

PRODUCTION OF ALUMINA FROM OUSE BAUXITE.

BY THE BAYER PROCESS.

by

N. C. Ashdown, B.Sc.

Presented to the University of Tasmania in fulfilment
of section I. of the details of the Honours Examination in
the Chemistry School.

March, 1944.

N. C. 1945

VT 137

I N T R O D U C T I O N .

Considerable bauxite deposits were discovered in Tasmania towards the end of 1941.

The purpose of this investigation was to carry out analyses of representative samples from the Ouse and Swansea deposits and to discover to what extent the Bayer Process was suitable for the extraction of alumina from the Ouse bauxite.

This thesis embodies details of the above two aspects together with outlines of the methods of analyses employed. Preliminary work on the dry extraction process using sodium carbonate is also included.

Analyses of four samples of clay occurring in the immediate vicinity of the Ouse deposits are listed in the Appendix.

PRINCIPAL SECTIONS.

| | <u>PAGE.</u> |
|--|--------------|
| 1. ANALYSIS OF SAMPLES. | 1. |
| 2. BENEFICIATION EXPERIMENTS. | 3. |
| 3. EXTRACTIONS AT ATMOSPHERIC PRESSURE. | 4. |
| 4. EXTRACTIONS UNDER PRESSURE. | 6. |
| 5. PRECIPITATION, PREPARATION, AND ANALYSIS OF ALUMINA. | 12. |
| 6. SILICA CONTENT OF ALUMINATE LIQUOR | 13. |
| 7. EXTRACTION OF ALUMINA FROM ROASTED BAUXITE. | 15. |
| 8. FILTERING RATES ON RESIDUE (RED MUD CAKES). | 15. |
| 9. ALUMINA EXTRACTION BY ROASTING WITH SODIUM CARBONATE. | 16. |
| 10. APPENDIX A. OUTLINE OF METHODS OF ANALYSIS USED. | 17. |
| 11. APPENDIX B. ANALYSIS OF CLAYS ASSOCIATED WITH OUSE BAUXITE. | 20. |

ANALYSIS OF SAMPLES.

I. Locality and Description.

Samples Nos. 0, 1, 2 and 3 were from the Lachlan Vale Estate, Ouse while Nos. 1B, 2B, 3B, 4B, 5B and 6B came from selected areas of the Swansea Municipality.

All samples varied in appearance. Nos. 0 and 1 were reddish-brown and of rather massive structure while Nos. 2 and 3 were softer and of a clay like nature. The Swansea samples were distinctly yellow studded with white veins. These samples were much softer than the first group.

2. Preparation for Analysis.

Each sample was broken to pieces of approximately 1 inch in diameter. The whole was then coned and quartered and about 3 lbs. ground to -90 mesh. This quantity was then sampled again and about 5 grams ground in an agate mortar. Of this portion, the moisture was determined and the remaining determinations carried out on the dried sample.

3. Quantities Taken.

0.5 grams of the dried sample was weighed into a platinum crucible and fused with 4 grams of A.R. fusion mixture. These fused mass was removed from the crucible and dissolved in excess 6N. HCl. After the precipitation and filtration of the silica, the volume of the filtrate was made up to 250 mls. The titanium, iron, and aluminium were determined on 25 ml. samples while 50 mls. were taken for each manganese determination. If the alumina content of the original was below 10%, it was found advisable to work on a 50 ml. sample. The sodium was determined on approximately 3 gram samples.

(2)

4. Results.

TABLE NO. I.

| Sample | 0 | 1 | 2 | 3 | 1B | 2B | 3B | 4B | 5B | 6B |
|--------------------------------|------|------|------|------|------|------|------|-------|------|-------|
| Moisture | 3.5 | 3.9 | 0.6 | 3.2 | 4.0 | 2.3 | 4.9 | 2.2 | 4.8 | 3.3 |
| T/H ₂ O | 19.1 | 23.3 | 24.7 | 29.9 | 23.0 | 23.2 | 22.9 | 24.9 | 24.7 | 24.9 |
| SiO ₂ | 5.3 | 4.4 | 2.0 | 3.1 | 14.8 | 15.2 | 9.6 | 5.2 | 4.5 | 4.8 |
| TiO ₂ | 2.4 | 1.8 | 1.6 | 2.2 | 1.0 | 1.1 | 2.2 | 0.6 | 1.7 | 1.3 |
| Fe ₂ O ₃ | 29.7 | 24.8 | 28.8 | 21.0 | 26.2 | 22.7 | 20.7 | 28.0 | 33.8 | 34.0 |
| MnO | 0.1 | 0.07 | 0.1 | - | 0.1 | 0.1 | - | - | - | - |
| Na ₂ O | - | 0.2 | 0.2 | - | - | - | - | - | - | - |
| Al ₂ O ₃ | 43.2 | 45.3 | 42.4 | 43.7 | 34.4 | 37.6 | 44.4 | 43.3 | 35.1 | 35.1 |
| | 99.8 | 99.9 | 99.8 | 99.9 | 99.5 | 99.9 | 99.8 | 100.0 | 99.8 | 100.1 |

5. Discussion of Results.

The above results show that the Ouse bauxites are comparatively low in silica and rather high in their iron oxide content. The Swansea samples are different in chemical character containing a larger percentage of silica and hence a lower percentage of uncombined alumina. It should be noted that all samples contain approximately the same amount of combined water. The sodium and manganese contents were not determined on all samples as these results were unnecessary for the calculation of extractions of alumina.

BENEFICIATION EXPERIMENTS.I. Experimental.

50 grams of finely ground bauxite were dispersed in water of slight alkalinity. The bauxite settled out in two distinct layers which were easily separated. The two portions were filtered, washed, dried and then analysed.

2. Results.

For the purpose of comparison, the analysis of the original samples is given at the beginning of each section.

T A B L E No. 2.

| | No.0 | Colloidal | Granular | No. I | Colloidal | Granular | No.2 | Colloidal | Granular |
|--------------------------------|------|-----------|----------|-------|-----------|----------|------|-----------|----------|
| Percent | - | 30 | 70 | - | 27.5 | 72.5 | - | 41.5 | 58.5 |
| T/H ₂ O | 19.1 | 22.5 | 17.0 | 23.3 | 24.1 | 23.5 | 24.7 | 24.0 | 22.0 |
| SiO ₂ | 5.3 | 8.3 | 4.0 | 4.4 | 5.7 | 3.8 | 2.0 | 2.8 | 2.2 |
| TiO ₂ | 2.4 | 1.9 | 2.7 | 1.8 | 1.7 | 2.1 | 1.6 | 1.5 | 1.6 |
| Fe ₂ O ₃ | 29.7 | 25.4 | 31.2 | 24.8 | 18.5 | 26.4 | 28.8 | 23.9 | 33.6 |
| Al ₂ O ₃ | 43.2 | 38.9 | 45.0 | 45.3 | 49.3 | 43.6 | 42.4 | 47.6 | 40.4 |
| | 99.8 | 97.0 | 99.9 | 99.6 | 99.3 | 99.4 | 99.5 | 99.8 | 99.8 |

3. Discussion of Results.

It was hoped by the above experiments, to obtain a greater proportion of the alumina in the granular portion but this was not achieved to any appreciable extent. This treatment may be applicable to ores much higher in silica as in each case the silica in the granular portion was lower than in the original sample, but the effect of this decrease is offset by the increase in the percentage of ferric oxide. It is noted that the ratio $\text{Al}_2\text{O}_3 : \text{Fe}_2\text{O}_3$ in the colloidal portions of samples Nos. 1 and 2, is greater than the same ratio for the corresponding original samples.

EXTRACTIONS AT ATMOSPHERIC PRESSURE.

1. Experimental.

About 1 kilogram of No. 1 was ground to -150 mesh. Portions of this were digested at atmospheric pressure with caustic soda solution. A study of extraction of the alumina with relation to (i) strength of caustic soda used, (ii) time of digestion, (iii) temperature of digestion, was made.

