THE PRODUCTION OF BARIUM SALTS FROM BARYTES.

By G. M. Adhikari, J. J. Sudborough and H. E. Watson.

INTRODUCTION.

Barium compounds are used commercially for the following purposes:—

1. The peroxide is used on the large scale for the manufacture of oxygen by Brin's process.

2. At one time barium hydroxide was used in sugar refineries for separating cane sugar from the molasses, but, owing to the poisonous nature of these compounds, it is now customary to use strontium, and not barium hydroxide.

3. Precipitated barium carbonate is manufactured for use as a rat poison and is also used in the glass and pottery industries.

4. The nitrate is manufactured on a large scale for use in pyrotechny for giving green-coloured lights.

5. Finely ground barytes is used as a reducer for white lead in the paint industry, but is practically never used by itself as a pigment owing to its low covering power. The fine powder is often used as a base on which different colours can be precipitated, e.g. paranitraniline reds and bright greens. It is also used as a 'filler' in the rubber and paper industries. The precipitated sulphate is largely used as a pigment under the name of 'blanc fixe' or permanent white.

6. The white pigment 'lithopone' is a mixture of zinc oxide, zinc sulphide and barium sulphate and is manufactured by mixing solutions of barium sulphide and zinc sulphate, the barium sulphide being manufactured by the reduction of barytes.

7. Certain luminous paints contain barium compounds.

The two chief sources of barium compounds are the carbonate, witherite, and the sulphate, barytes. The conversion of the carbonate into salts, such as the nitrate, chloride or precipitated sulphate, is a simple operation.
In India no appreciable deposits of witherite have so far been found, so that all barium compounds made from indigenous materials would have to be manufactured from the sulphate. Deposits of barytes, on the other hand, are met with in a number of different localities in India, viz. on the Sanmowli River and lower slopes of the Pab range in Baluchistan; in the neighbourhood of the Bawdwin lead-zinc-silver mines in the North Shan States of Burma; near the Mohan River of Central India; near Betamchelera in the Kurnool District of Madras and near Alangayan in the Salem District of the same Presidency.

The initial step in the conversion of barytes into other barium compounds is its reduction to sulphide and this is accomplished by heating 100 parts of powdered barytes with twenty parts of fine coal-slack or charcoal. When the latter is employed greater care in mixing is required as otherwise the reaction is not complete owing to the non-fusibility of the mass. When slack is used the bituminous materials permeate the mass and facilitate reduction. The addition of rosin, oil, gasworks asphalt etc. to charcoal produces similar effects, and common salt is also sometimes added to facilitate fusion.

The sulphide is soluble in water and the aqueous solutions on treatment with hydrochloric or nitric acid give the corresponding barium salts. Solutions of such salts yield 'blanc fixe' on precipitation with sulphuric acid and artificial barium carbonate on precipitation with ammonium carbonate. The latter compound can also be manufactured by heating powdered barytes (10 parts) with charcoal (2 parts) and potassium carbonate (5 parts) and lixiviating with water when barium carbonate, contaminated with iron, is left behind.

The reduction of powdered barytes by means of coal-slack (Rs. 8 per ton) in Bengal or charcoal (Rs. 45 per ton) in South India appears to be a feasible proposition. The relatively high prices of nitric and hydrochloric acids in India as compared with Europe and America would militate against the second stage in the process for manufacturing barium salts.

An alternative to the use of hydrochloric acid is the employment of magnesium chloride, and as this is now manufactured by the Pioneer Magnesia Works at Kharaghoda and put on the market at Rs. 9 per cwt., this appears to be a cheaper method of converting the barium sulphide into chloride.

The fusion of powdered barytes with charcoal and calcium chloride has been used for producing barium chloride, and Shroff

2 Indian Patent 4266 of March 7, 1919.
has described a similar process by using magnesium chloride in place of calcium chloride which is not manufactured in India.

The matters dealt with in this paper are grouped under the three headings:—

I. Reduction of barium sulphate (barytes) to barium sulphide.

II. Conversion of barium sulphide into barium chloride and recovery of hydrogen sulphide by means of magnesium chloride.

III. Simultaneous action of carbon and magnesium chloride on barium sulphate.

I. REDUCTION OF POWDERED BARYTES WITH CHARCOAL.

The reduction of barium sulphate to barium sulphide is a reaction which has been utilised for a number of years and in many factories the actual yields of water soluble barium sulphide amount to 60 to 70 per cent. of the theoretical. It is only recently, however, that systematic investigations of the reactions involved appear to have been undertaken. According to Mostowitsch barium sulphate is stable up to a temperature of 1400° in a current of air, but at 1500° begins to dissociate into barium oxide and sulphuric anhydride (or sulphur dioxide and oxygen). It can be reduced with coal or carbon monoxide; the reduction begins at 600° with coal or 650° with carbon monoxide and is complete at 800°. He states that at lower temperatures the reaction proceeds according to the equation:—

$$\text{BaSO}_4 + 2C \rightarrow \text{BaS} + 2\text{CO}_2$$

whilst at higher temperatures a portion decomposes in accordance with the equation:—

$$\text{BaSO}_4 + 4C \rightarrow \text{BaS} + 4\text{CO}.$$  

He further states that barium sulphide in the absence of air is stable up to 1200°.

L. Marino has studied the reduction of the sulphate in presence of combustible gases, such as methane, hydrogen, coal gas and water gas, and states that reduction occurs at lower temperatures than when powdered coal is used. With coal gas and water gas the most favourable temperature is 520 to 540° and hydrogen gives even better results. It is stated that the temperature can be even further lowered by the use of suitable catalysts and it is claimed that the process is cheaper than the older one in which powdered coal is used. According

2. Gazzetta, 1913, 43, i, 416.
to calculation each ton of barytes requires 500 cm. meters of water gas for complete reduction.

