

THE CHEMICAL REMOVAL OF SULPHATES USING BARIUM SALTS

DECLARATION OF CANDIDATE

I, the undersigned, declare that the work submitted herein for the degree of Master of Science in Engineering, is my own work and has not been submitted for a degree or other qualification to any other university or institution.

by

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A thesis submitted in partial fulfilment of the requirements of the
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G.E. Trusler

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ABSTRACT

The increasing level of dissolved solids in the water of the Vaal Barrage is having dire economic consequences. Sources of saline effluent have been identified in the Vaal River drainage region and their effect quantified; it was discovered that four mines contribute 38% of the total salt load, mainly in the form of sulphates.

In this study desalination of such effluents with barium carbonate and lime has been investigated. The advantages of using these chemicals are low toxicity, efficient sulphur removal and ease of reuse.

Recycle of barium is achieved by reduction of barium sulphate with coal to barium sulphide which is extracted by leaching with water. The leach liquor is then reacted with carbon dioxide to regenerate barium carbonate and produce hydrogen sulphide for conversion to sulphur.

The reaction kinetics of barium carbonate with aqueous calcium, magnesium and sodium sulphates are given. The magnesium and sodium sulphate systems require calcium hydroxide addition to ensure complete sulphate removal. Calcium carbonate seed crystals increase reaction rates.

Barium sulphate/calcium carbonate mixtures were reduced and it was found that reaction rates increase with temperature but that sintering occurs at 1 200°C. Calcium enhances the water soluble portion of the barium sulphide melt by reacting with silicates. Solid phase products were predicted using a thermodynamic computer algorithm and were identified by X-ray techniques.

Reacting barium carbonate with a typical mine effluent stream produced the following results (units in mg/l): the TDS was reduced from 3 750 to 905, SO_4 from 2 300 to 350, Fe from 60 to 0, Mg from 140 to 74, Ca from 560 to 10 and the pH was raised from 3,6 to 9,1. The addition of lime ensured complete SO_4 , Mg and Ca removal and raised the pH to 11,6.

The chemistry of the overall process has been shown to be feasible. The raw materials (coal and barium sulphate) are abundant in South Africa while the products (water and sulphur) are in demand. Implementation of the process will decrease the total dissolved solids in the Vaal Barrage, benefiting all water consumers in the Vaal Basin.

NOTATION

Abbreviations

AA	-	Atomic Absorption
ADA	-	Anthroquinone Disulphonic Acid
DRD	-	Durban Roodepoort Deep Mine
DWA	-	Department of Water Affairs
EPA	-	USA Environmental Protection Agency
ERGO	-	East Rand Gold Operations
ERPM	-	East Rand Proprietary Mines
HDS	-	High Density Slurry
IX	-	Ion Exchange
PSA	-	Pressure Swing Absorption
PWVS	-	Pretoria-Witwatersrand-Vereeniging-Sasolburg
RWB	-	Rand Water Board
Sallies	-	South African Land Exploration Company
SS	-	Suspended Solids
SSRO	-	Seeded Slurry Reverse Osmosis
TDS	-	Total Dissolved Solids
XRD	-	X-Ray Diffractometry

Nomenclature

abiotic	-	in the absence of life
aerobic	-	in the presence of free oxygen
anaerobic	-	in the absence of free oxygen
aragonite	-	orthorhombic calcium carbonate
barytes	-	natural barium sulphate
calcite	-	rhombahedral calcium carbonate
vaterite	-	spherulitic calcium carbonate

Subscripts

s	-	solid
aq	-	aqueous complex
T	-	total species concentration in any form

Superscript

°	-	uncharged complex
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Symbols

[]	-	concentration of the enclosed species
K_G	-	growth rate constant
f_D	-	activity coefficient for divalent ions
K_{sp}	-	solubility product
t	-	time
T	-	temperature
↓	-	precipitate

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1 INTRODUCTION

South Africa is a relatively arid country with an average rainfall of 497 mm compared to a world average of 860 mm. The rainfall is uneven and about one third of the country receives an annual rainfall of less than 300 mm. It is estimated that South Africa's exploitable surface runoff is 33 000 million m³/annum. Present usage is about 18 000 million m³/annum and demand is rising rapidly (Dept. Water Affairs, 1986).

At present there are regional water imbalances between supply and demand. The Pretoria-Witwatersrand-Vereeniging-Sasolburg (PWVS) complex is the most notable as it relies heavily on imported water resources to meet its consumption. Additional water resources are imported from neighbouring catchments such as the Orange, Tugela, Usutu and Komati. Construction on the Lesotho Highlands Water Scheme is progressing rapidly to provide additional water.

The Vaal catchment produces 8% of the mean annual runoff in the country but has the highest concentration of urban, industrial, mining and power generation development in South Africa. In 1980 it contributed 59% of the gross national product, is home to some 5,8 million people and is the focal point for much of South Africa's future development (Braune and Rogers, 1987).

This pressure on rivers, streams and impoundments leads to water being recycled on macroscale. One third of the water reticulated has been used before in the same basin. In the southern PWVS region 64% of supplied water is returned in the form of effluent. As a result the total dissolved solids (TDS) level of most streams in the catchment is rising steadily.

At the Rand Water Board's (RWB) Vereeniging intake, the average TDS rose from 135 to 220 during the period 1935 to 1962 i.e. 3 mg/ℓ/year. By 1979 the TDS had risen to 660 mg/ℓ which is a rise of 26 mg/ℓ/year from 1962 to 1979. Forecasts indicate that unless some action is taken the TDS in the Vaal Barrage could be 1 000 mg/ℓ by the end of 1990 (Heynike and McCulloch, 1982).

The recommended limits for TDS in drinking water is set out in SABS Specification 241-1984 as 455 mg/ℓ. The maximum allowable limit suitable for domestic use in extreme circumstances is 1950 mg/ℓ (Dept. Water Affairs, 1986).

This increasing level of mineral salt content progressively limits the number of cycles of industrial reuse and industries require a larger quantity of water to keep discharge TDS at acceptable levels. More irrigation water is required to counteract the deleterious effects of salt on the soil. This increasing consumption leads to suppliers like the RWB enlarging their water treatment facilities and local authorities having to increase their storage capacity to maintain a 36 hour retention volume. Higher salt levels promote corrosion, encourage scaling in boilers and heat exchangers and serve as a substrate for organisms implicated in biocorrosion.

Heynike (1987) assumed a TDS level in the Vaal Barrage of 300 mg/ℓ and calculated the total additional cost if this level should rise to 800 mg/ℓ to be 252,7 million Rand (1983) per annum.

Conventional water treatment processes remove organic but not mineral pollutants hence salt addition to the Vaal River is now seen as an incremental load. The Vaal River is not a salt sink because in the context of an integrated water system the water and consequently the TDS is recycled.

A large proportion of the salt influent is in the form of sulphates and chlorides of calcium and magnesium and, to a lesser extent, bicarbonates. Mineral pollution can only be reduced by costly demineralisation processes.

High quality water for dilution is available in limited quantities from neighbouring catchments. The dilution effect is a temporary measure because in the long term there is a general water shortage in the subcontinent.

It is thus imperative to decrease salt addition to the Vaal River. Minewater pumpage contributes only 5% of the flow but accounts for 25% of the salt load in the Vaal catchment. This thesis examines the nature and sources of mineral effluents and then proposes and develops a suitable treatment process which is simple and unsophisticated. It is proposed to use barium carbonate to treat high sulphate mine effluents. The barium is recycled and the sulphur is collected in the form of hydrogen sulphide.

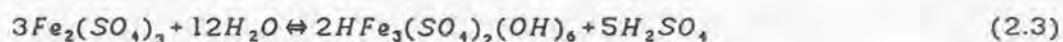
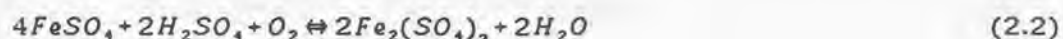
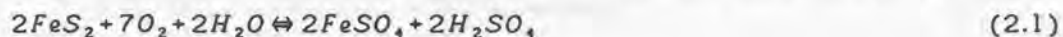
2 ORIGIN AND NATURE OF SULPHATE EFFLUENTS

2.1 Chemical Origins of Sulphates in Effluents

South Africa's two largest mining sectors, namely gold and coal, extract ores containing substantial quantities of pyrite. Coal seams often contain up to 2,5% sulphur.

The ore in the Durban Roodepoort Deep (DRD) gold mine contains up to 3,2% sulphur and East Rand Proprietary Mines (EPRM) 1,7% sulphur.

Acid mine water occurs wherever pyritic formations come into contact with air and water. The reactions occurring are given by Ivarson, Ross and Miles (1987) as:



Reactions (2.1) and (2.2) are oxidation reactions which require aerobic conditions while reaction (2.3), which produces the most acid, can occur in anaerobic conditions but relies on (2.1) and (2.2) to produce ferric and sulphate ions.

Below a pH value of about 4 the chemical oxidation of ferrous sulphate is very slow and is normally catalysed by the bacterium Thiobacillus Ferrooxidans.

Stumm and Morgan (1970) agree with reactions (2.1) and (2.2) but give an alternative acid producing reaction as:

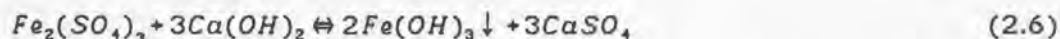


At a pH of less than 3 the increased solubility of iron results in an abiotic increased rate of oxidation of pyrite by ferric ions.

This oxidation takes place both underground and on mine dumps.

Before neutralisation, minewater typically contains 6 800 mg/l TDS. This is neutralised using lime which raises the pH to around 8,0. In addition the TDS is reduced to 3 600 mg/l. Lime is an inexpensive and effective alkali and also serves a TDS reductant.

The liming process is represented by the following reactions:



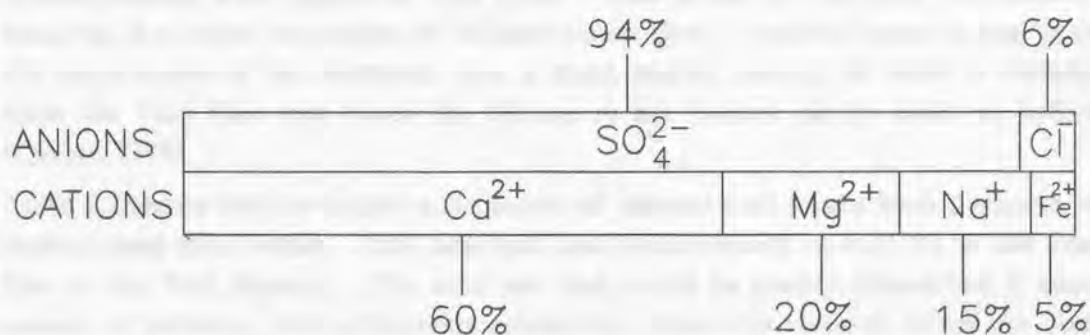
The reactions for ferrous sulphate and aluminium sulphate, if present, are similar to that for ferric sulphate in (2.6).

At ERPM 64 000 m³/d of mineralised effluent is partially neutralised underground and then pumped to the surface where it is treated by high density slurry (HDS) neutralisation and discharged to the Vaal River downstream of the Vaal Dam.

A typical effluent analysis from ERPM after liming is given in Table 2.1 and graphically presented in Figure 2.1.

TABLE 2.1 : A Typical Analysis of an ERPM Discharge (Funke, 1987)

SO ₄ ²⁻	(mg/l)	2 400
Cl ⁻	(mg/l)	120
Na ⁺	(mg/l)	180
K ⁺	(mg/l)	16
Ca ²⁺	(mg/l)	636
Mg ²⁺	(mg/l)	130
Fe ²⁺	(mg/l)	80
TDS	(mg/l)	3 562
pH		8.0

**FIGURE 2.1 : Anionic and Cationic Equivalents of a Typical ERPM Discharge**

Liming thus ameliorates but does not solve the problem as the product waters are saturated with the sparingly soluble calcium sulphate. Calcium sulphate has a negative temperature coefficient of solubility thus tending to form scale on pipes and fouling hydraulic equipment. It is therefore unsuitable for inhouse process water and is pumped into the river system adding to the salt load.

Some industries, such as the pulp and paper factories, discharge sulphate-rich effluent resulting from spent sulphuric acid. ERGO effluent contains calcium sulphate formed in the flotation plant during pH adjustment with sulphuric acid, for an acid medium float, and subsequent neutralisation with lime.

2.2 Sources of Sulphate Effluents

Hydrological surveys undertaken by the Department of Water Affairs indicate that the major problem areas lie in the Northern and Mid-West Middle Vaal and the Northern Upper Vaal where the Waterval, Molspruit, Klip and Suikerbosrand are highly polluted rivers (van Vliet and Nell, 1986). These rivers are subject to influences by diffuse and point sources. The RWB draws about one third of its supply from the Vaal Dam and about two thirds from the highly mineralised Vaal Barrage hence the mineral content of the Barrage has a major effect on the quality of water in the distribution systems (Braune and Rogers, 1987).

The water quality of the Vaal Dam is relatively stable while the Barrage water quality is deteriorating with respect to TDS level. This is due to increased consumption resulting in a higher proportion of effluent return flow. Another reason is that since the construction of the Bloemhof Dam a much smaller amount of water is released from the Vaal Dam and hence the Barrage is not flushed out as much as before (Laburn, 1979).

Table 2.2 shows that the largest point source of mineral load results from pumpage of underground mine water. This large salt load is contributed in only 5% of the total flow to the Vaal Barrage. The total salt load would be greatly diminished if these sources of pollution were effectively eliminated, hence this research effort has been concentrated on removing the contribution by these sources.

A large portion of the diffuse salt load results from drainage of sand and slime dumps. They are estimated to cover 80 km² on the Witwatersrand. Braun (1981) estimated that each of the 30 large sand dumps around the Witwatersrand could produce 7 000 tons of sulphuric acid per year. Slimes dams, because of the finer nature of the tailings contained in them, are less porous and consequently seepage and leaching is significantly less.

Slimes dam acidification occurs to a depth of 2 m from the surface, with a zone of maximum acidity at about 0,3 m at which point pH values of 1,5 may be encountered. Oxidation can only occur during the limited periods of exposure between the application of new layers of slime. The downward movement of water due to seepage is slow and thus the chemical pollution potential of slimes dams is low. Numerous surveys have shown that "inactive" slimes dams have a negligible contribution to the flow and pollution load of the Klip River system. (Funke, 1987).

From Table 2.3 it can be seen that the Klip River is the largest single contributor to the pollution load of the Vaal Barrage. The relative contributions to the highly mineralised character of the Klip River are given in Table 2.4. With the future expansion of mining operations it can be assumed that their contribution to the pollution load will increase.

Major point sources of salt load and their individual contributions are presented in Table 2.5. Characterisation of the major effluents revealed the analyses which are presented in Table 2.6.

TABLE 2.2 : Salt Mass Discharged into the Vaal Barrage (August 1977 to August 1978) (Stewart, *et. al.*, 1979)

Source of salt mass	Annual salt mass		Relative Volume Flows
	(ton/a)	(%)	(%)
Point sources:			
Mine pumpage	137 400	25	4,5
Municipal sewage	77 000	14	24,0
Industrial (direct discharge)	17 500	3	4,5
Total	232 300	42	33,0
Diffuse sources	<u>315 000</u>	<u>58</u>	<u>67,0</u>
Combined total	547 300	100	100,0

TABLE 2.3 : Total Flow and Load Contribution into the Vaal Barrage, 1982/1983 (Funke, 1987)

River	Metering Station (Fig. 2.2)	Daily flow		TDS		Sulphate	
		Ml /d	%	tons/d	%	tons/d	%
Engelbrecht's Drift	V2 (1)	606 000	74,4	117 441	40,5	10 390	12,5
Suikersbosrand River	S2 (2)	4 900	0,6	5 800	2,0	1 995	2,4
Klip River	C2M21 (3)	199 000	24,0	159 198	54,9	66 911	80,5
Rietspruit Lochvaal	RV2 (4)	6 500	0,8	7 540	2,6	3 740	4,5
Taaibosspruit	T1 (5)	1 100	0,1	150	-	60	0,1
	TOTAL	817 500	100	290 129	100	83 096	100
Vaal River	Lindeque's Drift V18	167 926		15 127		44 210	

TABLE 2.4 : Klip River: Point Source Contribution of Flow, TDS and SO₄
(Funke, 1987)

Point Sources	Mℓ/a	TDS tons/a	SO ₄ tons/a
ERPM HDS Plant	8 928	36 482	18 516
ERPM ex Hercules Shaft	6 222 15 150	18 431	10 128
ERGO Complex	7 290	25 360	15 488
ERGO Tailing Dam	4 379 11 669	16 021	9 388 Natal Spruit/
* Rondebult	12 794	11 109	1 918** Riet Spruit
* Dekama (-15% to irrigation)	10 996	6 317	1 499**
* Vlakplaas	14 600	11 884	2 190
* Waterval	9 512	6 317	1 499**
* Klip Spruit	100% to irrigation		
* Goudkoppies	41 975	25 185	6 716
* Olifantsvlei	54 750	25 460	6 570
ex Orlando Power sta.	3 650	2 665	1 022
Durban Deep	4 140	13 786	8 694
TOTAL	179 236	199 017	83 628
C2M21A	199 000	159 198	66 911

* Sewage works.

** The SO₄ load for Germiston Sewage Works was based on an assumed SO₄ concentration of 155 mg/ℓ, equivalent to that for the Johannesburg and Benoni Works.

TABLE 2.5 : Percentage Contribution of Point Sources to the Klip River
(Funke, 1987)

	Flow	TDS load	SO ₄ load
ERPM	8,5%	27,6%	34,3%
ERGO	6,5%	20,8%	29,7%
Durban Deep	2,3%	6,9%	10,4%
All Sewage Works	82,7%	44,7%	25,6%

TABLE 2.6 : Analytical Data of Centralised Mine Effluents
(Funke, 1987)

	Grootvlei into Blesbokspruit	Sallies/ERGO into Rietspruit	ERPM ex HDS plant into Elsburgspruit	Roodepoort Durban Deep into Klip River
pH	7,9	6,6 - 7,5	6,4 - 8,1	4,7 - 10,0
Cond (mS/m)	240	310 - 350	400 - 460	160 - 310
TDS (mg/l)	1 840	2 900 - 3 300	3 800 - 4 350	1 500 - 2 900
SO ₄ (mg/l)	900	1 780 - 2 880	1 750 - 3 000	1 000 - 2 280
Cl (mg/l)	165	180 - 245	100 - 140	35 - 75
Na (mg/l)	170	200 - 300	140 - 220	60 - 130
K (mg/l)	9	38 - 64	13 - 20	6
Ca (mg/l)	400	520 - 600	520 - 680	400 - 800
Mg (mg/l)	160	140 - 200	50 - 170	40 - 140
Cu (mg/l)	-	-	0,1 - 0,3	0,1 - 0,8
Fe (mg/l)	4	0,1 - 0,8	3 - 120	5 - 105
Mn (mg/l)	5	0,1 - 1,0	1 - 13	3 - 15
Ni (mg/l)	0,7	0,2 - 3,3	0,5 - 4,8	1,3 - 6,2
Al (mg/l)	2,6	0,1 - 0,2	0,3 - 39	2,3 - 48

TABLE 2.7 : Pollution from Active Mines in the Vaal Barrage Area
(Funke, 1987)

Mine	Receiving River	Flow Ml/a	TDS ton/a	SO ₄ ton/a
Grootvlei	Blesbokspruit	4 000	6 800	2 600
Wit Nigel	Blesbokspruit	no effluent		
Manievale	Blesbokspruit	no effluent		
Modderfontein B	Blesbokspruit	no effluent		
Modderfontein 74	Blesbokspruit/ Benoni Canal	no effluent		
ERPM ex SW Shaft/ HDS Plant	Elsburgspruit	9 000	36 500	18 500
ERPM ex Hercules Shaft	Cinderella Dam/ Elsburgspruit	6 200	18 400	10 100
Durban Roodepoort Deep	Klip River	4 100	13 800	8 700
Western Areas	Rietspruit/ Lochvaal	57 000	74 100	39 600

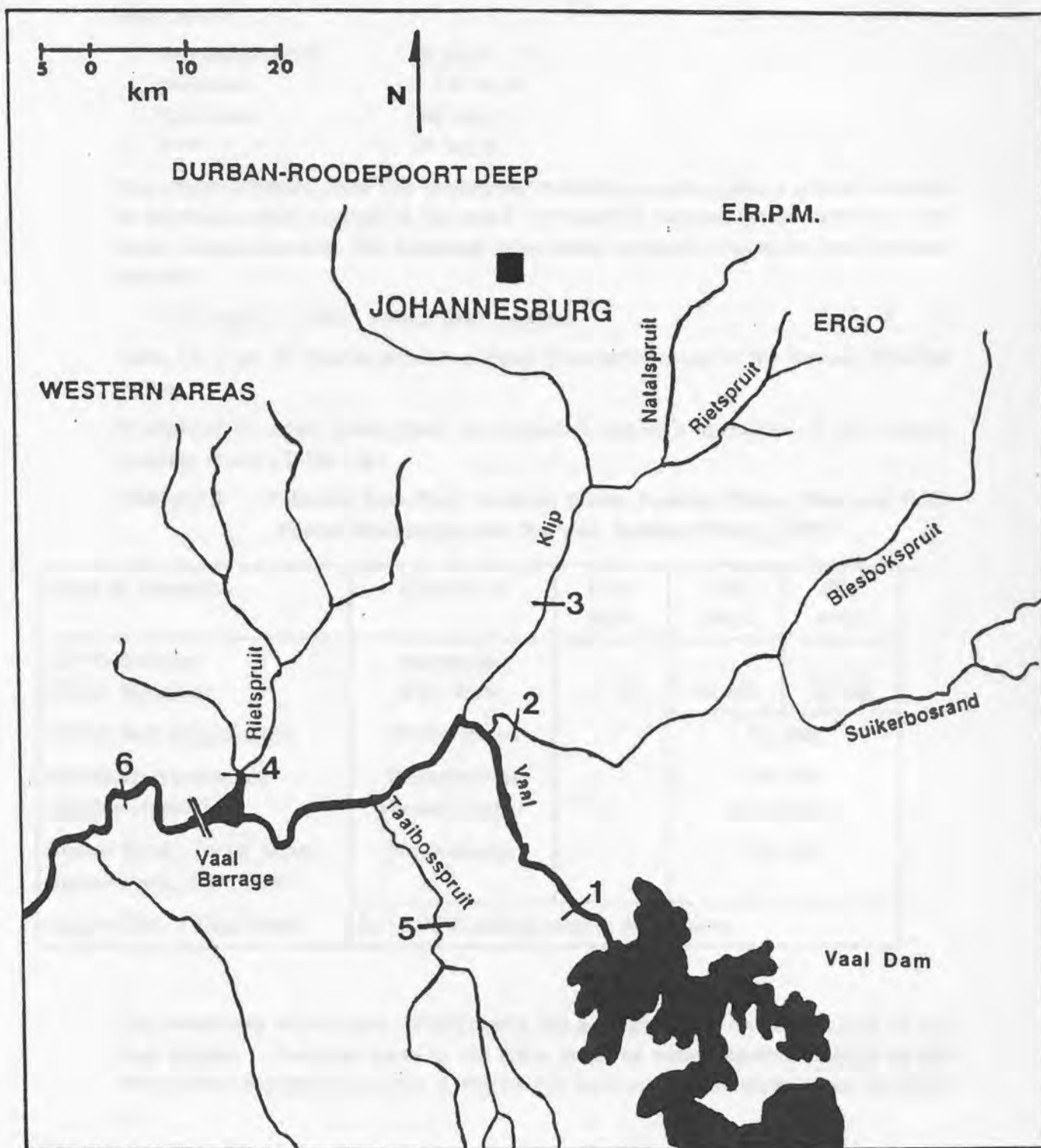


FIGURE 2.2 : Map of the Vaal Drainage Region

Continuous on line monitoring of mining effluents will produce more representative results than those obtained by analysing grab samples. White (1986) developed the necessary equipment and analysed the water quality at DRD producing the following mean results:

Suspended solids	70 mg/ℓ
Sulphates	2 700 mg/ℓ
Chlorides	100 mg/ℓ
Fe ²⁺	20 mg/ℓ

The results obtained from this continuous monitoring showed that a sudden increase in suspended solids resulted in decreased TDS possibly because the particles provided nuclei for precipitation. The following relationship between conductivity and TDS was deduced:

$$\text{TDS (mg/ℓ)} = 0.88 * \text{conductance (μS/cm)}$$

Table 2.7 gives all possible effluent streams from active mines in the Barrage drainage region.

In addition to active mines there are numerous recovery operations in the Barrage drainage region (Table 2.8.).

TABLE 2.8 : Pollution from Gold Recovery Plants Treating Slimes Dams and Sand Dumps Discharging into the Vaal Barrage (Funke, 1987)

Name of Operation	Effluent to	Flow Mℓ/a	TDS ton/a	SO ₄ ton/a
ERGO Brakpan ERGO Simmergo	Rietspruit/ Klip River	11 700	41 000	24 900
ERGO East Daggafontein	Blesbokspruit		No data	
Goldfields Vlakfontein Modderfontein 74	Blesbokspruit (Benoni Canal)		No data No effluent	
Barlow Rand, Crown Mines Barlow Rand, City Deep	No discharge		No data	
Anglo-Vaal, Village Main	As backfill underground - no effluent			

The dewatering of dolomite compartments has a major effect on the salt load of the Vaal Barrage. Readings taken by the DWA metering station number C2MO5 on the Rietspruit at Kaalplaats (see No. 4, Figure 2.2) were used to calculate values for Table 2.9.

TABLE 2.9 : Flow Rate and Salt Load of the Rietspruit in 1985 and 1987

	1985	1987
Flow rate (Mℓ/a)	9 776	62 441
TDS (mg/ℓ)	1 151	881
SO ₄ (mg/ℓ)	489	493
TDS load (tons/a)	11 249	55 000
SO ₄ load (tons/a)	4 778	30 770

The increased flow rate of 144 Mℓ/day in the Rietspruit from 1985 to 1987 is almost totally due to the dewatering of the Gemsbokfontein dolomite compartment by Western Areas Gold Mine. The water quality of the Rietspruit has improved but its salt load and consequently the salt load of the Vaal Barrage has increased by 120 tons/day. This dewatering will continue for approximately 8 to 10 years.

The actual dewatering flow is estimated to be 160 Mℓ/day with a sulphate content of 500 to 750 mg/ℓ (Funke, 1987). Evaporation losses and bacterial reduction of the sulphates in reed beds have lead to a slight decrease in the effect on the flow rate and TDS level of the Rietspruit.

West Rand Consolidated is pumping out about 2 900 Mℓ/a of water at an average concentration of 1 300 mg/ℓ SO₄ (Funke,1987). This effluent drains into a northerly flowing stream.

TABLE 2.10 : Volume and Composition of Surplus Water Disposed of by Far West Rand Mines into the Vaal Barrage (Funke,1987)

	Flow Mℓ/a	TDS mg/ℓ	SO ₄ mg/ℓ
Western Deep Levels	2 700	550	185
East Driefontein			
West Driefontein	35 200	630	100
Blyvooruitzicht	1 300	1 260	580
Doornfontein	2 100	1 060	400
Deelkraal	2 000	-	-
Elandsrand	<u>1 600</u>	-	-
Total	<u>44 900</u>		

Figure 2.3 shows the large contribution of the Klip River to the salt load of the Vaal Barrage. Since 1984 the flow and mineral load from ERGO has decreased due to improved water management. Presently it is estimated that only 53 Mℓ/a is discharged from ERGO. The reduced intake by ERGO of water from Sallies has resulted in a corresponding increase in effluent volume discharged by Sallies (Rogans, 1988). Grootvlei Mine pumps water out at Sallies to prevent flooding of its own workings. The contribution by ERPM and DRD will remain unchanged or even increase as mining operations seem stable. The contribution of Western Areas to the Western Rietspruit has shown a dramatic increase since mid 1986, as seen in Table 2.9, and can be expected to last until at least 1996. They have however been attempting to use more of this water in their in-house processes.

2.3 The Effect of Removing Selected Point Sources

The Klip River contributes 54,9% of the TDS load to the Vaal Barrage. Three mines, ERPM; DRD and ERGO contribute 55% of the TDS load but only 17% of the flow to the Klip River. These are thus concentrated effluent streams.

TABLE 2.11 : The Effect of Treating Major Sulphate Contributors to the Klip River

Mines	Flow Mℓ/a	Present TDS ton/a	Removable* TDS ton/a	TDS in treated effluent ton/a
ERPM	15 150	54 900	50 000	4 900
ERGO	11 700	41 000	34 400	6 600
DRD	4 100	13 800	12 800	1 000
Total	30 950	109 700	97 200	12 500

Table 2.11 indicates that by treating three effluent sources with barium carbonate and lime, 42% of the point source effluent TDS and 18% of the total mineral load to the Vaal Barrage can be removed.