Throughout all experiments in this section, 70 grams of bauxite and the same excess (150%) of caustic soda were used.

The cooks were carried out in the inner container of an iron glue pot. The pulp was stirred mechanically and the volume of solution maintained by water dripping from a restricted tube. The variation in temperature was obtained by employing heating liquids with the required boiling points and also by the use of varying strength caustic soda solutions.

The pulp was diluted and filtered by the use of the vacuum pump. After the cake had been washed free of aluminate, the filtrate was made up to volume in a standard flask and the alumina content determined by the precipitation as the basic succinate.

2. Observations-

- (a) The residue was redder than the original ore.
- (b) The pulp, using 600 g/l caustic soda, was very viscous
- (c) The aluminate solution was reddish-brown in colour and this became much darker as the temperature of digestion increased.

3. Results.

T A B L E No. 3.

| Number | NaOH | Time | Temperature | Extraction |
|--------|------|------|-------------|------------|
| | g/l | hrs | °C | % |
| 1 | 600 | 2.5 | 112 | 68.5 |
| 2 | 600 | 4.0 | 112 | 72.2 |
| 3 | 600 | 6.0 | 112 | 73.8 |
| 4 | 600 | 8.0 | 112 | 74.4 |
| 5 | 100 | 8.0 | 104 | 60.4 |
| 6 | 200 | 8.0 | 106 | 62.3 |
| 7 | 300 | 8.0 | 107.5 | 69.0 |
| 8 | 400 | 8.0 | 109 | 72.2 |
| 9 | 500 | 8.0 | 110.5 | 73.8 |
| 10 | 600 | 8.0 | 100 | 68.5 |
| 11 | 600 | 8.0 | 105 | 71.6 |
| 12 | 600 | 8.0 | 109 | 73.6 |
| 13 | 600 | 20.0 | 112 | 75.0 |

4. Graphs.

The following graphs were plotted:-

- No. 1. Extraction/Time:- using results of digestions 1,2,3, 4, and 13.
- No. 2 . Extraction/Strength of Caustic:- using results of digestions 4,5,6,7,8, and 9.
- No. 3. Extraction/Temperature:- using results of digestions 4,10,11, and 12.

5. Discussion of Results:

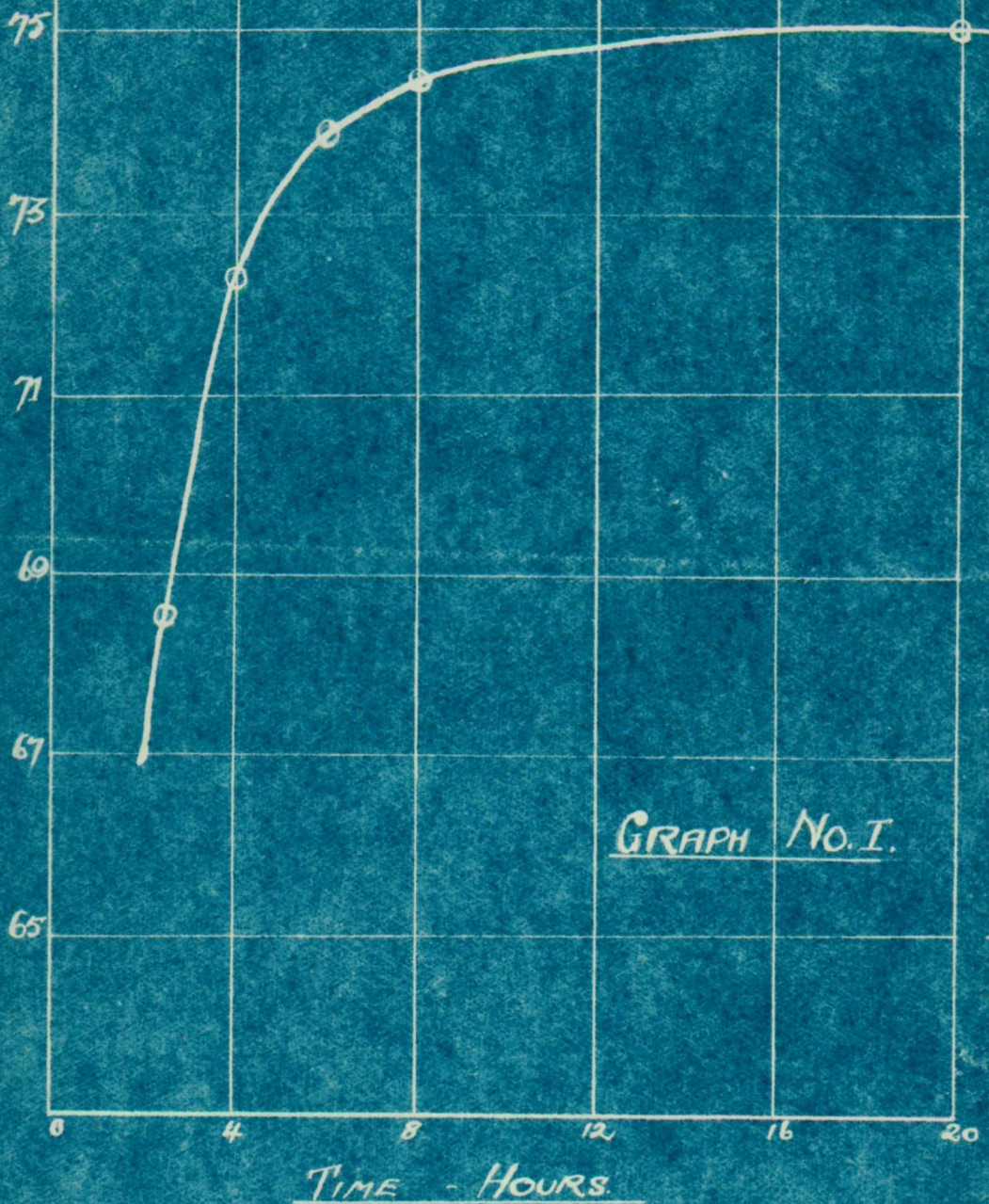
The percentage extraction increases with increasing strength of caustic soda used, up to a strength of 600/g/l. At this point, the increase in extraction is not sufficient to warrant the use of a solution of greater strength.

Digestion at the boiling point of the caustic soda solution used gives a greater comparative increase in extraction. Graph No. 3. shows an almost linear increase which suggests that extraction of the alumina is favoured by digestion under pressure.