A. E. Wells appears to have carried out the most extensive series of experiments hitherto recorded. As the result of experiments made with finely pulverised barytes and carbon intimately mixed and heated in crucibles in a muffle furnace and in the absence of outside air or of the products of combustion of the fuel, it is shown that a high degree of reduction, namely 90 per cent. or more, can be obtained at temperatures between 850 and 1000\(^{\circ}\) when the carbon added is about 15 per cent. of the weight of the barium sulphate. With less carbon the reduction is not so complete, although the carbon efficiency is greater, and with more than 15 per cent. the carbon efficiency decreases rapidly.

Wells draws particular attention to the necessity of preventing atmospheric oxygen from coming into contact with the reduced product. This he accomplished by having a well-fitting cover to the crucible and, in some cases, in having a protecting layer of fine coal on the top of the mixture. Even with such precautions slight reversion of sulphide to sulphate was noticed in one or two cases, and this was attributed to the slight porosity of some of the crucibles used.

Table I gives the results of the experiments made in porcelain crucibles with covers and with a protecting layer of carbon.

Experiments were also made with mixtures of barium sulphate and carbon placed in an electrically heated porcelain tube through which a current of nitrogen was passed and the results obtained were similar to those given by the crucible experiments.

Another series of experiments was made with briquettes of precipitated barium sulphate and lamp black and, after 1.5 to 3 hours in an oil-heated furnace in which the products of combustion (reducing gases containing 4 per cent. of carbon monoxide) were passed over the briquettes, gave the following results:

- 82.5 per cent. of the total barium as water soluble sulphide.
- 13.8 " " " acid soluble oxide or carbonate.
- 3.7 " " " insoluble sulphate.

Larger briquettes made of pulverised barytes and lamp black gave only 70 per cent. of the barium as sulphide and as the briquettes remained hot for a relatively long period, the tendency to reoxidation to sulphate was great.

Experiments were also made in a small multiple-hearth roasting furnace and a small rotary cement furnace. In the latter with a temperature of 1050° and with a mixture of powdered barytes and pulverised coal or charcoal only 2 to 3 per cent. of the barytes was left unacted on, but the water-soluble sulphide was only 85 to 87 per cent. and the acid soluble oxide or carbonate 10 to 12 per cent.

Thus in direct fired furnaces the proportion of acid soluble barium compounds, oxide and carbonate, is higher and the proportion of water-soluble sulphide is less than in an indirect fired furnace, e.g. a muffle furnace.

**TABLE 1.**

*Reduction of barium sulphate in porcelain crucibles (Wells.)*

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Time min.</th>
<th>Per cent. carbon to BaSO₄</th>
<th>Per cent. of total barium in product</th>
<th>Per cent. of total carbon consumed</th>
<th>Carbon consumed per cent. of BaSO₄ reduced to BaS.</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>60</td>
<td>10·5</td>
<td>50</td>
<td>58</td>
<td>42</td>
</tr>
<tr>
<td>800</td>
<td>120</td>
<td>10·5</td>
<td>62</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>850</td>
<td>60</td>
<td>10·5</td>
<td>66</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>850</td>
<td>120</td>
<td>10·5</td>
<td>78</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>900</td>
<td>60</td>
<td>10·5</td>
<td>80</td>
<td>85</td>
<td>15</td>
</tr>
<tr>
<td>900</td>
<td>120</td>
<td>10·5</td>
<td>85</td>
<td>86</td>
<td>14</td>
</tr>
<tr>
<td>950</td>
<td>30</td>
<td>10·3</td>
<td>80</td>
<td>83</td>
<td>17</td>
</tr>
<tr>
<td>950</td>
<td>60</td>
<td>10·3</td>
<td>78</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>1050</td>
<td>30</td>
<td>10·3</td>
<td>54</td>
<td>97</td>
<td>3</td>
</tr>
<tr>
<td>1150</td>
<td>20</td>
<td>10·3</td>
<td>82</td>
<td>96</td>
<td>2</td>
</tr>
</tbody>
</table>
By effecting the reduction rapidly at high temperatures, e. g. above 1000°, the proportion of oxide and carbonate is less than when the reduction takes place at lower temperatures. Below 750° the reduction is too slow to be of any value commercially.

We had begun our experiments on the reduction of powdered barytes by charcoal both in crucibles and in closed tubes before our attention was drawn to Wells' work. Our experiments confirm Wells' conclusions and a brief summary of them is given.

**Experimental.**

1. **Materials used.**—The barium sulphate was a high-grade crystalline barytes of 99.7 per cent. purity from the Madras Presidency and before use it was ground in an iron edge-runner mill until it passed a 200-mesh sieve.

The carbon employed for the reduction was ordinary wood charcoal and was ground to pass a 100-mesh sieve. The sample of charcoal gave 1 per cent. of ash insoluble in dilute hydrochloric acid.

The magnesium chloride was either pure white crystals of nearly 100 per cent. purity or the fused Indian magnesium chloride made at Kharaghoda. The latter contained 97 per cent. of MgCl₂, 6H₂O and a trace of sulphate.

The magnesia used in some of the experiments was 'heavy magnesia containing 82 per cent. MgO and in others 'light' magnesia containing 55 per cent. MgO. The impurities were water and carbonate.

The nitrogen used for displacing the air in the tube experiments was made by bubbling air through concentrated ammonia solution and leading the mixture over red-hot copper turnings.

2. **Method of determining percentage conversion.**—In the earlier experiments where the mixture was made by grinding the dry materials in a mortar the following method was adopted:—When cold the furnace product was weighed and one gram taken for analysis. This was extracted with boiling water and the soluble barium compounds, chiefly sulphide, precipitated as barium sulphate, filtered with the aid of a Gooch crucible and weighed.