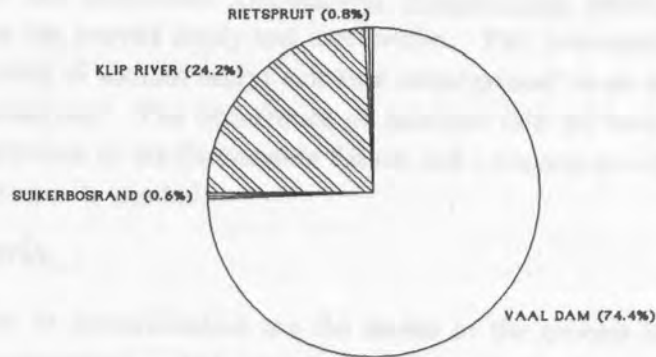
Western Area's expected increase in mineral contribution to the Rietspruit could be reduced by 46 000 tons/a*.

The application of this treatment process to numerous smaller effluent produces will have a lesser but still significant effect on the salt load of the Vaal River.

* If the effluent were treated with barium carbonate and lime as described in Section 5.3.4.

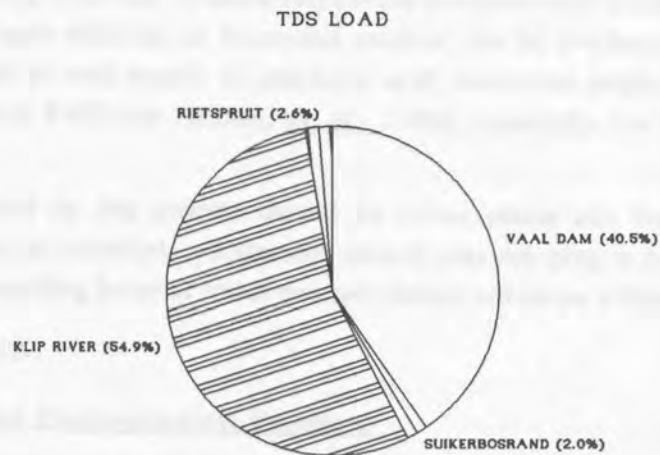
SHOWING A SUT PRATE VOLUMETRIC FLOW

The volume of the water flowing into the Vaal Dam is shown in the pie chart below. The Vaal Dam is the largest contributor to the total flow, accounting for 74.4% of the total. The Klip River and Rietspruit contribute 24.2% and 0.8% respectively, while Suikerbosrand contributes 0.6%.



Showing TDS Load

The TDS load is shown in the pie chart below. The Klip River is the largest contributor to the TDS load, accounting for 54.9% of the total. The Vaal Dam contributes 40.5%, Rietspruit contributes 2.6%, and Suikerbosrand contributes 2.0%.



Showing Sulphate Load

The sulphate load is shown in the pie chart below. The Klip River is the largest contributor to the sulphate load, accounting for 80.6% of the total. The Vaal Dam contributes 12.5%, Rietspruit contributes 4.5%, and Suikerbosrand contributes 2.4%.

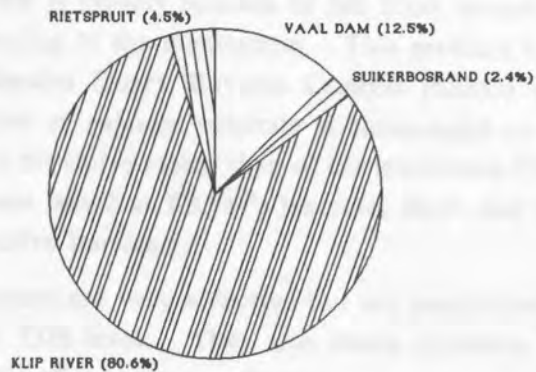


FIGURE 2.3 : Total Flow and Salt Contribution to the Vaal Barrage (1982/1983)

3 CHOOSING A SULPHATE REMOVAL PROCESS

The inhibition of the bacterium Thiobacillus Ferrooxidans which catalyses pyrite oxidation reactions has proved costly and ineffective. This preventative treatment has involved the spraying of sodium lauryl sulphate underground in an attempt to prevent sulphuric acid formation. The occurrence of sulphate rich effluent waters will thus continue to be a problem in the foreseeable future and a process to reduce the pollution impact of such streams is needed.

3.1 Decision Criteria

The largest sources of mineralisation are the mines so the process should be suitable for use in that environment. The process should be simple to operate, make use of technology available in South Africa, be kind to operator error and must be inexpensive. Since sulphates are being removed, valuable sulphurous products such as sulphur dioxide, sulphuric acid, hydrogen sulphide or elemental sulphur can be produced. Although the Witwatersrand has an over supply of sulphuric acid, elemental sulphur is imported at great cost, presently R460/ton (Maree, et. al., 1986), especially for use at coastal factories.

Raw materials required by the process should be either cheap and freely available locally or they should be recycled. Reactants should also not pose a toxic hazard to potential users. The resulting brine or solids product should not cause a disposal problem.

3.2 Possible Processes

(1) Membrane and Electrochemical Processes

Reverse osmosis involves the forcing of water under pressure through a specially designed membrane which has the capability of allowing the passage of pure water while rejecting impurities.

Reverse osmosis produces a pure and useful water product but the solubility limit of calcium sulphate is rapidly reached in the brine stream. This leads to precipitation and fouling of the membranes. This problem has led to the development of the Seeded Slurry Reverse Osmosis (SSRO) system where preferential precipitation of calcium sulphate is encouraged on recirculating crystals introduced with the slurry rather than on the membrane (Harries, 1984). Both processes have been tested at ERPM's Hercules Shaft and the SSRO has been shown to be effective but costly.

Ion Exchange (IX) columns are very effective but are prohibitively expensive for waters with a high TDS level. They also create problems of having to deal with a large amount of regenerating liquor.

Electrodialysis involves removing inorganic ions from water by impressing an electrical potential across the water, resulting in the migration of cations and anions to the cathode and anode respectively. Continuous reversal of the

potential prevents fouling of the membranes. This Electro Dialysis Reversal (EDR) process is effective but has high capital and operating costs (Randol International, 1984).

(ii) **Biological Sulphate Removal**

Various biological processes which utilise bacterium to remove the sulphates in solution have been extensively studied even up to pilot plant scale (Maree, *et al.*, 1987). The bacterium require a carbon source for nutrition. If effectively controlled the process performs well. The economics and applicability of biological processes vary greatly with location and site specific conditions, including climatic constraints. There is a waste disposal problem in the form of dead bacterium and the remains of the carbon source. Some of the precipitated metal sulphides may reoxidise and the whole effluent stream has to be treated to strip off the product hydrogen sulphide. Large retention times are necessary in the reactors for effective sulphate removal.

(iii) **Chemical Sulphate Removal**

Soluble barium compounds are an apparent choice to remove soluble sulphates in a chemical removal system because of the extreme insolubility of barium sulphate. Barium salts are expensive (barium carbonate US\$520/ton, Kirk and Othmer, 1982) and any process utilising them necessarily has to include a recycle loop. The production routes for various barium salts are shown in Figure 3.1.

Barium may be added in the form of various soluble salts such as the hydroxide, nitrate and chloride. Although they will effect rapid and complete sulphate removal the numerous production steps involved in their manufacture greatly adds to their cost. They also introduce another anion into solution in the place of sulphate. In order to reduce the number of production steps use could be made of barium sulphide. The addition of barium sulphide to sulphate containing waters results in the evolution of hydrogen sulphide and stripping this gas from a large quantity of water is inefficient. If barium is added in the form of a soluble salt extreme care must be taken during addition to prevent overdosage as soluble barium is extremely toxic (EPA recommended limit is 1 mg/l as barium).

Barium carbonate is not an automatic choice for sulphate removal because of its relative insolubility, however, a process utilising barium carbonate can meet the criteria mentioned in Section 3.1. The stable nature of barium carbonate ensures that it may be conveniently transported and handled and that the risk of producing a toxic product water through overdosing is minimised. When reacted with mine effluents a high quality water and extremely inert solids are obtained. Barium carbonate may be produced from raw materials available in South Africa and it is easily recycled using existing technology. The sulphur contained in the sulphate is removed as a concentrated stream of hydrogen sulphide which is amenable for processing into elemental sulphur. The sulphate removal process using barium carbonate as the reactant is described in Section 4.

THE PROPOSED PROCESS FOR THE REMOVAL OF SULPHATES USING BARYTES

The development of the process for the removal of sulphates from wastewater using barytes is the subject of this study.

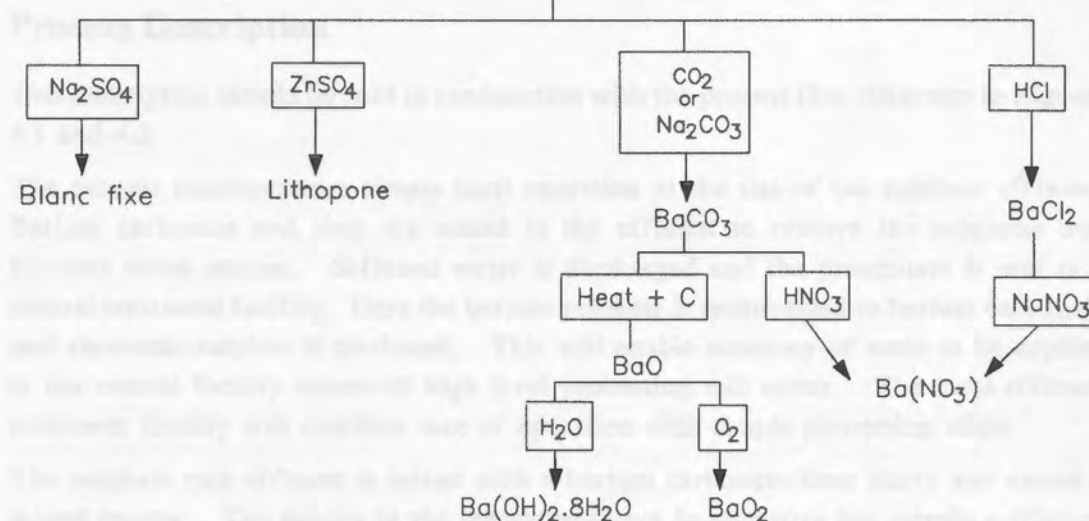


FIGURE 3.1 : Production Routes for Barium Salts
(Kirk and Othmer, 1982)

4 THE PROPOSED PROCESS FOR THE REMOVAL OF SULPHATES USING BARIUM CARBONATE

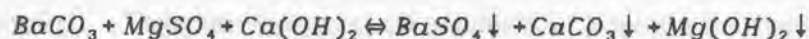
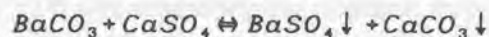
The development of the overall process and an examination of the individual unit operations was the subject of this thesis.

4.1 Process Description

This description should be read in conjunction with the process flow diagrams in Figures 4.1 and 4.2.

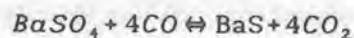
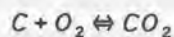
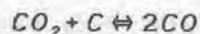
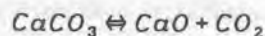
The process incorporates a simple local operation at the site of the sulphate effluent. Barium carbonate and lime are added to the effluent to remove the sulphates and bivalent metal cations. Softened water is discharged and the precipitate is sent to a central treatment facility. Here the barium sulphate is reconverted to barium carbonate and elemental sulphur is produced. This will enable economy of scale to be applied at the central facility where all high level processing will occur. The local effluent treatment facility will combine ease of operation with simple processing steps.

The sulphate rich effluent is mixed with a barium carbonate/lime slurry and enters a mixed reactor. The mixing in the reactor need not be excessive but merely sufficient to maintain a uniform suspension. Calcium carbonate seed crystals encourage precipitation. Retention time should be 45 minutes. In the reactor the following reactions will occur:

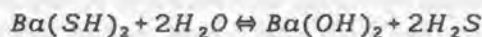
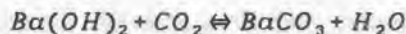
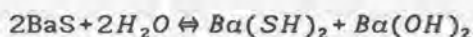


From the reactor the slurry enters a thickener where softened water is decanted off for use on the mine and for sale to other consumers. The product water has a high pH and to neutralise it a small amount of sulphuric acid might have to be added. The thickened slurry is filtered and dried and sent to the central treatment facility (Figure 4.1).

At the central treatment facility the barium sulphate/calcium carbonate mixture is mixed with pulverised coal and pelletised. These pellets are fed into a rotary kiln and reduced at 1 000 to 1 150°C. The following reactions occur:



The black ash kiln product is discharged into a wet ball or rod mill and then into a series of leaching tanks where barium sulphide is extracted with water. The insoluble portion containing mainly ash, lime and unreacted coal will be discharged. The barium sulphide solution is reacted with the flue gas from the kiln to precipitate out barium carbonate and to produce hydrogen sulphide by the following reactions:



Elemental sulphur is produced from the hydrogen sulphide using a commercial process. The barium carbonate is filtered, dried and then transported back to the local facilities for reuse (Figure 4.2).

4.2 Advantages of this Process

The contaminants distributed in a large effluent stream are concentrated into a small stream with no disposal problems. Useful water is produced from the effluent streams for use on the mines or for sale to other consumers.

Elemental sulphur is in short supply in South Africa and is imported at high cost. This process will substantially reduce the amount imported with consequent savings in foreign exchange.

The TDS and especially the sulphate level of public watercourses will be significantly lowered. The largest point source contributors of mineral load would have been eliminated. Together with good management to decrease the contribution by diffuse sources the cost incurred by rising TDS would be greatly reduced.

Barium is added in a very insoluble form and hence does not pose a severe toxicity hazard. Barium sulphate has a solubility level of 2,5 mg/l as barium sulphate. If excess reactant were added the maximum possible barium in solution would approach the solubility limit of barium carbonate which is approximately 10 mg/l as barium. This is in excess of the EPA recommended maximum of 1 mg/l as barium. For use as potable water the product stream requires further treatment and at these concentrations the use of an ion exchange column would be viable. Handling of the dry chemicals presents no hazard and this prevents the imposition of various strict control measures.

The unit operations used at the local facilities such as agitated reactors, thickeners and filters are easy to construct and maintain and are readily available. They do not require any skilled or intensive manpower to operate. At the central facility the required rotary kiln is a standard first processing step in producing any barium salt from barytes (natural barium sulphate) world-wide. Leach tanks and solution precipitation reactors are standard processing equipment. The wet scrubbing of hydrogen sulphide containing gas streams and the subsequent conversion to sulphur is also proven technology.

The barium is reused, hence saving the most expensive component. Input of raw material is in the form of barytes and coal. Coal is a cheap and readily available source of energy and reducing carbon. Barytes deposits occur in numerous places in South Africa, the largest of which is 50 km west of Pofadder in the N.W. Cape Province. The observed length of strike of this barytes deposit is 1 160 m dipping at angles between 30° and 50°. Reserves are calculated as 2 767 000 tons for every 30 m down dip (Brabers, 1976). The reserves at Gamsberg are approximately 2.5 million tons and of this 60 000 tons have been mined over the past 30 years. Mining costs are thought to be low as it is a surface operation (Kostlin, 1988). Numerous smaller deposits such as those in the Pietersburg area and along the Swaziland border could possibly be exploited for make-up purposes.

No pretreatment is necessary to remove the suspended solids present in the mining effluent. Most of the solids will be removed in the settler.

The sulphurous product in the form of hydrogen sulphide is produced in a small concentrated stream which is amenable to further processing such as sulphur production.

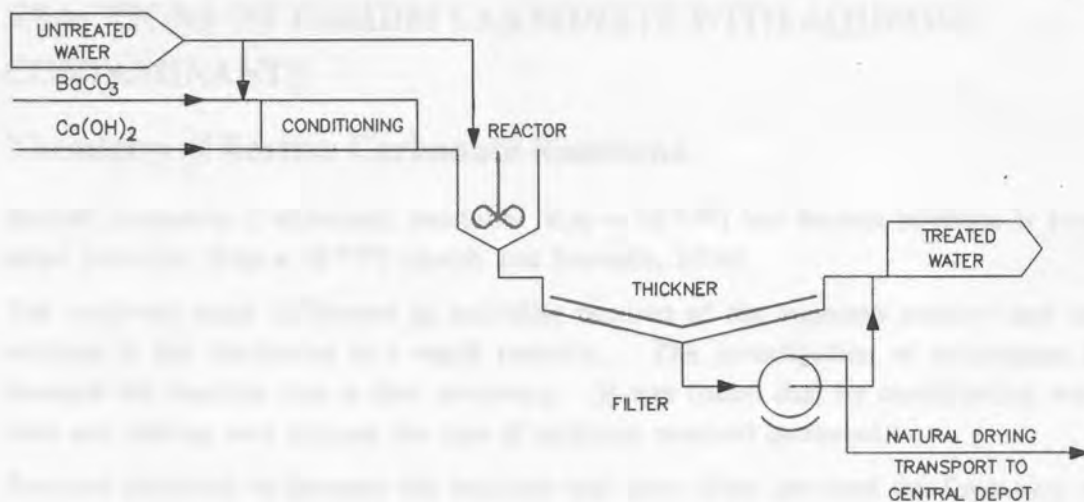


FIGURE 4.1 : Process Flow Diagram for the Treatment of Sulphate Rich Water with Barium Carbonate

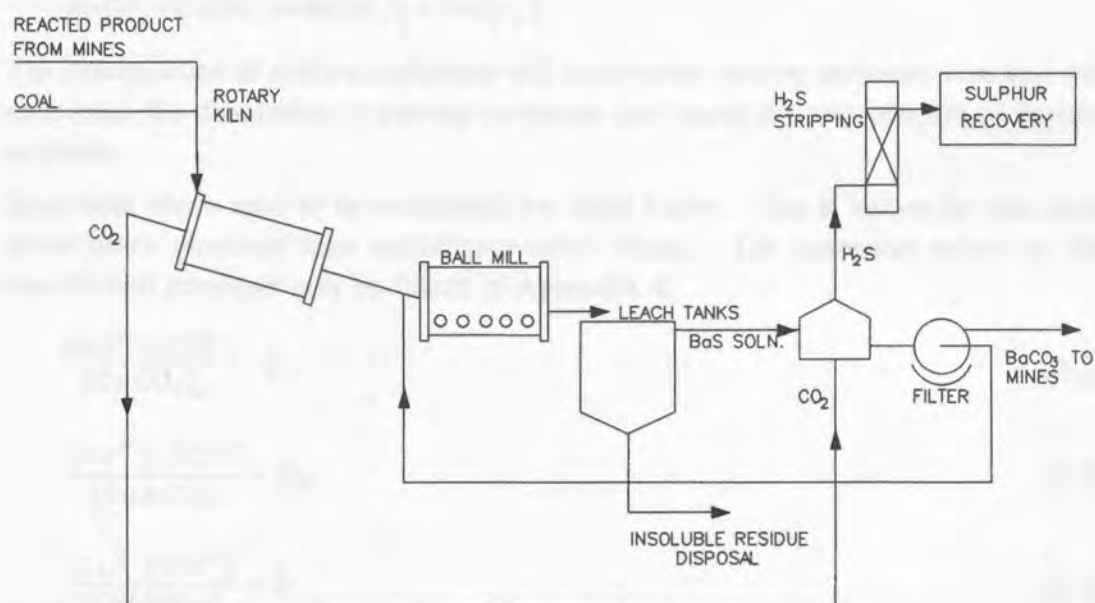


FIGURE 4.2 : Process Flow Diagram for the Regeneration of Barium Carbonate and the Recovery of Sulphur

5 REACTIONS OF BARIUM CARBONATE WITH AQUEOUS CONTAMINANTS

5.1 Chemistry of Barium Carbonate Reactions

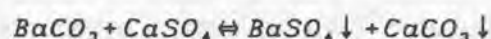
Barium carbonate is extremely insoluble ($K_{sp} = 10^{-8.30}$) but barium sulphate is even more insoluble ($K_{sp} = 10^{-9.96}$) (Smith and Martells, 1976).

The relatively small difference in solubility product of the expected product and the reactant is not conducive to a rapid reaction. The investigation of techniques to increase the reaction rate is thus necessary. It was found that by conditioning with lime and adding seed crystals the rate of sulphate removal increased.

Previous proposals to increase the reaction rate have often involved the formation of the soluble barium bicarbonate. This may be formed by the addition of mineral acid to, or the bubbling of carbon dioxide through, a barium carbonate slurry. In the proposed process these routes are not feasible due to the additional costs involved and the formation of soluble calcium bicarbonate which eliminates the removal of calcium.

5.1.1 With Calcium Sulphate

The main reaction with barium carbonate will be:



The precipitation of calcium carbonate will continually remove carbonate ions and will encourage the dissolution of barium carbonate and hence the precipitation of barium sulphate.

Equilibria which need to be considered are listed below. The K values for the solids listed below represent their solubility product values. The numerical values for the equilibrium constants may be found in Appendix 4.

$$\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]_{aq}} = K_1 \quad (5.1)$$

$$\frac{[Ca^{2+}][HCO_3^-]}{[CaHCO_3^+]} = K_2 \quad (5.2)$$

$$\frac{[Ca^{2+}][OH^-]^2}{[Ca(OH)_2]_s} = K_3 \quad (5.3)$$

$$\frac{[Ca^{2+}][SO_4^{2-}]}{[CaSO_4]_{aq}} = K_4 \quad (5.4)$$

$$\frac{[Ca^{2+}][CO_3^{2-}]}{[CaCO_3]_{calcite}} = K_5 \quad (5.5)$$

$$\frac{[Ba^{2+}][OH^-]}{[BaOH^+]} = K_6 \quad (5.6)$$

$$\frac{[Ba^{2+}][OH^-]^2}{[Ba(OH)_2 \cdot 8H_2O]} = K_7 \quad (5.7)$$

$$\frac{[Ba^{2+}][CO_3^{2-}]}{[BaCO_3]_s} = K_8 \quad (5.8)$$

$$\frac{[Ba^{2+}][CO_3^{2-}]}{[BaCO_3]_{aq}} = K_9 \quad (5.9)$$

$$\frac{[H^+][CO_3^{2-}]}{[HCO_3^-]} = K_{10} \quad (5.10)$$

$$\frac{[H^+][HCO_3^-]}{[H_2CO_3]} = K_{11} \quad (5.11)$$

$$\frac{[Ba^{2+}][SO_4^{2-}]}{[BaSO_4]_s} = K_{12} \quad (5.12)$$

Computations were performed using the MINEQL computer programme (Westall *et al.*, 1976) for chemical equilibrium in aqueous systems. All calculations were performed at 25°C and infinite dilution free energies of formation.

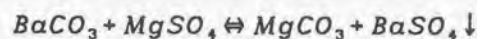
The following equilibria values were obtained using MINEQL for a $1,56 \times 10^{-2}$ mol/l barium carbonate and $1,56 \times 10^{-2}$ mol/l calcium sulphate solution:

Calcium	1,1% as Ca_{aq}^{2+} 98,9% as solid $CaCO_3$
Sulphates	100% as solid $BaSO_4$
Barium	100% as solid $BaSO_4$
Carbonates	98,9% as solid $CaCO_3$ 1,1% as CO_3^{2-}
pH	9,89

5.1.2 With Magnesium Sulphate

After calcium sulphate this is the next most concentrated contaminant in the effluents examined.

The reaction expected is:



Apart from K_8 through K_{12} above, we also need to consider the following equilibria:

$$\frac{[Mg^{2+}][CO_3^{2-}]}{[MgCO_3]_s} = K_{13} \quad (5.13)$$

$$\frac{[Mg^{2+}][CO_3^{2-}]}{[MgCO_3]_{aq}} = K_{14} \quad (5.14)$$

$$\frac{[Mg^{2+}][SO_4^{2-}]}{[MgSO_4]} = K_{15} \quad (5.15)$$

$$\frac{[Mg^{2+}][OH^-]^2}{[Mg(OH)_2]_s} = K_{16} \quad (5.16)$$

$$\frac{[Mg^{2+}][HCO_3^-]}{[MgHCO_3^+]} = K_{17} \quad (5.17)$$

The following equilibrium values were obtained using MINEQL for a $1,56 \times 10^{-2}$ mol/l barium carbonate and $1,56 \times 10^{-2}$ mol/l magnesium sulphate solution:

Magnesium 32,4% as Mg_{aq}^{2+}
 38,2% as $MgCO_3^0_{aq}$
 3,9% as $MgHCO_3^+_{aq}$
 24,7% as solid $Mg(OH)_2$

Barium 98,9% as solid $BaSO_4$
 1,1% as solid $BaCO_3$

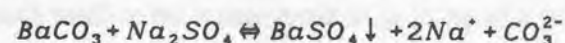
Sulphates 98,9% as solid $BaSO_4$

Carbonates 10,8% as $CO_3^{2-}_{aq}$
 38,2% as $MgCO_3^0_{aq}$
 3,9% as $MgHCO_3^+_{aq}$
 46,0% as HCO_3^-
 1,1% as solid $BaCO_3$

pH 9,39

5.1.3 With Sodium Sulphate

The reaction expected is:



No carbonate ions are precipitated and hence the driving force permitting the dissolution of barium carbonate decreases with reaction extent.

Apart from K_6 through K_{12} the following complexes may be formed:

$$\frac{[Na^+][OH^-]}{[NaOH^0]} = K_{18} \quad (5.18)$$

$$\frac{[Na^+][HSO_4^-]}{[NaHSO_4]} = K_{19} \quad (5.19)$$

The following equilibrium values were obtained using MINEQL for a $2,5 \times 10^{-2}$ mol/l sodium sulphate and $2,5 \times 10^{-2}$ mol/l barium carbonate solution :

Sodium	85,7% as Na^+_{aq}
	14,0% as $NaCO^+_{3aq}$
Barium	95,5% as solid $BaSO_4$
	4,5% as solid $BaCO_3$
Sulphates	3,9% as $SO^{2-}_4_{aq}$
	95,5% as solid $BaSO_4$
Carbonates	61,9% as $CO^{2-}_3_{aq}$
	27,9% as $NaCO^+_{3aq}$
	5,7% as HCO^-_{3aq}
	4,5% as solid $BaCO_3$
pH	11,06

5.2 Crystallisation

The driving force for reaction in the systems under consideration is low and hence the precipitation of reaction products should be encouraged so as to maximise the driving force.

Crystal growth rather than nucleation should be encouraged so as to improve the settling characteristics and filterability of the product. Seeding is also essential to prevent calcium carbonate scaling on the reactor vessel.

If seed is present in sufficient quantities and if the supersaturation does not exceed a certain critical level then nucleation could be expected to be minimal and the predominant mechanism should be growth (Stumm and Morgan, 1970).

Mine effluents contain various ions at different concentrations in solution and it was necessary to conduct an investigation of the literature in order to determine what effect these ions would have on the precipitation of the major reaction products, namely barium sulphate and calcium carbonate. The various parameters affecting crystal growth need to be investigated so as to be able to interpret the results and to understand what parameters need to be controlled in the aqueous reaction experiments.

There are various resistances to reaction such as the dissolution of the barium carbonate, diffusion of the ions, successful reaction collisions and then precipitation of the aqueous product.

Crystal growth occurs in successive reaction steps: the transport of the solute to the crystal interface, the adsorption of the solute at the surface and the incorporation of the crystal constituents into the lattice (Stumm & Morgan, 1970). The back reaction for crystal dissolution should also be considered. Growth kinetics depend on the rate limiting step. Causes of growth rate limitation are:

- 1) Diffusion controlled growth.
- 2) Interface controlled growth.

Diffusion controlled growth can be described by:

$$\frac{dC}{dt} = kS(C - C_o) \quad (5.15)$$

where C_o = equilibrium concentration of salt being precipitated.

C = salt solution concentration at time t

S = precipitate surface area.

k = rate constant.

Interface controlled growth may be empirically characterised by the following rate equation:

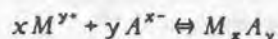
$$\frac{dC}{dt} = kS(C - C_o)^n \quad (5.16)$$

n = order of reaction.

Equations (5.15) and (5.16) are only valid for equivalent amounts of cations and anions (Stumm and Morgan, 1970).

Nancollas and Purdie (1964) have demonstrated that the kinetics of surface controlled crystal growth for solutions containing non-equivalent concentrations of cations and anions of a salt being precipitated may be expressed by an equation similar to (5.16) by replacing the term C by the geometric mean concentration of the cation and anion species.

In the following general reaction:



where M = cation with charge $y+$.

A = anion with charge $x-$.

The rate equation will be:

$$\frac{-dm}{dt} = k \cdot S \cdot \left(([M^{y+}]^x [A^{x-}]^y)^{1/x+y} - K_{sp}^{1/(x+y)} \right)^{x+y} \quad (5.17)$$

where m = mass of the salt precipitated.

k = rate constant.

S = surface area of crystal.

K_{sp} = solubility product of salt M_xA_y .

Equation (5.17) has been shown to be valid for the precipitation of barium sulphate for cation to anion ratios of 0.25 to 4.0 (Nancollas and Purdie, 1964).

5.2.1 Barium Sulphate Precipitation

Nancollas and Purdie (1963) showed that the rate of growth of barium sulphate was second order after an initial fast period and was not diffusion controlled. This held for equivalent as well as unequal molar concentrations. They suggested that the initial fast period was due to nucleation occurring on the surface of the seed crystals.

Bovington and Jones (1970) showed that the rate of dissolution of barium sulphate is also second order for at least 85% of saturation levels. They did not observe diffusion control and found that the stirrer speed did not affect the dissolution. Growth and dissolution were found not to be reciprocal processes. The rate of dissolution was found to be controlled by the rate at which unexposed units of the crystal enter the monolayer surrounding the crystal.

