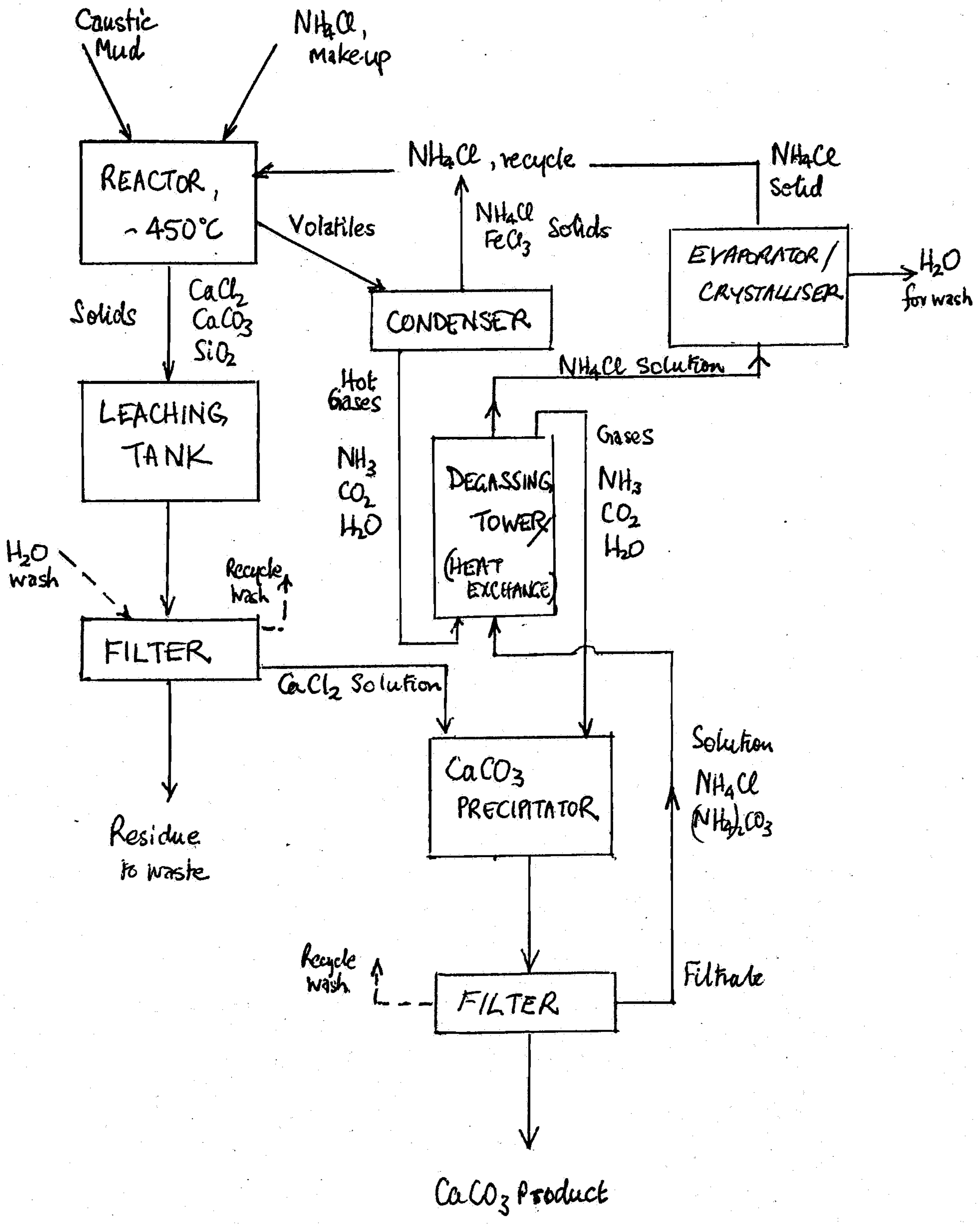


FIG. 8 : PROPOSED PROCESS FLOWSHEET

The Australian Mineral Development Laboratories

Flemington Street, Frewville
South Australia 5063
Phone Adelaide 79 1662
Telex AA82520

Please address all correspondence to
P.O. Box 114 Eastwood
SA 5063
In reply quote:

amdel

19 August 1983

OD 3/0/0

The Director-General
South Australian Department of Mines
and Energy
PO Box 151
EASTWOOD SA 5063

Attention: Mr R.L. Wildy

REPORT: OD 5620/83 - PART 2 AND FINAL

YOUR REFERENCE:	Your letter of 30 May 1983 File No. 11.20.1200
MATERIAL:	Calcium Carbonate Waste ('Caustic Mud')
LOCALITY:	ex ICI Australia Operations Pty Limited, Osborne, SA
WORK REQUIRED:	Preliminary Estimate of Costs for Purification Process

Investigation and Report by: R.J. Allen

Acting Manager, Operations Division: Ian W. McPheat

IW McPheat

for Brian S. Hickman,
Managing Director

cc. The Managing Director
Piber Contractors Pty Limited
26 Wingfield Road
WINGFIELD SA 5013

Attention: Mr T.L. Nicholls

rm

Head Office:
Flemington Street, Frewville
South Australia 5063
Telephone (08) 79 1662
Telex: Amdel AA82520
Pilot Plant:
Osman Place
Thebarton, S.A.
Telephone (08) 43 5733
Branch Laboratories:
Melbourne, Vic.
Telephone (03) 645 3093
Perth, W.A.
Telephone (09) 325 7311
Telex: Amdel AA94893
Townsville
Queensland 4814
Telephone (077) 75 1377

CONTENTS

76

1. INTRODUCTION

'Caustic mud' is the waste solids separated from the causticiser at the ICI alkali plant, wherein a solution of soda ash (Na_2CO_3) is converted to caustic soda (NaOH) by treatment with lime {$Ca(OH)_2$}, derived from calcined limestone.

$$\underset{}{Ca(OH)_2 + Na_2CO_3} \rightarrow \underset{\text{caustic mud}}{CaCO_3\downarrow} + NaOH$$

In addition to calcium carbonate - the principal component - caustic mud contains a little of the excess lime and of the caustic soda product, plus some minor impurities derived from the original limestone.

