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PRODUCTION OF BARIUM CHEMICALS IN SOUTH AUSTRALIA

by

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SUMMARY

Background

At the request of the South Australian Department of Mines, Amdel agreed to investigate the potential for establishing a barium chemical industry in South Australia.

Objectives

The aims of the project were as follows:

(1) To examine details of the Australian market for barium chemicals and to define the types of barium chemicals used, sources of supply, quantities used, prices and specifications.

(2) To establish the required grade of barite for use in manufacture of barium chemicals and consider methods for beneficiation.

(3) To note the effects of strontium content.

(4) To prepare order of magnitude capital and operating costs and assess the economic viability of a barium chemicals plant.

Summary of Work Done

A letter sent to companies believed to trade in barium chemicals failed to elicit sufficient information on the imports of barium chemicals and the total import figures published by the Bureau of Statistics were therefore used as a basis for sizing a barium chemicals plant. As over 90% of the listed imports are $BaCO_3$ the plant was costed only for production of $BaCO_3$. The capital cost of a plant treating 7000 t barite per annum is estimated to be $\$2.75 \times 10^6$ and the estimated production cost is \$340/t $BaCO_3$. Credits allowed for by-product recovery and sale and for interest-free capital would reduce the production cost to about \$250/t $BaCO_3$. As the present selling price of imported $BaCO_3$ is about \$250/t, the proposed process would be uneconomic unless substantial tariff protection were given.

Conclusions and Recommendations

The production of barium chemicals in South Australia is not economically viable at present.

If market conditions vary sufficiently to warrant further investigation, laboratory tests are required to confirm some aspects of the process.

Several South Australian barite deposits could supply a barium chemicals plant without the need for beneficiation.

There appears to be no market requirement for the removal of strontium from barium chemicals.

1. INTRODUCTION

At a meeting between officers of the South Australian Department of Mines and Amdel, held in November 1976, it was agreed that Amdel should investigate the potential for the establishment of a barium chemical industry in South Australia. The investigation was to be carried out as follows:

(1) Obtain details of the Australian market for barium chemicals; including details of the types of barium chemicals currently sold, sources of supply, uses, quantities used, prices, specifications for various barium chemicals and various grades of the different chemical, etc. This aspect is to be given most emphasis.

(2) Establish grade requirements for barytes to be used for the manufacture of barium chemicals. The possibility of upgrading barytes is to be considered briefly.

(3) Establish whether strontium in the barytes feed to a barium chemicals plant will have a deleterious effect on product grades; whether strontium can be separated during processing of barytes; and whether a saleable strontium product can be produced.

(4) Preparation of order-of-magnitude capital and operating cost estimates for a barium chemicals plant in order to establish the minimum viable size for such a plant.

(5) On the basis of (1) to (4) comment as to whether a barium chemicals plant in South Australia might be economically viable and whether an investigation in greater depth might be warranted.

2. BARIUM CHEMICALS - DESCRIPTION, USES AND MARKETS

2.1 Natural Barite - $BaSO_4$

Barite is the major barium mineral throughout the world. It is found in three geologically different kinds of deposit: vein deposits, sedimentary deposits and residual deposits. In the pure form barium sulphate crystals are colourless and rhombic and have a specific gravity of 4.5. Barite decomposes at 1580°C and is practically insoluble in water. Barite deposits may contain silica and iron impurities and these may result in the massive form appearing various colours from white to brown or black.

A list of the barite occurrences within South Australia has been supplied by the Department of Mines, and is given as Table 1. The list includes estimates of the deposit sizes and grades.

Over 80% of the world's production of barite is used as an ingredient of oil drilling mud, which is used as a lubricant for the drill and stem, to flush out core fragments, to seal the walls of the hole, and because of its high density, to help in confining the high pressures encountered in oil or gas strata. Because barite is a fairly common mineral, the crude barite used for oil drilling mud is inexpensive and deposits close to the areas being drilled are favoured.

Good quality, crushed barite is used in the glass manufacturing industry as a flux, and to add clarity and brilliance to the product. Finely-ground high grade barite is used as a filler or pigment extender in the paint, rubber and paper industries, where whiteness of the product is not important.

Barite is a good absorber of radiation and may be used as aggregate in concrete used for shielding of nuclear reactors, X-ray laboratories or isotope stores. Other uses for barite include a filler for rubber or asphalt paving and a constituent of some ceramic wares.

There do not appear to be any immediate potential markets for natural barite. In the longer term, however, renewed activity in oil exploration could increase the local demand for barite, and the use of barite as aggregate in concrete shielding should be considered in the design of projected nuclear power stations, enrichment plants and uranium mines.

2.2 Barium Carbonate - $BaCO_3$

Commercial barium carbonate is a fine white powder produced from barite via barium sulphide. It has a specific gravity of 4.25 and a bulk density of 650 to 2500 kg/m^3. The commercial grade chemical assays 98 to 99% $BaCO_3$, 0.2 to 1% $BaSO_4$ and 0.06% BaS. The particle size varies from 0.1 to 10 μm depending upon the conditions of manufacture. The dry product includes many agglomerates.

Barium carbonate is used as a raw material for manufacture of other barium compounds; as a purification medium for the removal of sulphates from aqueous solutions; as a flux in ceramics manufacture, as an ingredient in optical and fine glassware; and as a carbon carrier in case-hardening baths.