It thus appears that both the rate of precipitation and dissolution of barium sulphate is controlled at the crystal interface. They are both second order processes but with different rate constants. Agitation of the reaction mixture should thus not affect the rate of precipitation or of dissolution.

5.2.2 Calcium Carbonate Precipitation

Pure Calcium Carbonate Systems

The following expression for the rate of change of total dissolved calcium with time has been proposed by Reddy and Nancollas (1971):

$$\frac{d[Ca_T^{2+}]}{dt} = k_c M \left\{ [Ca^{2+}][CO_3^{2-}] - \frac{K_{sp}}{f_D^2} \right\} \quad (5.18)$$

- where $\frac{d[Ca_T]}{dt}$ = rate of change of total dissolved calcium species with time
- k_c = rate constant for crystal growth
($\ell \text{ mol}^{-1} \text{ min}^{-1}$)/(mg seed ℓ^{-1}).
- [] = enclosed species concentration.
- K_{sp} = calcite solubility product ($\text{mol}^2 \ell^{-2}$).
- f_D = activity factor for divalent ions.
- { } = degree of supersaturation ($\text{mol}^2 \ell^{-2}$).
- M = CaCO_3 seed concentration suspended in solution
(mg seed/ ℓ).

The rate constant, k_c , is temperature dependent according to the Arrhenius relationship below.

$$k_c = A \cdot e^{-E/RT}$$

- where A = constant.
- E = activation energy (kcal mol^{-1}).
- R = gas constant ($\text{kcal mol}^{-1} \text{ K}^{-1}$).
- T = absolute temperature (K).

The value for E is $10.3 \pm 0.9 \text{ kcal mol}^{-1}$.

Sturrock, Benjamin, Loewenthal and Marais (1976) proposed the following expression for the rate of calcium carbonate precipitation:

$$-\frac{\delta[\text{CaCO}_3]}{\delta t} = k \cdot M \cdot f_D^2 \{ [\text{Ca}^{2+}]^{\frac{1}{2}} [\text{CO}_3^{2-}]^{\frac{1}{2}} - \left(\frac{K_{sp}}{f_D^2} \right)^{\frac{1}{2}} \}^2 \quad (5.19)$$

- where k = rate constant of precipitation
 ($\ell \text{ mol}^{-1} \text{ min}^{-1}$)/(mg seed ℓ^{-1}).
 $[\]$ = enclosed species concentration.
 K_{sp} = calcite solubility product ($\text{mol}^2 \ell^{-2}$).
 f_D = activity factor for divalent ions.
 $\{ \}$ = degree of supersaturation ($\text{mol}^2 \ell^{-2}$).
 M = mass of seed (moles/ ℓ).

This equation held for batch and continuously stirred tank reactor systems. The rate constant for precipitation is limited to a particular source, size and type of calcium carbonate seed crystals.

Wiechers (1978) found that seed levels in excess of 400 mg/ ℓ held no additional benefits for the precipitation rate of calcium carbonate. Different sources of calcium carbonate for seed crystals were found to affect the rate constant by up to a factor of 5 times. He found it difficult to quantify the active sites available for precipitation.

He also found that $[\text{Ca}^{2+} \text{CO}_3^{2-}]$ ion pair formation was followed by a period of induction. The induction period decreased with increasing oversaturation, however, even at high values of oversaturation (120 mg/ ℓ as CaCO_3) the induction period was still significant (120 seconds).

The induction period was followed by a period of rapid precipitation. The almost instantaneous pH drop after mixing the carbonate and calcium solutions indicated that ion pairing reactions were very rapid.

Wiechers (1978) recommended that plug flow reactors without recycling should not be used in calcium carbonate precipitating systems. Continuously stirred tank reactors, even without sludge recycle, should in time develop sufficient crystal seed to eliminate the induction period.

The Effect of Foreign Ions

The growth rate determining step has frequently been found to be controlled at the interface hence small concentrations of soluble foreign constituents may strongly alter the growth rate and morphology of the precipitated crystals (Stumm and Morgan, 1970).

The presence of soluble magnesium during calcium carbonate precipitation has the following effects:

- (i) The calcite phase is distorted as magnesium is adsorbed onto or incorporated into the calcium carbonate crystal;
- (ii) Calcite (a crystal form of calcium carbonate) precipitation is inhibited;

- (iii) Other phases of calcium carbonate such as the mono- and hexa-hydrate are precipitated (Brooks, Clark and Thunot, 1951).

Kitano (1962) found that during very slow crystallisation of calcium carbonate no magnesium was coprecipitated with the calcite and that no magnesium was removed from solution. This could mean that magnesium merely retards calcite nuclei formation.

Groot and Dwyvis (1966) found that the presence of magnesium ions retarded or even stopped the formation of calcite nuclei.

Doner and Pratt (1969) observed the solubilities and crystalline products when calcium carbonate was precipitated in the presence of various salts at atmospheric carbon dioxide partial pressures. In sodium chloride solutions the solubility was that of calcite. In magnesium chloride solutions the solubility of the precipitate was greater than that of calcite, both calcite and aragonite (both crystallographic forms of calcium carbonate) were detected and magnesium was coprecipitated in the solid phase. In sodium sulphate solutions the solubility was greater than in the case of magnesium chloride solutions and both calcite and vaterite (another crystallographic form of calcium carbonate) were detected. In solutions of magnesium sulphate the solubility of the precipitate was intermediate between that of the magnesium chloride solutions and the sodium sulphate solutions.

Berner (1975) found that dissolved magnesium at sea water concentrations (1 200 mg/l) appeared to have no effect on the rate of crystal growth of aragonite but had a strong retarding effect on that of calcite. The role of inhibition by magnesium was considered to be due to its incorporation within the calcite crystal structure during growth which caused the resulting magnesian calcite to be considerably more soluble than pure calcite.

All the above results were obtained for simple systems. In real situations where numerous ions are in solution the aggregate affect may be different from that expected by examining their individual contributions.

Benjamin *et al.* (1977) investigated the precipitation kinetics of calcium carbonate in the presence of magnesium and described it in terms of the hypothesis of Davis and Jones for calcite seeded solutions.

$$-\frac{\delta[Ca^{2+}]}{\delta t} = KMf_b^2 \left\{ [Ca^{2+}]^{\frac{1}{2}} [CO_3^{2-}]^{\frac{1}{2}} - \left(\frac{K_{spa}}{f_b^2} \right)^{\frac{1}{2}} \right\}^2 \quad (5.20)$$

where K_{spa} = apparent solubility product for $CaCO_3$

K = the precipitation rate constant for magnesian calcite $(\text{min}(\text{moles}/\ell)^2)^{-1}$.

The apparent solubility product, K_{spa} , is related to the solubility product for magnesian calcite, K_{spm} , as follows:

$$K_{spa} = \frac{K_{spm}}{(Mg^{2+}/Ca^{2+})^x}$$

where x = mole fraction of $MgCO_3$ in the magnesian calcite.

Both the solubility product for magnesian calcite, K_{spm} , and the precipitation rate constant, K , vary with the ratio of magnesium to calcium in the aqueous solution:

$$pK_{spm} = 8.40 - 0.0349 \{Mg^{2+}/Ca^{2+}\}$$

$$K = K_0^{-0.366(Mg^{2+}/Ca^{2+})}$$

where K_0 = precipitation rate constant for pure calcite
($\text{min}(\text{mol}/\ell)^2$)⁻¹.

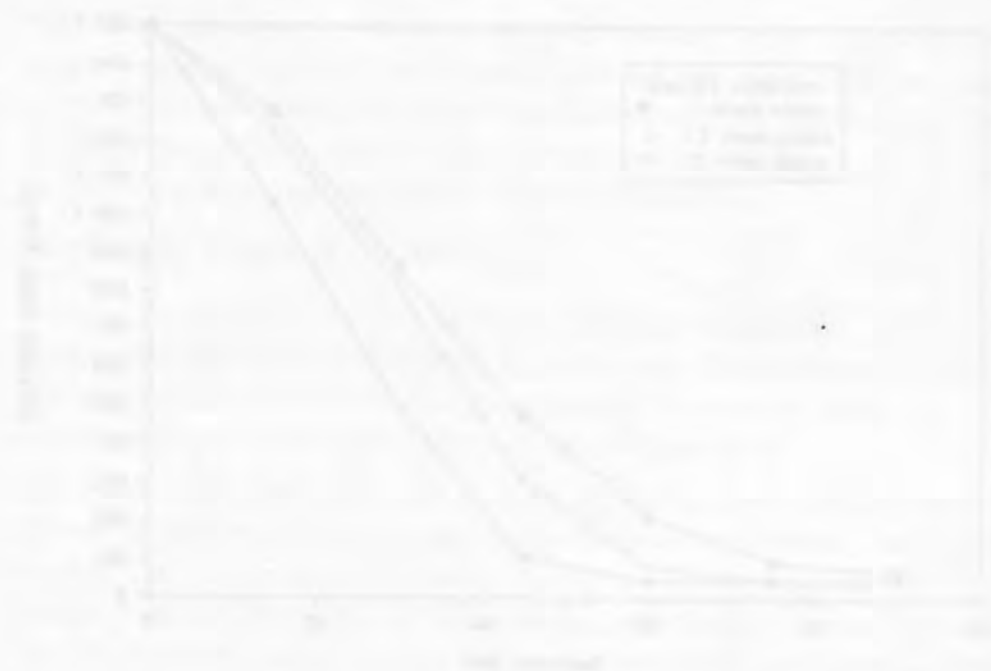


FIGURE 5.1 / Precipitate Removed from a Calcium Saturated Solution Using Sodium Carbonate

Barium carbonate is effective in removing calcium from a calcium sulfate solution in 30-60 minutes. Therefore, the reaction rate will depend on the solution used and longer periods of time will be required. A smaller volume will also require a less intense pump to be applied.

5.3 Experimental

5.3.1 Calcium Sulphate

(i) Reaction Kinetics

Reactions were carried out in 2 l batches at ambient temperatures using saturated calcium sulphate solutions. The reactor was continually stirred to maintain a uniform suspension.

Analytical grade barium carbonate was added in a slurry form (200 g/l) to prevent particle agglomeration. The aqueous sulphate concentration was inferred from measurements of the calcium in solution as well as by gravimetric determination of the sulphates by adding barium chloride to a hydrochloric acid acidified solution. All solids were removed by filtration through glass microfibre filters (size GF/C) to arrest any further reaction which might occur before the samples were analysed. The reaction kinetics are shown in Figure 5.1. The values used to plot this figure may be found in Appendix 1.

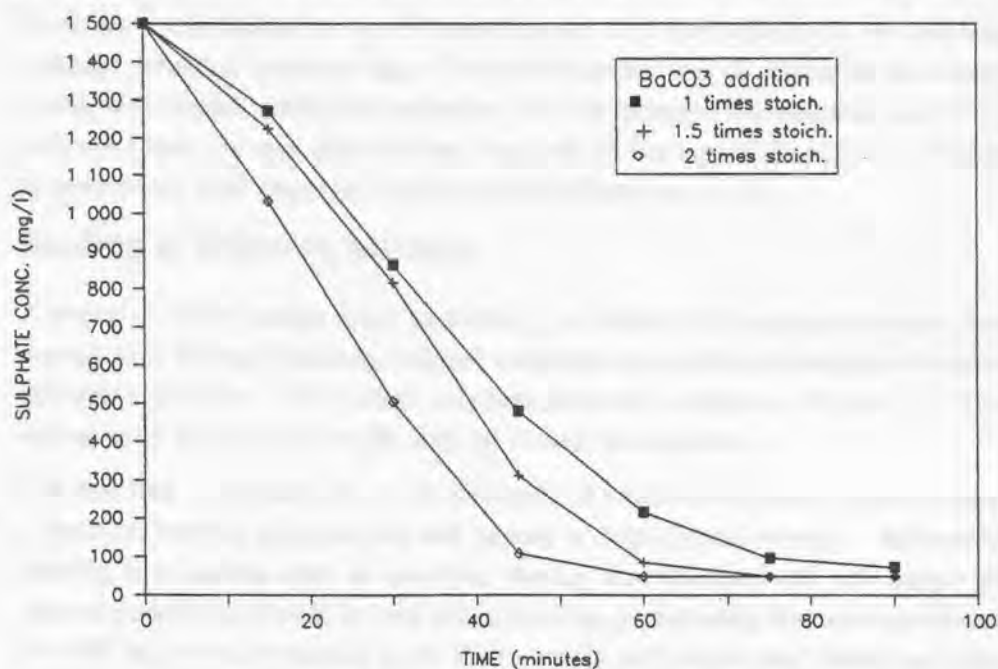


FIGURE 5.1 : Sulphate Removal from a Calcium Sulphate Solution Using Barium Carbonate

Barium carbonate is effective in steadily removing sulphate from a calcium sulphate solution in 60-90 minutes. Speeding up the reaction rate will shorten the residence time and hence decrease the size of the reactor required. A smaller reactor will save power as less volume needs to be agitated.

The first attempt at increasing the reaction rate involved decreasing the particle size of the barium carbonate reagent. This was achieved by attritioning the analar barium carbonate in a DENVER attritioning cell using fine quartz as the grinding medium. The average particle size (d50) was decreased from 4.5 micron to <1 micron. The subsequent increase in reaction rate using the finer reagent was less than 5%.

The next attempt at increasing the reaction rate involved producing the soluble barium bicarbonate by bubbling carbon dioxide through the reaction mixture. This did effect rapid sulphate removal but inhibited the removal of calcium by the formation of the soluble calcium bicarbonate. After 15 minutes no sulphate was detectable in solution but the residual calcium level was 485 mg/l. Levels of 1.5 g/l barium bicarbonate were obtained but this appears to be too low to be useful. The bicarbonate may also be formed by the addition of a mineral acid. The addition of sulphuric acid would increase the consumption of barium carbonate and hydrochloric acid would be prohibitively expensive and both would add to the TDS. Acidification involves the risk of soluble barium occurring in the product water.

Tests were conducted to see if stirrer speed had any effect on the calcium sulphate solution reaction rate. It was observed that if reactants were kept evenly distributed additional agitation did not increase the reaction rate. This indicated that the rate determining step was at the crystal interface. This is in agreement with previous workers results (Section 5.2.1).

(ii) Seeding of Reaction Mixture

A series of experiments were undertaken in which the reaction mixture was seeded with barium sulphate, calcium carbonate and a barium sulphate/calcium carbonate mixture. The rate of sulphate removal is shown in Figure 5.2. The values used to plot this graph may be found in Appendix 1.

The reaction is speeded up by the presence of calcium carbonate seed crystals. A seed of barium sulphate did not appear to benefit the system. Sequential seeding (i.e. adding seed at intervals during the reaction) did not appear to have any additional benefits over initial seeding, presumably because it exceeded the 400 mg/l seed threshold level above which additional seed would not hold additional benefit (see Section 5.2.2).

The dominant precipitation mechanism appears to be one of crystal growth rather than nucleation judging by the particle size distribution of product crystals. Size analyses were conducted by means of a MALVERN 3 600 Series E particle size analyser using a laser detection technique. A typical size analysis is given in Table 5.5.

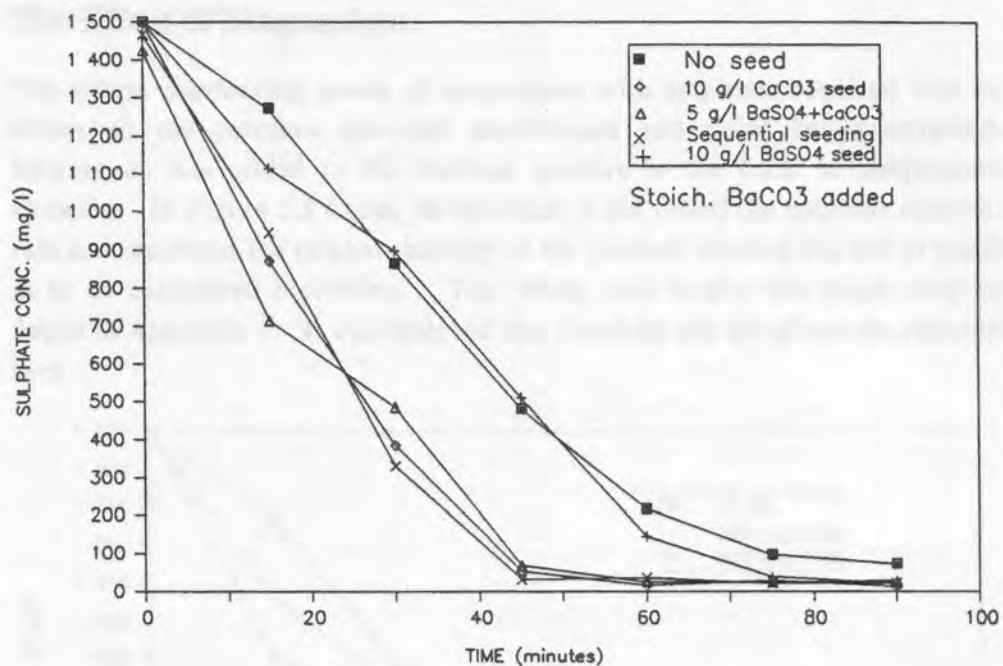


FIGURE 5.2 : Sulphate Removal from a Calcium Sulphate Solution: The Effect of Various Seed Crystals

(iii) The Effect of Magnesium

The strong complexing power of magnesium with sulphates required that its effect on the reaction rate and equilibrium end point be investigated. Magnesium was added to the reaction mixture in the form of magnesium chloride. In Figure 5.3 it may be seen that it did retard the sulphate removal rate and increased the sulphate content of the product solution but not so much as to be considered a problem. The values used to plot this graph may be found in Appendix 1. It was observed that chlorides did not affect the reaction rate.

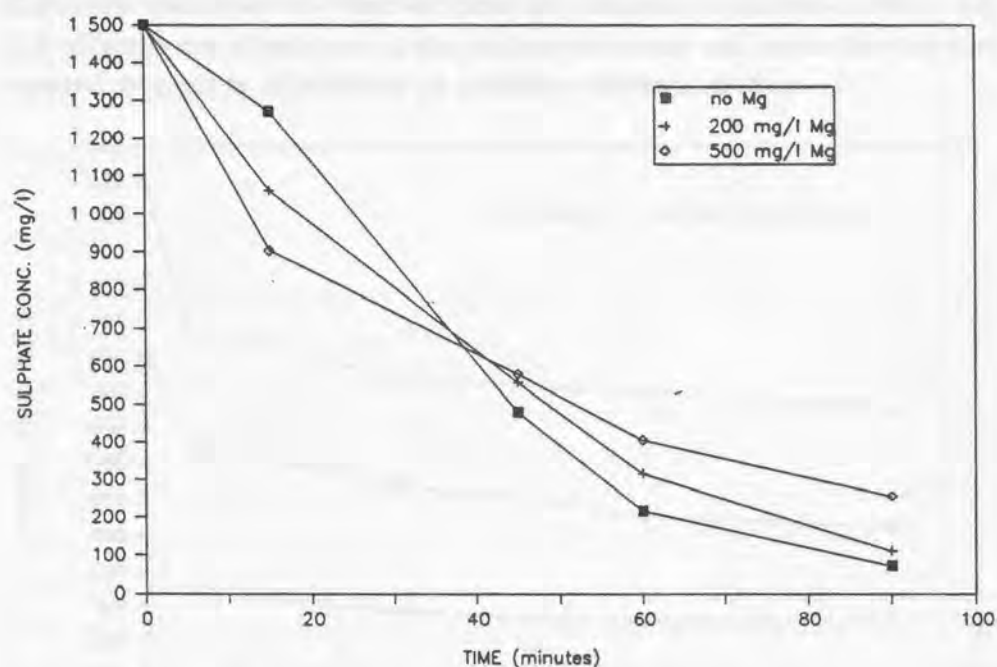


FIGURE 5.3 : Sulphate Removal from a Calcium Sulphate Solution: The Effect of Magnesium Chloride

5.3.2 Magnesium Sulphate

(i) Reaction Kinetics

Various concentrations of magnesium sulphate were reacted batchwise with barium carbonate at ambient temperatures. Sulphate levels were analysed gravimetrically. The rate of sulphate removal is given in Figure 5.4. The values used to plot this graph may be found in Appendix 1. Residual sulphate levels are higher than expected and some magnesium is removed, e.g. from 380 to 195 mg/l in the 1 500 mg/l sulphate test.

Carbonate ions were not removed from the magnesium sulphate solution and this affected the dissolution of the barium carbonate and hence the sulphate removal was not as effective as in a calcium sulphate solution.

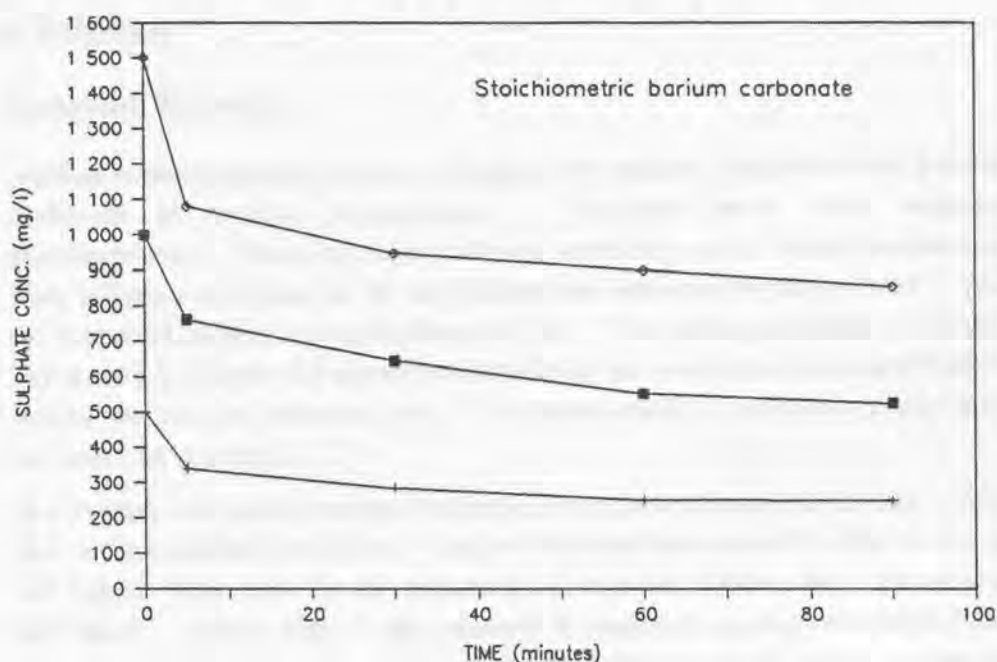
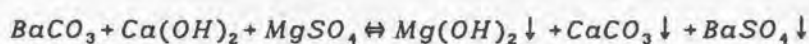


FIGURE 5.4 : Sulphate Removal from a Magnesium Sulphate Solution Using Barium Carbonate

(ii) The Addition of Slaked Lime

A reagent was thus needed to remove aqueous carbonate ions and to liberate the barium for reaction with the sulphates. It was decided to use slaked lime for this purpose as not only would it remove the aqueous carbonates but it would also aid magnesium removal in the form of the highly insoluble magnesium hydroxide. The following reaction will occur:



A magnesium sulphate solution (2 000 mg/ℓ as SO_4) was seeded with 500 mg/ℓ calcium carbonate and reacted with its molar equivalent of calcium hydroxide and with barium carbonate, which was 25% in excess of stoichiometry. The calcium carbonate was conditioned with the barium carbonate and the calcium hydroxide before addition to the magnesium sulphate solution. An analysis of the reaction mixture gave the following results:

Time (min)	0	15	30
SO_4 (mg/ℓ)	2 000	152	0
Mg (mg/ℓ)	507	-	3

It is seen that adding lime in addition to the barium carbonate increases the rate of reaction and also effects almost total sulphate and magnesium removal.

5.3.3 Sodium Sulphate

(i) Reaction Kinetics

Various concentrations of sodium sulphate were reacted batchwise with barium carbonate at ambient temperature. Sulphate levels were analysed gravimetrically. There appeared to be an extremely rapid initial reaction but with subsequent tailing off at far higher than expected sulphate levels. The pH remained constant at approximately 10.6. The reaction kinetics are shown in Figure 5.5. Figure 5.6 shows that increasing the dosage does not significantly reduce the residual sulphate level. The values used to plot these graphs may be found in Appendix 1.

In a further test excess barium carbonate was agitated continuously for 3 days in a sodium sulphate solution. The residual sulphate level fell from 2 440 to 620 mg/ℓ. When left for an additional 14 days the sulphate level dropped to 320 mg/ℓ. About 50% of the sulphate is removed quickly whereafter the presence of carbonate ions in solution retards the dissolution of barium carbonate thus imposing a kinetic restraint upon the system.

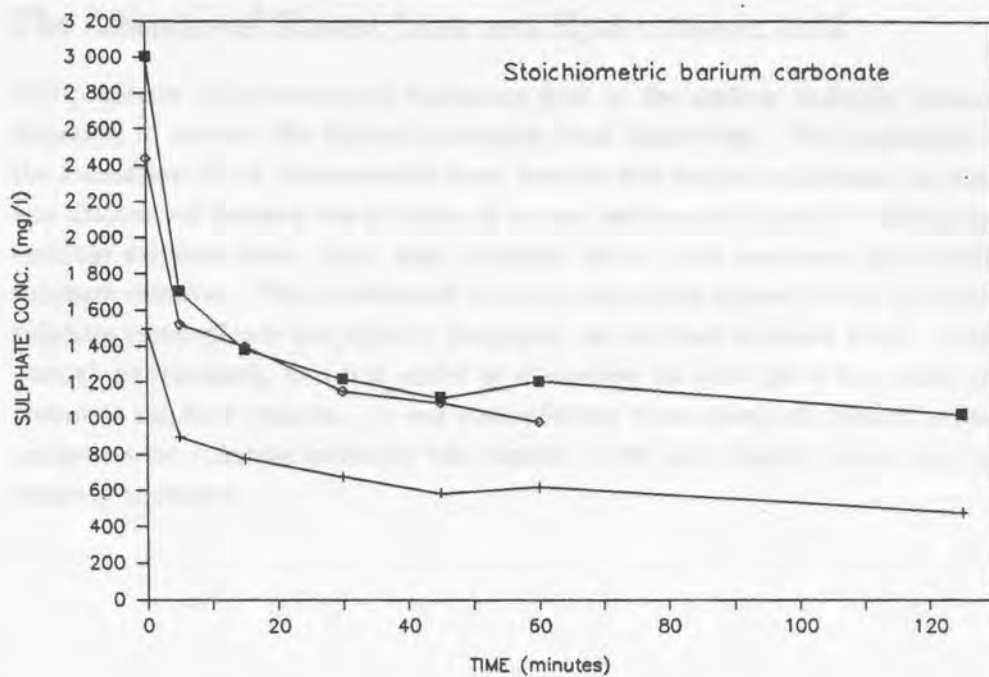


FIGURE 5.5 : Sulphate Removal from a Sodium Sulphate Solution Using Barium Carbonate

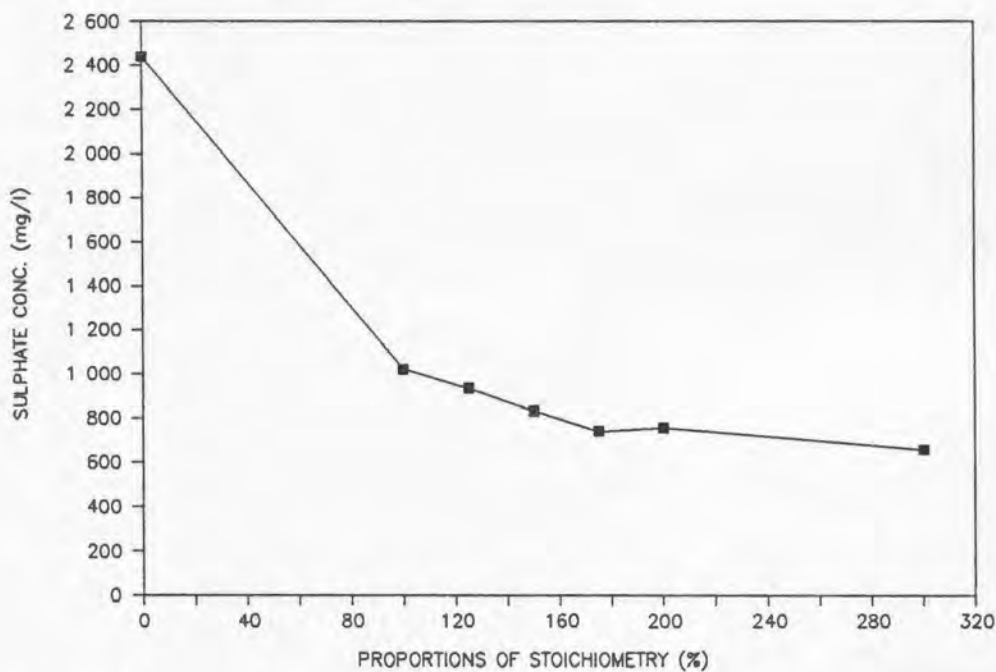


FIGURE 5.6 : Sulphate Removal from a Sodium Sulphate Solution Using Increasing Amounts of Barium Carbonate

(ii) The Addition of Slaked Lime and Hydrochloric Acid

The presence of uncomplexed carbonate ions in the sodium sulphate solution appeared to prevent the barium carbonate from dissolving. The possibility of the formation of an impermeable layer around the barium carbonate particles was discounted because the addition of excess barium carbonate still left a high residual sulphate level. Very long reaction times were necessary for further sulphate removal. The addition of calcium hydroxide slowed down the initial sulphate removal rate but slightly decreased the residual sulphate level. When enough hydrochloric acid was added to neutralise the lime there was rapid and complete sulphate removal. It was observed that when using attritioned barium carbonate the sulphate endpoint was slightly lower and slightly faster sulphate removal occurred.