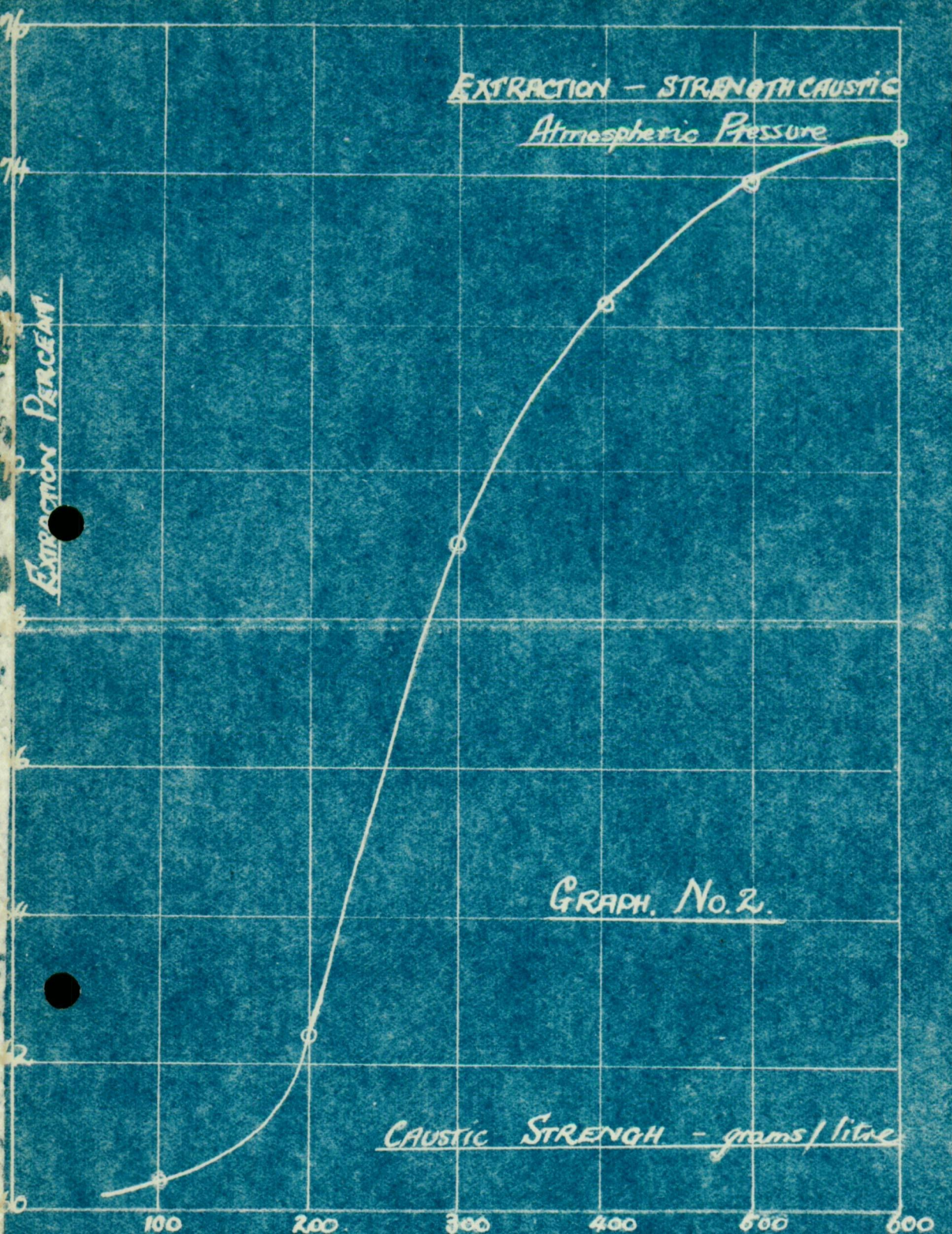
The extraction - time graph reveals that while percentage extraction increases with time, digestions for longer than 8 hours do not give a sufficient increase in extraction to warrant their use.

EXTRACTION - TIME
Atmospheric Pressure

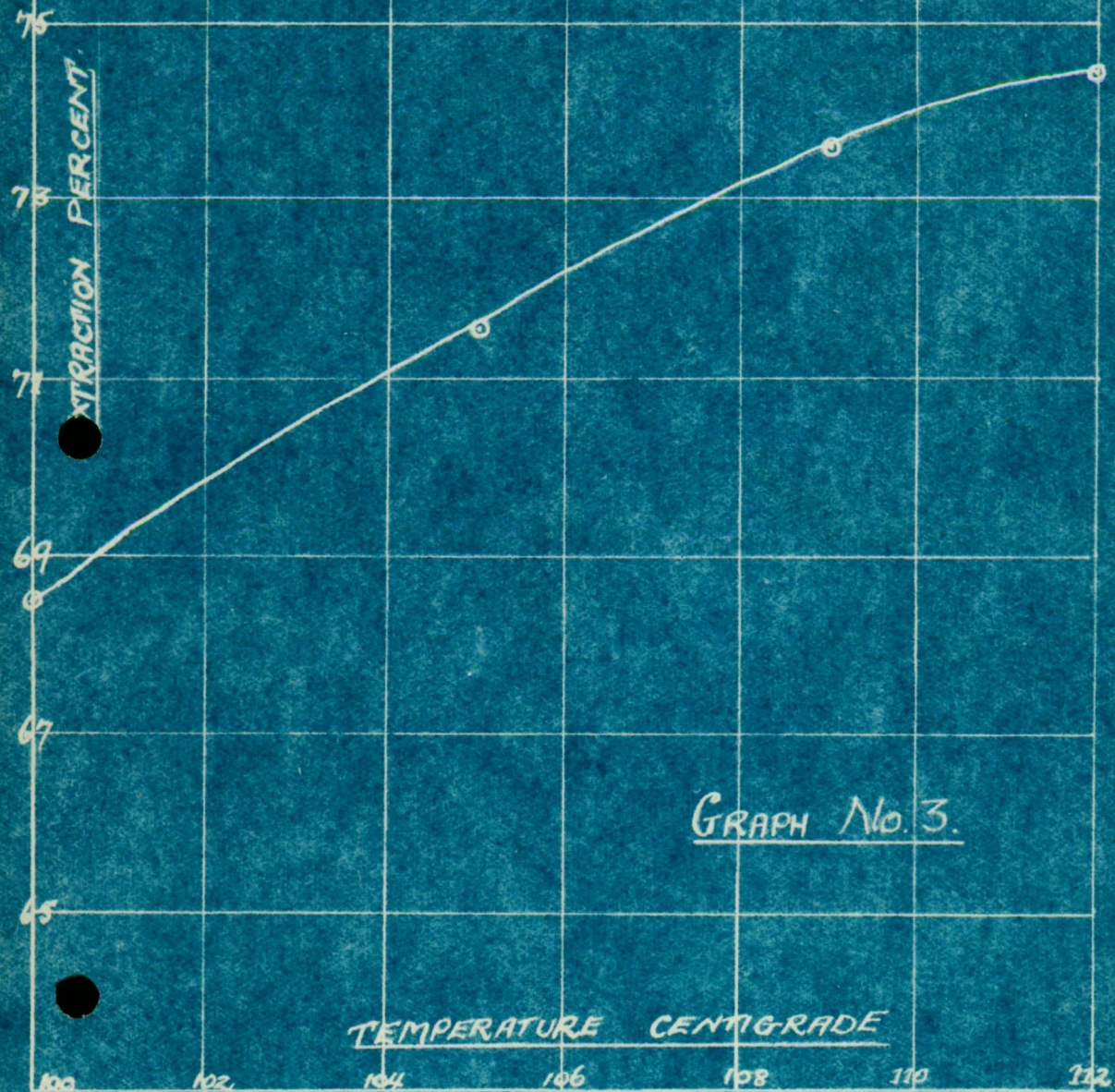
EXTRACTION PERCENT



GRAPH NO. I.



EXTRACTION - TEMPERATURE
Atmospheric Pressure



Hence the optimum conditions of extraction at atmospheric pressure are,

(i) 600 g/l NaOH, (ii) Time of digestion - 8 hours,

(iii) Temperature of digestion - the boiling point of the caustic soda solution used.

EXTRACTIONS UNDER PRESSURE.

I. Apparatus.

The autoclave used consisted of a cylindrical iron pipe, 1/4 in. thick, 18 ins. long and 6 ins. in diameter. It was flanged at each end. The bottom of the vessel was fixed while to the lid was connected a gauge reading absolute pressure. The most satisfactory gasket was 1/16 in. "Jointite", one thickness of which lasted two digestions. The whole was supported horizontally and rotated manually by means of a handle attached to the fixed end.

A single leaf vacuum filter was made from 5/8 in. Brass tubing, was used to filter the pulp. The annular portion of the filter was 7 inches in diameter. 1/8 inch holes were drilled 1 in. apart on the inside diameter of the annulus, which was then covered with a double thickness of cotton duck. This cloth withstood the action of the strong caustic but replacement was necessary after five filtrations.