Barium carbonate is a convenient raw material for production of other barium compounds, especially water-soluble salts, as it dissolves readily in acids, giving a pure solution of the desired salt.

The greatest use of $BaCO_3$ is as purification medium. Even though it is considered to be insoluble in water (0.002 g/100 g) it is ten times more soluble than $BaSO_4$ and the carbonate is converted slowly to sulphate when agitated in a solution containing sulphate ions. If the solution contains calcium or magnesium, these elements are co-precipitated as carbonates. This property of $BaCO_3$ is used in the chlor-alkali industry to remove sulphates from brine prior to electrolysis. In brick manufacture, the presence of gypsum or magnesium sulphate in the clay or the pugging water can cause a white scum to form on the surface of the bricks during the drying process. This scum is caused by slow diffusion of the slightly soluble salts to the surface of the bricks and their crystallisation during drying. On firing the bricks, the salt crystals can act as a flux giving an irregular finish. This problem can be overcome by adding $BaCO_3$ to the clay during pugging at a rate of 4-5 kg/1000 bricks. The $BaCO_3$ reacts to form $BaSO_4$ which does not diffuse to the brick surface.

Barium carbonate is used in the ceramic industry as a flux ingredient in enamels, glazes and bodies. If sodium carbonate is present it forms silicates at temperatures as low as 400°C. In enamels, $BaCO_3$ improves gloss, mechanical strength, elasticity and resistance to organic acids. Barium is not sensitive to combustion gases or to cast iron having a high carbon content, both of which tend to reduce lead or zinc oxides commonly present in enamels. The $BaCO_3$ content can vary from 7% in low-alkali sheet iron enamels to 12% in lead-free sanitary-ware cast iron enamels. It should not be used when sulphur is present, as $BaSO_4$ is formed and affects the finish. $BaCO_3$ makes a good flux for glazes and promotes a matt finish. However, it should not be used in ratios greater than 0.1 equivalent, as the glaze becomes too refractory. In pottery bodies $BaCO_3$ seems to impart better translucency but reduces the vitrification range. It increases the strength, but causes excessive shrinkage and blistering.

Barium carbonate is used as a fluxing agent and as an ingredient in optical and special glassware. Some bottle, plate and television tube glass may contain 0.5% barium, which imparts properties of density, brilliance and durability intermediate between those imparted by calcium and lead. The main advantage of barium glass is that it is not reduced by combustion gases, and may therefore be melted in open tanks or pots without discolouration. Special glasses may contain up to 30% BaO, but glasses containing appreciable quantities of barium are corrosive to refractories and must be made in special equipment.

The Bureau of Statistics data of Table 2 indicate that imports of $BaCO_3$ were about 1000 t/a for several years, but in 1975/6 and 1976/7 the quantity has suddenly risen to over 5000 t/a. Our enquiries account for only 700 to 800 t of this. However, the major consumption is probably as a descumming agent in brick and tile manufacture.

2.3 Barium Chloride - $BaCl_2.2H_2O$

Hydrated barium chloride is a fine, white crystalline solid produced by the action of hydrochloric acid upon either barium sulphide solution or barium carbonate. The crystals have a specific gravity of 3.1, and lose the water of crystallisation at 100°C. The anhydrous barium chloride has a specific gravity of 3.85. The salt is soluble in water and is poisonous.

The major use for barium chloride is as a raw material for the manufacture of blanc fixe paste for photographic paper.. It is also used as a raw material for other barium chemicals and in heat treatment baths.

When blanc fixe is used as a pigment it is sometimes preferred to produce it just prior to use in order to prevent the formation of agglomerates during drying. Manufacture of blanc fixe paste via barium chloride enables the removal of sulphide impurities which could affect the silver emulsion coating on the finished paper.

Barium chloride is used in heat treatment baths. It melts at 960°C, but readily forms with chlorides of potassium, sodium and calcium eutectics which have melting points in the range 630 to 680°C.

The Bureau of Statistics data in Table 2 indicates that imports of $BaCl_2$ have been variable from 50 t/a to 2000 t/a. Our enquiries have accounted for only 15 t of the estimated 260 t imported in 1967/7. We are unable to suggest the likely destination of the imported $BaCl_2$, but a representative of Kodak said that they imported photographic paper ready to use.

2.4 Barium Sulphate - $BaSO_4$ (blanc fixe)

Blanc fixe is a precipitated barium sulphate formed by the action of a soluble sulphate ion with a soluble barium salt. It is normally made by adding sodium sulphate to barium sulphide solution, but if a sulphide-free product is required it is made by adding sodium sulphate to barium chloride solution. The particle size of the blanc fixe may be varied by controlling the conditions of reaction.

Blanc fixe is used as a pigment extender, as a filler, as a paper coating, and in medical X-ray photography.

Blanc fixe may be used as a pigment extender for paint, varnish and printing ink. It improves resistance to attach by acids and alkalis, and to weathering.

As a filler, blanc fixe may be used in the manufacture of moulded plastics, linoleum and oilcloth.