In the greater number of the experiments the mixing was done wet in an edge-runner mill and the total barium contents of the mixture were determined after the experiment was complete. The total furnace product was weighed when cold, then 1 gram was taken
and ignited in a porcelain crucible to burn off the excess carbon, the white residue was transferred to a beaker, boiled with dilute hydrochloric and sulphuric acids and the precipitated barium sulphate filtered and weighed. The water-soluble barium compounds in 1 gram of the furnace product were determined and the percentage conversion to sulphide or percentage reduction thus ascertained.

A slight error was introduced in the estimation of the total barium by this method, as the ash from the charcoal contained 1 per cent. of acid insoluble ash. As the amount of charcoal used was usually 30 per cent. of the weight of the barytes, this means a positive error of about 0.2 in the percentage of total barium calculated as sulphate.

3. Crucible Experiments.—Morgan fireclay crucibles were used and were heated in an electric muffle furnace, the temperature of which was raised before the crucibles were introduced. Temperature measurements were made by means of a nickel-nichrome thermocouple, the junction of which was placed near the crucible. In the earlier experiments the substances were finely ground and mixed dry in a mortar, packed closely in open crucibles and heated in the furnace. The results given in Table II show that even when a large excess of charcoal is used the percentage reduction is relatively small.

Subsequent experiments were made in crucibles with closely fitting lids. The crucibles were provided with a disc of asbestos board and on this was placed a disc of alundum which was luted with alundum cement. The results, recorded in Table III, are better than in the first experiments, but the percentage reduction is still not good.

A final set of experiments was made by grinding several hundred grams of barytes with water and the required amount of charcoal in an edge-runner mill for two to three hours, drying the mixture and heating portions of it in closed crucibles in the muffle furnace. The results given in Table IV show that nearly complete reduction can be attained under such conditions.

**TABLE II.**

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Proportions of ingredients</th>
<th>Temperature in degrees Centigrade</th>
<th>Hours</th>
<th>Percentage reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Barytes:Charcoal 1:1</td>
<td>900</td>
<td>4</td>
<td>50.0</td>
</tr>
<tr>
<td>2</td>
<td>Barytes:Charcoal 1:3</td>
<td>900</td>
<td>4</td>
<td>61.0</td>
</tr>
<tr>
<td>3</td>
<td>Barytes:Charcoal 1:4</td>
<td>800</td>
<td>4</td>
<td>25.0</td>
</tr>
<tr>
<td>4</td>
<td>Barytes:Charcoal 2:0</td>
<td>800</td>
<td>4</td>
<td>36.7</td>
</tr>
<tr>
<td>5</td>
<td>Barytes:Charcoal 2:0</td>
<td>900</td>
<td>4</td>
<td>53.0</td>
</tr>
</tbody>
</table>
TABLE III.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Proportions of ingredients</th>
<th>Temperature in degrees Centigrade</th>
<th>Hours</th>
<th>Percentage reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>2</td>
<td>900</td>
<td>4</td>
<td>80.0</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>900</td>
<td>4</td>
<td>78.0</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>900</td>
<td>4</td>
<td>68.0</td>
</tr>
</tbody>
</table>

TABLE IV.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Proportions of ingredients</th>
<th>Temperature in degrees Centigrade</th>
<th>Hours</th>
<th>Percentage reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>2</td>
<td>900</td>
<td>4</td>
<td>87</td>
</tr>
<tr>
<td>10</td>
<td>2</td>
<td>900</td>
<td>4</td>
<td>95</td>
</tr>
<tr>
<td>11</td>
<td>3</td>
<td>900</td>
<td>4</td>
<td>97</td>
</tr>
</tbody>
</table>

4. Tube Experiments.—The furnace consisted of a quartz tube 48 cm. long and 23 mm. internal diameter and a length of 29 cm was wound with 9 meters of No. 16 S.W.G. nichrome wire. The winding was covered with a paste of ground chromite, asbestos and water and over this was placed a thick layer of alundum paste. The whole was allowed to dry in the sun and the tube thus prepared was placed in an asbestos box $34 \times 20 \times 15$ cm., which was packed with magnesia. The ends of the tube which projected 7 cm. from the ends of the box were closed with well-fitting rubber stoppers: one of these was double bored and carried a delivery tube and also a small quartz tube closed at one end and into this tube the nickel-nichrome thermocouple was introduced. The delivery tube was connected by means of wash bottles containing (1) sulphuric acid, and (2) alkali pyrogallate solution, to the gasholder containing nitrogen.

The charge was placed in a porcelain boat $9.5 \times 1.5$ cm., which was introduced into the tube so that the end touched the junction of the thermocouple. The thermocouple was compared with a standard pyrometer and the variations in temperature along the length of the tube was determined in one or two experiments. The maximum temperature was observed at about the middle of the boat and the two ends were usually $10^\circ$ cooler.

In Experiment No. 9 the materials were ground for one hour and in Experiments Nos. 10 and 11 for three hours.
The results of a series of experiments are recorded in Table V and show that at 900° almost complete reduction occurs in 1.5 hours, but that at lower temperatures the reduction is much less in the given time.

**TABLE V.**

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Time in Hours</th>
<th>Temperature</th>
<th>Percentage reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>1.5</td>
<td>900</td>
<td>98.5</td>
</tr>
<tr>
<td>13</td>
<td>1.5</td>
<td>900</td>
<td>99.2</td>
</tr>
<tr>
<td>14</td>
<td>1.5</td>
<td>800</td>
<td>65.0</td>
</tr>
<tr>
<td>15</td>
<td>1.5</td>
<td>700</td>
<td>34.0</td>
</tr>
</tbody>
</table>

**II. ACTION OF MAGNESIUM CHLORIDE ON BARIUM SULPHIDE.**

Shagnor and Helbig\(^2\) appear to have been the first to observe the reaction between an aqueous solution of magnesium chloride and sulphides of the alkali earths. Chance\(^3\) worked out the details of the reaction in connection with the disposal of alkali waste. He found that calcium sulphide is quantitatively decomposed into hydrogen sulphide and calcium chloride by an aqueous solution of magnesium chloride.

\[
\text{CaS} + \text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaCl}_2 + \text{Mg} (\text{OH})_2 + \text{H}_2\text{S.}
\]

Sulphides of strontium and barium behave in a similar manner and in several patents it has been suggested that the reaction might be utilised in the production of barium chloride and hydrogen sulphide from barytes.