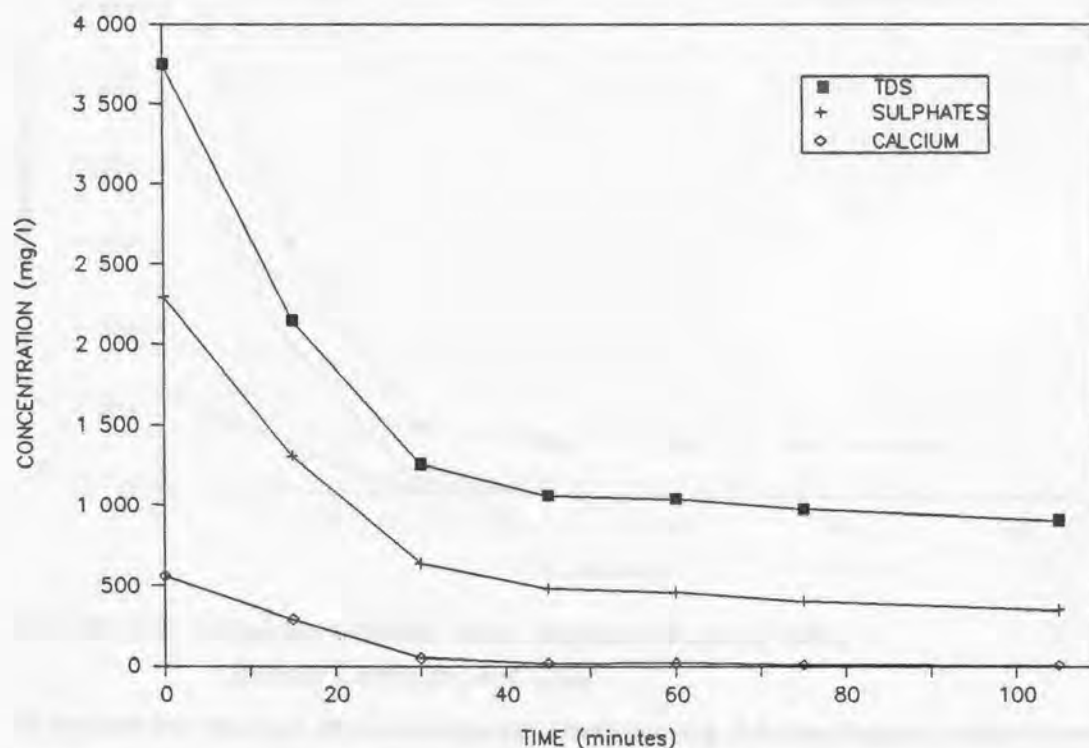
5.3.4 Reactions with minewater

Simulated samples of ERGO and ERPM effluent were prepared. The mixtures were seeded with 500 mg/l calcium carbonate and a 25% stoichiometric excess of barium carbonate was used.

The results from a simulated typical ERGO effluent is given in Table 5.1. A gradual reaction and incomplete sulphate removal was observed due to sodium and magnesium sulphate being present. Reaction kinetics are graphically presented in Figure 5.7.

**TABLE 5.1 : Salt Removal from a Simulated ERGO Effluent
Using Barium Carbonate**

Time (min)		0	15	30	45	60	75	105
TDS (mg/l)		3 750	2 150	1 256	1 058	1 039	970	905
SO ₄ (mg/l)		2 300	1 306	636	484	456	403	351
Cl (mg/l)		210	210	210	210	210	210	210
Fe (mg/l)		60	0	0	0	0	0	0
K (mg/l)		50	40	30	30	40	40	30
Na (mg/l)		250	220	250	235	230	230	230
Ca (mg/l)		560	290	50	20	20	10	10
Mg (mg/l)		140	84	80	79	83	77	74
pH		3,4	7,8	8,0	8,2	8,5	8,7	9,0

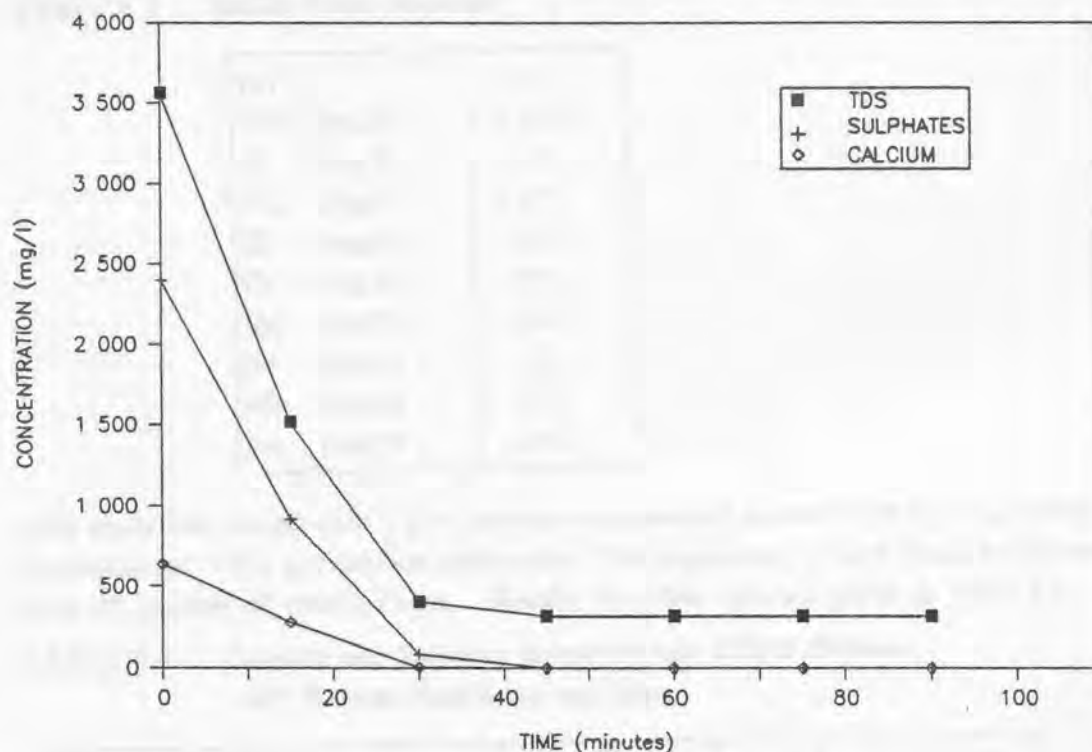


**FIGURE 5.7 : Simulated ERGO Water Sulphate Removal Using
Barium Carbonate**

For a simulated ERPM effluent an amount of calcium hydroxide was added which was stoichiometrically equivalent to the magnesium sulphate and sodium sulphate present. The result was rapid and complete sulphate removal accompanied by a large drop in the TDS as shown in Table 5.2 and graphically presented in Figure 5.8.

**TABLE 5.2 : Salt Removal from a Simulated ERPM Effluent
Using Barium Carbonate and Lime**

Time (mins)	0	15	30	45	60	75	105
TDS (mg/l)	3 562	1 519	407	318	318	318	318
SO ₄ (mg/l)	2 400	920	86	0	0	0	0
Cl (mg/l)	120	120	120	120	120	120	120
K (mg/l)	16	16	16	16	16	16	16
Na (mg/l)	180	180	180	180	180	180	180
Fe (mg/l)	80	0	0	0	0	0	0
Ca (mg/l)	636	280	4	1	1	1	1
Mg (mg/l)	130	3	1	1	1	1	1
pH	3,6	10,80	10,86	10,82	10,85	10,94	11,01



**FIGURE 5.8 : Simulated ERPM Water Sulphate Removal Using
Barium Carbonate and Lime**

No barium was detected in the supernatant solution using AA spectroscopy with a lower concentration limit of 1 mg/l. Thus the water produced conformed to the EPA standards regarding barium. The pH of the supernatant solution was 10,82 and required 2,65 mmol/l of sulphuric acid for neutralisation to pH 7.

The solid residue proved very easy to filter in a batch test and the cake had a moisture content of 50%. The settling properties of the solid particles were fairly good but, as the particles were slightly positively charged, with the addition of an anionic polyelectrolyte the settling characteristics improved remarkably. The solids concentration of 11,2 g/l required only 1 mg/l polyelectrolyte (0,09 mg poly./g dry solids) for adequate settling.

The calcium hydroxide and barium carbonate should be conditioned together to obtain an equilibrium of the form:



The equilibrium constant for this reaction is approximately 0,028. The small amount of soluble barium hydroxide will immediately react with any sulphates in solution when added to the effluent.

A sample of water was obtained (15 March 1988) from ERGO to see if it would react in the same way as the simulated mixture. It appeared reddish, probably due to suspended hematite, and also contained other suspended solids. The water analysis is given in Table 5.3.

TABLE 5.3 : ERGO Water Analysis

pH	4.1
TDS (mg/l)	4 112
SS (mg/l)	126
SO ₄ (mg/l)	2 527
Cl (mg/l)	207
Ca (mg/l)	653
Mg (mg/l)	152
Fe (mg/l)	5,6
Mn (mg/l)	7,5
Na (mg/l)	242

This water was seeded with 1 g/l calcium carbonate and reacted with 6,477 g/l barium carbonate and 0,811 g/l calcium hydroxide. No magnesium or iron could be detected after 15 minutes of reaction time. Results for other ions are given in Table 5.4.

**TABLE 5.4 : Calcium and Sulphate Removal from ERGO Effluent
with Barium Carbonate and Lime**

Time (min)	0	15	30	45	60	75	90
SO ₄ (mg/l)	1 870	1 236	372	0	0	0	0
Ca (mg/l)	653	610	490	120	10	2	1
pH	4,1	10,55	10,57	10,58	11,60	11,65	11,65

The product size analysis is given in Table 5.5 for the ERGO salt removal reaction. The small proportion of crystals in the very small size ranges indicates that the predominant precipitation mechanism is one of crystal growth.

TABLE 5.5 : Aqueous Reaction Product Size Analysis

Weight in Band (microns)	%
188 - 87,2	0,0
87,2 - 53,5	0,0
53,5 - 37,6	0,1
37,6 - 28,1	0,6
28,1 - 21,5	1,6
21,5 - 16,7	3,5
16,7 - 13,0	9,0
13,0 - 10,1	20,9
10,1 - 7,9	27,0
7,9 - 6,2	14,1
6,2 - 4,8	7,0
4,8 - 3,8	7,5
3,8 - 3,0	4,4
3,0 - 2,4	1,6
2,4 - 1,9	1,1

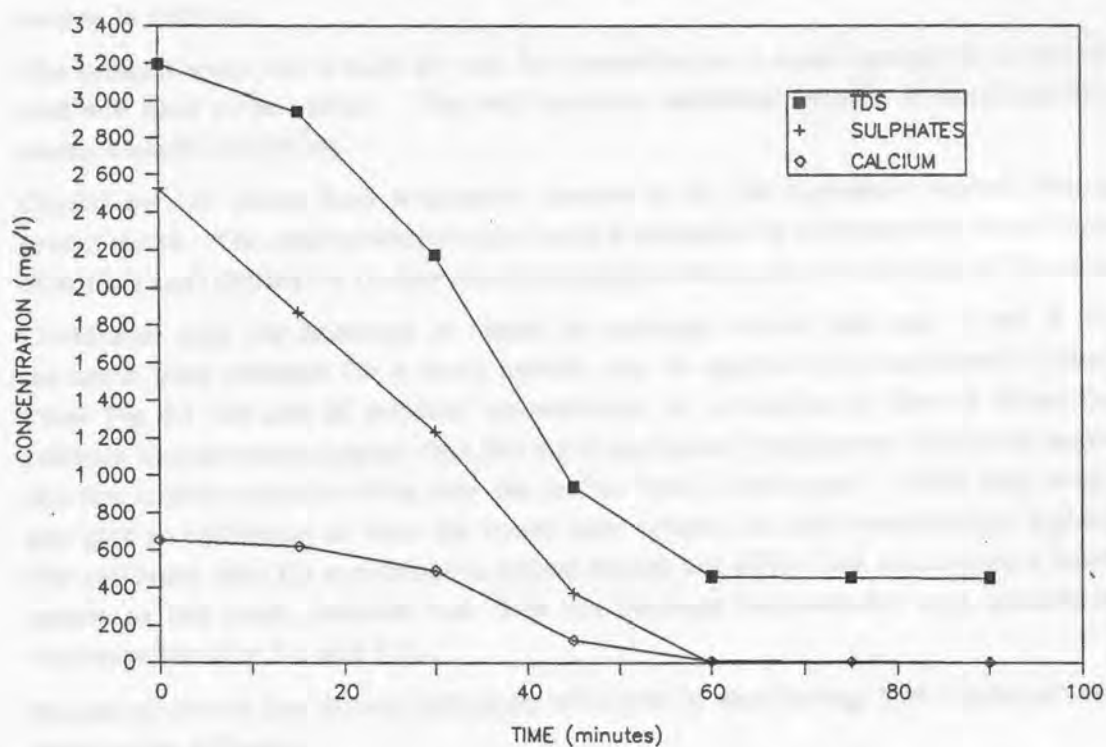


FIGURE 5.9 : Sulphate Removal from Real ERGO Water Using Barium Carbonate and Lime

5.4 CONCLUSIONS

Reacting barium carbonate with calcium sulphate solutions is very effective as both calcium and sulphate are removed from solution. The reaction rate is increased with the addition of excess barium carbonate and calcium carbonate seed crystals. The effect of the seed crystals is probably to eliminate the induction period and to encourage the removal of carbonates from solution thus encouraging the dissolution of barium carbonate. There is a limit above which additional seed does not increase the reaction rate. Sufficient agitation ensures that diffusion of products and reactants in the bulk solution is not rate limiting. Considering the rate of reaction the formation of product ion pairs is not likely to be rate limiting. The limiting step is thus expected to be either the dissolution of barium carbonate or interface control at the surface of the product crystal.

The introduction of calcium hydroxide in addition to barium carbonate in magnesium sulphate solutions and mine effluents helps lower the final sulphate and TDS level and increases the rate of reaction. It has the additional benefit of removing almost all aqueous magnesium and iron. Care should be taken not to add more lime than is required as it may add to the TDS of the product water. In the absence of calcium hydroxide the presence of magnesium retains sulphate in solution.

The residual sulphate content resulting from reacting barium carbonate with a sodium sulphate solution is higher than expected. This appears to be caused by a kinetic restraint imposed upon the dissolution of barium carbonate by the presence of carbonate species in solution.

The product water has a high pH and for neutralisation a small amount of sulphuric acid will need to be added. This will have the additional benefit of removing any excess barium in solution.

Crystal growth rather than nucleation appears to be the dominant process during precipitation. The solid precipitate produced is amenable to concentration in the form of settling and filtering for further processing and should present no handling difficulties.

Continuous tests are necessary to obtain an optimum reactor size and to see if the residence time obtained for a batch system may be applied to a continuous system. From Fig 5.1 the plot of sulphate concentration as a function of time is linear for sulphate concentrations greater than 200 mg/l, and hence it appears as though the major reaction is zero order in which case the reactor type is irrelevant. These tests would also give an indication of what the steady state crystal size and concentration will be. The residence time for a continuous system should not differ that much from a batch system as the batch reaction rate does not decrease substantially with decreasing concentration (Fig 5.1 and 5.2).

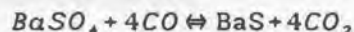
Barium carbonate has proved extremely effective in desalinating both simulated and actual mine effluents.

6 THE THERMAL REDUCTION OF A BARIUM SULPHATE / CALCIUM CARBONATE MIXTURE

6.1 Literature Overview

6.1.1 Reduction Mechanism of Barium Sulphate

The overall reaction used to describe the reduction of barium sulphate is:



Considerable debate exists as to what the actual mechanism of reduction is.

Lozhkin *et al.* (1974) viewed the reduction of barium sulphate as involving two inter-related steps:

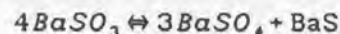
- (i) the oxidation of C to CO and CO₂;
- (ii) the reduction of barium sulphate by CO.

They studied the kinetics of barium sulphate reduction at 900 to 1 200°C. At lower temperatures the rate was limited by carbon gasification kinetics and at 1 200°C by the diffusion of the gaseous products into the barium sulphate.

The reaction mechanisms could involve an initial conversion of the barium sulphate to form barium sulphite:

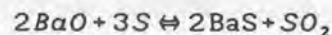
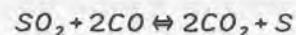
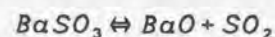


The barium sulphite can then undergo two possible series of reactions, firstly it may disproportionate;

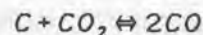


(Mellor, 1946)

or the sulphite may be further reduced to the sulphide.



The carbon monoxide is regenerated by means of the Boudouard reaction.



Alekseev (1977) described the kinetics of reaction as follows:

$$kt = 1 - (1 - \alpha)^{\frac{1}{3}}$$

where k = kinetic constant.

t = time.

α = fraction of barium sulphate reduced.

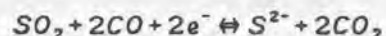
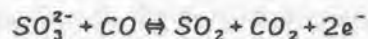
This only applies for $\alpha > 0,7$ and $900^\circ\text{C} < T < 1\,020^\circ\text{C}$.

Akmetov (1974) contended that barium sulphite dissociated during heating to form barium sulphide and sulphur dioxide and did not form a sulphate/sulphide mixture. He says that at high temperatures barium sulphide and barium thiosulphate are converted to the sulphate. His hypothesis for the formation of barium sulphide included the following:

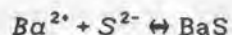
Barium sulphate dissociation:



Sulphate reduction:

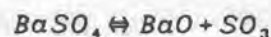
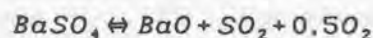
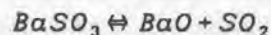


and then the sulphide and barium ions react to form barium sulphide:



He refuted the contention that barium sulphite dissociates with the formation of the oxide and sulphide. Various contradictions in the interpretation of the mechanism of the reaction consist in the different treatment of the conversion of sulphur from +VI to the +II state.

Shakhtakhtinskii *et. al.* (1980) examined 32 possible reduction reactions of barium sulphate with methane, carbon monoxide and hydrogen. They concluded that the reduction of barium sulphate produced barium sulphide, barium sulphite or barium oxide. Barium sulphate and sulphite can only dissociate to form barium oxide at temperatures $>2\,000\text{ K}$ ($1\,723^\circ\text{C}$) i.e. the dissociation reactions:



are only possible at temperatures $>2\,000\text{ K}$ ($1\,723^\circ\text{C}$).

They found that the temperature interval $1\,073$ to $1\,123\text{ K}$ (800 to 850°C) is the most favourable for the formation of barium sulphide using methane or natural gas.

Tanutrov *et. al.* (1985) studied the mechanism and kinetics of the reduction of barium sulphate with graphite. They found that the reduction and thermal dissociation of the barium sulphate was diffusion controlled at $<1\,540$ to $1\,580^\circ\text{C}$ when the heating was 5 to $10^\circ/\text{min}$ and that it occurred simultaneously when the graphite : barium sulphate ratio was >3 . The reduction and thermal dissociation ceased at $1\,540$ to $1\,580^\circ\text{C}$ regardless of the presence of graphite. This was regarded as being due to the sintering of the particles. Their findings with regard to the thermal dissociation of barium sulphate at temperatures $<1540^\circ\text{C}$ are in contradiction with the contentions of Shakhtakhtinskii above.

6.1.2 Barium Sulphate Reduction Processes

In barium sulphate reduction rotating kilns are generally used which are kept below 1 200°C, the melting point of barium sulphide. The production of almost all barium chemicals commences with the reduction of barium sulphate.

Ivanov *et. al.* (1970) used coke, anthracite, coal and charcoal as reducing agents and found the optimum C : BaSO₄ ratio was 1 : 4 and the optimum temperature was 900°C. A reaction time of 1 to 2 hours gave 80 to 90% conversion regardless of the nature of the reducing agent.

Videnov *et. al.* (1977) described a unique method for heating the kiln charge. A baryte containing 84,5% barium sulphate was reduced to barium sulphide by mixing it with 20% coke; pressing the mixture at 2 MPa and heating it to 1 150 to 1 200°C by passing an electric current directly through the mixture. After 30 minutes of heating the conversion was >95%.

Kashkarova *et. al.* (1980) found that using petroleum coke instead of blast furnace coke increased the production of barium sulphide by 20 to 30% and decreased the concentration of sulphur dioxide in the waste gas by 20 to 30%. They found optimum coke particle size to be 0,05 to 0,06 mm; the baryte : coke ratio 6 : 1; temperature 1 100°C and the reaction time 2,5 minutes.

Shakhtakhtinskii (1982) obtained a 98 to 99% reduction at 800 to 850°C and 1 hour residence time in a continuously operating kiln using natural gas. The optimum excess amount of reducing gas was 5% above the theoretical required.

Kashkarova (1983) again showed the advantages of petroleum coke over high ash blast furnace coke. The petroleum coke [C is 85 to 90%, S is 3 to 5%, volatiles are 8 to 12% and ash is 0,2 to 0,8%, calorific value 8 500 kcal/kg (35,6 MJ/kg)] used at 1 100°C gave 91,7% soluble barium salts and a reduction degree of 98,1%. Increasing the amount of coke above 12% had no added beneficial effect on the degree of reduction.

Annopolski *et. al.* (1985) also found that by using petroleum coke instead of blast furnace coke the proportion of water soluble barium compounds increased.

Dimitrova *et. al.* (1972) described a rotary furnace 8 m long, 0,54 m in diameter and a 2° slope rotating at 0,53 to 3,00 rpm. Furnace temperatures were measured 2,0 m, 6,0 m and 7,2 m from the exit. Optimum temperatures seemed to be 1 050 to 1 070 ; 700 to 800 and 400 to 500°C respectively in the 3 zones. Temperatures above 1 070°C caused barium sulphide to melt and stick to the wall. Oxygen in the exit gas was 1 to 4% and the yield was 140 kg/hour of barium sulphide.

Brambilla *et. al.* (1975) described a mathematical model and simulation of a rotating furnace as applied to the process of reducing barium sulphate for a kiln with a 6 tons/h feed of barium sulphate.

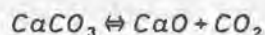
Strigunov *et. al.* (1976) reported an increase in the degree of reduction of baryte with carbon and a prevention of the oxidation of barium sulphide at elevated temperatures by adding 1 to 3% ferrous sulphate based on the mass of barium sulphate.

Lipinski (1965) noted that disagreements existed as to what the optimum particle size of the baryte feed should be. Too fine a feed resulted in some product being lost through the chimney. Large particles of barytes decrepitated in the kiln thus renewing the reaction surface and offsetting any loss of reaction rate due to lack of initial surface area. He noted the industrial practise of preparing the charge by mixing baryte and coal in a 4 : 1 weight ratio.

Nishev *et al.* (1971) gave suitable binders for the kiln pellets as 1% sulphite liquor (based on dry weight of the charges) or 0,5% water glass or 0,5% dextrin.

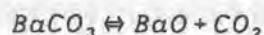
6.1.3 Decomposition of Barium and Calcium Carbonate

The decomposition of calcium carbonate occurs according to the following reaction:



The decomposition of calcite to produce calcium oxide is a massive industry world-wide. The evolution of carbon dioxide above 847°C occurs easily and rapidly and the rate of decomposition increases rapidly with increasing temperature. The particle sizes expected to be found in this process will ensure complete decomposition. Sintering is not a possibility as lime only melts at 2 100°C (Kirk and Othmer, 1982).

If any unreacted barium carbonate should re-enter the kiln it will undergo a similar reaction to that of calcite:



This reaction is very slow when there is a significant partial pressure of carbon dioxide but this kinetic constraint may be overcome at elevated temperatures.

6.1.4 Reactions with Components in the Coal Ash and Natural Barytes

These reactions are important because of the possible formation of water insoluble barium salts which would lead to decreased barium recoveries and increased recycle costs.

The process presented in this thesis includes a new aspect in the thermal reduction of barium sulphate in that substantial quantities of calcium carbonate are present in addition to the normal contaminants found in coal ash and natural barytes.

Brabers (1976) found that South Africa's largest baryte deposit (see Section 4.2) in the Namaqualand District of the Cape Province had the following constituents.

BaSO ₄	85,18 to 98,77%.
SiO ₂	1,09 to 8,25%.
Fe ₂ O ₃	0,64 to 8,47%.

A typical coal ash analysis is given in Section 6.3.2. The major contaminants that have to be considered are thus silicates, aluminates and ferrites. Numerous compounds could possibly be formed between these contaminants and barium and calcium.

Lipinski (1965) reported that each percent of silica in the baryte could bind from 3.6 to 10.8% of the barium sulphate and each percent of iron from 4 to 12%. He stressed the importance of keeping a check on their levels in coal used for reduction. He found that the presence of calcium and magnesium oxides did not detrimentally affect the reduction process.

Nishev (1971) reported adding 10% lime to a baryte kiln feed in order to form calcium silicates and ferrites preferentially to barium silicates and ferrites. It was found that above 10% no additional benefits were derived.

Kadic (1981) explained the positive effect of calcium on the formation of the desirable water soluble portion of barium sulphide melts. High negative values of the free enthalpies of the reaction of calcium oxide with natural materials (mullite, andalusite, kyanite, sillimanite, hercynite, hematite, alumina, cristobalite) at 1 500 K (1 223°C) confirmed that calcium oxide reacted with these impurities which are present in the barytes and coal and so improved the water soluble portion of the black-ash.

If barium aluminates are formed during the reduction it would not be detrimental to the process as they are moderately soluble in water and are easily decomposed by it. They have been very well studied especially in the first half of this century as they were used to desalinate boiler feed water. They dissociated to give barium hydroxide and alumina (Thorpe, p644). The barium reacted with the soluble sulphates and carbonates to form the insoluble barium salts; whilst the gelatinous aluminium hydroxide precipitated by hydrolysis carried with it other impurities. Barium aluminate had the obvious advantage over many other water softeners in that no soluble salts were formed (Thorpe, p284). The fact that it did not remove all soluble calcium and its high cost ensured that its use was discontinued.

(i) Silicates

Silicates are the major constituents of coal ash. Barium and calcium silicates are insoluble and it would be advantageous for this process if the silicates preferentially reacted with calcium and so increased the proportion of water soluble barium salts.

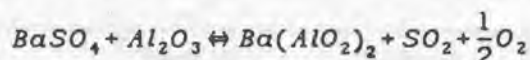
Akhmetov (1972) found that silica underwent allotropic modification at 1 021°C and that there was no significant reaction between barium sulphate and silica at 1 100°C. In a $\text{BaSO}_4/\text{SiO}_2/\text{C}$ mixture the reduction commenced at 1 005°C i.e. at a higher temperature than if the mixture contained only BaSO_4/C . Calcium carbonate dissociated at a lower temperature in the presence of silica. Calcium monosilicate formed at 902°C. In $\text{BaSO}_4/\text{C}/\text{CaCO}_3$ mixtures the reduction of calcium carbonate commenced at 907°C and the reduction of barium sulphate at 949°C.

Silicates form numerous compounds with barium and calcium and in the temperature range being considered (1 100-1 400 K) the formation of the following silicates are possible: $\text{CaO} \cdot \text{SiO}_2$, $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{SiO}_2$, $\text{BaO} \cdot \text{SiO}_2$, $2\text{BaO} \cdot \text{SiO}_2$ and $3\text{BaO} \cdot \text{SiO}_2$.

(ii) Aluminates

As with silicates numerous barium and calcium aluminates exist and in the temperature range considered we could expect the following aluminates: $\text{BaO} \cdot \text{Al}_2\text{O}_3$; $3\text{BaO} \cdot \text{Al}_2\text{O}_3$; $\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

Avgustnik *et. al.* (1947) studied the kinetics of the reaction:



The constants were obtained for the Arrhenius equation:

$$K = C e^{\alpha/T}$$

where α = 81 700 to 86 900 cal/mol (342 to 364 kJ/mol).
 q = αR = 170 000 cal/mol (711 kJ/mol).
 C = 10^{18} to 10^{20} .
 R = Universal gas constant.
 q = Activation energy.

Addition of 5% calcium oxide at low temperature speeded up the reaction and lowered α to 65 000 cal/mol (272 kJ/mol).

(iii) Ferrites

Ferrites have been well studied as they have caused many problems in baryte reduction by helping the mixture to sinter and by forming the insoluble barium ferrites.