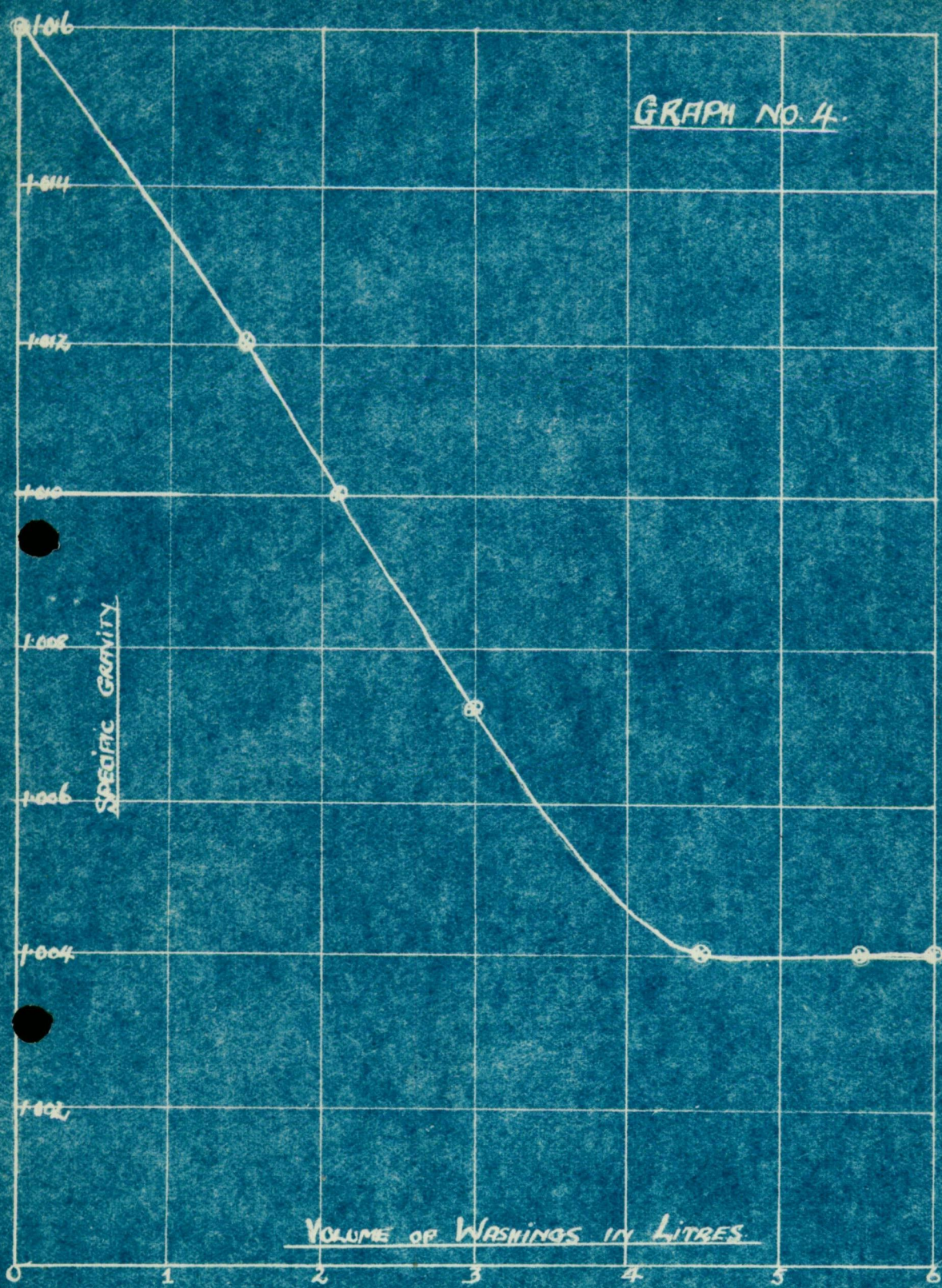
2. Experimental.

The charge unless otherwise stated, was two kilograms of moisture-free bauxite (Sample No. I.) and in each digestion the pressure was 75 lbs./sq. in. absolute. After the addition of the requisite amount of caustic soda solution the autoclave was evacuated and then heated until the required pressure was reached. The source of heat was regulated to maintain this pressure and the vessel rotated to keep the charge thoroughly mixed. After digestion the charge was allowed to cool, transferred to an enamelled container and allowed to settle overnight. This latter procedure considerably increased the filtering rate. The leaf filter was placed in a settled solution, a vacuum applied, and the filtrate caught in a Buchner flask.

3. Washing of Cake.

A washing curve was obtained from the residue of digestion

GRAPH NO. 4.



8A (see table 5). As much as possible of the aluminate solution was filtered off. The cake was then washed and readings of the volume of the washings and their corresponding specific gravity taken until a constant gravity was reached. The readings were plotted as shown on Graph No. 4.

T A B L E No. 4.

| Vol. of Washings ml. | Specific Gravity. |
|-------------------------|----------------------|
| 0 | 1.016 |
| 1500 | 1.012 |
| 2100 | 1.010 |
| 3000 | 1.007 |
| 4500 | 1.004 |
| 5500 | 1.004 |
| 6000 | 1.004 |

The graph shows that washing is complete at specific gravity 1.004 and that 4.5 litres of water are required to achieve this.

This quantity of wash water is three times the volume of the original solution. All residues were washed until the filtrate reached a specific gravity of 1.004.

4. Digestions.

Experiments were carried out to determine the relationship between percentage extraction and (i) excess of caustic soda, (ii) strength of caustic soda, (iii) time of digestion, (iv) fineness of bauxite.

All the digestions, except No. 8B, were carried out using sample No. I. No. 4R was a re-extraction of the residue of No. 4, using the excess of the caustic as shown. No. 8A. and No. 8A2 were two component digestions of a cyclic process. The same caustic liquor was used for both but in No. 8A2 any caustic losses were made up while sufficient raw ore was added to make the combined alumina content of both ore and solution equivalent to the alumina content of the ore used for No. 8A. No. 8B was carried out on sample 2 using the optimum conditions found for sample I.

TABLE No. 5.

| Digestion Number | Mesh I.M.M. | NaOH g/l | Time hours | Excess NaOH% | Residue % | Extraction % |
|------------------|-------------|----------|------------|--------------|-----------|--------------|
| 1. | 40 | 600 | 8 | 25 | 59.6 | 80.3 |
| 2. | 40 | 600 | 4 | 25 | 61.4 | 77.9 |
| 3. | 40 | 600 | 20 | 25 | 57.7 | 80.5 |
| 4. | 90 | 600 | 4 | 25 | 61.1 | 83.4 |
| 4R. | 90 | 600 | 8 | 550 | 84.1 | 95.1 |
| 8B. | 90 | 600 | 8 | 25 | 48.8 | 84.5 |
| 7. | 90 | 600 | 8 | 100 | 57.4 | 90.5 |
| 8A. | 90 | 600 | 8 | 25 | 56.0 | 85.2 |
| 8A2 | 90 | 600 | 8 | 25 | 56.1 | 91.1 |
| 10. | 90 | 600 | 20 | 25 | 60.0 | 85.5 |
| 11. | 90 | 600 | 8 | 300 | 54.3 | 93.5 |
| 12. | 90 | 400 | 8 | 25 | 61.0 | 75.0 |
| 13. | 90 | 300 | 8 | 25 | 65.7 | 71.2 |
| 14. | 90 | 200 | 8 | 25 | 69.1 | 68.5 |
| 15. | 150 | 600 | 8 | 25 | 56.2 | 86.1 |