The production of pure calcium carbonate from caustic mud has been studied at laboratory scale by AMDEL*.

A market survey† revealed that currently, only about 2500 tonnes per annum of pure, precipitated calcium carbonate are imported into Australia; this premium-grade material commands a price of $400 to $600 per tonne, delivered. The balance of the calcium carbonate consumed in Australia, around 70,000 tonnes per annum, which comprises finely-milled local limestone, would be priced in the range $50 to $250 per tonne, depending on particle size and purity.

The South Australian Department of Mines approved an AMDEL proposal to prepare a preliminary estimate of the costs of producing calcium carbonate by the process being developed at AMDEL.

2. BASIS

The caustic mud contains calcium carbonate, calcium hydroxide and sodium hydroxide, plus minor quantities of silica and iron oxide.

By reaction with solid ammonium chloride for 2 hours at 450°C, approximately 85% of the calcium in the mud can be converted to calcium chloride.

For the preliminary cost study, the caustic mud is assumed to have the composition shown in Table 1. Two scales of operation have been assumed, viz 4000 tonnes caustic mud per annum (0.5 tph) and 20,000 tonnes per annum (2.5 tph).

The plant will be sited in the Osborne area, adjacent to the ICI plant which generates the caustic mud waste. The plant will operate continuously, 7 days per week, for an operating year of 330 days, with an assumed plant life of 10 years.

Make-up chemicals, to compensate for minor losses in the essentially cyclic process, will be obtained from the adjacent ICI plant.

Because of the corrosiveness of ammonium chloride, and other chloride solutions, all equipment pumps and pipelines must be rubber-lined. To permit operation at about 450°C, the main reactor will be a rotary kiln, lined with acid-proof refractory bricks.

---

*See AMDEL Service Report Nos OD 5043/81, dated 12 May 1981
OD 5825/81, dated 9 July 1981
OD 5620/83, Part 1, dated 29 July 1983.

†See AMDEL Service Report No. OD 2714/82, dated 2 February 1982.

3. PROCESS DESCRIPTION

A mass balance for the process, based on 1 tonne of caustic mud, is shown in Fig. 1. A flowsheet for the proposed treatment plant is given in Fig. 2.

The main steps in the process, and the equipment envisaged, are described below.

3.1 Feed

The caustic mud will be reclaimed from a stockpile by a front-end loader. It is assumed to have drained and air-dried to an average of 20% free moisture. At the low rate of production, 0.50 tonnes per hour of the caustic mud will be fed to the pug-mixer, via conveyor and weigh feeder.

3.2 Ammonium Chloride

This will be mainly recycle material, discharged from the crystalliser at an assumed 5% moisture. The balance of ammonium chloride (zero moisture), to make up for losses, will be purchased in bags from the adjacent ICI plant.

The ammonium chloride will be fed by conveyor to the pugmixer at the rate of 0.37 tonnes per hour.

3.3 Ammonia, Carbon Dioxide

To make up for minor losses of ammonia from the pugmixer and the evaporator/crystalliser, ammonia will be purchased in large cylinders from the ICI plant, and introduced into the calcium carbonate precipitator.

Combustion products from the burning of natural gas in the kiln will provide carbon dioxide equivalent to the calcium hydroxide component of the mud, and will compensate for losses of CO_2.

Through the above measures, an excess of NH_3 and CO_2 will be maintained in the precipitator, ensuring efficient precipitation of $CaCO_3$ product.

3.4 The Reaction of Caustic Mud with NH_4Cl

The intimately mixed mud and NH_4Cl will be discharged from a rubber-lined pugmixer into the reactor, a counter-currently gas-fired rotary kiln with a lining made of acid-proof refractory brick to withstand the chemically aggressive ammonium chloride at 450°C. The assumed retention time is 2 hours. The reactor of 20 tpd capacity, will be gas-tight to prevent escape of noxious and corrosive gases, and to ensure complete recovery of NH_4Cl, NH_3 and CO_2, essential to the cyclic operation of the process.

The product gas stream will be drawn back through the kiln where volatilised NH_4Cl will recondense, and heat will be transferred to the incoming solids.

3.5 Recovery of Ammonia and Carbon Dioxide

Ammonia and carbon dioxide in the exhaust gases will pass from the kiln up through the degassing tower which will be held at a sufficient temperature to remove additional NH_3 and CO_2 from the filtered supernatant liquor.

This combined stream of gas, rich in NH_3 and CO_2 will pass directly into the $CaCO_3$ precipitation tank. Piping will be electrically heated to 100°C to prevent recondensation of solid ammonium carbonate.

3.6 Leaching of Calcium Chloride

The reaction product is directly discharged from the reactor into the leaching tank which is rubber-lined and fitted with a rubber-coated agitator. The leaching tank will receive a flow of 0.50 tph of water recycled from the evaporator and 0.38 tph of wash water, recycled from the two filters. The capacity of the leaching tank is such (1.5 m^3) as to give an average retention time of one hour. The rubber-coated agitator is driven by a 1.5 kW motor.