R. Heinz\(^4\) has pointed out that if the grey product obtained by reducing barytes is employed, the magnesium hydroxide produced according to the equation:

\[
\text{BaS} + \text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{BaCl}_2 + \text{Mg} (\text{OH})_2 + \text{H}_2\text{S}
\]

is not white and contains all the impurities present in the grey mass. If, however, the grey reduction product is extracted with water only barium sulphide and a little hydroxide are dissolved. When this solution is heated with magnesium chloride the reaction is very slow.

---

\(^{1}\) These figures were obtained by extracting the product with dilute hydrochloric acid and not water and hence include not only the sulphide but also the small amounts of oxide and carbonate formed (cf. Wells, *loc. cit.*, p. 771).


\(^{4}\) *P. R. P.*, 1887, 738 of January 3, 1907.
but under pressure becomes more rapid, proceeds smoothly and colourless barium chloride and magnesium hydroxide are obtained and also a good yield of hydrogen sulphide.

This reaction, or the analogous reaction with calcium sulphide, appears to have been utilised in Germany to a large extent during the war for the production of sulphur for sulphuric acid manufacture, as the importation of foreign pyrites or sulphur was impossible.

III. REDUCTION OF BARYTES WITH CHARCOAL IN THE PRESENCE OF MAGNESIUM CHLORIDE.

It appears quite clear from the preceding sections that it is possible to get good yields of barium chloride and hydrogen sulphide and hence sulphur from barytes provided the operation is conducted in the two stages, namely, first reduction to the sulphide and then the decomposition of a solution of the sulphide by magnesium chloride under pressure.

It would obviously be much more convenient if the whole change could be effected in one stage, namely by heating barytes with carbon and magnesium chloride. Shroff 1 claims to have accomplished this and recommends it as a method for preparing barium chloride, magnesia and sulphuretted hydrogen.

When crystallised magnesium chloride, MgCl₂·6H₂O, is heated above 160° it is decomposed into magnesia and hydrogen chloride. Studies of the statics and dynamics of the reactions involved show that, though there are minor intermediate reactions, the charge may in the main be represented by the equation:

\[ \text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HCl} \]

If a mixture of barytes, charcoal and crystallised magnesium chloride is heated quickly to the temperature of reduction, it is probable that the following reactions occur:

\[ \text{BaSO}_4 + 4\text{C} \rightarrow \text{BaS} + 4\text{CO} \quad (1) \]
\[ \text{MgCl}_2 + \text{H}_2\text{O} \rightarrow \text{MgO} + 2\text{HCl} \quad (2) \]
\[ \text{BaS} + 2\text{HCl} \rightarrow \text{BaCl}_2 + \text{H}_2\text{S} \quad (3) \]

Good yields of the products represented in equation (3) will be obtained only if the reactions represented by (1) and (2) start simultaneously and proceed with equal velocity or if reaction (1) proceeds more rapidly than reaction (2).

1 Ind. Pat. No. 4266 of March 7, 1919.
We have carried out a number of small scale experiments with the object of testing the yields of water-soluble barium salt formed under specific conditions, also the percentage of acid-soluble barium salts left in the residue and the form in which the sulphur is evolved.

The apparatus used was the electrically heated silica tube furnace described on p. 90, with the addition of wash bottles attached to the exit end of the tube in order to collect the volatile sulphur compounds formed. The first wash bottle contained a little water which did not quite touch the bottom of the tube through which the gases entered the bottle. The object of this bottle was to catch the hydrogen chloride evolved and also to condense all the elemental sulphur produced during the reaction. Sulphuretted hydrogen and also any sulphur dioxide were absorbed in bottles containing dilute sodium hydroxide solution. When the boat was placed in position and the wash bottles connected up, the whole apparatus was tested for leaks, after which a fairly rapid current of nitrogen was passed for 20 to 30 minutes in order to displace the air in the tube. The electric current was then switched on and when the correct temperature was attained, the rate of passage of the gas was reduced. After maintaining the temperature at the fixed point for a given time, in most experiments 1.5 hours, the current was switched off and a rapid stream of nitrogen passed in order to remove the residual gases from the tube. Some sulphur which condensed in the outlet end of the tube was driven over into the first wash bottle by gently warming.

I. Method of estimating the products of the reaction.

1. The residue in the boat was extracted with boiling water and the filtered extract made up to 500 cc. 50 cc. were taken for total water-soluble barium compounds which were weighed as barium sulphate. The quantity of barium sulphate originally present in the mixture was determined in a second sample as described on p. 88 and consequently the percentage conversion or ratio of soluble barium salts expressed as sulphate to the weight of barium sulphate originally present could be calculated.

2. The extract contained sulphide and probably polysulphides of barium. The total sulphur content of the extract was estimated by oxidising 50 cc. of the solution to sulphate by means of sodium hypobromite and weighing as barium sulphate, and multiplying by 10. This amount deducted from the percentage of total barium brought into water-soluble form and expressed as sulphate gives the percentage of total sulphur which had been eliminated during the experiment as sulphur, sulphur dioxide or hydrogen sulphide.
3. The contents of bottles II and III were made up to 500 cc. Sulphuretted hydrogen was estimated in 50 cc. by adding cadmium sulphate solution and treating the precipitated and washed cadmium sulphide with excess of iodine and titrating the excess with 0.1 N sodium thiosulphate solution.

4. A second 50 cc. of the alkaline liquid was oxidised with sodium hypobromite and the resulting sulphate precipitated and weighed as barium sulphate, thus giving the total sulphur eliminated as sulphur dioxide and sulphuretted hydrogen calculated as barium sulphate.