6. Graphs and Discussion of Results.a. Graph No. 5. :Extraction/Excess Caustic.

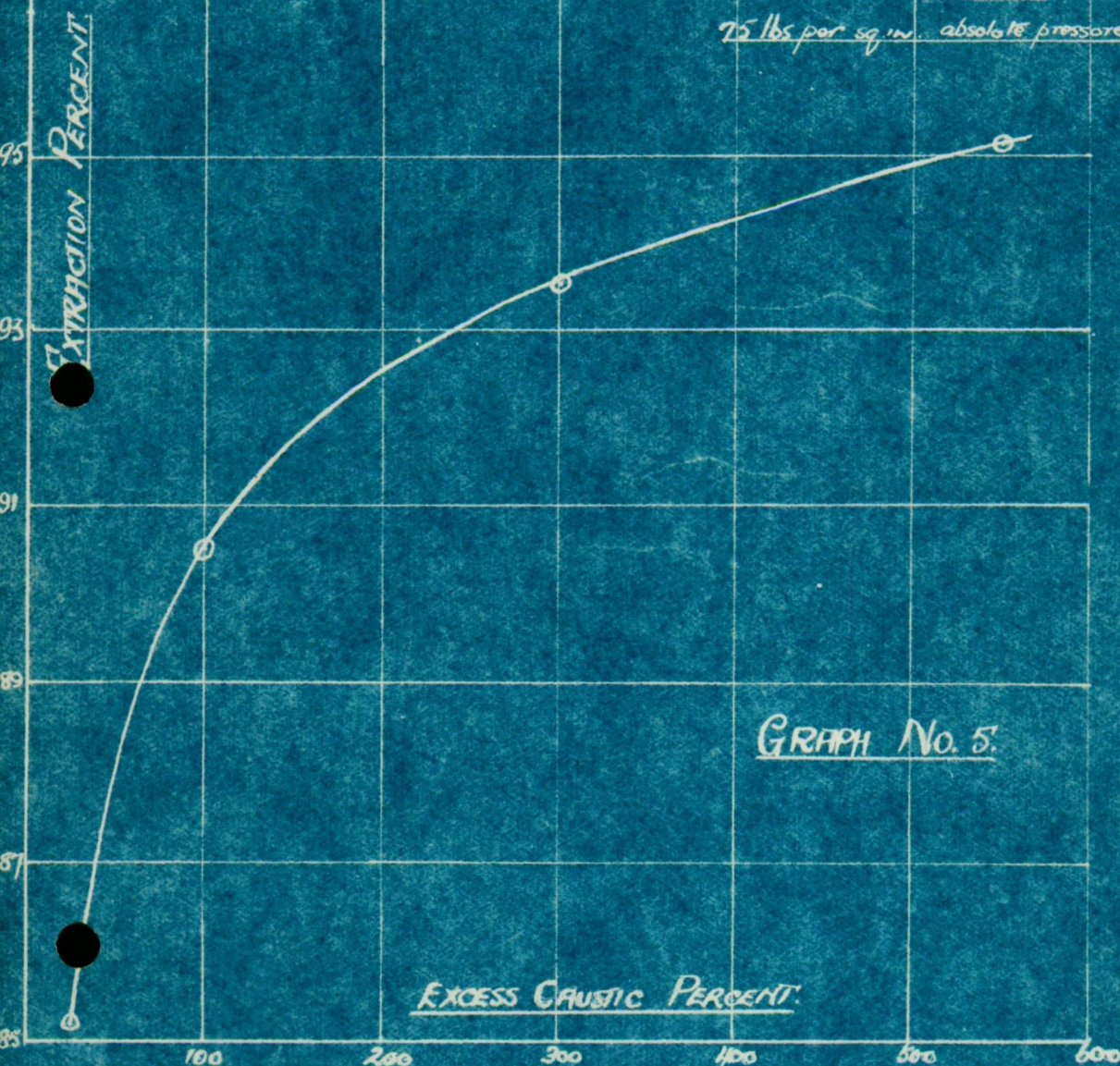
The results of digestion 8A, 7, 11, 4R were used. It is obvious that the greater the excess of caustic the greater the extraction rising to 95.1% when there is a 550% excess. The following table shows the percentage increase in extraction for a given percentage increase in excess caustic.

| Percent. Increase in Excess Caustic | Percent Increase Extraction | % Increase Extracn % Increase Excess Caustic. |
|-------------------------------------|-----------------------------|--|
| ... | | |
| 75 | 5.3 | 0.071 |
| 275 | 8.3 | 0.030 |
| 525 | 9.9 | 0.018 |

From this table it is evident that a greater percentage increase in extraction per unit increase in percentage excess caustic is given by an excess of caustic nearer 25%.