Blanc fixe may be used in the manufacture of coated papers, especially photographic papers. It is reported to have superior whiteness, weight, insolubility and ability to take tinting dyes. It is used for photographic papers because it may be manufactured to very high purity, and is inert to the photographic emulsion. In order to achieve the best finish, blanc fixe is used in the form of a paste so as to eliminate any particle agglomeration which would occur during drying.

Because of its extremely low solubility, barium sulphate may be used as a contrast medium for X-ray diagnostics. Its use derives from its property of absorbing X-rays which enables the stomach and intestines to be examined.

The Bureau of Statistics data in Table 2 indicates a fairly stable market of 250 to 400 t/a. Our enquiries have accounted for about 90 t of the estimated 280 t imported during 1976/77. We assume that most of the material is being used as an extender in paint manufacture.

2.5 Minor Barium Chemicals

Barium acetate - Ba $(C_2H_3O_2)_2$ is of minor importance. It can be made by reacting $BaCO_3$ or BaS with acetic acid.

Barium bromate - Ba $(BrO_3)_2.H_2O$ may be used in the manufacture of other bromates. It is poisonous.

Barium bromide - $BaBr_2$ is a white crystalline solid, soluble in water, and poisonous. It is made by the reaction of barium hydroxide with hydrobromic acid.

Barium chlorate - Ba $(ClO_3)_2.H_2O$ is made by the reaction of barium chloride with sodium chlorate. It may be used in pyrotechnics.

Barium chromate - $BaCrO_4$ is made by the precipitation of a soluble barium salt with a chromate or dichromate solution. It may be used in metal primers or in pyrotechnics. It may also be used in the production of chrome yellow in overglazes. One respondent to our circular letter indicated that they were importing 3 to 4 t/a.

Barium cyanide - $Ba(CN)_2$ has no commercial use.

Barium ferrite - $BaO.6Fe_2O_3$ may assume permanent magnetism. It may be cast and used as door fasteners for refrigerators, cupboards, etc.

Barium fluoride - BaF_2 has no commercial use.

Barium fluosilicate - $BaSiF_6$ is the least soluble fluosilicate. It may be used as an opacifier in enamel frits, or in insecticides or fungicides.

Barium formate - $Ba(COOH)_2$ has no commercial use.

Barium iodide - BaI_2 is a colourless crystalline solid, soluble in water.

It decomposes in air to iodine and $BaCO_3$.

Barium hydride - BaH_2 is made by the reaction of hydrogen with barium metal. It could be used as a reducing or condensing agent in organic reactions, but is too costly to make.

Barium hydrosulphide - $Ba(HS)_2$ has no commercial use.

Barium hydroxide - $Ba(OH)_2$ is a white crystalline solid. It is produced by dissolving barium oxide in hot water, clarifying the liquor and cooling to form the $Ba(OH)_2.8H_2O$ crystals. It is used in clarification of sugar-beet juice, as a detergent additive in lubricating oils, as a descumming agent in ceramics, and as an ingredient of barium greases. Two respondents to the circular letter indicated that they imported a total of about 50 t/a of the monohydrate, which is used to manufacture barium soaps of fatty acids and phenates. These latter compounds are sold as a part of a heat stabiliser for PVC. The monohydrate is also used as a starting material in the production of barium ferrite.

Barium nitrate - $Ba(NO_3)_2$ is a colourless crystalline solid, soluble in water. It may be made either by the reaction of barium carbonate with nitric acid, or by the reaction of barium chloride with sodium nitrate. It is used in pyrotechnics, giving a green light in fireworks, signal flares and tracer bullets. It is also used in primers and detonators. Small quantities have been used in ceramics to replace alkali metal nitrates.

Barium nitrite - $Ba(NO_2)_2$ has no commercial use.

Barium oxide - BaO is a colourless crystalline solid. Because of its high reactivity with water and/or carbon dioxide and the high heats of formation of the hydroxide and carbonate, it is a fire hazard and may cause spontaneous ignition. It is manufactured by the decomposition of $BaCO_3$ with carbon at high temperature.

Barium oxide was previously used to manufacture barium peroxide, which used to be the major raw material in the manufacture of hydrogen peroxide. However, the process became obsolete. It has since been used in the manufacture of lubricating oil detergents, but has largely been replaced by the safer hydroxide.

Barium perchlorate - $Ba(ClO_4)_4$ has no commercial use.

Barium peroxide - BaO_2 has no commercial use but was formerly the raw material for hydrogen peroxide.

Barium stannate - $BaSnO_3$ is prepared by the calcination of barium carbonate with stannic oxide. It is used as an additive to barium titanate bodies for use as capacitors.

Barium sulphite - $BaSO_3$ has no commercial use.

Barium titanate - $BaTiO_3$ is produced by calcining barium carbonate with titanium dioxide. It is used in the electronics industry because of its high dielectric constant, its piezoelectric properties and its ferroelectric properties. It is used in miniature electronic and communications equipment, such as underwater sonar, guided missiles, acoustic mines, ultrasonic cleaning, sound reproduction, etc.

Lithopone - a mixture of ZnS and $BaSO_4$.

It is produced by the reaction of $ZnSO_4$ and BaS, after removal of impurities from the solutions. It has been used as a white pigment since 1871, but has been steadily losing its market to TiO_2 pigments. It is still used for some undercoat paints and in filling pastes and putties, emulsion paints and wallpaper.