5. Elemental sulphur, together with small quantities of sulphur dioxide or sulphuretted hydrogen which collected in bottle No. 1, was boiled with bromine water and nitric acid, evaporated to a small bulk and then treated two or three times with about 5 cc. of a 3 per cent. solution of bromine in carbon tetrachloride and the sulphuric acid so obtained estimated as barium sulphate, thus giving the amount of free sulphur evolved as such but calculated as barium sulphate.

The sum of (4) and (5) gives the total sulphur eliminated during the reaction and this figure should agree with that obtained by deduction as shown in Section (2) above and the agreement actually obtained was usually within 4 per cent.

2. **Crucible Experiments.**

Experiments made in crucibles were far from decisive. The main disturbing factor was the tendency of the mixture to froth vigorously. This took place in the earlier stages of the experiment and either blew off the lid or made a large gap. Thus reoxidation and loss vitiated the experiment. Table VI gives the results of a series of experiments in which the reaction was conducted in two stages as follows:—Barytes and charcoal were mixed with half the theoretical amount of magnesium chloride and heated in a closed crucible for two hours. When cold the charge was mixed with the remaining half of the magnesium chloride and reheated for a further period of two hours.
TABLE VI.

Reduction of barytes with charcoal in closed crucibles in the presence of magnesium chloride at 900°.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Weights of ingredients in grams</th>
<th>Time in hours</th>
<th>Percentage conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barytes</td>
<td>Charcoal</td>
<td>Mag. Chloride</td>
</tr>
<tr>
<td>16</td>
<td>9·4</td>
<td>9</td>
<td>4·7</td>
</tr>
<tr>
<td>17</td>
<td>9·4</td>
<td>9</td>
<td>4·7</td>
</tr>
<tr>
<td>18</td>
<td>20</td>
<td>6</td>
<td>10·0</td>
</tr>
<tr>
<td>19</td>
<td>20</td>
<td>6</td>
<td>10·0</td>
</tr>
</tbody>
</table>

The experiments show that under the given conditions only 70–78 per cent. of conversion into chloride takes place.

3. Closed Tube Experiments.

A series of experiments was made in the nitrogen-filled quartz tube in order to ascertain the manner in which the sulphur is eliminated and the amount of barium sulphide left in the residue in the boat.

A mixture which would serve for a series of experiments was made as follows:—100 grams of powdered barytes and 30 grams of wood charcoal were ground together wet in an edge-runner mill for three hours. The mixture\(^1\) was dried and analysed for total barium sulphate content (cf. p. 88). 30 grams of this mixture were added to the calculated quantity of magnesium chloride, viz. equimolecular proportions of barium sulphate and magnesium chloride, the mixture moistened with a little water and ground in a porcelain mortar and dried in the steam oven. Small portions weighing about five grams were heated in the tube furnace and the results obtained in three experiments at 900° are given in Table VII.

\(^1\) The same mixture was used for Experiment No. 11.  Cf. Table IV.
Table VII.

Tube experiments with mixtures of barytes, charcoal and magnesium chloride at 900°.

<table>
<thead>
<tr>
<th>No. of</th>
<th>Percentage of total barytes reduced to water-soluble barium salts (sulphide)</th>
<th>Percentage of total sulphur present in the aqueous extract</th>
<th>Percentage of total sulphur eliminated as</th>
<th>Percentage of barytes converted into acid soluble barium compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂S</td>
<td>SO₂</td>
<td>S</td>
</tr>
<tr>
<td>20</td>
<td>87</td>
<td>37</td>
<td>39·5</td>
<td>7·5</td>
</tr>
<tr>
<td>21</td>
<td>89</td>
<td>41</td>
<td>33·0</td>
<td>8·0</td>
</tr>
<tr>
<td>22</td>
<td>94</td>
<td>41</td>
<td>34·4</td>
<td>13·8</td>
</tr>
</tbody>
</table>

Barytes, when mixed with charcoal alone in the proportions used in the above experiments, is almost completely reduced in 1·5 hours at 900° as is shown in Table V. On the addition of magnesium chloride the average conversion at 900° to water-soluble barium compounds is 91 per cent. In addition the residue after extraction with water contains about 3 to 4 per cent. of barium compounds soluble in dilute acid as shown in column 5 of Table VII. Thus on an average the percentage reduction is 95, showing that magnesium chloride has only a very slight inhibiting effect on the reduction.

The sulphur evolved is not recovered wholly as sulphuretted hydrogen as represented in equation (3) formulated on p. 92. Sulphur and sulphur dioxide are also formed.

Only about half the sulphur corresponding with the water soluble barium salts is eliminated, the remainder is found in the residue in the boat as barium sulphide and perhaps polysulphides.

4. Reduction of barytes in presence of magnesium chloride and magnesia.

If the reactions:

\[
\text{MgCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + 2\text{HCl}
\]

and

\[
\text{BaSO}_4 + 4\text{C} \rightarrow \text{BaS} + 4\text{CO}
\]

proceeded with equal velocities at the same temperature nearly the whole of the barium sulphate should be transformed into barium chloride. Table VII shows that only about 50 per cent. of the total sulphur is eliminated, and this proves that the above condition is not satisfied. Actually the first reaction starts at a much lower temperature than the second one. For a short time the two reactions occur
simultaneously and finally all the magnesium chloride is decomposed
and the second reaction continues giving rise to sulphide and not
chloride of barium.

It is thus evident that if the temperature at which the first re-
action takes place could be raised a larger quantity of the barium
sulphide, formed according to the second reaction, would be converted
into chloride.

Moldenhauer has pointed out that the addition of magnesia
raises the decomposition temperature of magnesium chloride to 500°
and hence the effects of the addition of magnesia to the reaction
mixture used in Experiments 20-22 have been studied.