Alekseev *et. al.* (1978) showed in a theoretical thermodynamic examination that the formation of $\text{BaO} \cdot \text{Fe}_2\text{O}_3$ and $2\text{BaO} \cdot \text{Fe}_2\text{O}_3$ is thermodynamically possible. Of the two the more stable compound was $2\text{BaO} \cdot \text{Fe}_2\text{O}_3$. The thermal decomposition of barium ferrites was thermodynamically unlikely to occur.

6.2 Thermodynamic Predictions

Thermodynamic calculations were performed to determine the equilibrium conditions of compounds used in the reduction process. The computations were performed using the Villars-Cruise-Smith (VCS) Algorithm for Optimised Stoichiometry as found in Smith and Missen (1982). Thermodynamic data for barium ferrites were obtained from Alekseev *et. al.* (1978) and for all other constituents from Barin *et. al.* (1976). Detailed results are given in Appendix 2.

The thermodynamic calculations showed that the reduction of barium sulphate and the decomposition of calcium carbonate is possible in the range 1 100 to 1 400 K (827 to 1 127°C) provided sufficient carbon is present. The amount of sulphur dioxide and elemental sulphur formed is negligibly small. At 1 400 K the $\text{CO} : \text{CO}_2$ ratio is 99,8 : 0,2 and at 1 100 K it is 92 : 8. If insufficient carbon is present then not all the barium sulphate is reduced and the predominant gas is carbon dioxide.

The equilibrium calculations showed that at 1 400 K (1 127°C) all silica present reacted with the calcium to form $\text{CaO} \cdot \text{SiO}_2$, all ferrites formed $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$ and the aluminates $3\text{CaO} \cdot \text{Al}_2\text{O}_3$.

The products predicted by thermodynamic equilibrium calculations are tabulated in Table 6.1.

Table 6.1 Thermodynamically Predicted Reduction Products

Input	Temp (K)	Products
BaSO_4 CaCO_3 C	1 100-1 400	BaS CaO CO CO ₂
BaSO_4 CaCO_3 C SiO_2	1 400	BaS CaO CO CO ₂ $\text{CaO} \cdot \text{SiO}_2$
BaSO_4 CaCO_3 C Al_2O_3	1 400	BaS CaO CO CO ₂ $3\text{CaO} \cdot \text{Al}_2\text{O}_3$
BaSO_4 CaCO_3 C Fe_2O_3	1 400	BaS CaO CO CO ₂ $2\text{CaO} \cdot \text{Fe}_2\text{O}_3$

6.3 Experimental Reductions

6.3.1 Description of Thermobalance

All thermal reductions were carried out in an isothermal thermobalance wherein an inert atmosphere was created by a constant purge of nitrogen. It allowed for mass measurement and mass data capture on a micro-computer (den Hoed, 1984).

The reactant was placed in an alumina crucible which in turn was placed on a supporting rod. The rod was connected to the load cell pin of a Mettler PC 2 000-S2 balance which allowed for data transmission to the computer; an Apple II Plus. The computer received, manipulated, displayed and stored data on a diskette. It did not control any variables.

The temperature of the sample was measured by means of a thermocouple positioned just above the crucible. The temperature was controlled by a Eurotherm temperature controller.

The construction of the thermobalance allowed for isothermal gravimetry as the sample was only raised into the reaction zone once the required temperature and atmosphere had been established. The sample was heated up to just below the reaction temperature before insertion into the high temperature zone.

The cross-section of the thermobalance is depicted in Figure 6.1.

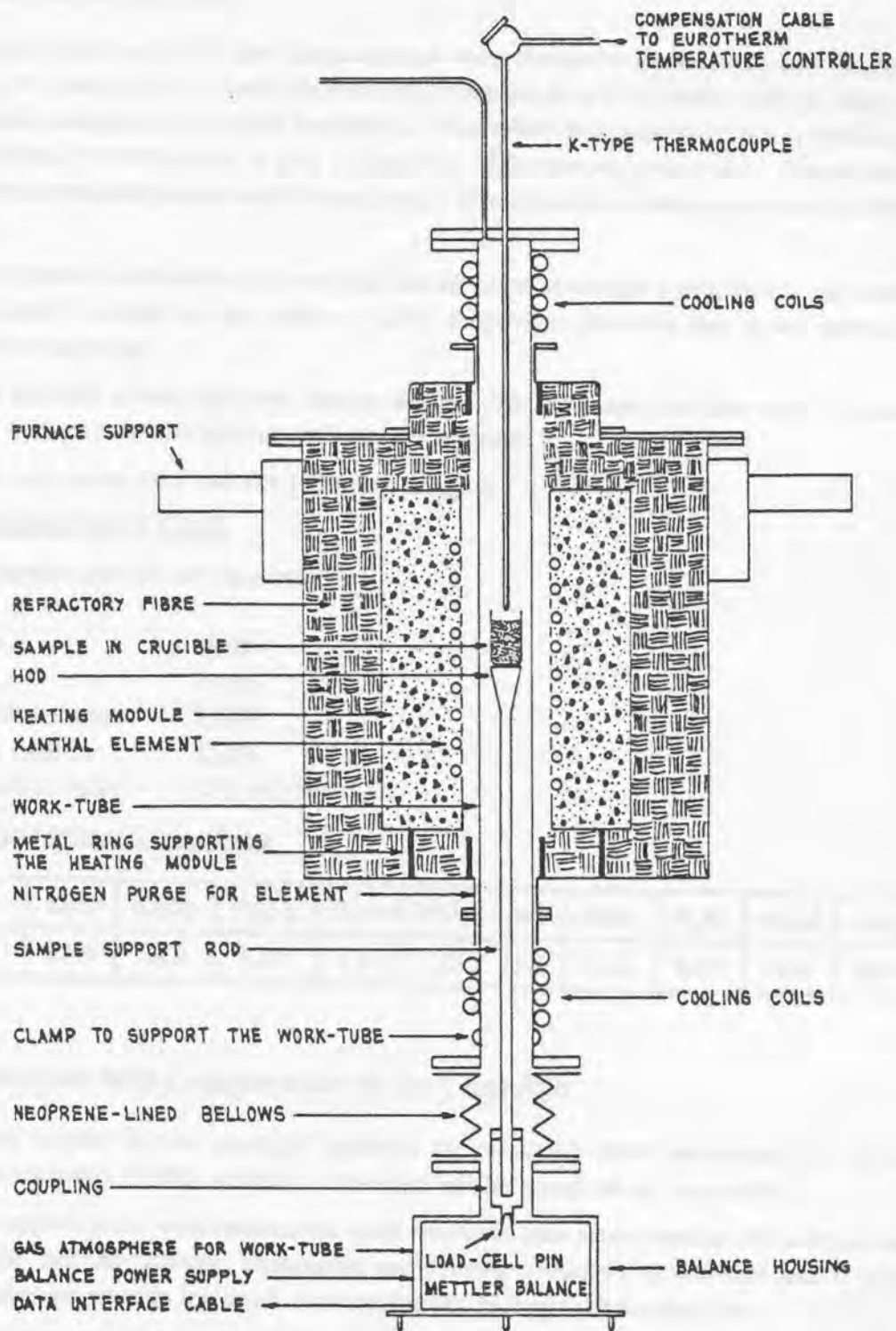


FIGURE 6.1 : Thermobalance Cross-section

6.3.2 Reduction Kinetics

Sample sizes for use in the thermobalance were limited to between 20 and 30 g each due to crucible size. Reaction mixtures consisted of a 1 : 1 molar ratio of analytical barium sulphate and calcium carbonate. Pulverised Bosjesspruit coal was used as the reductant and was added in a 5 : 1 mass ratio of barium sulphate : coal. The reduction mixture was well mixed before being used. The reduction kinetics are shown in Figure 6.2.

The kinetics indicate that the reaction should occur at as high a temperature as possible but that it should be kept below 1 200°C to prevent sintering due to the melting of barium sulphide.

Size analysis of the reduction charge showed that the mean coal size was 15 microns and barium sulphate/calcium carbonate 5 microns.

The coal being used had the following analysis:

BOSJESSPRUIT COAL

Proximate analysis (air dry basis)

H ₂ O	3,9%
Ash	20,9%
Volatile matter	21,9%
Free carbon	53,3%
Calorific value	31,0 MJ/kg

Mineral Matter Composition

Component	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	TiO ₂	CaO	MgO	K ₂ O	Na ₂ O	SO ₃
Mass %	43,6	26,3	6,47	1,43	1,43	11,8	3,64	0,57	0,60	4,06

6.3.3 Reactions with Components of the Coal Ash

Phases present in the products obtained by reduction were determined by X-Ray Diffractometry (XRD) analysis. Detailed results are given in Appendix 5.

The experimental work established what reactions take place between the calcium and barium and the silicates, aluminates and ferrites contained in the coal ash. Other components were in too small a concentration to warrant investigation.

The XRD pattern obtained for the products of the reduction using coal as the reductant (as described in Section 6.3.2) is very complicated. Analysis of this pattern was complicated by the fact that numerous possible products have overlapping peaks. It was thus unrealistic to name the products with certainty.

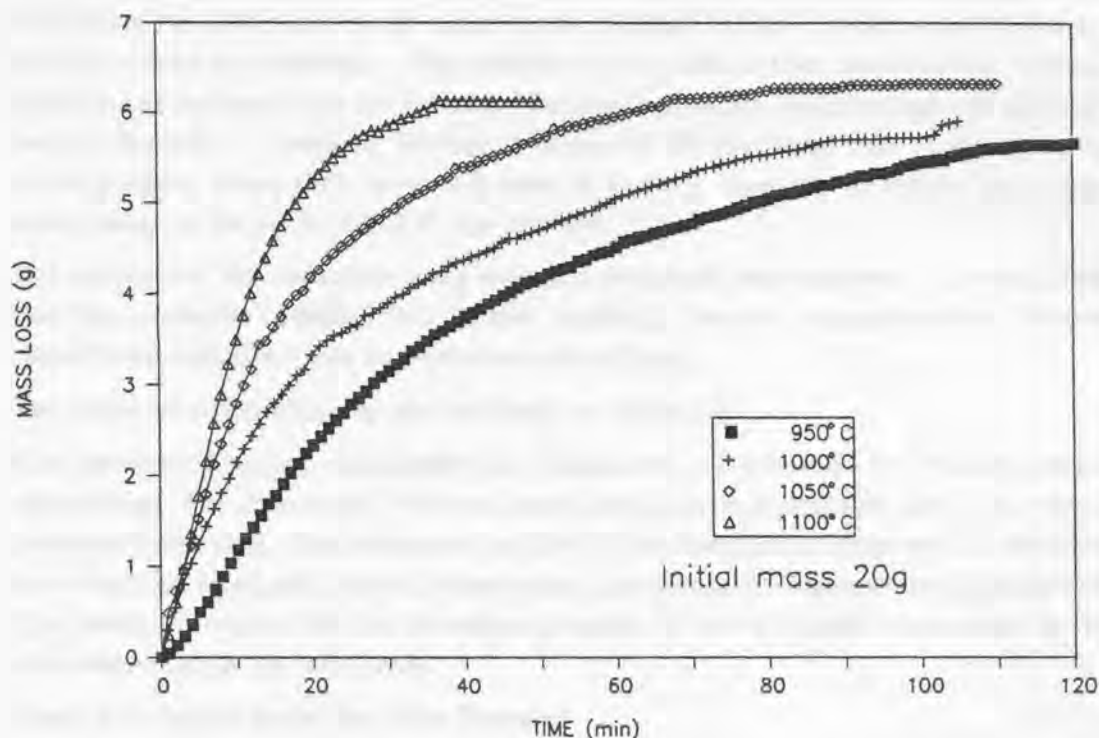


FIGURE 6.2 : Reduction Kinetics of Barium Sulphate and Calcium Carbonate Using Coal as a Reductant

In order to obtain a better understanding of the solid phase analysis it was decided to start with simple systems and to integrate the knowledge that these systems provided into an understanding of the true system.

It was thus decided to use a pure carbon source (lamp-black) and to react each constituent of the ash individually as a control so as to be able to interpret the results of the macro system. All these tests took place at 1 150°C and a reaction time of 90 minutes. The reaction mixture consisted of 20 g of an equimolar $\text{BaSO}_4/\text{CaCO}_3$ mixture to which 2,1 g of lamp-black was added and the sample well mixed.

The analysis of reaction products from a $\text{BaSO}_4/\text{CaCO}_3/\text{C}$ charge showed, as predicted by thermodynamics, that barium sulphide and calcium oxide were formed. It was observed that excess carbon and sufficient reaction time is necessary in order to reduce all the barium sulphate.

The $\text{BaSO}_4/\text{CaCO}_3/\text{C}$ mixture with 2% silica added formed calcium monosilicate, calcium oxide and barium sulphide. This is beneficial to the process as the presence of calcium will prevent barium from reacting with the chief component of the coal ash and so will aid barium recovery in a soluble form. It is also in agreement with the thermodynamic calculations.

The $\text{BaSO}_4/\text{CaCO}_3/\text{C}$ mixture with 2% alumina added formed barium monoaluminate, calcium oxide and barium sulphide. This implies a loss of sulphur in the off gas. These products are not detrimental to our process as barium aluminate is soluble.

The ferrites have very low peaks and on the XRD scan and so artificially high levels of ferric oxide (10%) had to be added to the $\text{BaSO}_4/\text{CaCO}_3/\text{C}$ mixture before ferrite products could be detected. The results showed that barium monoferrite, barium sulphide and calcium oxide are formed. Barium ferrites are insoluble and will decrease barium recovery. Levels of ferrites in excess of 2% (by mass) lead to the sintering of the product hence their level will have to be very carefully monitored especially when make-up baryte is added to the mixture.

The products of the reduction using coal as a reductant were analysed. It was found that the products consisted of: barium sulphide, barium monoaluminate, barium monoferrite, calcium oxide and calcium monosilicate.

The actual products obtained are tabulated in Table 6.2.

The presence of barium aluminates and ferrites was not predicted by thermodynamic calculations. The discrepancy between theory and practice is probably due to inaccurate thermodynamic data. The difference in Gibb's Free Energies between various products is so small that small differences in data could give rise to different product predictions. The possibility exists that the discrepancy might be due to kinetic constraints as the reactions occur in the solid state.

Table 6.2 Actual Reduction Kiln Products

Input	Temp (K)	Products
BaSO ₄ CaCO ₃ Coal	1 423	BaS CaO CaO.SiO ₂ BaO.Al ₂ O ₃ BaO.Fe ₂ O ₃

6.4 Summary

Carbon monoxide is responsible for the reduction of barium sulphate in the kiln and it was found to be industrial practise to use coal in a coal: BaSO_4 ratio of 1:4. The kinetics of the reduction increases with temperature but the kiln should be kept below 1 200°C to prevent sintering. The presence of calcium in the kiln is beneficial to the process in that it preferentially reacts with the silicates, thus increasing the water soluble portion of the barium sulphide melt. Thermodynamic calculations show that silicates, ferrites and aluminates should form compounds with the calcium oxide. It was found that only the silicate did. Barium aluminate is soluble and so its presence is no cause for concern. The formation of barium ferrite will result in a barium loss and possible complications due to aiding the sintering of the charge.

6.5 Conclusions

1. The kiln should be operated in the 1 000 to 1 150°C temperature range.
2. The level of iron in the coal ash and make up baryte should be kept extremely low.
3. Intimate mixing and an excess of reductant are necessary to ensure complete reduction.
4. Calcium is beneficial to the reduction process.

any barium oxide present in the reduction kiln product will hydrolyse as follows:



The solution is then extremely caustic, with a pH of 12.5, and when sulfur dioxide is passed through the solution it is readily absorbed as there is much available alkali. The following equilibria are established:



The barium hydroxide will react with the carbonates present in solution to form the insoluble barium carbonate:



The mainly reducing atmosphere and solution of barium carbonate being added to the precipitation. Some barium hydroxide appears to react with the sulfur dioxide between the hydroxide and the hydroxide ions:



The equilibrium concentrations of the various species in solution are established as follows:



In any given temperature the distribution of species present in solution will be pH dependent (Figure 3.11). Only when the pH drops below 8.3 will precipitation of barium carbonate occur.

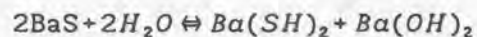
Measurements of the pH of the reacting mixture will give a good indication of the point of reaction.

The sulfur dioxide is provided for the conversion of the gas in the kiln. The reduction of barium sulfate with carbon monoxide and the decomposition of sulfuric acid must be there should be an excess of carbon dioxide available for the hydrolysis reaction.

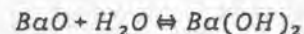
7 THE PRODUCTION OF BARIUM CARBONATE FROM REDUCTION KILN PRODUCTS

7.1 Chemistry of Barium Carbonate Production

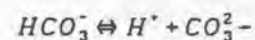
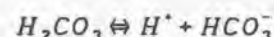
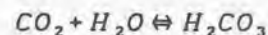
Barium sulphide dissolves readily in water and 10% of the aqueous barium sulphide dissociates as follows (Kirk and Othmer, 1982):



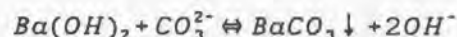
any barium oxide present in the reduction kiln product will hydrolyse as follows:



The solution is thus extremely caustic, with a pH of 12.9, and when carbon dioxide is bubbled through the solution it is readily absorbed to form a weak carbonic acid. The following equilibria are established:



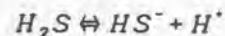
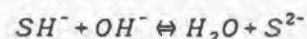
The barium hydroxide will react with the carbonate ions in solution to form the insoluble barium carbonate:



The caustic solution depresses the solubility of barium carbonate thus aiding the precipitation. Some barium hydrosulphide dissociates to maintain the equilibrium between the hydroxide and the hydrosulphide ions.



The equilibrium concentrations of the sulphides in solution are established as follows:



At any given temperature the distribution of sulphur components in solution will be pH dependant (Figure 7.1). Only once the pH drops below 6.5 will evolution of hydrogen sulphide occur.

Measurement of the pH of the reacting mixture will give a good indication of the extent of reaction.

The carbon dioxide is provided by the combustion of the coal in the kiln, the reduction of barium sulphate with carbon monoxide and the decomposition of calcium carbonate so there should be an excess of carbon dioxide available for the carbonation reactions.

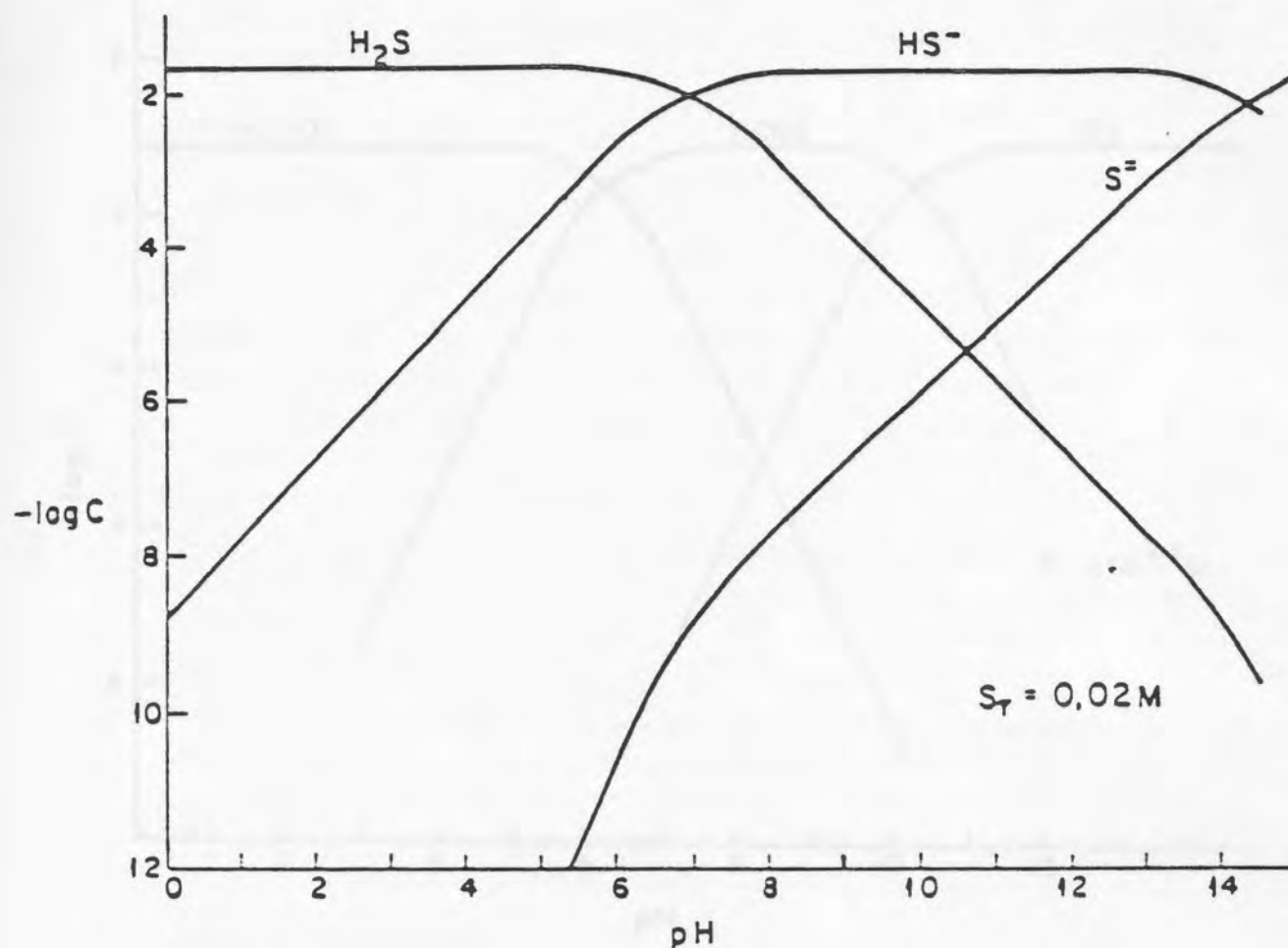


FIGURE 7.1 : Speciation of Sulphur in Solution vs pH (25°C)
(Volman, 1984)

7.2 Leaching with Dissolved Materials

7.2.1

Leaching is the process of extracting a substance from a solid material by a liquid solvent. This process is commonly used in the mining industry to extract metals from ores.

The leaching process involves the reaction of the solid material with the liquid solvent. The reaction is typically exothermic, meaning it releases heat. The rate of leaching is influenced by several factors, including the concentration of the solvent, the surface area of the solid material, and the temperature of the system. The leaching process is often used to extract metals from ores, such as copper, zinc, and lead.

Leaching is a key step in the production of many metals. It is also used in the chemical industry to produce various chemicals, such as acids and bases.

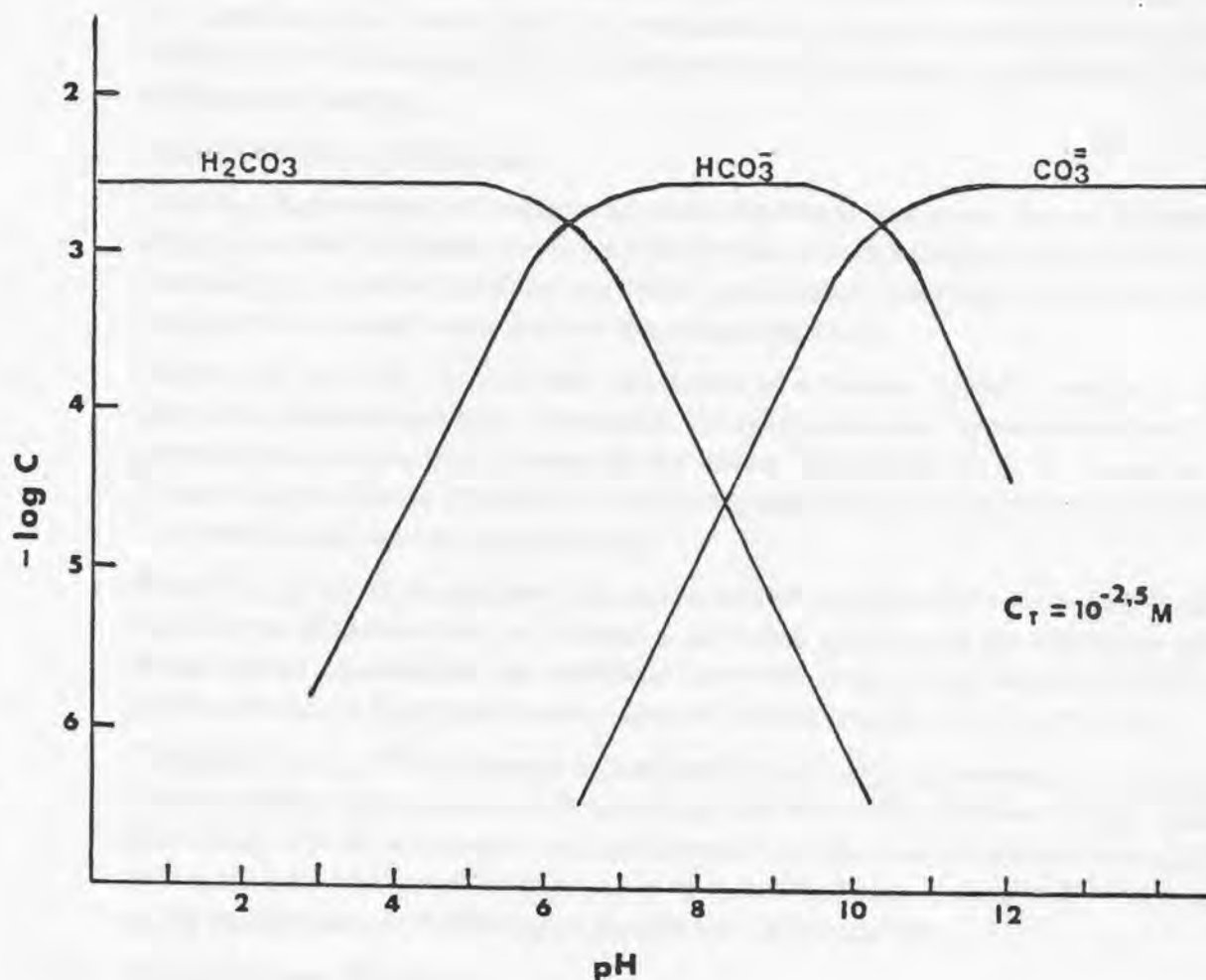


FIGURE 7.2 : Speciation of Carbonates in Solution vs pH (25°C)
(After Stumm and Morgan, 1970)

7.2 Leaching and Production Methods

Leaching

Black ash leaching is an exothermic process and generally occurs in a multi-stage countercurrent extraction system.

For leaching the black ash Pikon *et al.* (1979) proposed the following process. A screw conveyor fed the raw material (ground to -2 mm) into an inverted conical vessel where it was mixed with ascending hot water which was a 1 : (1-5) mixture of fresh solvent and recycled suspension. The suspension was withdrawn for recycling at a point which was located $>1/3$ of the extractor height. The aqueous mixture was then passed into a settling bath where it was stirred with a vibrator. Sludge was separated at the base and clarified liquid at the top.

Akhentov (1973) found that the completeness of the barium sulphide leach from the melt was increased when excess sulphide ions were present.

Semke (1977) proposed the automation of the barium sulphide leaching step by varying the feed of the leaching agent. Control was improved when the flow rate was varied as a function of the charge feed, the temperature of the baryte reduction zone, the temperature of the charge feed at the inlet to the leacher and the temperature of the product after leaching.

Barium Carbonate Precipitation

Recently a large amount of research has been directed at producing barium carbonate which is very low in sulphur and is very fine for use in the glass and ceramic industries. Generally this involves carefully controlled precipitation conditions and subsequent sulphur removal using oxalic acid or ammonium hydroxide.

Panushev *et al.* (1970) studied the carbonation of a barium sulphide solution in an absorption column using a $\text{CO}_2 : \text{N}_2$ mixture. They found that the carbonation efficiency increased with temperature. Increasing the carbon dioxide content in the gas resulted in lower carbon dioxide conversion. Increasing the flow rate of the solution resulted in a lower conversion of barium sulphide.

Pechter *et al.* (1970) investigated the carbonation in a pilot batch bubbler and found that the rate of carbonation, the utilisation of carbon dioxide and the production rate of the column depended on the superficial linear rate of gas in the column (0,0055 to 0,032 m/s) and on the initial concentration of barium sulphide (32,7 to 96,5 g/l).

Yahamada *et al.* (1977) proposed an interesting contacting arrangement. Aqueous barium sulphide and carbon dioxide (at 2,6 kg/cm²) was mixed continuously in a spiral tube which was 50 m long and 5 cm in diameter. A 190 second residence time gave 98% yield and a product of 0,4 micron. A 45 second residence time gave 97% recovery at 0,8 kg/cm² carbon dioxide and a particle size of 0,7 micron.

7.3 Solids Waste Disposal

The main calcium product from the reduction kiln will be calcium oxide. It is sparingly soluble in water (1,85 g/l) and will become slaked with the heat evolved from slaking varying according to the thermal history of the lime. The caustic barium sulphide solution should ensure that the dissociation of the slaked lime is severely depressed.

The calcium silicates are extremely insoluble and together with unreacted coal and coal ash will not affect the solution significantly.

The barium ferrites and unreacted barium sulphate will be lost as insoluble salts.