Manganese blue - a mixture of $BaSO_4$ and $BaMnO_4$.

It is a blue pigment used in building materials e.g. concrete, plaster; surface coatings, e.g. varnishes, laquers; plastics and paper. A respondent to our circular letter indicated the sale of 0.5 to 1.0 tonne annually.

Barium metaborate $BaB_2O_4.H_2O$. A patented modified form of barium metaborate is manufactured and marketed as Busan 11-M1 by Buckman Laboratories, Inc., Memphis, Tennessee, USA. It is sold as a pigment for paints and claims mould and bacterial resistance, corrosion resistance, fire resistance, chalk resistance, better colour retention and stain resistance. It is also sold as a fungicide and flame retardent in plastics and textiles. We understand that over 100 t is imported into Australia annually.

3. DESCRIPTION OF MANUFACTURING PROCESS

3.1 Barium Sulphide

Barite ore is ground to minus 1 mm and blended with a solid reductant, e.g. coal, coke, carbon. The mixture is fed to a gas or oil-fired rotary kiln operating at 1100 to 1300°C and the following reaction occurs:

$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

The presence of silica, iron or fluorite in the ore is detrimental to recovery. Silica consumes barite to form barium silicate, and iron may consume barite to form a barium ferrite. Iron or fluorite may form low-melting products which interfere with the operation of the kiln.

The hot reaction products are quenched in water and barium sulphide is dissolved. A wet rod mill or ball mill may be required to regrind agglomerates formed during roasting. The barium sulphide solution is recovered from the insoluble solids by counter-current decantation and filtration. The clean liquor is the basic raw material for the production of other barium chemicals.

3.2 Barium Carbonate
$BaCO_3$

Conversion of barium sulphide to barium carbonate can be accomplished by one of the following reactions:

$$BaS + CO_2 + H_2O \rightarrow BaCO_3 + H_2S \quad .. \quad .. \quad (1)$$

$$BaS + Na_2CO_3 \rightarrow BaCO_3 + Na_2S \quad .. \quad .. \quad (2)$$

In the first process, CO_2 is injected into a hot solution of barium sulphide and barium carbonate is precipitated. H_2S which dissolves in the liquor can be removed by sparging with air. The CO_2 may be either purchased or recovered from the off-gases from the barite reduction kiln. The H_2S produced by the reaction must be collected either for sale, or for the production of elemental sulphur.

In the second process, soda ash is agitated with the barium sulphide solution and the $BaCO_3$ is precipitated. The precipitate is washed by counter-current decantation, filtered and dried. The wash liquor must be treated to neutralise or recover the sodium sulphide.

3.3 Barium Chloride - $BaCl_2$

Hydrochloric acid is mixed with barium sulphide solution in an agitated rubber-lined tank.

$$BaS + 2HCl \rightarrow BaCl_2 + H_2S$$

The hydrogen sulphide formed must be collected either for sale or for the formation of elemental sulphur. The solution is concentrated by evaporation and barium chloride is crystallised, filtered, washed, dried and bagged.

3.4 Barium Sulphate - $BaSO_4$ (blanc fixe)

Barium sulphide solution is mixed with a purified solution of sodium sulphate and barium sulphate is precipitated.

$$BaS + Na_2SO_4 \rightarrow BaSO_4 + Na_2S$$

The size range of the precipitated barium sulphate particles can be varied by careful control of the concentrations of the solutions, the rate of mixing and the reaction temperature. The blanc fixe precipitate is washed and dried and then ground to break up agglomerates formed during drying.

The blanc fixe produced by this process is unsuitable for use on photographic papers, due to the presence of residual sulphides which would react with the silver emulsions. Blanc fixe required for photographic paper must be prepared from either purified barium carbonate or barium chloride.

4. COST ESTIMATES

Examination of import data shows that for the years 1975/76 and 1976/77, imports of $BaCO_3$, $BaCl_2$ and $BaSO_4$ have been equivalent to about 6500 to 7000 t $BaSO_4$. The treatment plant is therefore assumed to treat 7000 t barite per annum. As this is equivalent to about 1 t/h, on a 3 shift basis, the plant is sized and costed on the basis of operation on day shift, 5 days per week. Allowing 4 weeks down-time and 10 Public Holidays, available days are 230.

The treatment rate is therefore 30 t/d.

Equipment cost data and operating cost data are from Amdel files.

The estimated capital cost of the plant is $\$2.75 \times 10^6$.

The estimated production cost is \$340/t $BaCO_3$.

4.1 Capital Cost

The sizes and purchase costs of major equipment items on the flow sheet (Fig. 1) are estimated and factors applied to give the installed plant cost. The flow sheet is based on production of $BaCO_3$ only.

(1) Kiln 30 t/d barite

$$BaSO_4 + 4C \rightarrow BaS + 4CO$$

assume coal at 25% carbon.

Coal required is $30 \times \frac{48}{233} \times 4 = 25$ t/d

Total solids input 55 t/d

Assuming operation at 6 h/d to allow heat up period, treatment rate is 9.2 t/h.