Table VIII gives the results of several crucible experiments.
In Experiments 23-26 the mixing was accomplished by grinding the
dry materials by hand in a mortar. In Experiments 27 and 28 the
charge was ground wet in a power-driven edge-runner mill for three
hours and then dried in an oven. All these experiments were charac-
terised by a complete absence of the frothing observed when the
magnesia was omitted (see p. 94).

Table IX gives the results of a series of experiments carried out
in two stages as described on p. 94. For these experiments the
charge was ground wet in the power-driven mill. The temperature in
all the Experiments 23-31 was 900° and the time four hours.

**TABLE VIII.**

*Crucible experiments with mixtures of barytes, charcoal, magnesium chloride and magnesia.*

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Weights of constituents in grams</th>
<th>Percentage conversion into water-soluble barium salts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barytes</td>
<td>Charcoal</td>
</tr>
<tr>
<td>23</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>24</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>25</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>26</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>27</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>28</td>
<td>20</td>
<td>6</td>
</tr>
</tbody>
</table>

TABLE IX.

*Crucible experiments with mixtures of barytes, charcoal, magnesium chloride and magnesia.*

The charge was heated for two hours, the second half of the magnesium chloride added and the mass reheated for two hours.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Weights of constituents in grams</th>
<th>Percentage conversion into water-soluble barium salts</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barytes</td>
<td>Charcoal</td>
</tr>
<tr>
<td>29</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>30</td>
<td>20</td>
<td>6</td>
</tr>
<tr>
<td>31</td>
<td>100</td>
<td>30</td>
</tr>
</tbody>
</table>

5. *Tube experiments with mixtures of barytes, charcoal, magnesium chloride and magnesia.*

Table X gives the results of some early experiments in the tube furnace. The mixture was the same as that used in Experiments 27 and 28 (Table VIII) viz. barytes 20, charcoal 6, magnesium chloride 20 and magnesia 5. The percentage conversion to water soluble barium compounds is distinctly better than in the corresponding crucible experiments. On an average 66 per cent. of the total sulphur of the barytes is eliminated, mainly as hydrogen sulphide, but partly as sulphur dioxide and sulphur.
TABLE X.

Tube experiments with mixtures of barytes, charcoal, magnesium chloride and magnesia.

Temperature = 900°. Time = 3 hours. Molecular proportions—barytes 1, magnesia 0.75, magnesium chloride 1.2.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Percentage conversion to water: soluble</th>
<th>Percentage of total sulphur eliminated as</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barium salts</td>
<td>Sulphide</td>
</tr>
<tr>
<td>32</td>
<td>85·0</td>
<td>22·7</td>
</tr>
<tr>
<td>33</td>
<td>88·4</td>
<td>15·8</td>
</tr>
<tr>
<td>34</td>
<td>86·3</td>
<td>22·7</td>
</tr>
<tr>
<td>35</td>
<td>87·6</td>
<td>16·3</td>
</tr>
<tr>
<td>36</td>
<td>87·7</td>
<td>17·6</td>
</tr>
<tr>
<td>37</td>
<td>87·9</td>
<td>21·2</td>
</tr>
<tr>
<td>38</td>
<td>88·2</td>
<td>21·6</td>
</tr>
<tr>
<td>39</td>
<td>85·7</td>
<td>16·5</td>
</tr>
</tbody>
</table>

Experiments have also been made in which the amount of magnesia was varied between 0·55 and 1·0 equivalents. The results are tabulated in Table XI. In these experiments also no frothing was observed. In Experiments 40–44 the mixing was accomplished by hand in a mortar, whereas in Experiments 45–50 the mixture was prepared by grinding wet for three hours in an edge-runner mill. With the exception of Experiment 45, the percentage conversion varies from 83 to 90 and the maximum percentage of sulphur evolved is obtained by using equimolecular proportions of chloride and oxide, but in all cases an appreciable amount of sulphur remains in the residue in the form of sulphides of barium. A comparison of Experiments 40 and 45 indicates that wet mixing in the edge-runner mill is preferable to grinding dry by hand.
TABLE XI.

*Tube experiments using different amounts of magnesia. Temperature, 900°. Charcoal, 30 per cent.*

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Relative proportions of ingredients in gram molecules</th>
<th>Percentage of water-soluble barium compounds</th>
<th>Percentage of sulphur (calculated as BaSO₄) present in extract</th>
<th>Percentage of total sulphur eliminated as</th>
<th>Total percentage of sulphur eliminated</th>
<th>Calculated from sulphur in residue</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Barytes</td>
<td>Magnesium chloride</td>
<td>Magnesia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>1</td>
<td>1</td>
<td>0.55</td>
<td>87.4</td>
<td>38.8</td>
<td>35.1</td>
</tr>
<tr>
<td>41</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
<td>87.4</td>
<td>36.9</td>
<td>38.8</td>
</tr>
<tr>
<td>42</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
<td>85.7</td>
<td>28.6</td>
<td>49.0</td>
</tr>
<tr>
<td>43</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
<td>85.1</td>
<td>31.9</td>
<td>46.5</td>
</tr>
<tr>
<td>44</td>
<td>1</td>
<td>1</td>
<td>0.75</td>
<td>83.5</td>
<td>29.8</td>
<td>44.5</td>
</tr>
<tr>
<td>45</td>
<td>1</td>
<td>1</td>
<td>0.55</td>
<td>95.4</td>
<td>40.1</td>
<td>31.0</td>
</tr>
<tr>
<td>46</td>
<td>1</td>
<td>1.1</td>
<td>1.1</td>
<td>82.4</td>
<td>14.8</td>
<td>50.6</td>
</tr>
<tr>
<td>47</td>
<td>1</td>
<td>1.1</td>
<td>1.1</td>
<td>83.4</td>
<td>21.4</td>
<td>42.8</td>
</tr>
<tr>
<td>48</td>
<td>1</td>
<td>1.1</td>
<td>1.1</td>
<td>84.1</td>
<td>20.3</td>
<td>40.8</td>
</tr>
<tr>
<td>49</td>
<td>1</td>
<td>1.1</td>
<td>1.1</td>
<td>89.6</td>
<td>23.1</td>
<td>44.1</td>
</tr>
<tr>
<td>50</td>
<td>1</td>
<td>1.1</td>
<td>1.1</td>
<td>88.4</td>
<td>23.2</td>
<td>45.1</td>
</tr>
</tbody>
</table>
In Table XII are recorded the results of several experiments carried out at temperatures between 700 and 950°. The molecular proportions were the same in all the experiments, viz. \( \text{BaSO}_4 : \text{MgCl}_2 : 6\text{H}_2\text{O} : \text{MgO} = 1 : 1 : 1 : 0.75 \) and the charcoal was 30 per cent. of the weight of the barytes. The mixture was made by grinding wet in the edge-runner mill for three hours.