3.7 Filtration of Leach Liquor

The pulp overflowing from the leaching tank is filtered using a plate and frame filter. A filtration rate of 100 kg $m^{-2}h^{-1}$ is assumed requiring a filter area of 1 m^2.

The leach residue, comprising unattacked $CaCO_3$, as well as quartz, mica and iron oxide impurities is washed on the filter using fresh water, and discarded. The washings are directed to the leaching tank.

3.8 Precipitation of $CaCO_3$

The filtered leach liquor is a concentrated solution of calcium chloride (assumed 420 g/*l* $CaCl_2$, 17 g/*l* NaCl). This filtrate is pumped to the precipitation tank, where it contacts a suspension of calcium carbonate product in ammonium carbonate/ammonium chloride solution, this suspension is also continuously receiving a flow of ammonia/carbon dioxide from the degassing tower, equivalent to the incoming calcium chloride.

The conditions needed to produce calcium carbonate of specified particle size characteristics have not yet been studied. However, from the papers included in Appendix A, control of temperature during precipitation may be necessary.

The $CaCO_3$ precipitator is hence a rubber-lined tank, sealed to prevent escape of ammonia and carbon dioxide gases. A capacity of 2.0 m^3 has been provided to allow an average retention time of one hour. The tank has a rubber-coated agitator driven by a 2 kW motor, coils for steam heating, and temperature control equipment.

3.9 Filtration of $CaCO_3$ Product

The suspension of calcium carbonate in ammonium chloride-ammonium carbonate solution that overflows from the precipitation tank is pumped to a plate and frame filter. A filtration rate of 100 kg $m^{-2}h^{-1}$ is assumed, giving a requirement of 4 m^2 of filter area.

The product $CaCO_3$ is washed in the filter with fresh water which is then pumped to the leaching tank.

The washed $CaCO_3$ is finally dried using an indirectly gas-fired rotary dryer, (2.7 m long × 0.68 m diameter) having a heated surface of about 6 m^2.

3.10 Crystallisation of NH_4Cl

The filtered supernatant liquor from the $CaCO_3$ precipitation tank is pumped, via the degassing tower to the evaporator/crystalliser, where water is removed by evaporation (and condensed for use in washing of filter cakes). Crystalline NH_4Cl is allowed to drain to minimise the residual content of mother liquor. The mother liquor so separated is discarded as a bleed stream to remove sodium chloride from the system; this of course involves a concurrent loss of NH_4Cl, which requires making up with purchased NH Cl from the ICI plant.

The NH_4Cl (5% moisture), recovered in the crystalliser, is conveyed back to the pugmixer.

3.11 Miscellaneous

Also included in the estimate are the necessary pumps throughout the system

4. CAPITAL COST ESTIMATES

The total capital investment was estimated by the factored method and is based on the total delivered cost of the major items of equipment, multiplied by factors, derived from experience, for all other items.

An equipment schedule, together with estimated purchase costs is given in Appendix B (Table B1). The total capital investment is detailed in Table B2 of Appendix B.

5. PRODUCTION COST ESTIMATES

The total production cost is estimated in Table B3.

6. PROFITABILITY

At the treatment rate of 4000 tpa caustic mud (0.5 tph), 2455 tonnes of calcium carbonate would be produced per year, at an estimated cost of $735 per tonne.

This compares with a delivered price of $400-$600 per tonne for the 2500 tonnes of pure precipitated calcium carbonate imported annually into Australia.

The high production cost by the proposed new process is due principally to high capital investment costs (financial expenses, depreciation and maintenance contributing about 51% of the total costs), and high labour costs (23%) at this very small scale of production.

The calculations of Appendix C show that production costs could be reduced to an estimated $387 per tonne if the plant were scaled up five times. Under these conditions, part of the product might be solid profitably to replace the 2500 tonnes per year of imported material. However, the remaining bulk of the product would have to compete with finely milled pure limestone, whose suppliers could probably afford to cut prices to meet the competition.

Thus at the present level of demand in Australia, this process does not appear to be an economically attractive way to produce precipitated calcium carbonate.

TABLE 1: ASSUMED COMPOSITION OF CAUSTIC MUD FEED

	%
Calcium carbonate, $CaCO_3$	73
Calcium hydroxide, $Ca(OH)_2$	2.5
Sodium hydroxide, NaOH	3.5
Silica, SiO_2	1
Iron oxide, Fe_2O_3	0.25
Magnesium, potassium, aluminium	∿0.5
Moisture	20