EXTRACTION - EXCESS
CAUSTIC

75 lbs per sq. in. absolute pressure



EXTRACTION - CAUSTIC STRENGTH

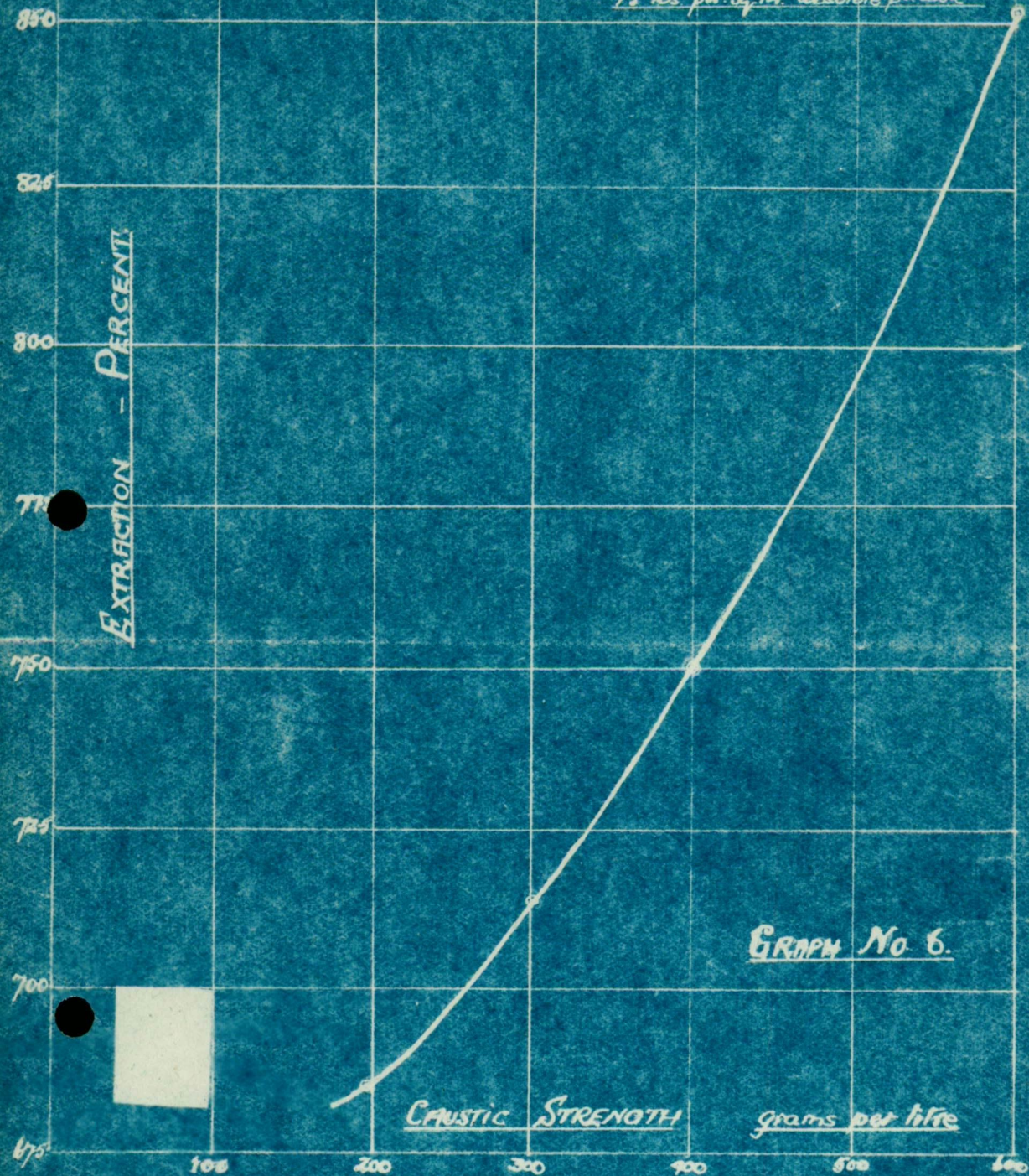
7.5 lbs. per sq. in. absolute pressure

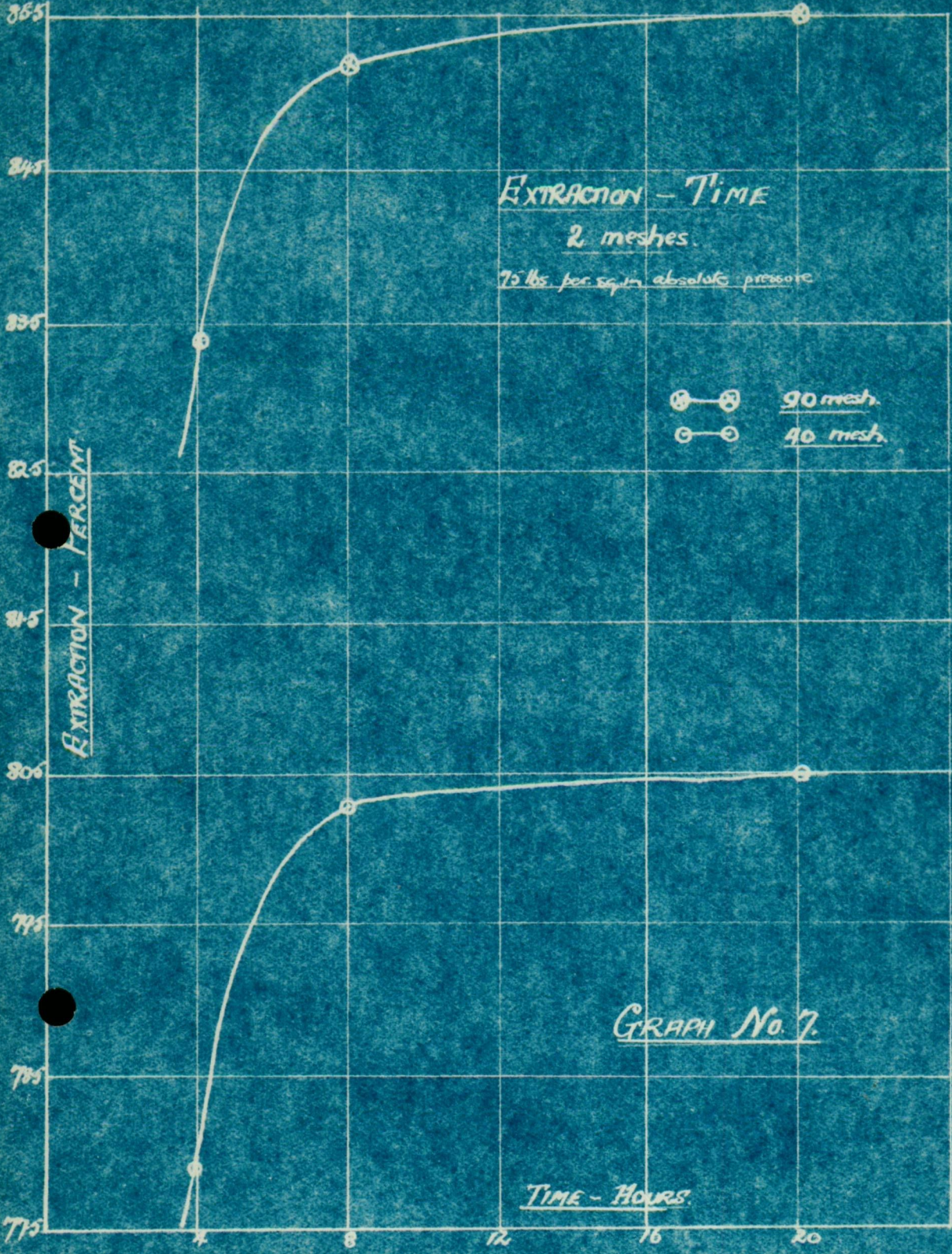
EXTRACTION - PERCENT.

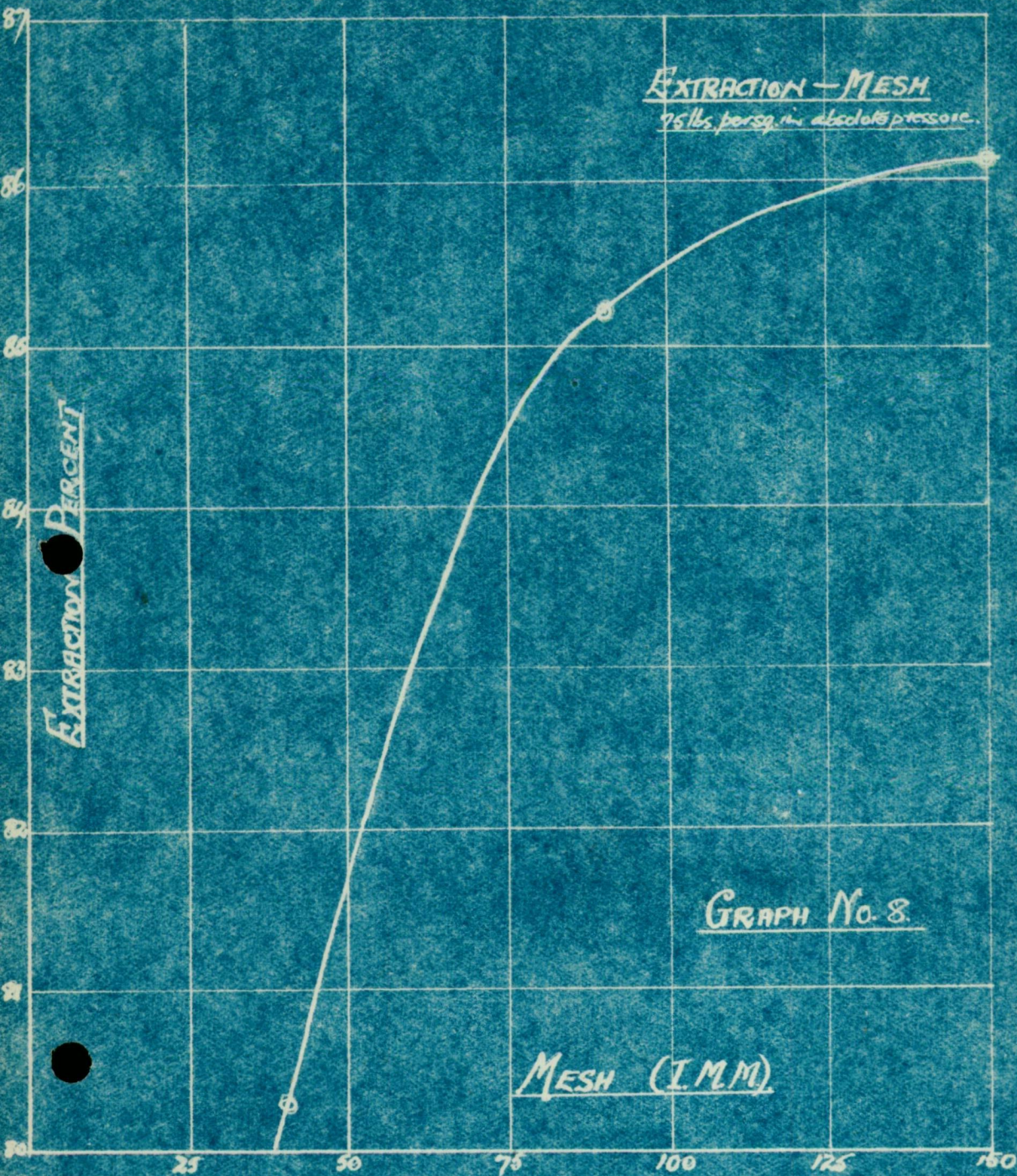
GRAPH No. 6.