Kiln size 220 t/d say 2.4 m ϕ × 45 m
Price (1977) $280,000

(2) Leaching 9.2 t solids/h

Assume leach at 50% solids, i.e. 9.2 t liquor

Allow 2 h leach time

Tank volume is $2\ (9.2 + \frac{9.2}{2.5}) = 26$ kl

Assume 2 stages, each 13 kl

Price per tank (1977) $9,000

Agitators. To stir 13 kl at 50% solids
Allow 0.8 kW/kl i.e. 10.4 kW
Price per agitator (1977) $8,000

Total price of leaching tanks $34,000

(3) Regrind Mill

Assume 20% of original solids require regrinding, i.e. 1.8 t/h

Size of mill 1.2 m × 0.9 m

Power consumption, about 22 kW

Price (1977) $30,000

(4) Thickeners

Assume an insoluble residue of 10% of the feed.

i.e. 0.92 t/h

Assume final liquor concentration is 200 g BaS/1

To treat 5 t $BaSO_4$/h, requirement is $5 \times 10^6 \times \frac{169}{233} \times \frac{1}{200} = 18.1$ kl/h

Assume a thickening rate of 1.5 m^2/t day

Hence area required is $1.5 \times 0.92 \times 24 = 33$ m^2

and thickener diameter is 6.5 m

Price per thickener (1977) $13,500

Washing efficiency with 1 unit is 95%

Washing efficiency with 2 units is 99.7%

Assume 2 units, price $27,000

(5) Clarifying Filter

Liquor flow rate is 18.1 kl/h

Assuming a design flow rate of 4.5 kl/h m^2, area required is 4 m^2.
Assume 2 units, each 2 m^2., i.e. 1.5 m diameter

Price per unit $3,500

(6) Product Storage Tanks

Allow 1 days storage, i.e. $6 \times 18.1 = 110$ kl
Price of tank (1977) $14,000

(7) Barium Carbonate Precipitation Tank

Assume a residence time of 10 minutes.

Capacity is $18.1 \times \frac{1}{6}$ kl BaS solution plus equivalent volume of Na_2CO_3 solution i.e. 6 kl

Price of tank (1977) $5,000

(8) $BaCO_3$ Thickener

Production rate 90 t/d for 6 h/day

Assume thickening rate is 1.5 m^2/t/d

Area required is 135 m^2 and diameter is 11.5 m

Thickener price (1977) $29,000

(9) <u>$BaCO_3$ Filter</u>

Assuming a filtration rate of 2 t/m^2 day, area required is 45 m^2

Assuming a rotary vacuum drum filter, price (1973) is $79,000

Price (1977) $121,000

(10) <u>$BaCO_3$ Drier</u>

Throughput is 90 t/d for 6 hours/day

Assume a rotary kiln drier 1.2 m diameter -10 m long

Price (1977) $7,000

(11) <u>$BaCO_3$ Mill</u>

Throughput 3.7 t/h

Price for mill (1977) $30,000

(12) <u>Bagging Plant</u>

Throughput 3.7 t/h

Assume 2 bags/min. - Price $12,000

(13) <u>Miscellaneous Pumps, Hoppers, Conveyors, Tankage</u>

Add 15% to total price i.e. $89,000

<u>Summary of Capital Costs</u>

1.	Kiln	$280,000
2.	Leaching	34,000
3.	Regrind Mill	30,000
4.	Thickeners	27,000
5.	Clarifiers	7,000
6.	BaS Storage Tank	14,000
7.	$BaCO_3$ Precipitation	5,000
8.	Thickener	29,000
9.	Filter	121,000
10.	Drier	7,000
11.	$BaCO_3$ Mill	30,000

Summary of Capital Costs (Continued)

12.	Bagging Plant	12,000
13.	Miscellaneous	89,000
Total Purchase Cost		$685,000

Installed cost is about 4 times purchase cost, i.e. $\$2.75 \times 10^6$

4.2 Production Costs

1. Materials

Barytes	7000 t/a	@	$30/t	$210,000
Coal	5750 t/a	@	$30/t	172,500
Na_2CO_3	3000 t/a	@	$130/t	390,000

2. Direct Labour

Assume 4 operators at $9000	36,000

3. Utilities

Water - Feed to CCD 19.1 kl/h for 6 h
i.e. 114.6 kl/d

Assume 70% recycle from $BaCO_3$ plant

Water use is $114.6 \times 0.3 \times 230 = 8000$ kl/a
cost at 17¢/kl 1,500

Power - allow 200 kW - 6 h/day i.e. 276000 kWh
cost at 2¢/kWh 5,500

Fuel - from Perry III - barite roasting uses
904 BTU/lb BaS, i.e. 2136 MJ/t

$$\text{Fuel requirement is } 7000 \times 0.9 \times \frac{169}{233} \times 2136$$

$$= 9.8 \times 10^6 \text{ MJ/a}$$

Cost at 0.2¢/MJ 19,500

4. Maintenance	allow 6% of capital	164,500
5. Supervision	allow 20% of direct labour	7,000
6. Operating Supplies	allow 10% of direct labour	3,500
7. Direct Manufacturing cost (1-6)		$1010,000