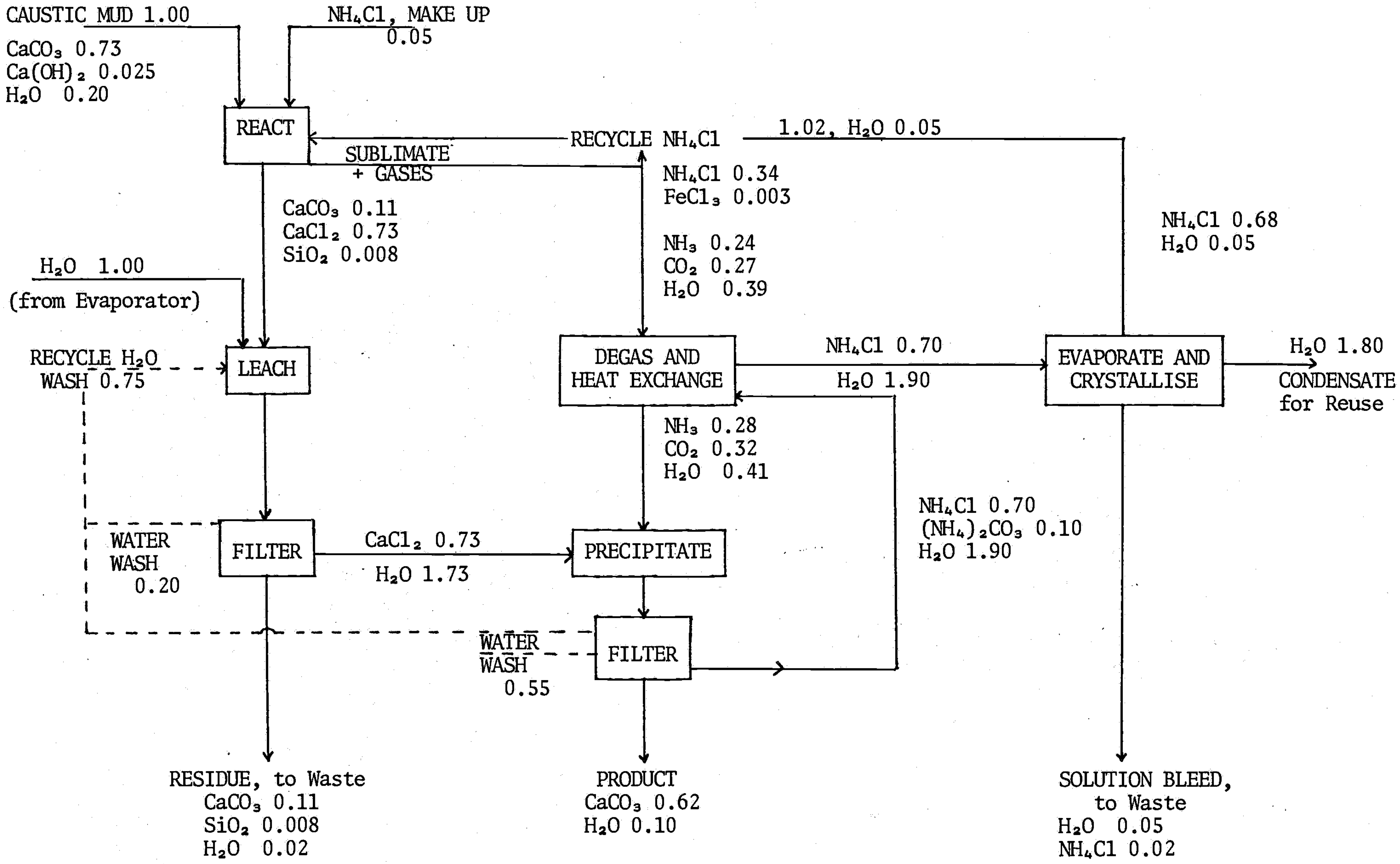


FIG. 1: MASS BALANCE (Basis - 1 tonne Caustic Mud)