The figures for temperatures between 850 and 950° show a nearly complete reduction to water-soluble barium compounds and the percentage of sulphur eliminated at temperatures between 800 and 950° is about 67. At lower temperatures the percentage reduction to water-soluble barium salts is less and the total percentage of sulphur eliminated is also less, although the actual amount of barium sulphide left in the residue is very small.

**TABLE XII.**

*Reduction of barytes at different temperatures in the presence of magnesium chloride and magnesia.*

Composition of mixture \( \text{BaSO}_4 : \text{MgCl}_2 : \text{MgO} = 1 : 1 : 1 : 0.75 \) and charcoal 30 per cent. of the weight of the barytes.

<table>
<thead>
<tr>
<th>No of Experiment</th>
<th>Temperature</th>
<th>Percentage of water-soluble barium compounds</th>
<th>Percentage of total sulphur present in aqueous extract</th>
<th>Percentage of total sulphur eliminated as ( \text{H}_2\text{S} ), ( \text{SO}_2 ), ( \text{S} )</th>
<th>Total sulphur eliminated</th>
<th>Found</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>700</td>
<td>94.0</td>
<td>28.5</td>
<td>44.5, 6.7, 11.0</td>
<td>62.2</td>
<td>66.5</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>700</td>
<td>93.8</td>
<td>32.1</td>
<td>48.8, 9.0</td>
<td>57.8</td>
<td>61.7</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>850</td>
<td>96.8</td>
<td>28.2</td>
<td>40.0, 4.75, 10.5</td>
<td>64.3</td>
<td>68.6</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>850</td>
<td>96.2</td>
<td>29.9</td>
<td>52.3, 10.0</td>
<td>62.3</td>
<td>66.3</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>800</td>
<td>89.5</td>
<td>21.5</td>
<td>46.4, 3.1</td>
<td>...</td>
<td>68.0</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>775</td>
<td>73.4</td>
<td>15.0</td>
<td>...</td>
<td>...</td>
<td>57.5</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>750</td>
<td>69.1</td>
<td>12.6</td>
<td>...</td>
<td>...</td>
<td>56.0</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>700</td>
<td>54.4</td>
<td>trace</td>
<td>...</td>
<td>...</td>
<td>54.4</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>700</td>
<td>51.6</td>
<td>trace</td>
<td>...</td>
<td>...</td>
<td>51.6</td>
<td></td>
</tr>
</tbody>
</table>
The foregoing experiments show that a suitably made mixture of barytes, magnesium chloride and magnesia in the molecular proportions, 1 : 1 : 0.75, can be reduced by charcoal at 850–950° in the course of two hours yielding 96 per cent. of the total barium in the form of water-soluble salts, whilst only 66 per cent. of the total sulphur is eliminated as hydrogen sulphide, sulphur dioxide or sulphur. The aqueous extract of the residue contains in the form of sulphides of barium about 30 per cent. of the total sulphur originally present. It will be found that the percentage conversion to barium chloride cannot be found by subtracting the percentage of water-soluble sulphur (calculated as BaSO₄) from the percentage of water-soluble barium salts (also calculated as BaSO₄).

### TABLE XIII.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Percentage conversion to water-soluble barium salts</th>
<th>Percentage of total sulphur as water soluble</th>
<th>Difference</th>
<th>Percentage conversion to barium chloride by estimation of soluble chloride</th>
</tr>
</thead>
<tbody>
<tr>
<td>45a</td>
<td>96.2</td>
<td>33.7</td>
<td>62.5</td>
<td>70.4</td>
</tr>
<tr>
<td>50</td>
<td>88.4</td>
<td>23.2</td>
<td>65.2</td>
<td>76.4</td>
</tr>
<tr>
<td>21</td>
<td>89.0</td>
<td>41.0</td>
<td>48.0</td>
<td>57.1</td>
</tr>
</tbody>
</table>

In the three experiments quoted in Table XIII the actual conversion into barium chloride is greater than this difference. This either means that there is a certain amount of magnesium oxychloride in solution or that a portion of the sulphur is present as polysulphides of barium. The latter appears to be the correct conclusion as on heating magnesium chloride at 900° water is incapable of extracting even a trace of chloride from the residue.

7. Addition of common salt in place of magnesia.

Several experiments were made by adding common salt in place of magnesia to the magnesium chloride mixture. Crucible experiments gave poor and discordant results. This was largely due to the fact that the sodium chloride and magnesium chloride fused and entered the pores of the crucible and probably carried some barium chloride with them.

Table XIV gives the results of a few experiments carried out in the tube furnace at 900° with a mixture containing equimolecular proportions of barytes, magnesium chloride and sodium chloride and charcoal equal to 30 per cent. of the weight of the barium sulphate.
TABLE XIV.