All insoluble solids may be easily disposed of by filtering the barium sulphide solution. The filter cake should be washed to recover any occluded barium sulphide solution and also to ensure a non-toxic waste. The solid residue will include extremely inert barium compounds, coal ash and lime. This slaked lime might be used as a neutralising agent in numerous other processes and could find use as a byproduct.

7.4 The Experimental Carbonation of Barium Sulphide Solutions

7.4.1 Description of Apparatus

All carbonation experiments were conducted on a batch basis in a 2 l glass reaction vessel sealed with a multiple port hood. A technical grade reagent (80% purity) was used.

The initial barium sulphide concentration was 60 g/l in 1,25 l. The gas reaction mixture was fixed at 20% carbon dioxide and 80% nitrogen to simulate conditions which would exist if all oxygen in the air fed to the kiln was reduced to carbon dioxide and the gas stream was not upgraded in any way.

Flow rates were controlled by means of rotameters. Product gas samples were taken immediately above the reaction mixture through a silicone septum using a gas syringe and were analysed on a GOW-MAC gas chromatograph with a VARIAN 4270 integrator recording the changing conductivity of the detector coil. The chromatograph columns were kept at a constant temperature of 42°C to ensure adequate peak separation between the carbon dioxide and the hydrogen sulphide.

A magnetic stirrer provided the agitation for the mixture to provide good gas dispersion and a large gas/liquid interface. Temperature was controlled by means of a temperature controller/sensor which was connected to the heating element of the stirrer. Control to within about 1°C was achieved. An extra mercury thermometer served as a check on the controller.

All product gases passed through an extensive water jacket to prevent changing the concentration of the reactants.

7.4.2 The Effect of Temperature

The results of constant gas flow rate and varying temperature may be seen in Figures 7.4 and 7.5. Figure 7.4 shows the carbon dioxide utilisation and Figure 7.5 shows hydrogen sulphide concentration in the product stream for various temperatures. Detailed results are given in Appendix 3.

In Figure 7.4 it is seen that with increasing temperature the carbon dioxide utilisation decreases with a consequent reduction in reaction rate. This is probably due to decreased carbon dioxide solubility at higher temperatures. The production rate of hydrogen sulphide is higher at lower temperatures due to increased carbon dioxide utilisation.

7.4.3 The Effect of Gas Flow Rate

The results of varying gas flow rates at a constant temperature are given in Figures 7.6 and 7.7. Figure 7.6 shows the carbon dioxide utilisation and Figure 7.7 shows the concentration of hydrogen sulphide in the product gas stream for various flow rates and a constant temperature. Detailed results are given in Appendix 3.

Figure 7.6 shows that increasing gas flow rates at a constant temperature lead to less utilisation of the carbon dioxide but to an increased reaction rate. The hydrogen sulphide production rate is consequently higher at larger gas flow rates and the larger flow rates result in hydrogen sulphide being less concentrated in the product stream.

At the start of the reactions total carbon dioxide utilisation is observed as any carbon dioxide entering the solution is immediately precipitated as barium carbonate resulting in a negligible mass transfer resistance. The speciation of carbonates in solution represented in Figure 7.2 shows that at high pH's the CO_3^{2-} ion predominates, thus aiding the precipitation of barium carbonate.

When the pH of the solution has dropped sufficiently to liberate hydrogen sulphide there is a dramatic reduction in carbon dioxide utilisation. This is possibly due to the higher concentration of carbonate species in solution, at the lower pH, providing resistance to carbon dioxide entering the liquid phase. The proportion of CO_3^{2-} ions is low thus slowing the reaction between soluble barium and carbonate ions.

For a period after the carbon dioxide utilisation has dropped to zero the evolution of hydrogen sulphide continues due to the stripping action of the reagent gas.

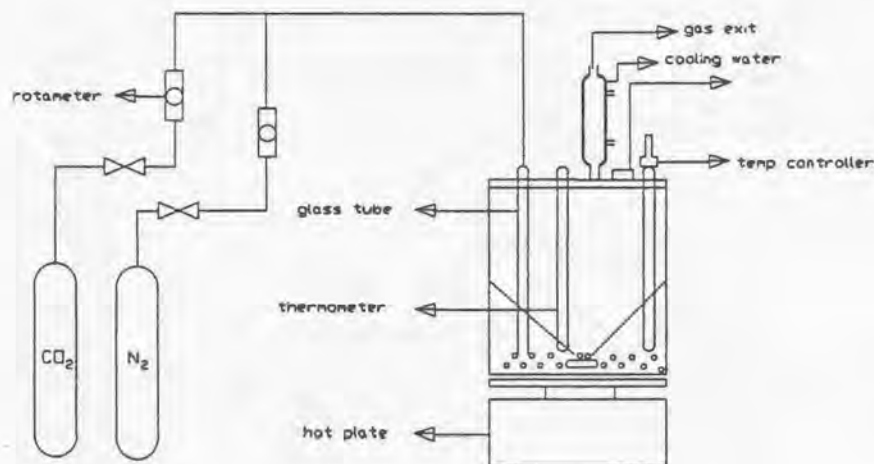


FIGURE 7.3 : Equipment Used for Barium Sulphide Carbonation Experiments

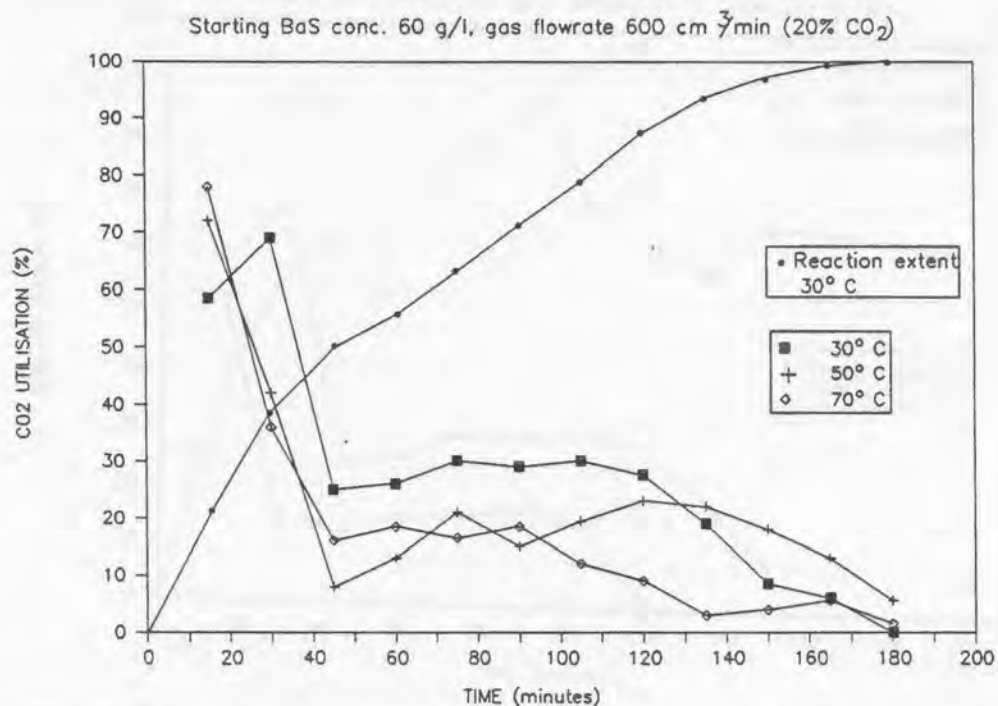


FIGURE 7.4 : Carbonation of Barium Sulphide : The Effect of Varying Temperatures on Carbon Dioxide Utilisation

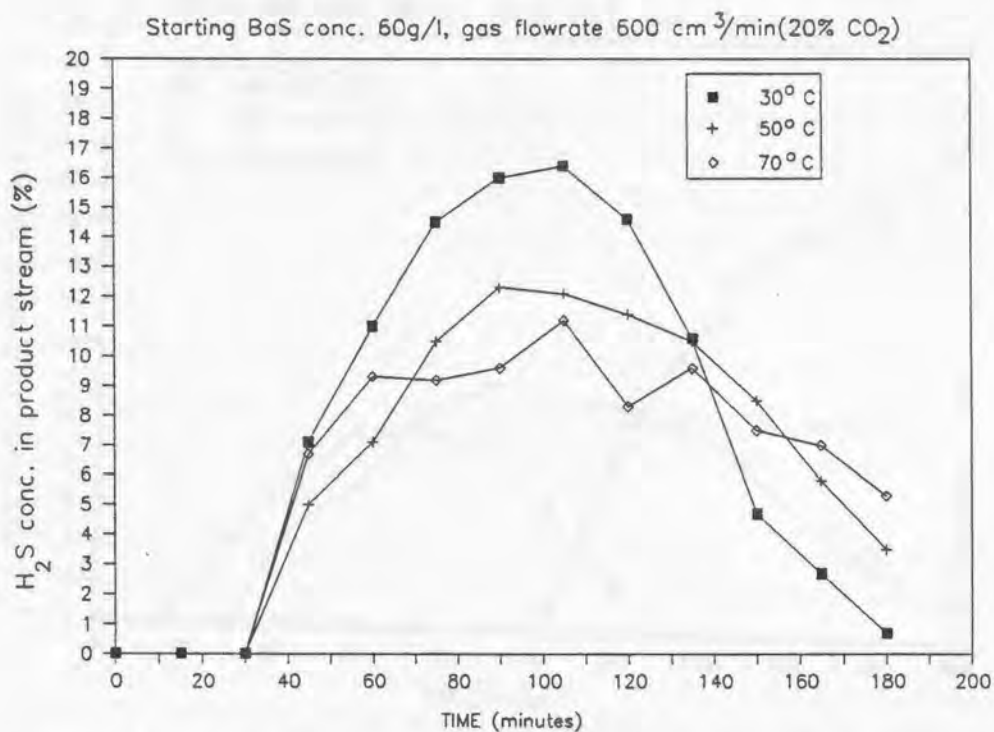


FIGURE 7.5 : Carbonation of Barium Sulphide : The Effect of Varying Temperatures on Hydrogen Sulphide Production

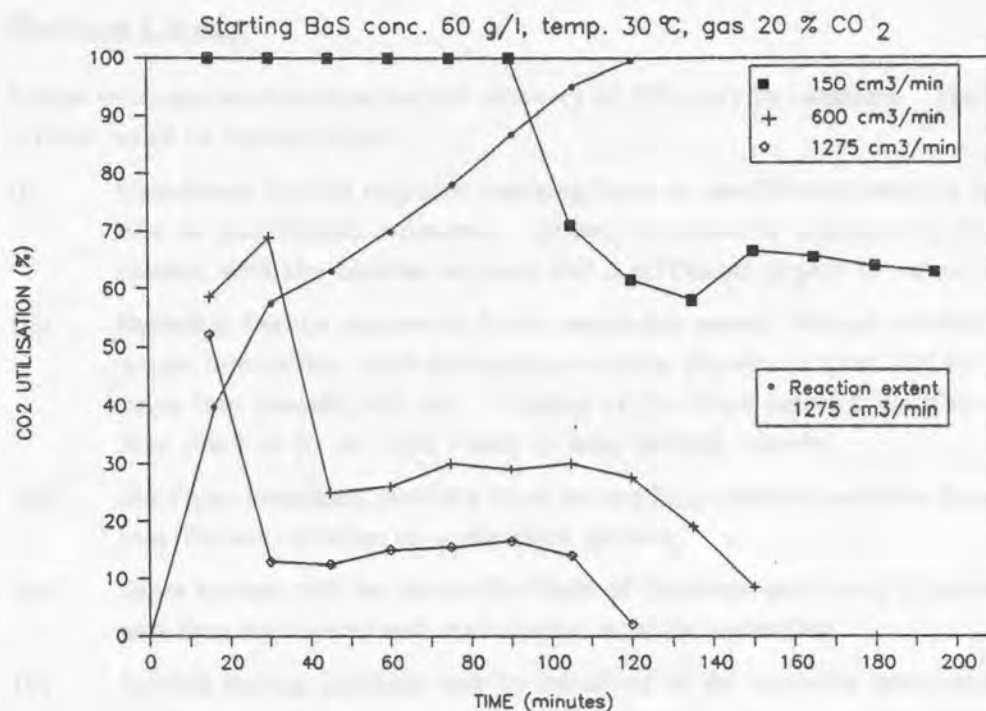


FIGURE 7.6 : Carbonation of Barium Sulphide : The Effect of Varying Flow Rates on Carbon Dioxide Utilisation

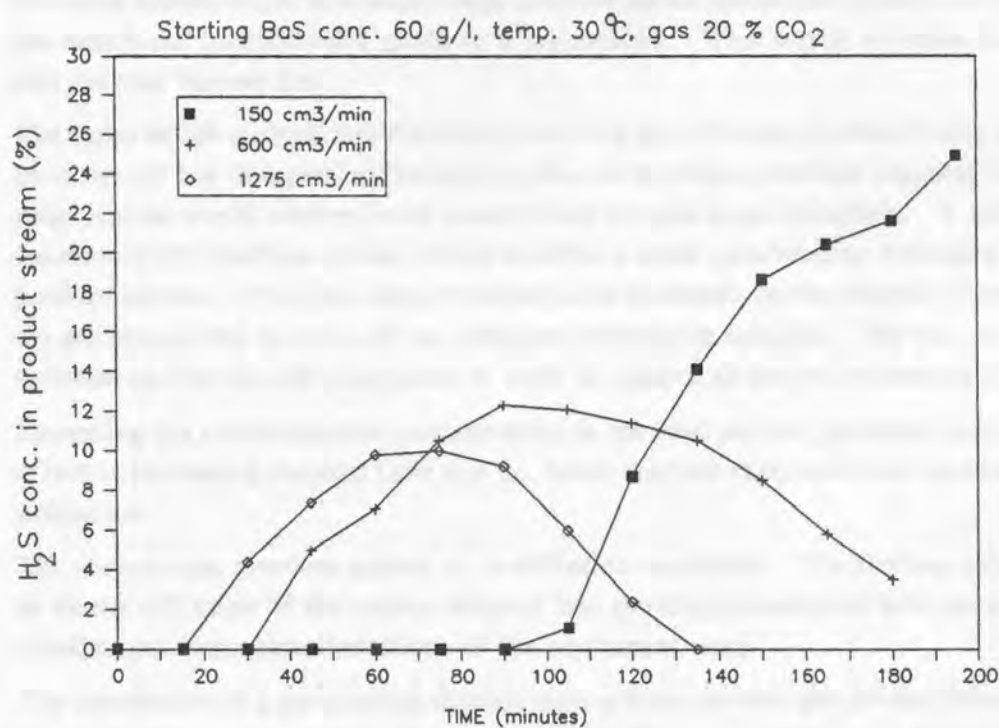


FIGURE 7.7 : Carbonation of Barium Sulphide : The Effect of Varying Flow Rates on Hydrogen Sulphide Production

7.5 Barium Losses

Under optimum conditions a barium recovery of 95% may be obtained. The following effects result in barium losses :

- (i) Unreduced barium sulphate resulting from an insufficient reaction time in the kiln or insufficient reductant. Excess reductant is necessary to ensure good contact with the barium sulphate and a sufficient degree of reduction.
- (ii) Insoluble barium carbonate forms when the caustic barium sulphide solution comes into contact with atmospheric carbon dioxide or when hot kiln products come into contact with air. Cooling of the black ash and leaching must thus take place in an air tight vessel to keep barium soluble.
- (iii) Inefficient leaching resulting from having large product particles from the kiln, insufficient agitation or a saturated solvent.
- (iv) Some barium will be lost in the form of insoluble salts such as barium ferrite and thus the baryte and coal quality must be controlled.
- (v) Soluble barium sulphide may be contained in the insoluble leach residue. The residue should thus be washed during filtering to recover this barium.

7.6 Conclusions

Leaching should occur in a multi-stage countercurrent extraction system to ensure that the maximum concentration gradient is maintained. This would optimise dissolution and prevent barium loss.

The shape of the carbonation reaction curve with no hydrogen sulphide being produced until the pH has dropped sufficiently to liberate hydrogen sulphide suggests that a two stage reactor would ensure better control than a single stage operation. A multi-stage countercurrent reaction system would result in a more concentrated hydrogen sulphide product stream. The first stage would be used to absorb carbon dioxide remaining in the gas stream and to drive off all hydrogen sulphide in solution. The last stage would optimise carbon dioxide absorption in order to remove all barium remaining in solution.

Increasing the carbon dioxide concentration in the feed gas will probably have the same effect as increasing the total flow rate i.e. faster reaction rates and lower carbon dioxide utilisation.

The carbonation reactions appear to be diffusion controlled. The limiting step appears to be the diffusion of the carbon dioxide into the barium sulphide solution noting the possible gas dispersion limitations of the equipment used.

The production of a pure carbon dioxide stream from the kiln gas product stream would result in a more concentrated hydrogen sulphide stream, decrease the size of the carbonation equipment and lead to better control of the reaction.

8 SULPHUR RECOVERY

Hydrogen sulphide is an extremely corrosive, poisonous and objectionable gas. When burnt in air it forms sulphur dioxide which too is corrosive and objectionable. The sulphur contained in the gas does however represent a valuable product.

Recovered sulphur now accounts for over 60% of the total world production of elemental sulphur. Practically all the elemental sulphur recovered from gas streams today is produced by processing hydrogen sulphide (Sander, *et al.*, 1984).

South Africa is in the situation of having an enormous oversupply of sulphuric acid in the mining regions of the country while importing large quantities of expensive elemental sulphur mainly for use at coastal factories. The cost of transporting sulphuric acid is prohibitive but elemental sulphur may be transported much more cheaply. The objective of this process should thus be to produce elemental sulphur to provide an income to cover the running expenses of the plant. The sulphur products contained in a large effluent stream will be concentrated into a relatively small, concentrated gas stream containing virtually no contaminants apart from carbon dioxide, carbon monoxide and nitrogen.

If the economics of sulphur production should be unfavourable or in the event of a pilot plant being constructed the hydrogen sulphide produced by the process could be fed directly into the sulphuric acid plants which exist in most mining complexes. The acid plant roaster would oxidise the hydrogen sulphide to sulphur dioxide which would in turn augment sulphuric acid production.

Hydrogen sulphide may be removed from gas streams by means of wet and dry processes. The dry process may involve reaction with iron oxide or adsorption onto activated carbon. These reactors are generally discontinuous in operation and are best suited to treating gas streams containing low concentrations of hydrogen sulphide.

Wet processes can generally be grouped in one of four categories:

- (i) Non-regenerative processes where hydrogen sulphide reacts with some chemical and is then discarded.
- (ii) Regenerative processes where the absorbing solution is recycled but the hydrogen sulphide is necessarily discarded.
- (iii) Regenerative processes where hydrogen sulphide is recovered as a gas.
- (iv) Regenerative processes where hydrogen sulphide is converted to elemental sulphur.

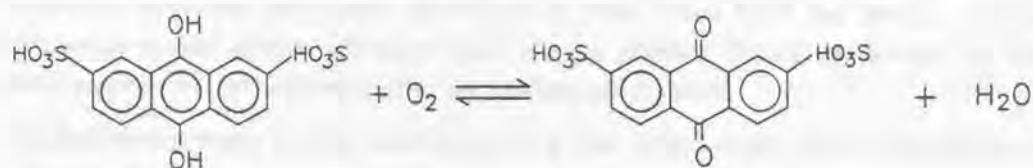
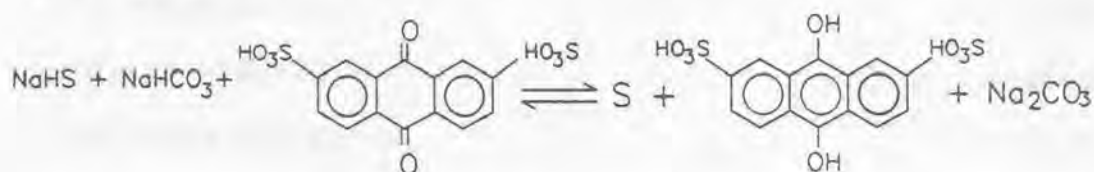
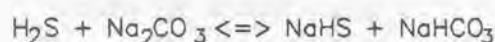
One of the aims of the process is to produce a valuable product from the gas stream and thus the last two separation routes mentioned above warrant investigation.

Regenerative processes, in which hydrogen sulphide is recovered, are used to upgrade and concentrate hydrogen sulphide containing streams. This has the obvious advantage in that further processing steps deal with a smaller flow of almost pure hydrogen sulphide with subsequent savings due to reduced plant size. These processes generally

involve reversible chemical or physical absorption in a liquid medium. Common processes include the use of amines to absorb the hydrogen sulphide or pressure swing absorption (P.S.A.) Techniques.

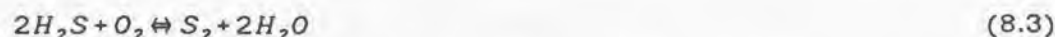
If carbon dioxide is selectively removed from the kiln gas product stream for reaction with the barium sulphide solution then the processing necessary to purify and concentrate the hydrogen sulphide stream may not be required.

Regenerative processes which recover the absorbed hydrogen sulphide in the form of elemental sulphur have the advantage that all reactions occur in the same medium and thus processing equipment may be kept to a minimum. These conversion processes use alkaline solutions containing mild oxidising agents which oxidise the hydrogen sulphide to sulphur and are then themselves regenerated by means of air. Currently the main commercial process of this type is the Stretford process. It was developed on the following chemical steps.



Metavanadate oxidises the bisulphide ions formed and is itself reduced to a lower valency state. The anthroquinone disulphonic acid (ADA) reoxidises the reduced vanadium values back to the metavanadate, being reduced to the phenolic form in the process. Aeration of the solution oxidises the phenolic form of the ADA back to the quinone form.

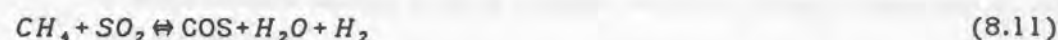
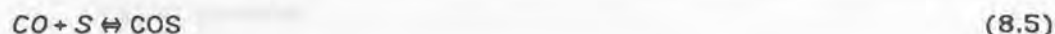
The most famous sulphur recovery route is the Claus Process. It was invented in 1883 and large scale use began in the 1950's. Principal chemical reactions are:



Instead of oxidising one third of the hydrogen sulphide stream via reaction (8.1) use could be made of the sulphur dioxide produced by the acid plant roasters on the mines which would augment the sulphur production substantially as well as reduce the present glut of sulphuric acid.

The reactions involved in the Claus process are extremely exothermic and the heat of reaction must be dissipated to ensure sufficient conversion. This energy may be used, for instance, to heat elution columns in a gold recovery operation. Two tonnes of steam at 5 bar may be raised per tonne of sulphur produced (Sander *et al.*, 1984). Since reaction rate drops with decreasing temperature suitable catalysts must be used to improve sulphur yields.

Possible side reactions include (Lurgi, 1984):



Despite the existence of all these side reactions the sulphur recovery is 97% plus. Numerous processes have been developed to treat Claus Plant tail gases. Obviously economics would dictate whether these tail gas streams should be treated to recover more sulphur or just directed into an existing acid plant.

The Sulfreen process is often referred to as a "low temperature Claus" process and from a chemical and technological point of view the two are very similar. Reactors are operated cyclically using an aluminium oxide catalyst which simultaneously acts as an absorbing agent. The catalyst is regenerated cyclically when the sulphur is desorbed. The lower reaction temperature shifts the equilibrium in equation (8.2) to the right. This process requires very few additional utilities and capital costs amount to about 30% of a two-stage Claus process.

Numerous possible processing routes thus exist and the choice of process will obviously depend on economic considerations.

9 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

- (i) The addition of barium carbonate and lime to sulphate mine effluents effectively removes all dissolved solids except for group I and VII ions.
- (ii) Calcium carbonate seed crystals enhance reaction rates.
- (iii) The sulphates in the effluents are captured in the form of a concentrated hydrogen sulphide stream which is amenable to further processing into valuable sulphur products.
- (iv) The barium salts may be effectively recycled with minimal make-up being required.
- (v) Barium is handled in its least toxic forms, namely the sulphate and the carbonate.
- (vi) The barium sulphate and carbonate precipitates may be readily thickened and filtered.
- (vii) The presence of calcium carbonate in the reduction step enhances the recovery of water soluble barium salts by reaction with the silicates contained in the coal and barytes.
- (viii) All unit operations are ideally suited to a mining environment.
- (ix) Technology required for this process is available.
- (x) The raw materials required, namely barytes and coal, exist in abundance in South Africa while the products, sulphur and water, are in demand.
- (xi) The establishment of a baryte reduction kiln could pave the way for the establishment of a barium chemicals industry in South Africa.
- (xii) There is no solids or brine disposal problem.
- (xiii) The treatment of mine effluents is an effective way of reducing the TDS level in the Vaal Barrage. This results in savings to all water consumers in the Vaal Basin.

9.2 Recommendations

- (i) Extensive economic evaluation of this process will reveal whether it is economically viable and where changes should be made to the process. It would also highlight areas which might require further investigation.
- (ii) Industry should be made aware of the existence of this process and its potential application in their processes. The potential uses for this process should not be confined to sulphate effluent treatment.
- (iii) Pilot plant runs will give accurate operating data for the design of a full scale plant.

- (iv) If this process is shown to be economically viable the government should not renew special permits to mines dumping sulphate effluents and should treat them on a par with other segments of industry. A wide cross-section of people will benefit from lower TDS levels in the Vaal catchment and so the government should consider subsidising the process initially.
- (v) Other uses for soluble barium salts in this country should be investigated.

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APPENDIX 1: RESULTS OF TEST WORK CONDUCTED ON**AQUEOUS CHEMICAL SYSTEMS****Nomenclature**

t = time (minutes).

T = temperature (°C).

Ca = total dissolved calcium (mg/l as Ca).

SO₄ = total dissolved sulphates (mg/l as SO₄).

Na = total dissolved sodium (mg/l as Na).

Mg = total dissolved magnesium (mg/l as Mg).

t = 0 corresponds to the system before reagent addition.

Reactions between CaSO₄ solutions and BaCO₃.**(i) Varying stoichiometry of BaCO₃**

T = ambient

BaCO ₃ added	t	SO ₄
Stoichiometric	0	1 500
	15	1 272
	30	864
	45	480
	60	216
	75	96
	90	72
1,5 x stoich	0	1 500
	15	1 224
	30	816
	45	312
	60	84
	75	48
	90	48
2 x stoich	0	1 500
	15	1 032
	30	504
	45	108
	60	48
	75	48
	90	48

- (ii) Investigating various seeding techniques with a stoichiometric amount of BaCO_3 .

Seed	t	SO_4
10 g/l BaSO_4	0	1 500
	15	1 114
	30	898
	45	509
	60	142
	75	38
	90	22
10 g/l CaCO_3	0	1 500
	15	871
	30	386
	45	53
	60	17
	75	29
	90	14
5 g/l CaCO_3 and 5 g/l BaSO_4	0	1 425
	15	715
	30	485
	45	67
	60	26
	75	24
	90	28
Sequential seeding with CaCO_3	0	1 466
	15	946
	30	331
	45	31
	60	26
	75	22
	90	22

- (iii) Investigating the effect of magnesium on sulphate removal with a stoichiometric amount of BaCO_3

Mg	t	SO_4
0	0	1 500
	15	1 272
	45	480
	60	216
	90	72
200	0	1 500
	15	1 059
	45	558
	60	316
	90	111
500	0	1 500
	15	903
	45	579
	60	405
	90	256

t	SO_4
0	1 500
15	1 272
45	480
60	216
90	72

- (iii) With varying proportions of stoichiometry after repeating the experiment on combinations: total SO_4 level was 2 640 mg/L

BaCO_3	SO_4
1 x stoichiometry	1 500
1.25 x stoichiometry	720
1.5 x stoichiometry	360
1.75 x stoichiometry	180
2.0 x stoichiometry	72
2.25 x stoichiometry	36

The Rate of Sulphate Removal from an Na_2SO_4 Solution

(i) Stoichiometric addition of BaCO_3

t	SO_4
0	3 000
5	1 704
15	1 378
30	1 215
45	1 114
60	1 203
125	1 023

0	1 500
5	896
15	774
30	675
45	584
60	618
125	474

t	SO_4
0	2 440
5	1 523
15	1 396
30	1 150
45	1 086
60	980

(ii) With varying proportions of stoichiometry after reacting for one hour at each concentration. Initial SO_4 level was 2 440 mg/l.

BaCO_3	SO_4
1 x stoichiometry	1 022
1,25 x stoichiometry	936
1,50 x stoichiometry	833
1,75 x stoichiometry	744
2,00 x stoichiometry	756
3,00 x stoichiometry	659

The Rate of Sulphate Removal from a MgSO_4 Solution Using a stoichiometric amount of BaCO_3

t	SO_4
0	500
5	341
30	285
60	253
90	250
0	1 000
5	761
30	645
60	553
90	526
0	1 500
5	1 080
30	947
60	900
90	854

APPENDIX 2: RESULTS OF WORK DONE ON THE THERMAL**REDUCTION OF BARIUM SULPHATE**

Thermodynamic Calculations Performed using the
Villars-Cruise-Smith Algorithm.

1.(i) Input

Temp. : 1 400 K

Pressure : 1 atm.