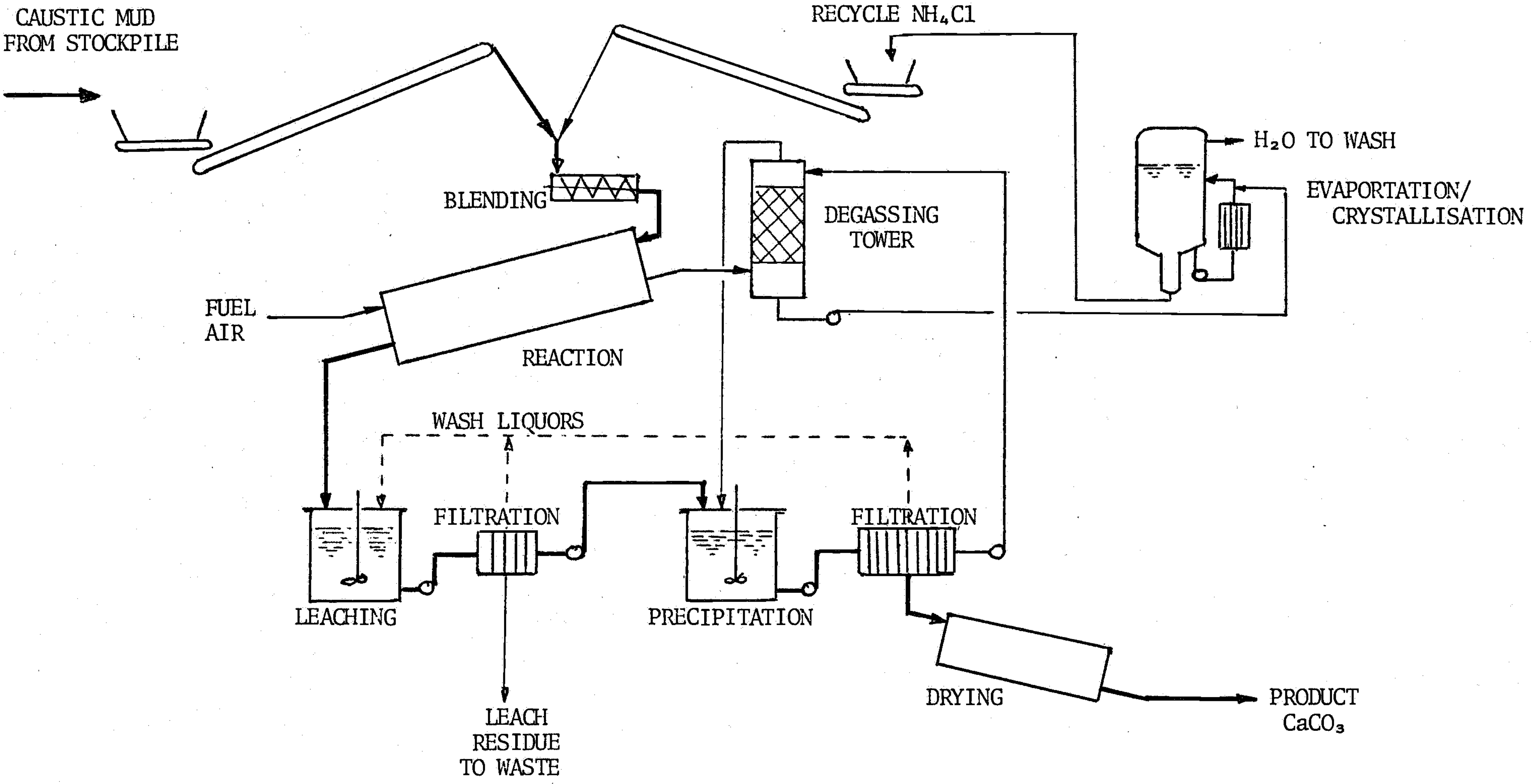


FIG. 2: PROCESS FLOWSHEET

APPENDIX A

PUBLISHED INFORMATION ON CONTROLLED PRECIPITATION OF CALCIUM CARBONATE

(1) ROTHON, R.N., and ASHLEY, R.J. (1982). 'Control of Particle Shape and Size in Calcium Carbonate Precipitation'. Paper, I. Chem. E. Jubilee Symposium, pp G35-G38.

(2) DIEKMANN, H., and ZAPP, K.H. (1963). 'Production of Precipitated Calcium Carbonate'. British Patent 921,077, 13 March.

£2-50

84

CONTROL OF PARTICLE SHAPE AND SIZE IN CALCIUM CARBONATE PRECIPITATION

R N Rothon and R J Ashley*

Precipitated calcium carbonates with a wide range of particle morphologies are prepared and used industrially. The main factors governing product shape and size in one widely used process, the carbonation of calcium hydroxide slurry are briefly discussed.

INTRODUCTION

Well over half a million tons of precipitated calcium carbonates are produced and used annually. Applications include rubber and plastics filling, paper coatings, cosmetics, pharmaceuticals and detergents and call for a wide range of particle morphology as the data in Table 1 shows.

TABLE 1 - Surface Area and Particle Size of some commercial Calcium Carbonates.

Calcium Carbonate	Surface Area m^2/g	Particle Size microns
1	87	0.03
2	20	0.07
3	10	2.5
4	4	8.0

---

* Technical Department, ICI Mond Division, Runcorn.

One of the most widely used industrial processes for producing precipitated calcium carbonates is the carbonation of a calcium hydroxide slurry. Despite its importance little has been written about this reaction, particularly with regard to control of product morphology. This paper outlines the main features of the reaction and shows how they control particle size and shape. The information comes from a combination of the authors' own experiments and a study of the patent literature.

The Carbonation Reaction

The raw materials are generally derived from limestone, the complete sequence of reactions being described by equations 1-3.

$$CaCO_3 \xrightarrow[\text{(kiln)}]{\text{heat}} CaO + CO_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

The final, carbonation reaction in which we are interested is usually carried out batchwise by blowing kiln gas containing up to 40% v/v carbon dioxide through a well agitated aqueous slurry of calcium hydroxide until the latter is completely converted to carbonate. This reaction can be broken down into three stages; nucleation, growth by precipitation and growth by ageing. All these stages play a part in controlling product morphology and are considered in more detail below.

Nucleation

This is the early part of the reaction where fresh product nuclei are being formed due to the supersaturation developed once carbon dioxide starts reacting. This stage determines how many product crystals initially form and how they aggregate and hence plays a major role in determining product morphology.

The low solubility of calcium carbonate is further depressed by the saturated calcium hydroxide solution and hence the reaction is characterised by very high initial supersaturations leading to very large numbers of nuclei, in excess of 10^{15} ml^{-1}, being formed. These nuclei have a pronounced tendency to aggregation but show little tendency to ripen in the saturated calcium hydroxide solution.

We have found temperature to be the most important factor controlling nucleation with the number of nuclei decreasing with increasing temperature. Thus in a series of experiments we found the relative number of nuclei formed at 25, 35 and 50°C to be in the approximate ratio 31:4:1. Temperature also affects the way the nuclei aggregate, they form chains at the lower temperature, cigar shaped aggregates at higher temperatures. Up to 50°C only calcite nuclei are formed, at higher temperatures aragonite is also formed.

Growth by Precipitation

Following nucleation we have a relatively long period where further calcium carbonate is produced by reaction between carbon dioxide and calcium hydroxide but this is deposited onto the existing nuclei rather than forming fresh nuclei. This leads to growth and consolidation of the aggregates formed during nucleation.

The calcium hydroxide concentration is the most important parameter here, the higher this is the longer the growth and consolidation of the aggregates occurs.

Ageing

At the end of the reaction the solution pH falls rapidly as the last of the calcium hydroxide is consumed. Ageing or Ostwald ripening processes which were suppressed at the higher pH's now become very significant. They result in increased crystal size and a reduction in aggregate strength, and the extent to which they are allowed to continue again has a marked effect on product morphology.