CAUSTIC STRENGTH

grams per litre







b. Graph No. 6. : Extraction/Caustic Strength.

The results of digestions 14, 13, 12, 8A were used. Since this graph has a positive slope extraction is favoured by increase in the caustic strength. No extraction was attempted with strength of caustic greater than 600 g/l., because filtering difficulties would have increased considerably.

c. Graph No. 7. : Extraction/Time

The results of digestions 1, 2, 3, 4, 8A, 10 were used. This graph shows extraction time in relationships for two meshes. The small increase in percentage extraction, after cooking for twenty hours, does not warrant digestion for a period longer than eight hours.

d. Graph No. 8. : Extraction/Mesh.

The results of digestions 1, 8A, 15 were used. It is obvious that the extra energy expended in grinding the sample to -150 mesh is not compensated by the increase in extraction. Grinding the sample to -90 mesh appears to be the most suitable.

e. General.

The optimum conditions for extraction of alumina from sample No. 1. were found to be,

- (i) a 25% excess of caustic,
- (ii) 600 g/l caustic soda solution,
- (iii) a digestion for eight hours,
- (iv) grinding of the sample to -90 mesh I.M.M.

Sample No. 2 when treated under the above optimum conditions gave results comparable with those obtained from Sample No. I.

The second stage, 8A2, of the cyclic process resulted in an increased percentage extraction. The caustic losses and precipitation of alumina will be considered later.

7. Residues.

For each digestion, the residue was washed, dried, weighed and analysed for combined water, silica, titania, ferric oxide, and alumina. The extractions were calculated from the percentage alumina found in the residue.

The following table gives the analysis of typical residues:-

TABLE No. 6.

| Digestion Number. | 3 | 4 | 4R | 7 | 8A | 8A2 | 12 | 10 | 8B |
|--------------------------------|------|------|------|------|------|------|------|------|------|
| T/H ₂ O | 13.9 | 14.1 | 10.4 | 11.9 | 14.1 | 12.9 | 14.4 | 14.2 | 11.3 |
| SiO ₂ | 7.3 | 7.3 | 9.0 | 8.3 | 8.0 | 8.9 | 7.0 | 8.7 | 4.2 |
| TiO ₂ | 2.2 | 2.9 | 3.2 | 2.8 | 3.5 | 3.0 | 3.0 | 3.2 | 2.9 |
| Fe ₂ O ₃ | 52.2 | 52.6 | 59.4 | 57.6 | 56.2 | 55.5 | 53.1 | 55.8 | 56.4 |
| Al ₂ O ₃ | 14.4 | 12.3 | 4.3 | 7.5 | 12.0 | 7.1 | 18.9 | 10.8 | 13.5 |

All residues have a ferric oxide content greater than 50% and hence there is the possibility of their use in the blast furnace. The average titania content is 67 lbs. per ton of residue. Here again there is the possibility of the residue being smelted to give ferrotitanium or chlorinated to remove the titanium as the tetrachloride.

The residue from pressure digestion No. 8A, i.e. for sample No. I. under optimum conditions is 56.0% of the total charge (table 5.) and the percentage residues for most extractions are near this figure. The percentage residue for sample No. 2 under optimum conditions is 7.2% lower than the corresponding figure for sample No. I.

8. Residue Factors.

TABLE No. 7.

| Digestion Number | Residue Factor by Fe ₂ O ₃ | Residue Factor by SiO ₂ | Residue Factor by TiO ₂ | Extraction % Al ₂ O ₃ |
|------------------|--|------------------------------------|------------------------------------|---|
| 3 | 47.5 | 60.3 | 81.8 | 86.9 |
| 4 | 47.1 | 60.3 | 62.1 | 89.0 |
| 7 | 43.1 | 53.0 | 64.3 | 94.4 |
| 8B | 51.1 | 50.1 | 55.2 | 87.8 |
| 8A | 44.1 | 55.0 | 51.4 | 90.8 |
| 8A2. | 44.7 | 49.4 | 60.0 | 94.3 |
| 10 | 44.5 | 50.6 | 56.3 | 91.4 |

The above factors were calculated thus - if there is x% of a constituent in the residue and y% of the same constituent in the original charge, then the residue factor by that constituent is (100 y/x).

The percentage extraction of alumina is the value of the expression.

$$100 - \left\{ \frac{\text{Residue Factor by Fe}_2\text{O}_3 \times \% \text{Al}_2\text{O}_3 \text{ in residue.}}{\% \text{Fe}_2\text{O}_3 \text{ in residue} \times 100.} \right\}$$

9. Nature of Residue and Undissolved Alumina.

a. Screening and Analysis of Residue from Digestion No.1.

The original charge was -40 mesh and the residue, after drying, was screened on a 90 mesh screen. The +90 fraction represented 31.7% and the -90 fraction 68.3% of the whole. An analysis of each of the fractions for ferric oxide, titania, and alumina gave the following results.

T A B L E No. 8.

| | -90 Mesh | +90 Mesh |
|---|----------|----------|
| TiO ₂ | 2.7 | 3.2 |
| Fe ₂ O ₃ | 45.2 | 47.1 |
| Al ₂ O ₃ | 23.8 | 24.8 |
| % Al ₂ O ₃ of Total Al ₂ O ₃ | 63.8 | 36.2 |

This reveals that the greater portion of the undissolved alumina is in the finer portion of the residue.

b. Gravity Separation and Analysis.

100 grams of the residue from digestion No.1 was allowed to settle in water. A layer of black particles collected at the bottom of the vessel. This layer was separated, washed, dried and analysed. The weight of the separated particles represented 22.3% of the total weight of the residue. The analysis is given in the following table.

T A B L E No. 9.

| | |
|--------------------------------|------|
| SiO ₂ | 3.9 |
| Fe ₂ O ₃ | 82.2 |
| TiO ₂ | 2.7 |
| Al ₂ O ₃ | 5.6 |

The above analysis shows that the iron in this portion of the residue may be in the form of haematite.

c. Acid Extraction of Residue.

5 grams of the residue from digestion No. 2 were boiled

with 300 mls. of the N/1 HCl (i.e. 150% excess) for one hour. The filtrate was analysed for alumina.

| | |
|--|----------------|
| Total alumina extracted by acid | = 810 mgrms. |
| Total alumina in residue | = 812.5 mgrms. |
| % Al_2O_3 not acid soluble | = 0.3% |

Thus practically all the alumina not dissolved by caustic soda under pressure is acid soluble.

PRECIPITATION, PREPARATION AND ANALYSIS OF ALUMINA.

I. Aluminate Solutions.

The aluminate solutions from all digestions were dark-brown in colour probably due to the presence of sodium ferrite. (Chemical Abstracts 32,8711). An analysis of several aluminate solutions showed that less than 0.1% of the Fe_2O_3 in the original sample had been dissolved by the caustic soda. Owing to prolonged exposure to the air, the solutions carbonated slightly and a representative solution contained Al_2O_3 70 g/l, Na_2O (as NaOH) 96 g/l, Na_2O (as Na_2CO_3) 24 g/l.

2. PRECIPITATION.

The specific gravity of the liquor was approximately 1.5 and before precipitation this was diluted considerably. Agitation over a period of time was the method adopted to facilitate auto-precipitation of the aluminium hydroxide.

The liquor was usually diluted to 1.20 specific gravity and a small seed charge of previously precipitated aluminium hydroxide ~~was~~ added to form a nucleus for precipitation. The solution was continuously agitated during the precipitation and it was found that 72 hours was sufficient to precipitate most of the hydroxide.

The precipitate was granular and is $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite). It was also noticed that precipitation continued until the ratio $\text{Al}_2\text{O}_3 : \text{Na}_2\text{O} = 1.6$

3. Calcination.

The filtered precipitate was washed free of alkali, dried at 130°C and calcined at 1050°C for 8 hours.