8.	Payroll Overhead allow 20% of direct labour	$7,000
9.	Plant Overhead allow 125% of direct labour	45,000
10.	Process Control allow 25% of direct labour	9,000
11.	Packaging allow 5% of direct costs	50,500
12.	Indirect Manufacturing Cost (8-11)	111,500
13.	Depreciation allow 8% of capital	219,000
14.	Property taxes, rent and insurance allow 1% of capital	27,500
15.	Fixed Manufacturing Cost (13-14)	246,500
16.	Manufacturing Cost (7 + 13 + 15)	1,368,000
17.	Administrative Expenses allow 3% of (16)	41,000
18.	Distribution and Marketing Expenses allow 5% of (16)	68,500
19.	Research and development allow 5% of (16)	68,500
20.	Financial Expenses allow 10% of capital	274,000
21.	Non-manufacturing Cost (17-20)	452,000
22.	Total Production Cost (16 + 21)	$1,820,000

Cost of producing 5325 t $BaCO_3$ is $\$1.82 \times 10^6$, i.e. $340/t

5. DISCUSSION

An attempt was made to obtain details of the barium chemicals imported into Australia by writing to 32 companies which are listed in various trade directories as either dealing in, or manufacturing barium chemicals. The letter requested information on the types of chemicals imported, the source, the quantity and the price. The response was disappointing, as only 13 companies replied, and of these, only 5 supplied positive information. The quantities of barium chemicals imported by these 5 companies are only a fraction of the total imports reported by the Commonwealth Bureau of Statistics.

The notes in Section 2 on the uses and markets for barium minerals are based, therefore, on published information and some of the uses described may not be applicable in Australia.

The Commonwealth Bureau of Statistics indicates that barium carbonate, chloride and sulphate are being imported at a rate equivalent to about 6800 t of $BaSO_4$ per annum. The cost estimate has been based upon the treatment of 7000 t barite per annum, to produce $BaCO_3$.

As the $BaCl_2$ and $BaSO_4$ products are of similar value to the $BaCO_3$, and as they together constitute less than 10% of the total imports, it is assumed that they can be made at the same cost as the $BaCO_3$, by production in batches according to demand.

The capital cost for the plant to treat 7000 t barite/annum, producing 5325 t $BaCO_3$/annum, is $\$2.75 \times 10^6$.

The production cost of the above plant is $340/t of $BaCO_3$.

An examination of the production cost shows that raw materials account for 42%, and non-manufacturing costs account for 25%. If carbon dioxide were substituted for the Na_2CO_3 used to make $BaCO_3$ the raw materials cost would be reduced by $222,000 and the production cost would be $300/t. This process would produce, however, gaseous H_2S, which would have to be confined and sold, or converted to sulphur and sold. It is assumed that the product is sold at neither loss nor profit although additional capital expenditure will be necessary.

If the use of Na_2CO_3 is retained, sodium sulphide is produced as a by-product. If all the Na_2S produced were recovered, the quantity would be about the same order of magnitude as the rate of import into Australia. The current price for Na_2S is about $300/t (PACE-1977), but as recovery involves evaporation at temperature up to 160°C to produce a crystalline solid, the profit available from the sale of Na_2S may be reduced to, say, $100/t. The effect of the sale of recovered by-product Na_2S would be a credit of $210,000 to the production cost for $BaCO_3$, which would be reduced to $302/t.

The major component of the non-manufacturing cost is the sum of $274,000 allowed for interest on borrowed capital. If interest-free funds were available, the effect on the production cost would be to reduce it to $290/t.

If both interest-free capital and by-product sales were achieved, the production cost would be about $250/t, which is approximately the same as the current imported price. There would therefore not be a profit on the production of $BaCO_3$ unless import tariff protection were available.

This report has assumed process details which would require confirmation before proceeding with a more detailed study of the process economics. Various references suggest the use of coal or carbon as the reducing agent during the barite roasting, and obviously a local brown coal would be preferred. However, the same references suggest that silica contained in the barites is undesirable because it consumes barium to form silicates. Although South Australia has barite containing low silica, the brown coal available contains high silica, and laboratory tests would be required to show whether the silica in the coal reacted with the barite.

Other aspects requiring laboratory confirmation include leaching temperature and time, thickening rates, and the selection of solution concentrations and temperatures to give desired product particle size.

A list of occurrences of barite in South Australia has been prepared by the Mines Department and is given as Table 1. The size of each deposit and its assay have been examined and the following list gives the preferred order of development. The minimum deposit size required for 10 years operation is 70000 t.

1. Oraparinna underground.
2. Pernatty Lagoon.
3. Nilpena 1 + 2
4. Weekeroo

Although of slightly lower grade, the Oraparinna deposit is preferred because of the existing mine workings which would eliminate development costs. The deposit at Pernatty Lagoon appears to be of very high grade, but requires further drilling to confirm the deposit size and grade.

Because the deposit in the above list have such good grades, there is no requirement for beneficiation.

None of the companies indicated a requirement for strontium-free barium chemicals, and probably only a few are aware that it is present.

6. CONCLUSIONS AND RECOMMENDATIONS

(1) The production of barium chemicals in South Australia is not economically viable at present. The estimated cost of production of $BaCO_3$ equivalent to the total imports of barium chemicals into Australia (5300 t/a) is \$340/t, compared with the present average import price of \$250/t. The estimated cost of the production plant is $\$2.75 \times 10^6$.

(2) If market conditions change sufficiently to warrant further investigation, laboratory tests should be made to confirm details of the process. Such tests would define the role of silica contained in indigenous coals upon barium recovery in the barite reduction stage, optimise leaching conditions, determine thickening rates, and study the effects of solution concentrations, temperatures and mixing rates upon the particle size of the product.