Aggregate Strength

The importance of aggregate strength must be emphasised as it controls the effective particle size in any given application. Thus weak aggregates will break down to the primary crystals in many applications and the primary crystal size and shape will be the important ones. One such product is shown in Figure 1, the crystal size being about 0.1 micron. With strong aggregates that don't break down in the end use, it is then the aggregate morphology rather than that of the primary crystal that are important. Two such products are shown in Figures 2 and 3, the spherical aggregates in Figure 3 actually contain crystals much smaller than those in Figure 1 but the effective particle size is much greater.

Conclusions

From the above it can be seen that reaction temperature, calcium hydroxide concentration and ageing processes interact in a complex way to determine product size and shape. The morphology of product aggregates is also often as important as that of the primary crystals.

It is only by understanding and using these parameters to the full that manufacturers are able to produce such a wide range of precipitated calcium carbonates.

Figure 1 Well dispersed crystals
42,000 X

Figure 2 Strong, spiky aggregates
5,000 X

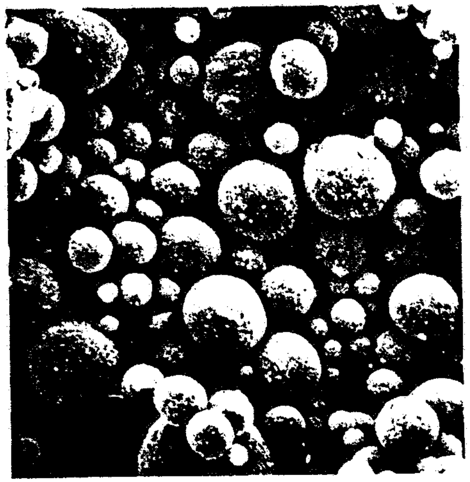


Figure 3 Strong, smooth aggregates
1,000 X

PRODUCTION OF PRECIPITATED CALCIUM CARBONATE

We, BADISCHE ANILIN- & SODA-FABRIN AKTIENGESELLSCHAFT, a German Joint Stock Company, of Ludwigshafen/Rhine, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:-

This invention relates to a process for the production of finely divided calcium carbonate. More particularly, the invention relates to the production of finely divided, substantially pure calcium carbonate from aqueous calcium salt solutions by precipitation with carbonates.

In the paper and dye industries, in the pharmeceutical and cosmetics industries and also in the rubber industry, precipitated calcium carbonate is used which should be as finely divided as possible. It is known to produce calcium carbonate of this kind by reacting calcium salt solutions with ammonium or alkali metal carbonate solutions in the presence of additives which are added to the reaction mixture during or after the reaction to prevent formation of large crystals or agglomeration of the finely divided $CaCO_3$ primarily formed. In the known process it is preferred to use as additives surface-active substances, for example organic sulfonates, alkyl amines or aryl amines and derivatives of higher fatty acids. It is known to use, as additives, complex-forming substances, for example salts of polybasic organic hydroxyacids, such as citrates or tartrates, or the so-called condensed phosphates, such as sodium tripolyphosphate or sodium hexametaphosphate. The considerable amounts of the substances used - about 20 parts of additive to 100 parts of calcium carbonate - may be reduced in known manner by the addition of a soluble fluoride or silicofluoride by up to half the amount necessary without the addition of a soluble fluoride or silicofluoride. These processes have the disadvantage that both the calcium carbonate and also the solution of alkali metal or ammonium slats which are formed simultaneously are heavily contaminated by the additives. The latter interfere especially wtih the processing of these alkali metal or ammonium salt solutions.

It is an object of the present invention to provide a process for the production of finely divided calcium carbonate. Another object of the invention is to provide a process for the production of finely divided calcium carbonate which is substantially free from impurities. A further object of the invention is to provide a process for the production of finely divided calcium carbonate which when dispersed in water has a low settling velocity. These objects are achieved by precipitating calcium carbonate in the presence of a water soluble fluoride as the sole active substance for producing the fine division. Even very small amounts of such fluorine compounds are sufficient for producing a finely divided $CaCO_3$. Calcium carbonate prepared with small amounts of water-soluble fluorine compounds contains less than 0.1% F and the ammonium or alkali metal salt solution which is formed simutaneously contains no detectable amounts of fluorine. By the process according to the present invention, therefore, the calcium carbonate and the ammonium or alkali metal salt solutions are obtained in high purity. The process may be carried out batch-wise or continuously. When carrying out the process continuously, the reaction components are preferably introduced into a reaction vessel provided with an overflow or into a mixing nozzle.

The present invention is limited to the sole addition of the said fluorine compounds as substances producing the fine division. Ad-mixture of substances inert in this respect, for example alkali metal or ammonium salts other than fluorides is possible.

Suitable fluorides include such water-soluble fluorides as potassium fluoride, sodium fluoride or ammonium fluoride.

The content of fluoride in the solution used for precipitation may be varied within wide limits. We prefer to apply from 0.05 to 5 parts by weight of fluoride per 100 parts by weight of carbonate. Only a slight contamination of the precepitated calcium carbonate occurs by using small amounts of fluoride (0.05% by weight) but the precipitated calcium carbonate is not so finely divided as when using larger amounts of fluoride. A very finely divided calcium carbonate is produced by using about 5% by weight of fluoride, but the fluoride content of the calcium carbonate increases above 0.1%. In no case can fluoride be detected in the filtrate which is separated after precipitation of the calcium carbonate.

By calcium salt solutions we understand aqueous solutions of calcium salts, for example calcium nitrate or calcium chloride. By carbonates we understand ammonium carbonate sodium carbonate and potassium carbonate.