Inerts : 0

Elemental Abundances Ba 1 (moles)
Ca 1 (moles)
S 1 (moles)
O 7 (moles)
C 6 (moles)

Species	Standard Chemical Potential (kcal/mol)
CO	-1,00284 E + 2
CO ₂	-1,77078 E + 2
CaO	-1,77358 E + 2
BaS	-1,49153 E + 2
S ₂	-5,43400 E + 1
CaCO ₃	-3,43681 E + 2
BaSO ₄	-4,26272 E + 2
SO ₂	-1,65848 E + 2
C (solid)	-5,75700 E + 0

1.(ii) Output

Species	Equilibrium Moles
CO	5,9796404 E + 0
CaO	1,0000000 E + 1
BaS	1,0000000 E + 1
CO ₂	1,0179809 E - 2
SO ₂	7,2663678 E - 19
C (solid)	1,0179809 E - 2
S ₂	4,7423166 E - 22
BaSO ₄	0,0000000
CaCO ₃	0,0000000

2.(i) Input

Temp. : 1 200 K

Pressure : 1 atm.

Inerts : 0

Elemental Abundances

Ba	1 (moles)
Ca	1 (moles)
S	1 (moles)
O	7 (moles)
C	6 (moles)

Species	Standard Chemical Potential (kcal/mol)
CO	-1,63544 E + 2
CO ₂	-8,86580 E + 1
CaO	-1,71928 E + 2
BaS	-1,41777 E + 2
S ₂	-4,10794 E + 1
CaCO ₃	-4,10903 E + 2
BaSO ₄	-3,32738 E + 2
SO ₂	-1,50575 E + 2
C (solid)	-4,30500 E + 0

(ii) Output

Species	Equilibrium Moles
CO	5,7855837 E + 0
CaO	1,0000000 E + 0
BaS	1,0000000 E + 0
CO ₂	1,0720816 E - 1
SO ₂	1,6065618 E + 19
C (solid)	1,0720816 E - 1
S ₂	5,7390181 E - 25
BaSO ₄	0,0000000
CaCO ₃	0,0000000

3.(i) Input

Temp. : 1 100 K

Pressure : 1 atm.

Inerts : 0

Elemental Abundances

Ba	1 (moles)
Ca	1 (moles)
S	1 (moles)
O	7 (moles)
C	6 (moles)

Species	Standard Chemical Potential (kcal/mol)
CO	-1,56937 E + 2
CO ₂	-8,29420 E + 1
CaO	-1,69373 E + 2
BaS	-1,38250 E + 2
S ₂	-3,44050 E + 1
CaCO ₃	-4,03623 E + 2
BaSO ₄	-3,27129 E + 2
SO ₂	-1,43102 E + 2
C (solid)	-3,64600 E + 0

3.(ii) Output

Species	Equilibrium Moles
CO	5,1565555 E + 0
CaO	1,0000000 E + 0
BaS	1,0000000 E + 0
CO ₂	4,2172223 E - 1
SO ₂	1,6106963 E - 18
C (solid)	4,2172223 E - 1
S ₂	6,4647576 E - 24
BaSO ₄	0,0000000
CaCO ₃	0,0000000

4.(i) Input

Temp. : 1 400 K

Pressure : 1 atm.

Inerts : 0

Elemental Abundances

Ba	1 (moles)
Ca	1 (moles)
S	1 (moles)
O	7 (moles)
C	6 (moles)
Si	0,2 (moles)

Species	Standard Chemical Potential (kcal/mol)
CO	-1,00248 E + 2
CO ₂	-1,77078 E + 2
BaS	-1,49153 E + 2
CaO	-1,77358 E + 2
CaO.SiO ₂	-4,45286 E + 2
2BaO.SiO ₂	-6,49015 E + 2
BaSO ₄	-4,26272 E + 2
C (solid)	-5,75700 E + 0
2CaO.SiO ₂	-6,20271 E + 2
3CaO.SiO ₂	-7,97814 E + 2
BaO.SiO ₂	-4,53624 E + 2
CaCO ₃	-3,43681 E + 2
SiO ₂	-2,46876 E + 2

4.(ii) Output

Species	Equilibrium Moles
CO	5,9791094 E + 0
CaO.SiO ₂	2,0000000 E - 1
BaS	1,0000000 E + 0
CO ₂	1,0445314 E - 2
2BaO.SiO ₂	1,4875000 E - 10
CaO	8,0000000 E - 1
BaSO ₄	0,0000000
C (solid)	1,0445314 E - 2
3CaO.SiO ₂	0,0000000
2CaO.SiO ₂	0,0000000
CaCO ₃	0,0000000
BaO.SiO ₂	0,0000000
SiO ₂	0,0000000

5.(i) Input

Temp. : 1 400 K

Pressure : 1 atm.

Inerts : 0

Elemental Abundances

Ba	1 (moles)
Ca	1 (moles)
S	1 (moles)
O	7,6 (moles)
C	7 (moles)
Al	0,4 (moles)

Species	Standard Chemical Potential (kcal/mol)
CO	-1,00248 E + 2
CO ₂	-1,77078 E + 2
CaO	-1,77358 E + 2
BaS	-1,49153 E + 2
CaCO ₃	-3,43681 E + 2
BaSO ₄	-4,26272 E + 2
C (solid)	-5,75700 E + 0
Al ₂ O ₃	-4,44162 E + 2
3CaO.Al ₂ O ₃	-9,88094 E + 2
BaO.Al ₂ O ₃	-6,45561 E + 2
CaO.Al ₂ O ₃	-6,31360 E + 2

5.(ii) Output

Species	Equilibrium Moles
CO	5,9791094 E + 0
CaO	6,0000000 E - 1
BaS	1,0000000 E + 0
CO ₂	1,0445314 E - 2
C (solid)	1,0104453 E + 0
BaSO ₄	0,0000000
CaCO ₃	0,0000000
Al ₂ O ₃	0,0000000
3CaO.Al ₂ O ₃	2,0000000 E - 1
BaO.Al ₂ O ₃	1,0000000 E - 18
CaO.Al ₂ O ₃	0,0000000

6.(i) Input

Temp. : 1 400 K

Pressure : 1 atm.

Inerts : 0

Elemental Abundances

Ba	1 (moles)
Ca	1 (moles)
S	1 (moles)
O	7,6 (moles)
C	7 (moles)
Fe	0,4 (moles)

Species	Standard Chemical Potential (kcal/mol)
CO	-1,00248 E + 2
CO ₂	-1,77078 E + 2
CaO	-1,77358 E + 2
BaS	-1,49153 E + 2
CaCO ₃	-3,43681 E + 2
BaSO ₄	-4,26272 E + 2
C (solid)	-5,75700 E + 0
Fe ₂ O ₃	-2,60372 E + 2
2BaO.Fe ₂ O ₃	-6,51636 E + 2
2CaO.Fe ₂ O ₃	-6,28080 E + 2
CaO.Fe ₂ O ₃	-4,46138 E + 2
BaO.Fe ₂ O ₃	-4,64404 E + 2

6.(ii) Output

Species	Equilibrium Moles
CO	5,9791094 E + 0
CaO	6,0000000 E - 1
BaS	1,0000000 E + 0
CO ₂	1,0445314 E - 2
C (solid)	1,0104453 E + 0
BaSO ₄	0,0000000
CaCO ₃	0,0000000
2CaO.Fe ₂ O ₃	2,0000000 E - 1
BaO.Fe ₂ O ₃	1,2652765 E - 18
2BaO.Fe ₂ O ₃	0,0000000
Fe ₂ O ₃	0,0000000
CaO.Fe ₂ O ₃	1,0000000 E - 10

Reduction of Barium Sulphate in a Thermobalance

(i) The reaction charge used was made up of an equimolar mixture of BaSO_4 and CaCO_3 . This was mixed in with pulverised coal with a BaSO_4 : coal ratio (mass) of 5 : 1. Reaction continued for 90 minutes.

Temp. of reduction ($^{\circ}\text{C}$)	950	1 000	1 050	1 100	1 150	1 200
mass of charge (g)	20,00	20,00	20,00	20,00	20,00	20,00
mass of product (g)	<u>14,06</u>	<u>13,85</u>	<u>12,95</u>	<u>12,94</u>	<u>12,83</u>	<u>12,66</u>
mass loss (g)	5,94	6,15	7,08	7,06	7,17	7,34

5 g of each product was agitated in 1 ℓ of water to determine the water solution portion.

Temp. of reduction ($^{\circ}\text{C}$)	950	1 000	1 050	1 100	1 150	1 200
Water Soluble (%)	51,5	51,1	67,7	69,2	69,6	67,5
Barium Recovery (%)	62	-	75	79	78	74

(ii) Reaction charge: BaSO_4 11,6 g
 CaCO_3 5 g
 Coal 4 g
 reaction time 3,5 hours
 barium recovery 94%

APPENDIX 3: EXPERIMENTAL RESULTS OF THE CARBO-
NATION OF A BARIUM SULPHIDE SOLUTION

F = flow rate of reactant gas (cm³/min).

T = temperature (°C).

H₂S = H₂S in product gas stream (%).

CO₂ = CO₂ in product gas stream (%).

t = time (minutes)

The BaS used was a technical grade reagent and the feed gas consisted of 20% CO₂ and 80% N₂.

RUN 1 BaS = 60 g/l

F = 600

T = 30

t	H ₂ S	CO ₂
12	0	5,6
13	0	4,6
15	0	8,3
26	0	6,2
28	0	6,2
41	6,1	14,8
53	8,2	15,1
68	13,5	14,3
75	14,5	14,0
88	16,0	14,2
105	16,4	14,0
120	14,6	14,5
135	10,6	16,2
150	4,7	18,3
176	0,7	21,0

RUN 2 BaS =60 g/l
 F =600
 T =50

t	H ₂ S	CO ₂
15	0	5,6
30	0	11,6
45	5,0	18,4
60	7,1	17,4
75	10,5	15,8
90	12,3	17,0
105	12,1	16,1
120	11,4	15,4
135	10,5	15,6
150	8,5	16,4
165	5,8	17,4
180	3,5	18,9

RUN 3 BaS =60 g/l
 F =600
 T =70

t	H ₂ S	CO ₂
2	0	2,0
15	0	4,4
32	0	12,8
45	6,7	16,8
60	9,3	16,3
75	9,2	16,7
90	9,6	16,3
105	11,2	17,6
120	8,3	18,2
135	9,6	19,4
160	7,5	19,2
165	7,0	18,9
180	5,3	19,7

RUN 4 BaS =60 g/l

F =1 275

T =30

t	H ₂ S	CO ₂
8	0	8,4
15	0	9,6
30	4,4	17,4
45	7,4	17,5
60	9,8	17,0
75	10,0	16,9
90	9,2	16,7
105	6,0	17,2
120	2,4	19,6

RUN 5 BaS =60 g/l

F =150

T =30

t	H ₂ S	CO ₂
15	0	0
30	0	0
45	0	0
60	0	0
75	0	0
90	0	0
105	1,1	5,8
120	8,7	7,7
135	14,1	8,4
150	18,6	6,7
165	20,4	6,9
180	21,6	7,2
195	24,9	7,1

APPENDIX 4 : SOLUBILITY PRODUCTS AND CRITICAL STABILITY**CONSTANTS**

The numbering for the K values refers to the equations in Section 5.1.1. and were obtained from Smith and Martells, 1976.

	<u>log K</u>
K1	0,32
K2	1,0
K3	-5,19
K4	0,43
K5	-8,35
K6	1,67
K7	-3,6
K8	-8,30
K9	0,36
K10	0,094
K11	0,157
K12	-9,96
K13	-7,46
K14	0,35
K15	0,45
K16	-11,15
K17	1,05
K18	-5,0
K19	1,43

APPENDIX 5 : THE X-RAY DIFFRACTOMETRY RESULTS FROM THERMOBALANCE PRODUCTS

Both reduction products and insoluble residues are examined.

The d-spacing may be obtained by using Bragg's Law i.e.

$$d = \lambda / 2 \sin \theta$$

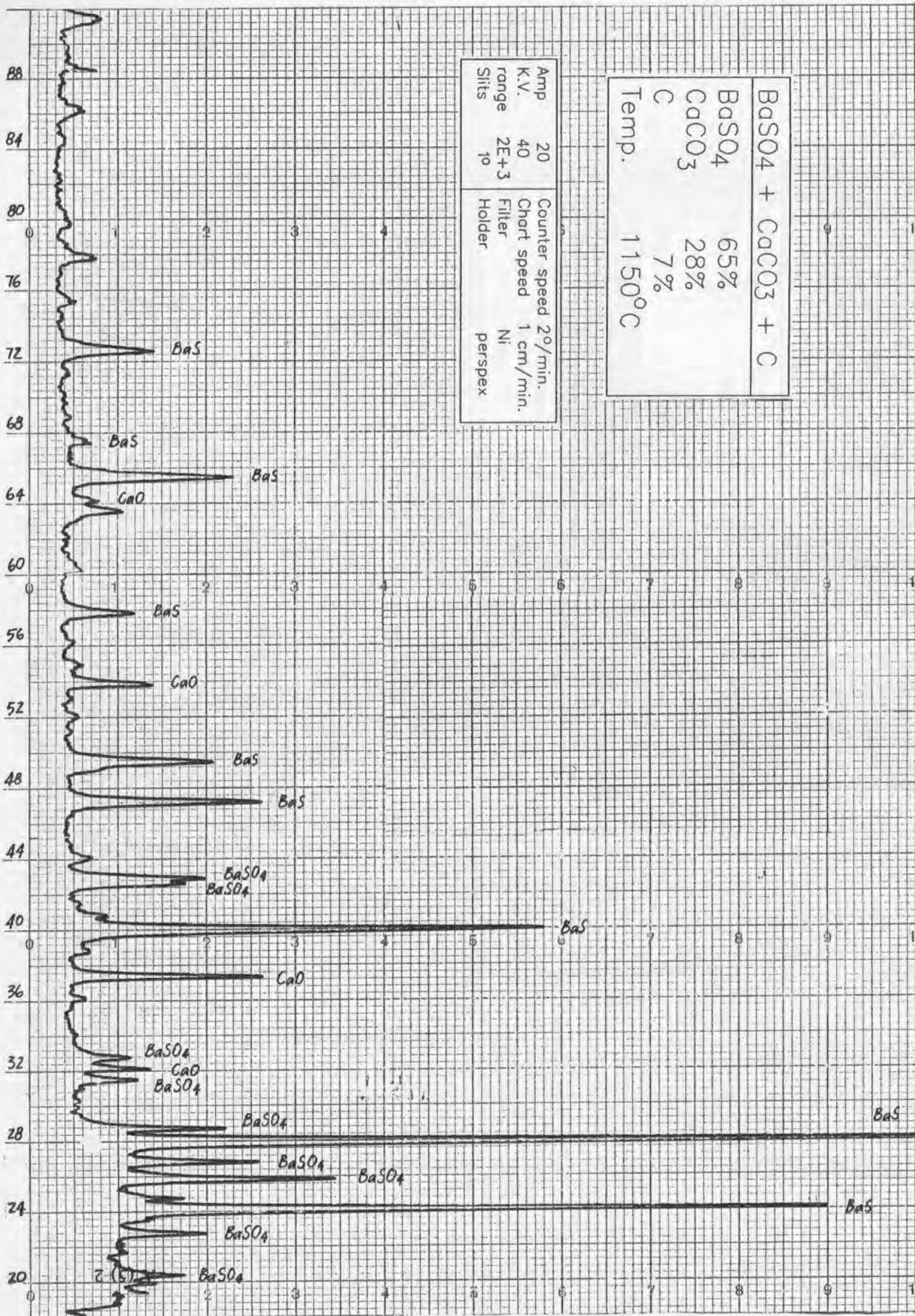
where θ = half the angle of incidence.

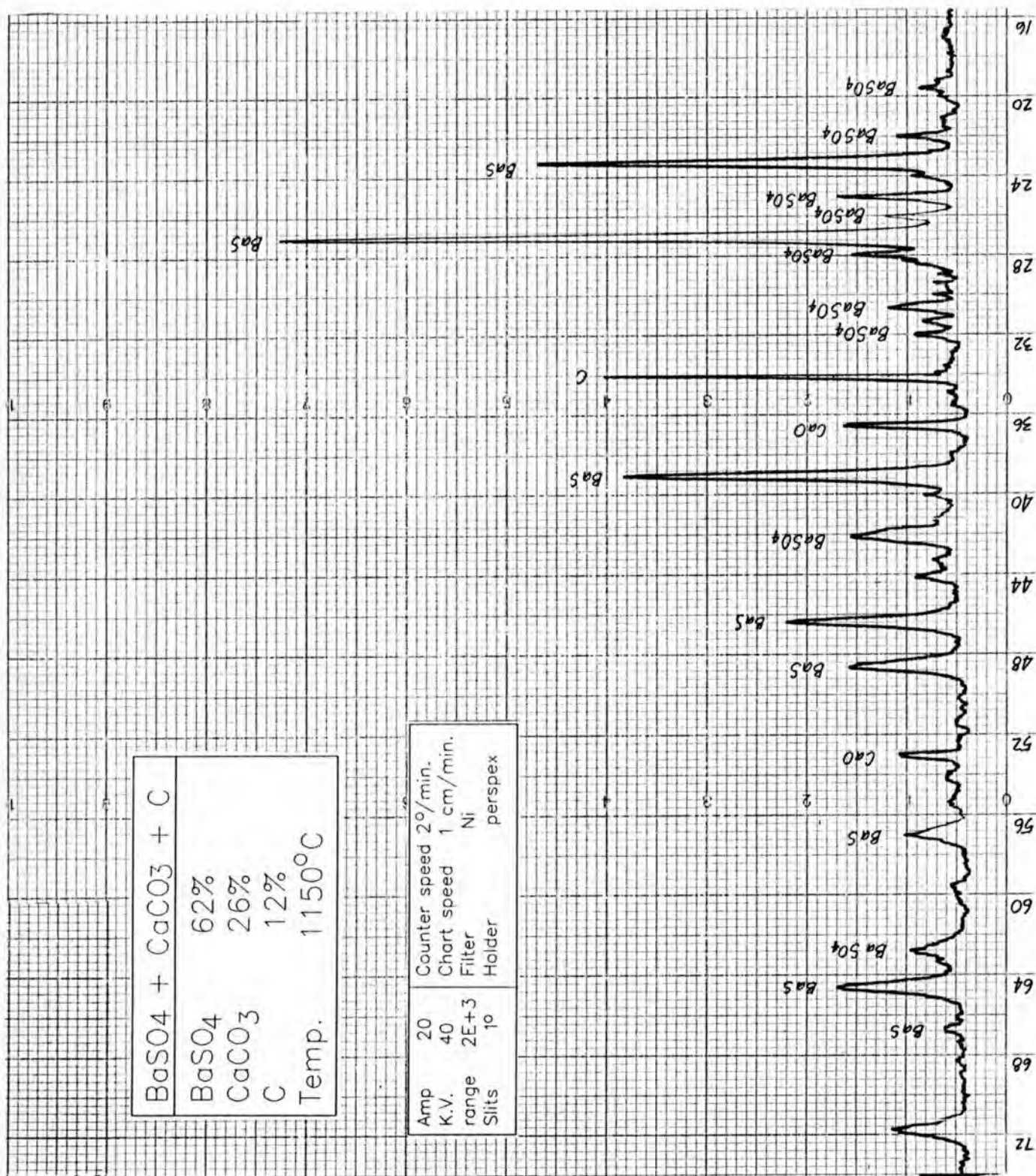
λ = 1,78896 in this case.

The angles of incidence are given on the x-axis.

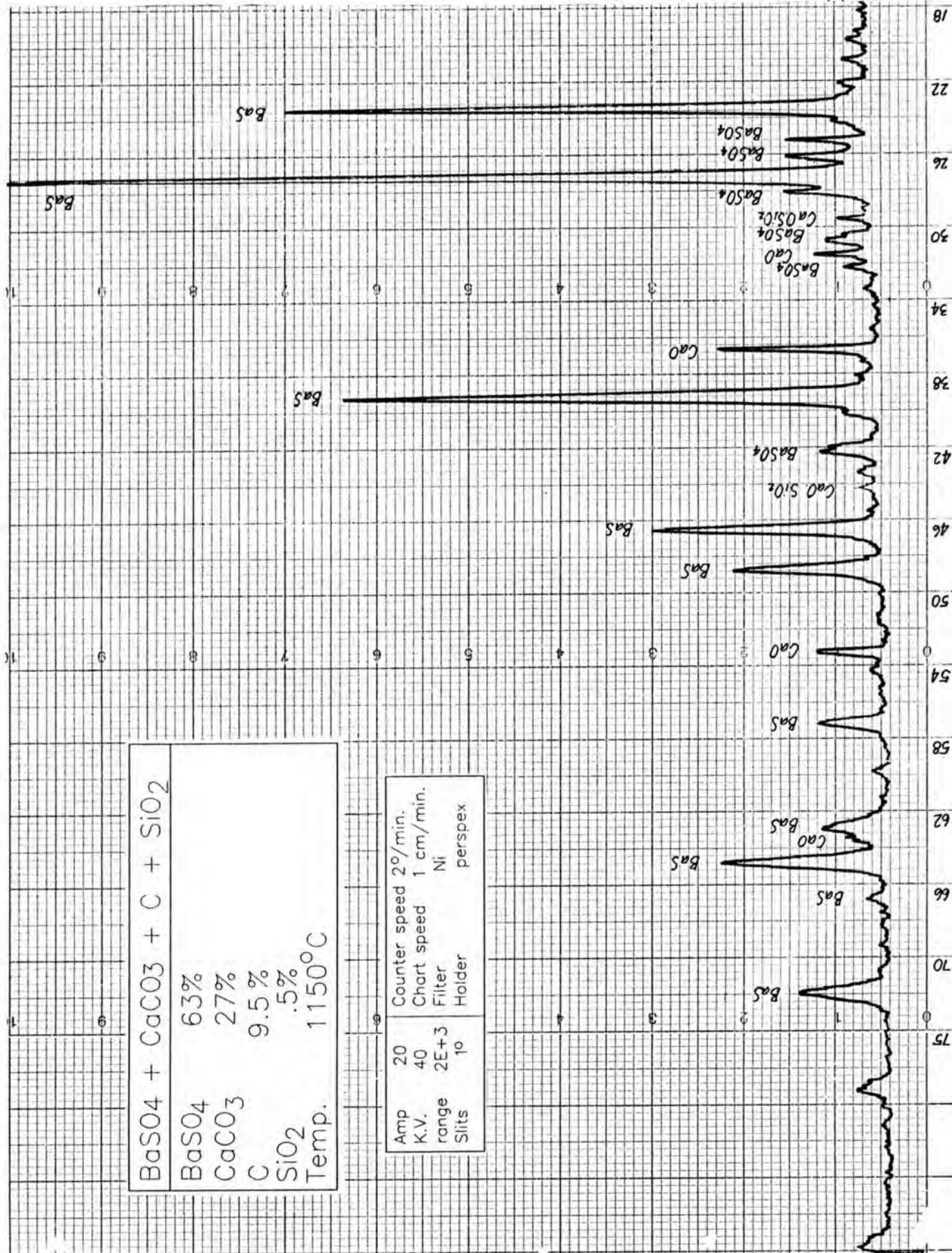
$\text{BaSO}_4 + \text{CaCO}_3 + \text{C}$
 BaSO_4 65%
 CaCO_3 28%
 C 7%
 Temp. 1150°C

Amp 20
 K.V. 40
 range 2E+3
 Slits 10
 Counter speed 2°/min.
 Chart speed 1 cm/min.
 Filter Ni
 Holder perspex