(3) The grades of several South Australian deposits of barite are sufficient to preclude the need for beneficiation.

(4) There appears to be no market requirement for the removal of strontium from barium chemicals.

TABLES 1 and 2

FIG. 1

TABLE 1: BARITE RESOURCES - SOUTH AUSTRALIA

Deposit	Reserves				Grade				Reference
	Measured	Indicated	Inferred	Estimated	$BaSO_4$	$SrSO_4$	SiO_2	Fe_2O_3	
Parachilna									
Oraparinna Underground	2,000	72,000	135,000	-	95	2.0	2.7	0.1	RB 73/110, Reid, 1969
Roberts Lode	5,000	-	20,000	-	95	2.0	3.0	0.1	RB 73/110
Bowering	-	-	-	8,000	-	-	-	-	Reid, 1974
Linkes	-	-	-	large	-	-	5.0	10.0	Reid, 1974
Bairstows	-	-	-	2,000	-	-	-	-	Reid, SML 325 - low grade
Howard	-	-	-	10,000	90	1.4	8.0	-	Reid, SML 325
Hall	-	-	-	6,000	-	-	10.0	-	Reid, 1974
Mt Haywood	-	-	-	2,000	95.0	4.8	0.1	-	Reid, SML 325
Matthews	-	6,000	8,000	-	91.4	3.8	4.03	0.12	RB 75/87 - dark barite
McRae 1	-	-	-	small	-	-	-	-	Unknown
2	-	-	-	small	-	-	-	-	Unknown
Carey Hill 2	-	38,000	21,000	-	93	3.0	4.0	0.5	RB 76/93
Carey Hill South	-	-	-	2,000	92.6	3.1	3.75	-	Reid, SML 325
Cement Square 1	-	7,500	7,500	-	96	3.4	0.6	0.05	RB 76/76 - dark barite
2	-	4,300	1,000	-	96	3.4	0.6	0.05	RB 76/76
Mt Falkland 1	-	3,700	8,400	-	96	3.0	0.1	0.03	RB 75/20
2	-	4,400	8,300	-	96	3.4	0.09	0.22	RB 75/21
3	-	4,500	7,000	-	96	3	0.1	0.03	RB 74/157
Moralana South	-	1,000	6,000	-	73	1.2	2.0	24.0	RB 75/58
North	-	-	-	2,000	-	-	-	-	Unknown, Reid 1974
Mt Frome	-	12,000	10,000	-	86	1.3	12.4	Tr	RB 76/86
Mt Neville	-	3,000	3,000	-	90	1.5	8.0	Tr	RB 76/68
Martins Well - Coad	-	-	-	-	-	-	-	-	Unknown
" " - East	-	-	-	2,000	92	1.3	2.5	-	Reid, SML 277
Weavers Well	-	-	-	5,000	92	1.5	3	-	Reid, SML 277
Artipena 1	-	-	-	8,000	96	1.0	2	-	Reid, SML 277
Black Hill 1	-	-	-	-	-	-	-	-	Unknown
2	-	-	-	-	-	-	-	-	Unknown
3	-	-	-	-	-	-	-	-	Unknown

Continued

TABLE 1: CONTINUED

Deposit	Reserves				Grade				Reference
	Measured	Indicated	Inferred	Estimated	$BaSO_4$	$SrSO_4$	SiO_2	Fe_2O_3	
<u>Copley</u>									
Beltana 2	-	2,000	-	-	90	2	5.7	1.3	RB 76/70
Nilpena 1	-	-	-	large	92-96	2.7-2.9	0.6	0.05-3.8	Amdel MT 148/76 & 149/76
2	-	-	-	medium	-	-	-	-	Unknown
Mt Serle 1	-	-	-	medium	-	-	-	-	Unknown
2	-	-	-	medium	-	-	-	-	Unknown
Mt Chambers	-	-	3,000	-	95	3.7	1.0	Tr	RB 76/12
Mt John	-	7,600	6,000	-	96	2.1	1.6	Tr	RB 76/130
Potato Patch	140	1,500	2,700	-	94	2.4	1.4	Tr	RB 76/130
Mt James	-	-	-	large	93	3.2	3.5	Tr	Amdel MT 148/76
Mt Coffin	-	300	300	-	97	2.0	0.2	Tr	RB 76/52
Nankabunyana	1,200	4,800	6,000	-	95	2.6	0.9	0.04	RB 76/142
Moolooloo	-	-	-	Small	98	1.5	0.2	Tr	Amdel MT 148/76
<u>Olary</u>									
Weekeroo	-	-	2,700,000	-	-94.0-		2.7	2.0	Amdel Rept. 234, RB 26/69
Ameroo Hill 1	-	-	-	medium	-	-	-	-	Similar to Mt Mulga
2		-	-	medium	-	-	-	-	" " "
Mt Mulga	-	89,000	-	-	76.3	1.87	13.2	6.8	RB 74/143
<u>Orroroo</u>									
Oladdie	-	-	-	minor	-	-	-	-	Low grade
Great Gladstone	-	-	-	-	-	-	-	-	Unknown
Yanyarrie	-	-	-	36,000/m	70.0	-	-	-	Gold-copper exploration
<u>Torrens</u>									
Pernatty Lagoon	-	-	-	16,000/m	96.4	2.59	0.05	0.05	M.Res.Rev. 135