Application of definite temperatures, speeds of stirring or pH-values during the reaction is unnecessary. Filtration of the $CaCO_3$ produced in accordance with this invention may be carried out a long time after the reaction without trouble.

The fine division of the $CaCO_3$ prepared according to this process is especially apparent from the high settling volume of a suspension in water. Whereas $CaCO_3$ which has been precipitated without the addition of fluorine compounds, in a suspension of 100 cm^3 has a settling volume of 50 to 60 cm^3/10 g of $CaCO_3$ after 2 hours, $CaCO_3$ which was precipitated under otherwise similar conditions after an addition of a potassium fluoride solution has, after suspension to 100 cm^3, a settling volume of 95 to 99 cm^3/10 g $CaCO_3$.

The invention is illustrated by, but not limited to, the following example.

EXAMPLE

Calcium carbonate is precipitated from a five per cent aqueous calcium chloride solution by the introduction with stirring of an approximately equivalent volume of a forty per cent aqueous ammonium carbonate solution which contains 0.2% of potassium fluoride. The ammonium carbonate solution contains 0.5 part by weight of potassium fluoride per 100 parts by weight ammonium carbonate. A stiff, creamy reaction mixture is formed by the precipitation. When precipitation is complete, the mixture is stirred for two more minutes and then filtered. The calcium carbonate produced in this way has a particle size of 0.1 µm and contains 0.09% F. The filtrate is free from fluorine. The settling volume of a suspension of 10 grams of the calcium carbonate thus obtained in 100 cm^3 of water is 99 cm^3 after 2 hours. No further sedimentation is observed within the subsequent 24 hours.

If a five per cent solution of calcium chloride is precipitated in known manner by additon of a soda solution which contains 10 parts by weight of alkali metal polyphosphate and 3 parts by weight of sodium silicofluoride to 100 parts by weight of soda, under otherwise similar conditions as described in the above experiment, a finely divided calcium carbonate is also obtained. The reaction mixture, however, precipitate and solution) contains 13 parts by weight of impurities to 100 parts by weight of precipitating agent, compared with only 0.5 part when working in accordance with the process of the present invention.

WHAT WE CLAIM IS:-

1. A process for the production of finely divided precipitated calcium carbonate by the reaction of calcium salt solutions with solutions

89

of carbonates in the presence of a water-soluble fluoride as the sole active substance for producing the fine division.

2. A process according to Claim 1 wherein 0.5 to 5 parts by weight of fluoride are used per 100 parts by weight of carbonate.

3. A process according to Claim 1 or 2 wherein sodium fluoride potassium fluoride or ammonium fluoride is used as the fluoride.

4. A process for the production of finely divided, precipitated calcium carbonate substantially as described in the foregoing example.

5. Finely divided, precipitated calcium carbonate when obtained by the process claimed in any one of Claims 1 to 4.

J.Y. & G.W. JOHNSON

Furnival House, 14 - 18, High Holborn,
LONDON, W.C.1

Chartered Patent Agents,
Agents for the Applicants.

APPENDIX B

DETAILS OF PROCESS COST ESTIMATES

TABLE B1: EQUIPMENT SCHEDULE AND ESTIMATED PURCHASE COST OF MAJOR ITEMS

Item	Description	Power kW	Purchase Cost $
1	Conveyor, caustic mud to weigh feeder, 0.5 tph, 200 mm × 25 m × 5 m lift	1.5	14,000
2	Conveyor, NH_4Cl to weigh feeder, 0.5 tph, 200 mm × 25 m × 5 m lift	1.5	14,000
3	Weigh feeders, 2 off plus bins	1	15,000
4	Pugmixer, 0.5 tonne capacity, rubber-lined	3	10,500
5	Reactor - rotary kiln, 16 m long × 1.5 m dia., internally gas-fired, lined with acid-resistant bricks	12	312,000
6	Leaching tank, 1.5 m^3, rubber-lined, with agitator, turbine, rubber coated	- 1.5	2,600 7,700
7	Leach pulp pump, 1 m^3/h	2	2,000
8	Leach residue filter, 1 m^3, rubber-lined with liquor storage tank	-	7,600
9	$CaCl_2$ filtrate pump, 1 m^3/h	2	2,000
10	Precipitation tank, 2.0 m^3, rubber-lined, closed, with agitator, turbine, rubber-coated	- 2	3,100 8,900
11	$CaCO_3$ suspension pump 1.5 m^3/h	2	2,000
12	Product filter 4 m^3 rubber-lined with liquor storage tank	-	17,000
13	$(NH_4)_2CO_3/NH_4Cl$ filtrate pump, 1.5 m^3/h	2	2,000
14	Degassing tower, 2 m^3 capacity, conical bottom	-	5,500
15	Evaporator/crystalliser	-	160,000
16	$CaCO_3$ product dryer, heating surface, 6 m^2	-	28,000
	Total	31	613,900
	Delivery cost, major items		61,400
	Delivered cost		675,000

Estimated Delivered Cost = $\$6.75 \times 10^5$

Estimated Power installed = 31 kW

In addition, for handling of caustic mud and $CaCO_3$ product, require

2 × 0.5 tonne capacity front end loader	38,400

i.e. additional capital cost for transport = $38,400

TABLE B2: TOTAL CAPITAL INVESTMENT ESTIMATE

		$\$10^3$
1.	Purchased equipment, delivered	675
2.	Installation, 30% of (1)	203
3.	Instrumentation, 15% of (1)	101
4.	Piping, 35% of (1)	236
5.	Electrical, 15% of (1)	101
6.	Buildings, 20% of (1)	135
7.	Foundations and structures, 20% of (1)	135
8.	Land and yard improvements, 10% of (1)	68
9.	Utilities, 25% of (1)	169
	Total Direct Cost	1,823
10.	Engineering, construction and contractors' fees 25% of direct cost	456
11.	Contingency, 30% of direct cost	547
12.	Additional capital for transport	38
	Fixed Capital Investment	2,864
13.	Working capital, 3 months' operating costs	278
	Total Capital Investment	3,142