A (5) 4



BaSO₄ + CaCO₃ + C + SiO₂

BaSO₄ 63%

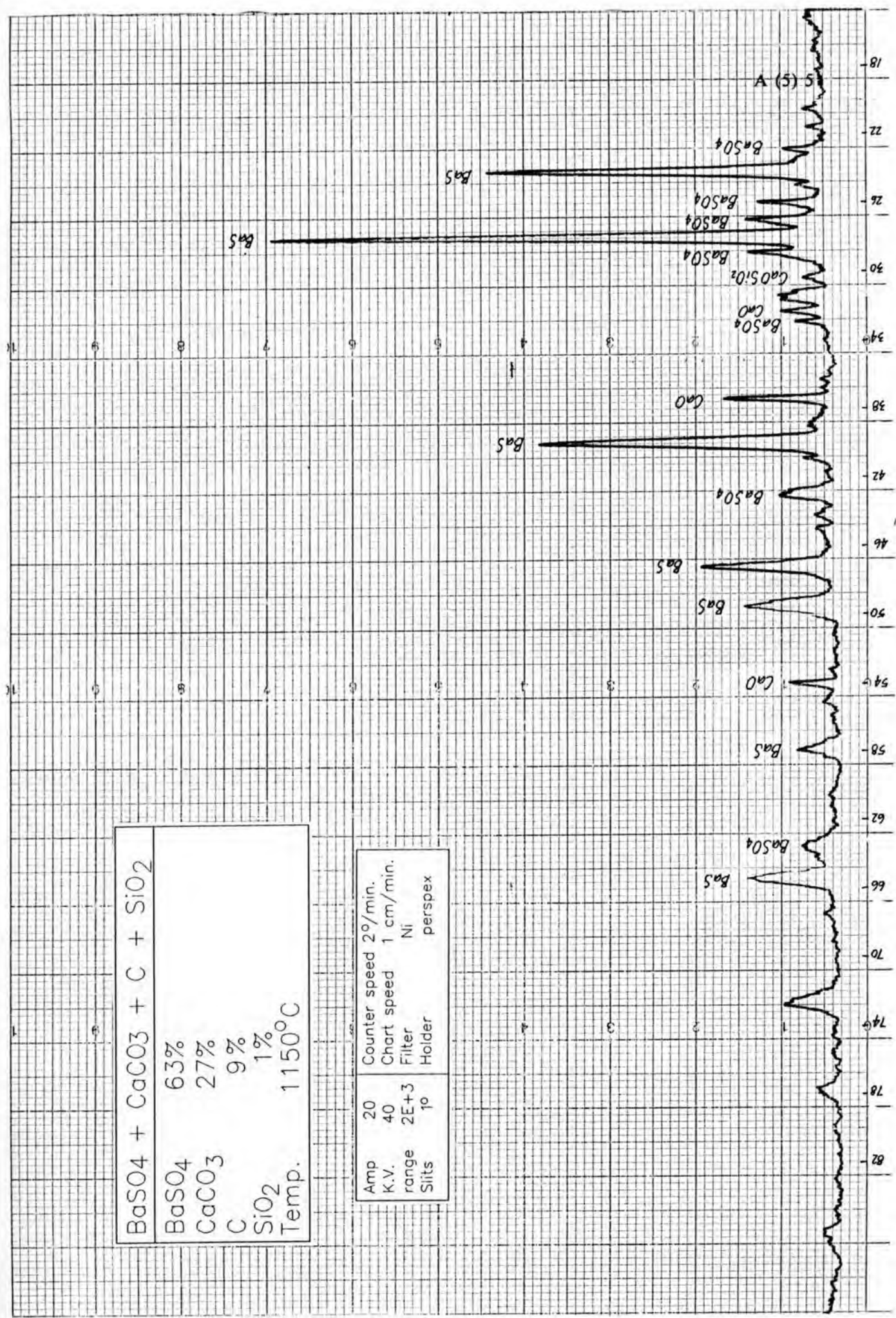
CaCO₃ 27%

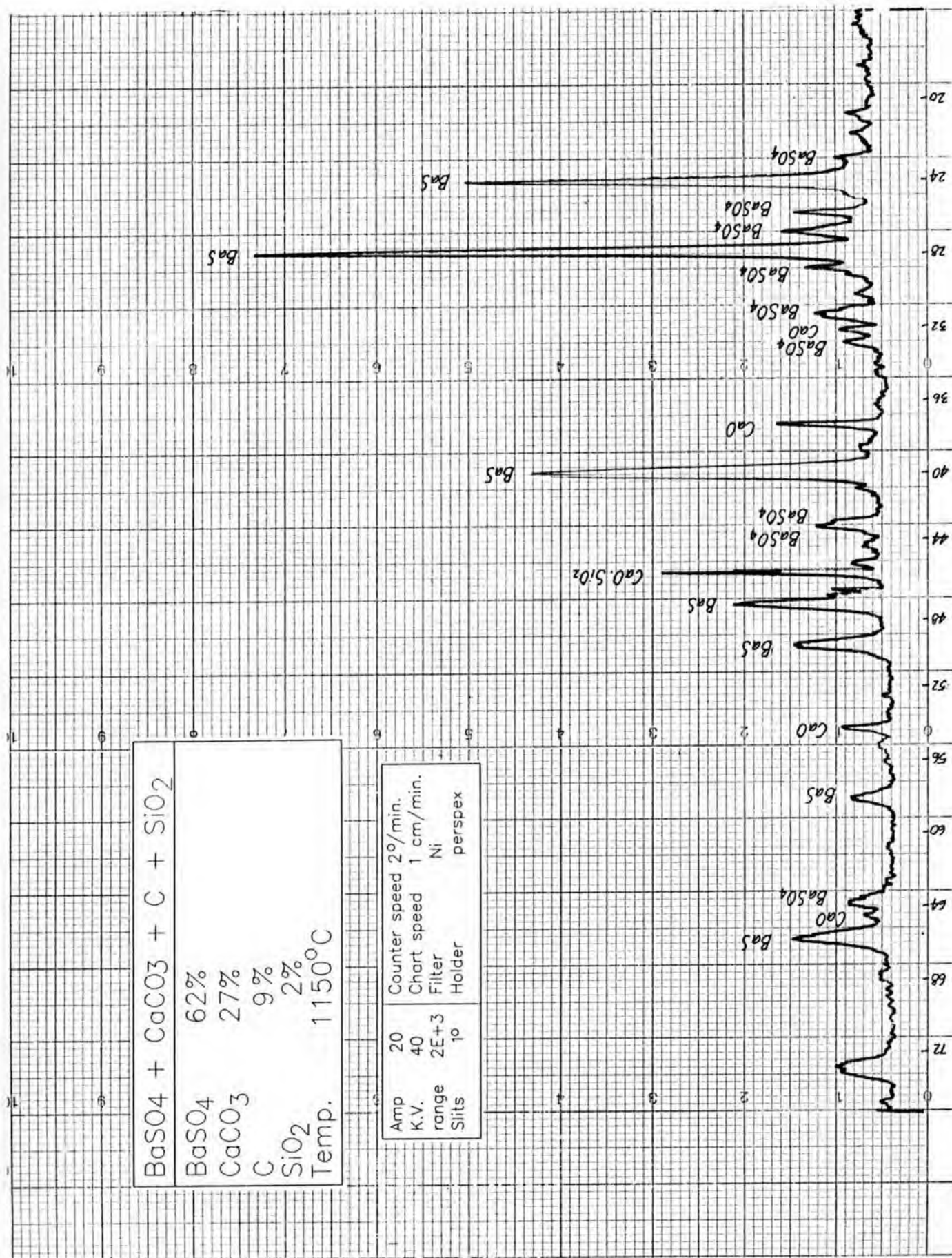
C 9%

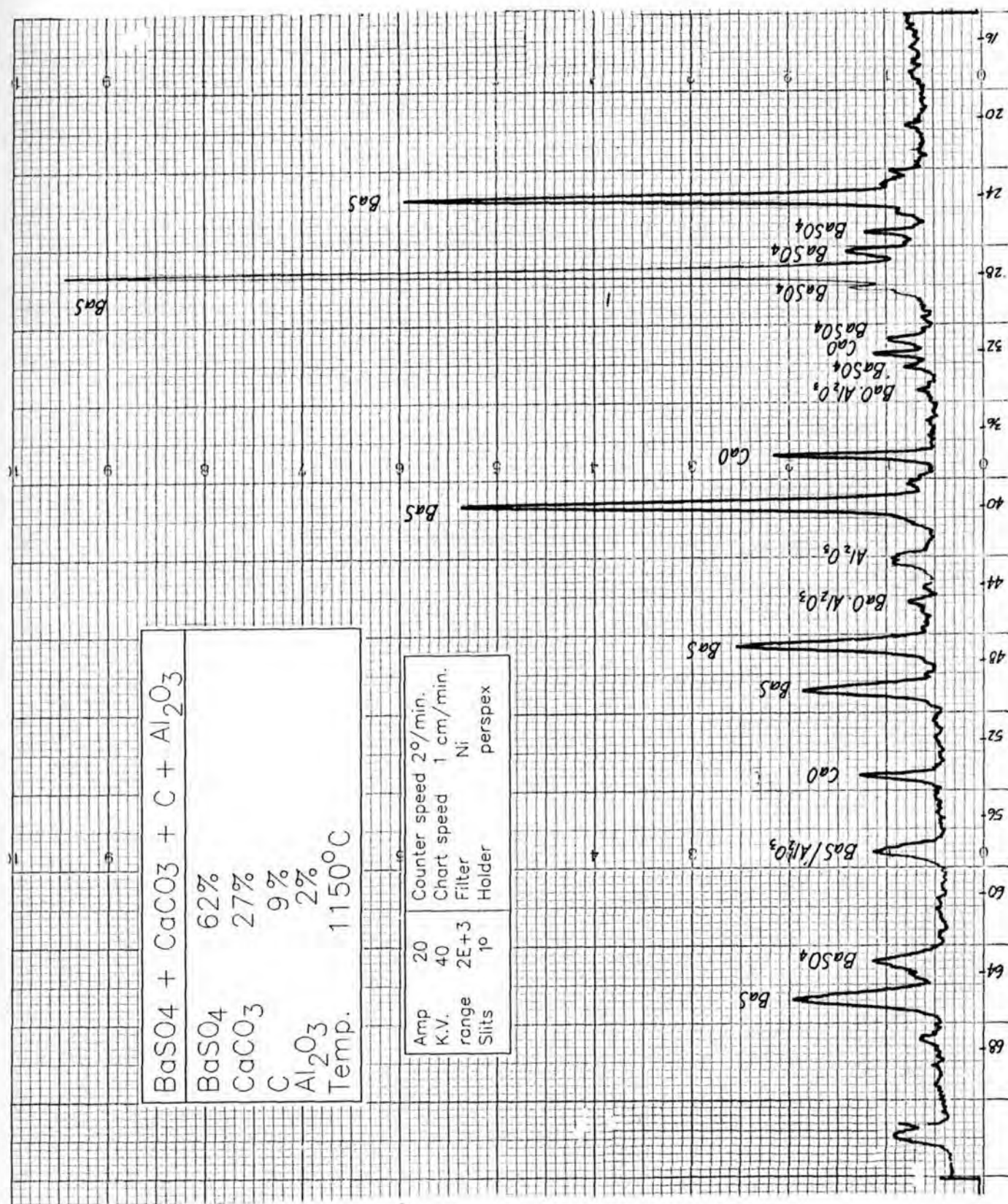
SiO₂ 1%

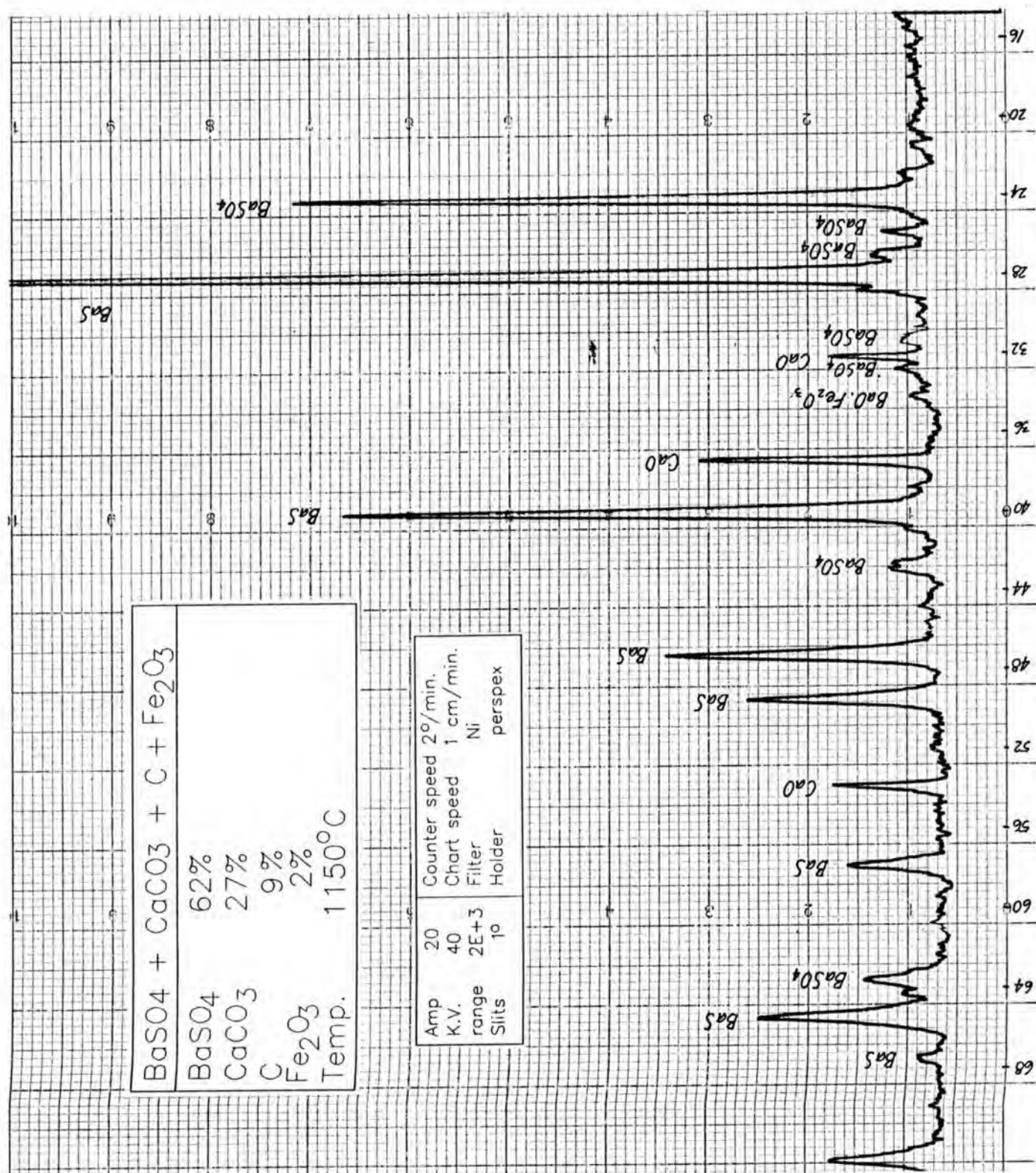
Temp. 1150°C

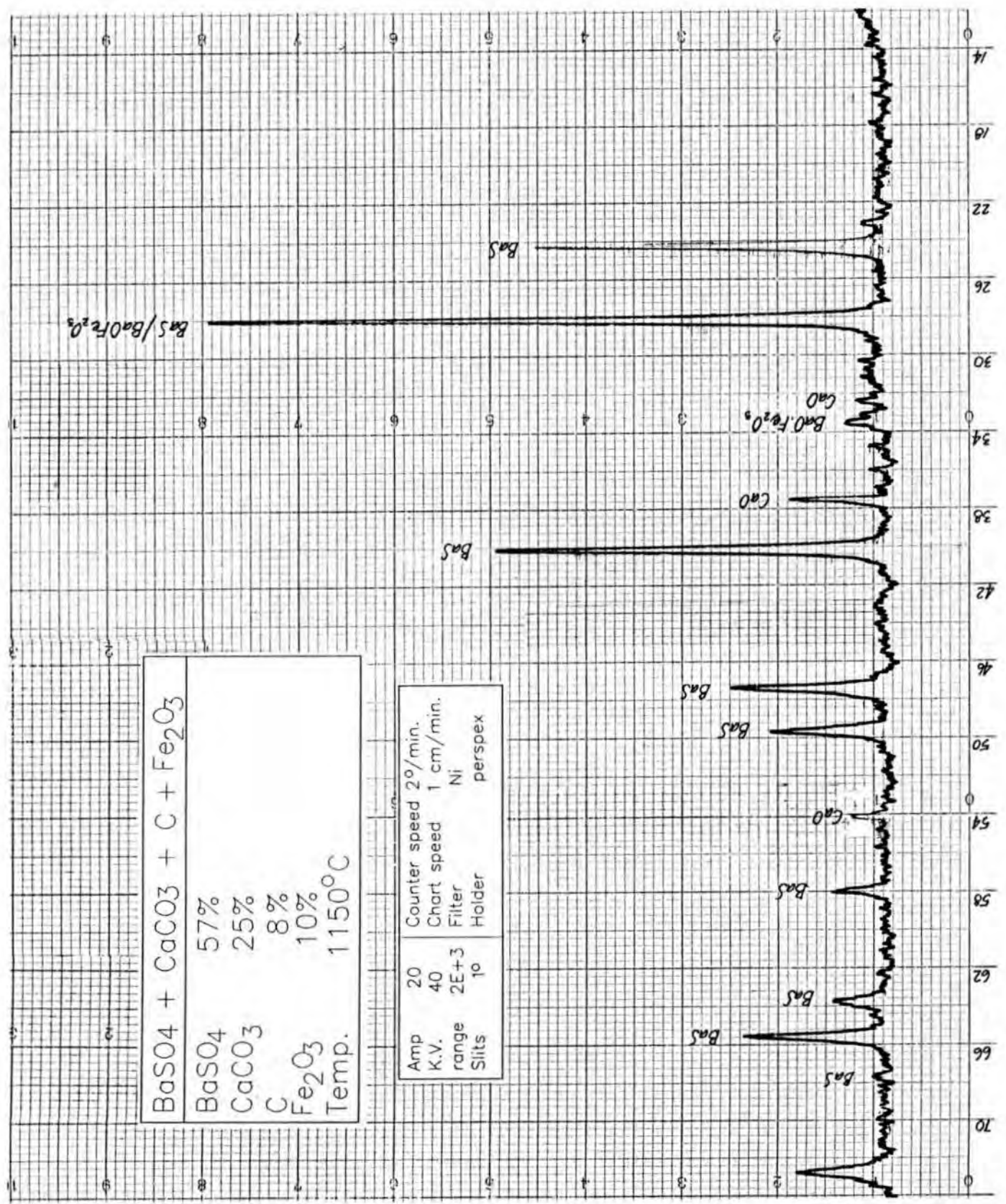
Amp	20	Counter speed	2°/min.
K.V.	40	Chart speed	1 cm/min.
range	2E+3	Filter	Ni
Slits	10	Holder	perspex

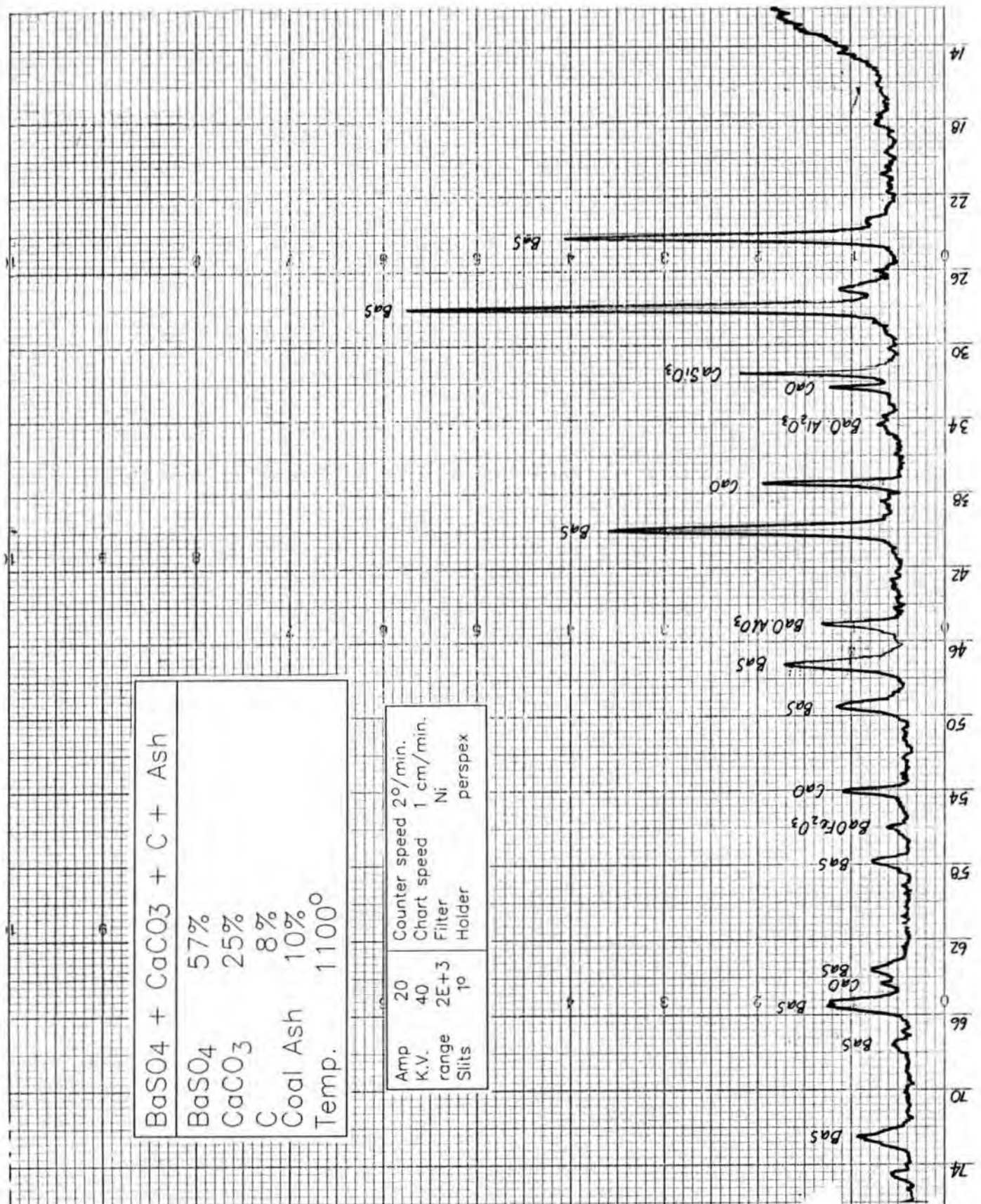


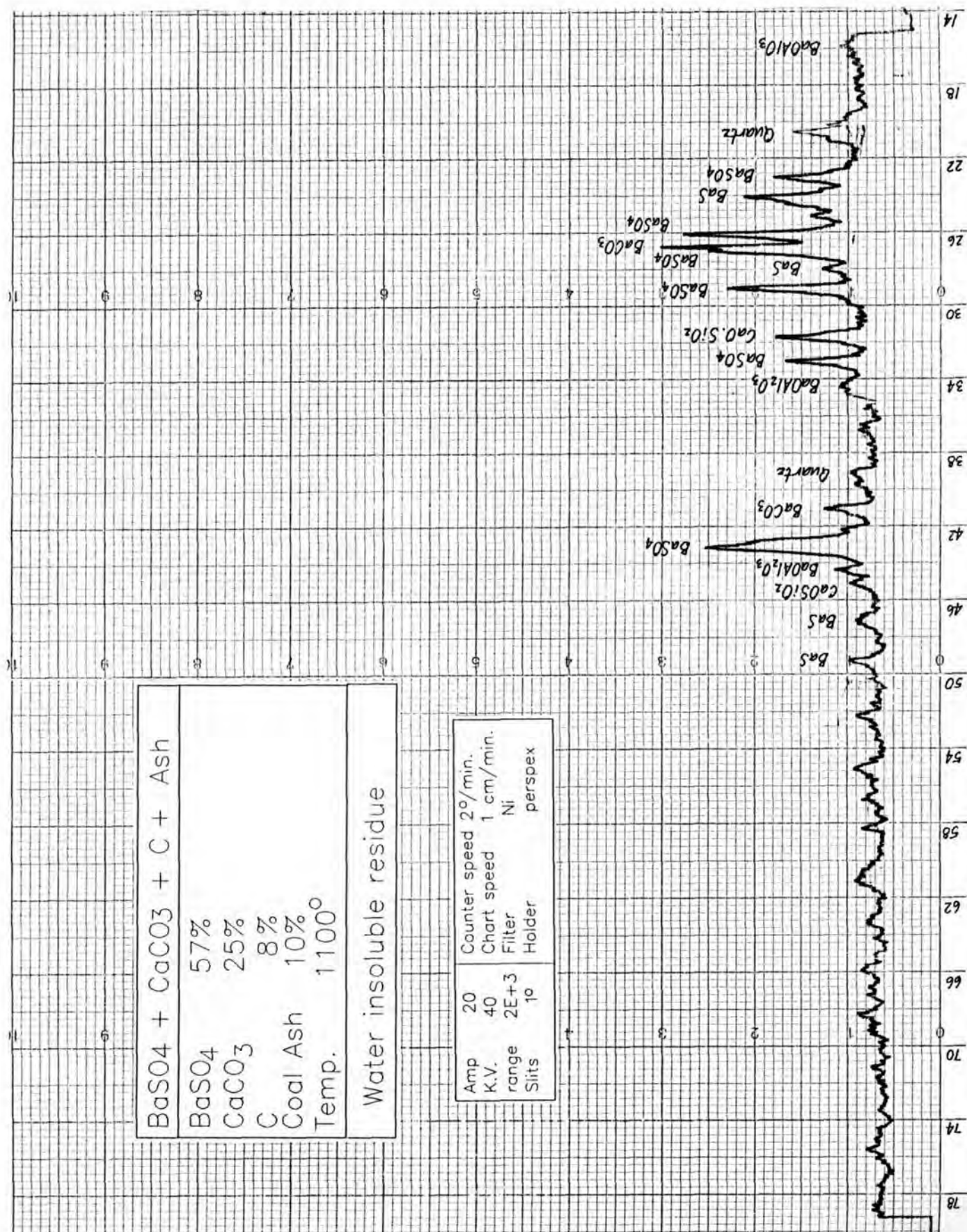






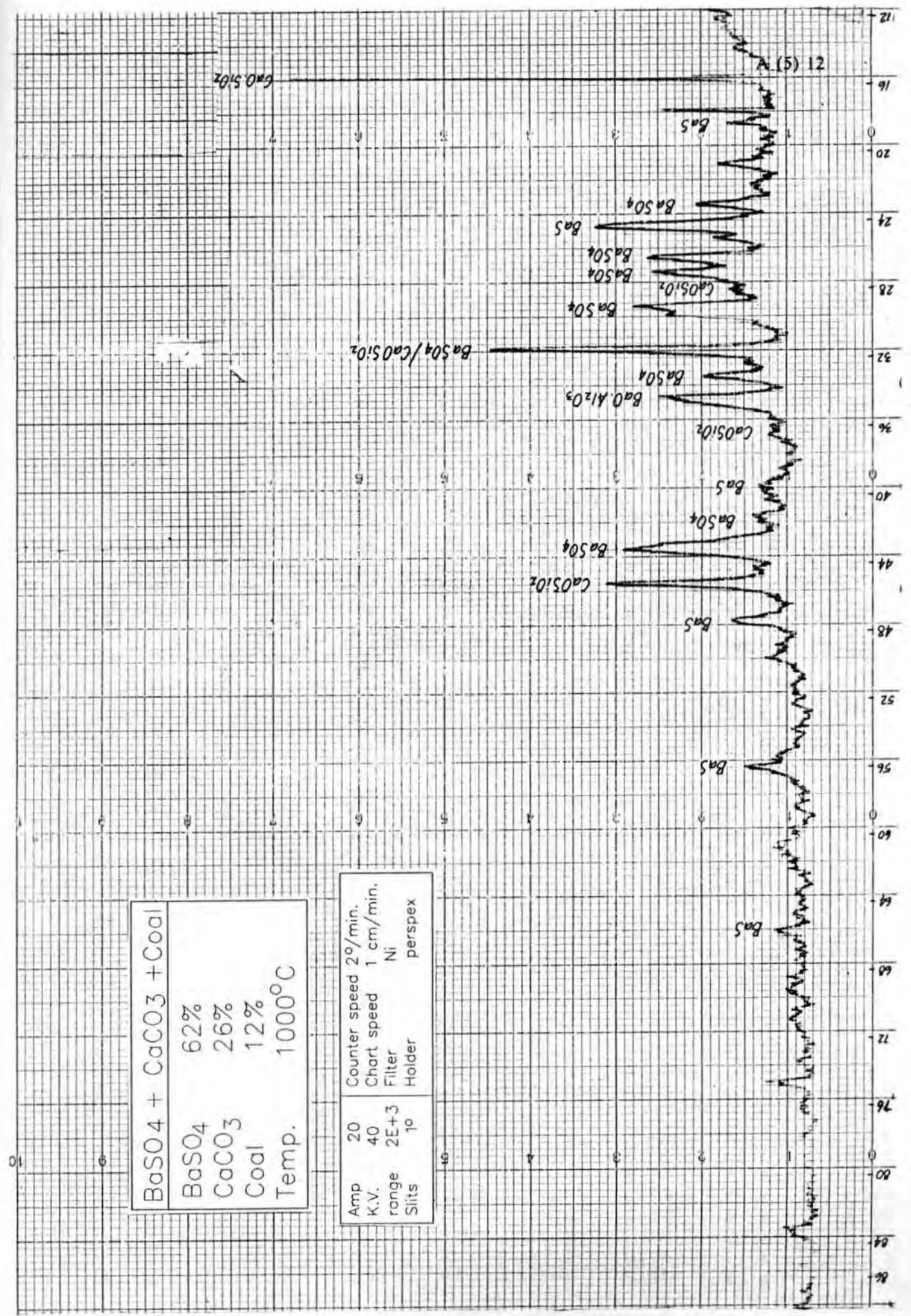






$\text{BaSO}_4 + \text{CaCO}_3 + \text{Coal}$
 BaSO_4 62%
 CaCO_3 26%
 Coal 12%
 Temp. 1000°C

Amp	20	Counter speed	$2^\circ/\text{min.}$
K.V.	40	Chart speed	1 cm/min.
range	$2\text{E}+3$	Filter	Ni
Slits	10	Holder	perspex



BaSO4 + CaCO3 + Coal

BaSO₄ 56%
 CaCO₃ 24%
 Coal 20%
 Temp. 1100°

Water insoluble residue

Listed DI file name : GTU.DI
 Raw data file name : GTU.RD
 Sample identification : GTU
 Date of measurement : 8-FEB-88
 Generator settings : 40 kV, 30 mA
 Step size, count time : 0.020 deg, 0.40 s
 Angle range (2theta) : 20.010 - 109.990 deg
 Al, A2 wavelengths : 1.78896, 1.79979 Ang
 Range in d-spacing : 1.0920 - 5.1486 Ang
 Monochromator used : Yes
 Maximum peak counts : 146. cts, 366. cps

Peak no	Angle (deg)	Tip width (deg)	Peak (cts)	Backg (cts)	D spac (Ang)	I/Imax (%)	Type Al A2 Ot	Qual
1	24.3925	0.64	17.	18.	4.2340	11.48	X X	1.07
2	27.0400	0.24	32.	21.	3.8261	22.19	X X	1.00
3	28.3500	0.20	88.	35.	3.6527	60.35	X X	3.80
4	28.8450	0.16	45.	35.	3.5913	30.66	X X	1.00
5	29.5325	0.24	13.	29.	3.5095	8.85	X X	0.89
6	30.7350	0.08	62.	30.	3.3753	42.63	X	0.93
7	31.5675	0.16	58.	30.	3.2885	39.45	X X	1.17
8	32.9325	0.32	10.	45.	3.1557	6.99	X X	0.95
9	34.1750	0.24	52.	30.	3.0442	35.41	X X	1.66
10	34.8700	0.08	146.	31.	2.9854	100.00	X	0.83
11	37.1750	0.12	66.	29.	2.8062	44.81	X	1.41
12	38.9325	0.32	27.	30.	2.6841	18.47	X X	0.91
13	39.9600	0.12	12.	31.	2.6178	8.37	X	0.95
14	40.4100	0.16	23.	31.	2.5898	15.74	X X	0.93
15	41.0000	0.12	32.	27.	2.5542	22.19	X	1.23
16	42.5950	0.40	24.	21.	2.4627	16.40	X X	1.58
17	46.7200	0.16	37.	22.	2.2559	25.41	X	0.83
18	48.4150	0.32	16.	30.	2.1814	10.93	X X	0.87
19	49.7125	0.24	50.	24.	2.1280	34.43	X X	2.34
20	50.8625	0.20	125.	24.	2.0830	85.68	X	1.45
21	52.2625	0.06	24.	44.	2.0309	16.40	X	0.81
22	53.0900	0.10	61.	38.	2.0015	41.55	X	0.78
23	55.2875	0.24	28.	27.	1.9279	19.19	X X	1.00
24	56.0825	0.24	36.	21.	1.9027	24.59	X X	1.07
25	57.2625	0.24	19.	31.	1.8667	13.22	X X	0.87
26	58.0475	0.32	14.	31.	1.8436	9.35	X X	0.89
27	61.6025	0.96	10.	18.	1.7468	6.99	X X	0.91
28	64.9675	0.24	24.	21.	1.6655	16.40	X	1.26
29	66.2450	0.24	16.	30.	1.6370	10.93	X	1.51
30	66.9300	0.32	11.	30.	1.6319	7.44	X	0.85
31	68.1775	0.48	10.	31.	1.5959	6.99	X X	0.76
32	72.0500	1.12	24.	22.	1.5209	16.40	X X	3.89
33	74.9875	0.40	17.	24.	1.4696	11.48	X X	1.55
34	78.5050	0.56	10.	32.	1.4137	6.99	X X	1.00
35	81.4575	0.40	18.	28.	1.3709	12.63	X X	1.41
36	83.3600	0.40	10.	30.	1.3451	6.99	X X	1.12
37	87.5150	0.48	11.	23.	1.2933	7.44	X X	1.12
38	89.3550	0.40	12.	25.	1.2722	8.37	X X	1.62
39	90.7475	0.40	18.	21.	1.2568	12.05	X X	0.76
40	92.8275	0.40	10.	29.	1.2349	6.99	X X	0.79
41	96.6825	0.40	10.	28.	1.1972	6.99	X X	0.79
42	98.6050	0.48	10.	26.	1.1798	6.99	X X	0.95
43	100.4500	0.64	10.	23.	1.1638	6.99	X X	1.48
44	103.1500	1.28	10.	25.	1.1418	6.99	X X	1.12
45	106.0650	0.64	14.	21.	1.1195	9.35	X X	0.76

45 peaks identified

45 crystalline