Data supplied by South Australian Department of Mines - 1977

TABLE 2: IMPORT STATISTICS - BARIUM CHEMICALS
Source - Commonwealth Bureau of
Statistics Materials Cleared for
Home Consumption

		$BaCO_3$	$BaCl_2$	$BaSO_4$
1970/71	tonnes	928	1258	310
	$	90,000	107,000	45,000
	$/t	97	85	145
1971/72	tonnes	1461	1364	293
	$	130,000	119,000	39,000
	$/t	89	87	133
1972/73	tonnes	1049	1910	350
	$	102,000	185,000	49,000
	$/t	97	97	140
1973/74	tonnes	811	2213	407
	$	103,000	238,000	53,000
	$/t	126	107	129
1974/75	tonnes	969	825	303
	$	211,000	164,000	90,000
	$/t	217	199	295
1975/76	tonnes	5350*	48	257
	$	1,247,000	1,600	4,600
	$/t	233*	341	178
1976/77	tonnes	5300*	260*	276*
	$	133,500*	78,000*	59,000*
	$/t	250*	298*	212*

* Estimates

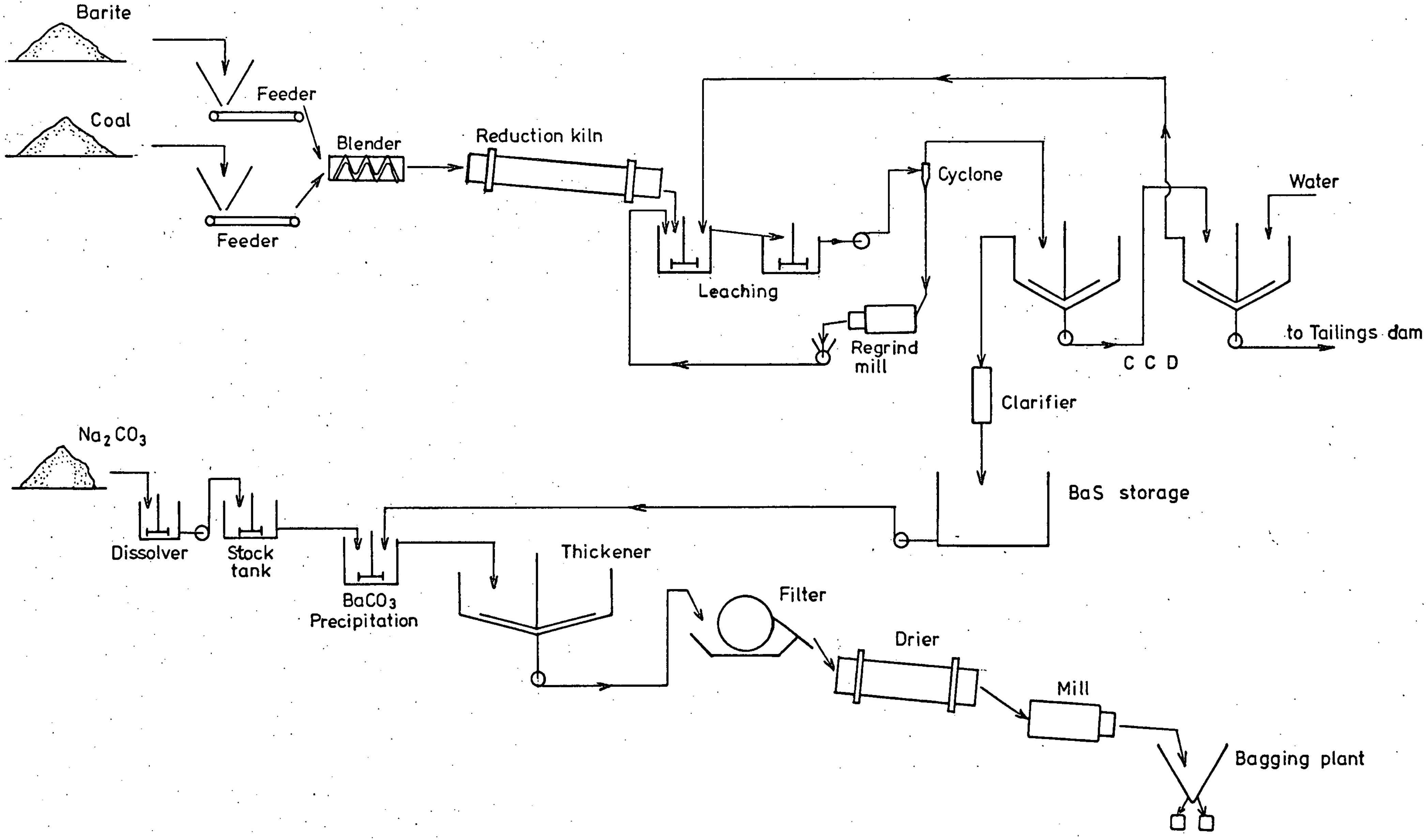

FIG. 1: FLOW SHEET FOR THE PRODUCTION OF $BaCO_3$ FROM BARITE