TABLE B3: TOTAL PRODUCTION COST ESTIMATE

		Cost $/annum
1.	Raw Materials	
	Caustic mud, 4000 t/a at zero cost	-
	NH_4Cl, make-up, 80 t/a at $470 per tonne	37,600
	NH_3, make-up, 80 t/a at $1146 per tonne	91,700
2.	Utilities	
	Power: 31 kW	49,100
	31 × 24 × 330 × $0.20/kWh	
	Gas: 4.06 GJ/h at $6.00/GJ	193,250
3.	Direct Labour, 2 men per shift, 4 shifts	256,000
	8 men at $32,000	
4.	Supervision, 4 shift supervisors at $40,000	160,000
5.	Maintenance	
	Materials and labour, 8% of fixed capital investment	229,100
6.	Operating Supplies	10,000
7.	Depreciation	
	10% of fixed capital	286,400
8.	Property Taxes and Insurance	
	1% of fixed capital	28,640
9.	Product Distribution Cost	
	$15/tonne	36,800
10.	Research and Development Cost	50,000
11.	Financial Expenses	
	12% of total capital investment	377,000
TOTAL PRODUCTION COSTS		1,805,600

APPENDIX C

CHANGES TO COST ESTIMATE FOR 20,000 TPA TREATMENT RATE

TABLE C1: CHANGES TO EQUIPMENT PURCHASE COSTS

Item	Description	Additional Cost, $	Additional kW
1,2	Conveyors, same size, 2.5 kW each	-	1
3	Weigh feeders, same size, 3 kW total	-	2
4	Pugmixer, 2.5 tonne cap., $29,500, 10 kW	19,000	7
5	Reactor, 100 tpd, 2.45 m × 24 m, $733,000, 35 kW	421,000	23
6	Leaching tank, 7.5 m^3, $10,000	7,400	-
	+ Agitator, $16,300, 5 kW	8,600	4
7	Leach pulp pump, 5 m^3/h, $3000, 4 kW	1,000	2
8	Leach residue filter, 5 m^3, $11,400	3,800	-
9	$CaCl_2$ filtrate pump, 5 m^3/h, $3000, 4 kW	1,000	2
10	Precipitation tank, 10 m^3, $14,300	11,200	-
	+ Agitator, $15,000, 6 kW	6,100	4
11	$CaCO_3$ suspension pump, 7.5 m^3/h, $3000, 4 kW	1,000	2
12	Product filters, 2 × 10 m^3, $39,000	22,000	-
13	$(NH_4)_2CO_3/NH_4Cl$ filtrate pump, 7.5 m^3/h, $3000, 4 kW	1,000	2
14	Degassing tower, 10^3 cap. $25,200	19,700	-
15	Evaporator/crystalliser, $450,000	290,000	-
16	$CaCO_3$ product dryer, 17 m^2 heating area, $56,000	28,000	-
	TOTAL ADDITIONAL	840,800	49
	FOR 4000 tpa plant	613,900	31
	TOTAL	1,454,700	80
	Delivery Cost	145,500	
	Total Delivered Cost	1,600,200	

Estimated Delivered Cost $\$1.600 \times 10^6$

Estimated Power Installed 80 kW

2 × 1 tonne capacity front end loaders = $126,800

TABLE C2: TOTAL CAPITAL INVESTMENT ESTIMATE, 20,000 TPA TREATMENT RATE

		$\$10^3$
1.	Purchased equipment, delivered	1,600
2.	Installation, 30% of (1)	480
3.	Instrumentation, 15% of (1)	240
4.	Piping, 35% of (1)	560
5.	Electrical, 15% of (1)	240
6.	Buildings, 20% of (1)	320
7.	Foundations and structures, 20% of (1)	320
8.	Land and yard improvements, 10% of (1)	160
9.	Utilities, 25% of (1)	400
	Total Direct Cost	4,320
10.	Engineering, construction and contractors' fees, 25% of direct cost	1,080
11.	Contingency, 30% of direct cost	1,296
12.	Additional capital for transport	127
	Fixed Capital Investment	6,823
13.	Working capital, 3 months' operating costs	771
	Total Capital Investment	7,594

TABLE C3: TOTAL PRODUCTION COST ESTIMATE, 20,000 TPA TREATMENT RATE

		Cost, \$/year
1.	Raw Materials	
	Caustic mud, 20,000 tpa at zero cost	-
	NH_4Cl, make-up	188,000
	NH_3, make-up	458,500
2.	Utilities	
	Power, 80 kW	126,800
	Gas, 20.3 GJ/h at \$6.00/GJ	966,250
3.	Direct Labour, as previously	256,000
4.	Supervision, as previously	160,000
5.	Maintenance, 8% of fixed capital investment	545,800
6.	Operating Supplies	50,000
7.	Depreciation, 10% of fixed capital	682,300
8.	Property Taxes and Insurance, 1% of fixed capital	68,200
9.	Product Distribution Cost, \$15 per tonne	184,000
10.	Research and Development Cost	150,000
11.	Financial Expenses, 12% of total capital	911,300
	TOTAL PRODUCTION COSTS	4,747,000