Tube experiments at 900° with mixture of magnesium chloride and sodium chloride.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Percentage conversion to water-soluble barium salts</th>
<th>Percentage of total sulphur evolved as</th>
<th></th>
<th></th>
<th></th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>H₂S</td>
<td>SO₂</td>
<td>S</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>84·5</td>
<td>34·5</td>
<td>38·3</td>
<td>4·2</td>
<td></td>
<td>63·8</td>
</tr>
<tr>
<td>61</td>
<td>83·8</td>
<td>34·2</td>
<td>49·8</td>
<td>9·8</td>
<td>4·2</td>
<td>58·1</td>
</tr>
<tr>
<td>62</td>
<td>92·1</td>
<td>32·0</td>
<td>44·9</td>
<td>9·7</td>
<td>3·5</td>
<td>62·4</td>
</tr>
<tr>
<td>63</td>
<td>91·3</td>
<td>...</td>
<td>45·5</td>
<td>12·7</td>
<td>4·2</td>
<td>62·4</td>
</tr>
</tbody>
</table>

By the use of common salt the frothing was checked, the percentage reduction was good and the percentage of sulphur evolved was rather higher than when magnesium chloride alone was used. (Cf. Table VII.)

8. Reaction between barium sulphate and magnesium chloride.

The formation of sulphur dioxide in the experiments in which magnesium chloride was used is probably due to the following series of reactions:

1. \( \text{BaSO}_4 + \text{MgCl}_2 \rightarrow \text{MgSO}_4 + \text{BaCl}_2 \)
2. \( \text{MgSO}_4 \rightarrow \text{MgO} + \text{SO}_2 + \text{O} \) (above 890°).
3. \( \text{MgSO}_4 + \text{C} \rightarrow \text{MgO} + \text{CO} + \text{SO}_2 \) (above 630°).

A few experiments were made by heating together a mixture of barytes and magnesium chloride in equimolecular proportions and estimating the percentage conversion into water-soluble barium salts and also the percentage of the total sulphur present evolved as sulphur dioxide. The results are given in Table XV.

TABLE XV.

Heating equimolecular mixture of barium sulphate and magnesium chloride.

<table>
<thead>
<tr>
<th>No. of Experiment</th>
<th>Percentage of total barytes present as water-soluble barium salts</th>
<th>Percentage of total sulphur evolved as sulphur dioxide</th>
<th>Temperature in degrees Centigrade</th>
</tr>
</thead>
<tbody>
<tr>
<td>64</td>
<td>6·9</td>
<td>6·2</td>
<td>1000</td>
</tr>
<tr>
<td>65</td>
<td>6·2</td>
<td>5·4</td>
<td>950</td>
</tr>
<tr>
<td>66</td>
<td>5·8</td>
<td>5·2</td>
<td>900</td>
</tr>
</tbody>
</table>

In the presence of charcoal the formation of sulphur dioxide will occur at a lower temperature owing to reaction (3).
IV. GENERAL SUMMARY AND CONCLUSIONS.

1. Barium sulphate is readily reduced to water-soluble barium compounds (sulphide) by heating with 30 per cent. of wood charcoal at 900° for 1.5 hours.

2. Good grinding and mixing is essential and the best results are obtained by grinding wet in an edge-runner mill.

3. Considerable care is required to prevent reoxidation and, if the decomposition is carried out in crucibles in a muffle furnace, air must be excluded as far as possible. Even a porous crucible admits air and produces reoxidation.

4. With direct heating there is a tendency for the formation of oxide and carbonate and the amounts of these tend to increase the longer the heating is continued. (Wells.)

5. At temperatures below 900° the reduction is much slower and is not complete in 1.5 hours.

6. The percentage reduction is not affected by the presence of magnesium chloride or a mixture of the chloride and magnesia.

7. The decomposition of magnesium chloride begins at a temperature much below that required for the reduction of the barium sulphate and hence with mixtures of magnesium chloride, barytes and charcoal, only 57 per cent. of the barytes is converted into chloride and only about 50 per cent. of the total sulphur is eliminated mainly as hydrogen sulphide but also as sulphur dioxide and free sulphur. The remainder of the sulphur is present as sulphides of barium and as unreduced sulphate.

8. The addition of magnesia (0.75 to 1 gram molecule per gram molecule of chloride) inhibits frothing and raises the yield of barium chloride to 73 per cent. and that of the sulphur eliminated to 66 per cent.

9. The addition of sodium chloride also inhibits frothing and raises the percentage of sulphur evolved to a slight extent.

10. The sulphur dioxide evolved appears to be due to the reduction of magnesium sulphate formed by double decomposition between the barytes and magnesium chloride.

11. The sulphur is probably due to the reaction between the sulphur dioxide and hydrogen sulphide.
12. It is clear that by heating together barytes, charcoal and magnesium chloride in a single charge, either with or without the addition of magnesia, it is impossible to obtain a good percentage reduction and a good yield of barium chloride. At $900^\circ$ the reduction proceeds nearly to completion, but the product is a mixture of chloride and sulphide; at lower temperatures, e.g. $700^\circ$, it is possible to obtain barium chloride free from sulphide, but only about 50 per cent. of the barytes is converted into chloride, the remaining half being unacted upon after four hours. By increasing the time the percentage reduction could probably be increased and sulphide but not chloride formed.

To convert completely the mixture of chloride and sulphide to chloride the residue after cooling might be mixed with a further quantity of magnesium chloride and reheated or the cold residue might be extracted with water and the solution heated with magnesium chloride under pressure.

Such processes, however, are not so simple as the older process of first reducing barytes to sulphide in the absence of magnesium chloride and then heating the aqueous solution of the sulphide under pressure with magnesium chloride. The advantages of this process are that ($a$) an excess of magnesium chloride is not required and ($b$) all the sulphur is evolved in one stage as sulphuretted hydrogen and not as mixture of sulphuretted hydrogen, sulphur dioxide and sulphur.

*Department of General and Organic Chemistry,*  
*Indian Institute of Science,*  
*Bangalore.*