4. Percent Alumina Precipitated.

Greater dilution increased the amount of hydroxide precipitated. At a gravity of 1.24, 37.4% of the total alumina in the solution was precipitated while at a gravity of 1.12, 70.9% was precipitated. It should be realised that in a cyclic process, too great a dilution would not favour the economics of the process. It appears that 1.20 is a workable gravity.

5. Analysis.

The calcined alumina was analysed employing methods as outlined in Appendix A.

T A B L E 10.

| Digestion Number | I | 2 | 8A | 12 |
|--------------------------------|--------|--------|--------|--------|
| Al ₂ O ₃ | 99.63 | 99.65 | 99.70 | 99.67 |
| Fe ₂ O ₃ | 0.16 | 0.17 | 0.25 | 0.15 |
| SiO ₂ | 0.03 | 0.03 | 0.01 | 0.02 |
| TiO ₂ | <0.007 | <0.007 | <0.007 | <0.007 |
| Na ₂ O | 0.18 | 0.15 | 0.04 | 0.16 |

The above table shows that it is possible to produce alumina from Tasmanian bauxite, which is within the limits of purity required for the electrolytic production of aluminium. It should also be noticed that the lower the specific gravity of the aluminate solution, the purer the alumina with respect to iron.

SILICA CONTENT OF ALUMINATE LIQUOR.

A measured volume of the solution was diluted with water, acidified, and 6N ammonium hydroxide added until precipitation was complete. The hydroxide was filtered and washed free of chloride. The precipitate was then dissolved in concentrated hydrochloric acid and the silica determined by the usual method.

The original digestion was carried out with 2000 grams of bauxite, Sample No. 2, ground to 40 mesh and treated with 1.5 litres of caustic soda of strength 600 g/l. The filtrate and washings measured 3,850 mls.

The silica content was found to be 0.0645 g/100 mls. of solution, i.e. a total silica content of 2.48 grams. Since the original charge contained 40 grams of silica, this means that 6.2% of the silica has been dissolved by the sodium hydroxide. Calculated in terms of 600 g/l caustic soda this represents 1.65 grams of dissolved silica per litre of sodium hydroxide solution.

A similar run was made on Sample No. 1. and this showed that the liquor contained 1.74 grams of silica per litre of 600 g/l caustic soda solution

EXTRACTION OF ALUMINA FROM ROASTED BAUXITE.

I. Conditions.

It was found that the following conditions were satisfactory for roasting bauxite to constant weight:-

- (a) Temperature - 600°C.
- (b) Time - 4 hours.

2. Experimental.

Digestions were carried out on samples Nos. 2 and 3. After roasting, it was found that each had lost about 26.5% in weight.

Roast No. 1. 1500 grams of the roasted ore were ground to -90 mesh and digested with 1.5 litres of sodium hydroxide of strength 600 g/l for eight hours under 75 lbs per sq. in. absolute pressure.

Roast No. 2. 2000 grams of Sample 2 were roasted and ground to -40 mesh and digested with 2 litres of 600 g/l sodium hydroxide for 8 hours under 75 lbs. per sq. in. absolute pressure.

3. Analysis of Roasted Ore.

T A B L E II.

| | No. 1. | No. 2. |
|--------------------------------|--------|--------|
| T/H ₂ O | 4.7 | 4.4 |
| SiO ₂ | 4.3 | 2.5 |
| TiO ₂ | 3.0 | 2.0 |
| Fe ₂ O ₃ | 28.5 | 31.4 |
| Al ₂ O ₃ | 59.3 | 59.0 |
| | 99.8 | 99.3 |

T A B L E No. 12.

| | No. 1. | No. 2. |
|--------------------------------|--------|--------|
| % Residue | 57.2 | 56.3 |
| T/H ₂ O | 18.8 | 20.7 |
| SiO ₂ | 7.4 | 4.0 |
| TiO ₂ | 4.7 | 3.4 |
| Fe ₂ O ₃ | 50.1 | 55.1 |
| Al ₂ O ₃ | 12.9 | 13.4 |
| % Extrac- tion | 87.6% | 87.2% |

5. Discussion of Results.

Owing to the shortage of time, little was done on this section of the work. It appears that the average extraction of alumina from roasted ore is about 2.2% greater than from natural unroasted ore. The roasting of Ouse bauxite, prior to extraction, would be economic as besides increased alumina extraction much less energy is required to grind the ore after roasting than before.

FILTERING RATES ON RESIDUE (RED MUD) CAKES.

1. Experimental.

Filtering rates were carried out on residue from digestions with natural and roasted bauxites, ground to different meshes.

The set-up consisted of an iron Buchner type filter about 8 inches in diameter with cotton duck as the filtering medium. All readings were taken at a pressure of 17 mms. of mercury i.e. 0.33 lbs per sq. in.

2. Results.

T A B L E No. 13.

| Ore | Mesh | Dilution | Thickness of Cake | Rate. Galls/ Sq.ft/hour |
|---------|------|----------|--------------------|----------------------------|
| Natural | -40 | 4:1 | 1 inch | 0.56 |
| Roasted | -90 | 3:2 | 1 inch | 0.004 |
| Roasted | -40 | 3:2 | 1 in ch | 0.15 |

3. Discussion of Results.

The results in the above table shows that the variation of filter rate with mesh and gravity of pulp is quite considerable.

ALUMINA EXTRACTION BY ROASTING WITH SODIUM CARBONATE.

Little work was done in this section as it was soon realised that the percentage extractions in this section did not compare favourably with those of the wet method.

1. Roasting.

Four roasts were made. In each the charge was 100 grams of -90 mesh bauxite mixed with 200 grams of -90 mesh anhydrous sodium carbonate i.e. a molar ratio of Al_2O_3 : Na_2CO_3 of 1.0 : 4.5.

Roasts A1 and A2 were carried out on samples, 1 and 2 respectively at 850°C for 5 hours and Nos. B1 and B2 on the same two samples at 1000°C for 6 hours. It was noticed that the sintering point had not been reached at 700°C . The sintered mass was quite red in colour.

In each case, the loss of weight on roasting, approximately represented the combined weights of the carbon dioxide content of the carbonate and the combined water in the bauxite. This was approximately 33% of the total charge.

2. Lixiviation.

The sintered mass was lixiviated with 600 mls. of water at 80°C . The solution was stirred vigorously to ensure maximum solution of the sodium aluminate. The red mud was separated by filtration and washed free of aluminate. The filtrate possessed a slight green colour probably due to a compound of iron. The alumina content of the solution was determined.

3. Results.

T A B L E No. 14.

| No. | % Residue | Wt. Al_2O_3 | % Extraction |
|-----|-----------|-----------------------------|--------------|
| A1 | 58.8 | 34.61 | 76.4 |
| A2 | 54.1 | 31.51 | 74.3 |
| B1 | 59.2 | 34.88 | 77.0 |
| B2 | 56.5 | 31.83 | 75.1 |

4. Discussion of Results.

The percentage residues obtained by this method are of the same order as those for the wet method, but the percentage extractions are much lower. It should be noted that roasts B1 and B2 were carried out under conditions recommended by the Aluminium Company of America.

5. Precipitation and Analysis of Alumina.

To recover the alumina, the aluminate solution was heated to 80°C. and saturated with carbon dioxide.

The precipitated hydroxide was filtered, washed, calcined and analysed. It was apparent that the alumina produced was of low purity. Two samples gave alumina contents of 85.3% and 86.2%. These figures are not sufficiently high for commercial utilization

C O N C L U S I O N .

The samples of bauxite from Ouse were much lower in silica than the Swansea deposits. All bauxites analysed showed a high ferric oxide content. The percentage main constituents of both bauxites are now given. The quoted figures are the averages of all samples analysed.

| | <u>OUSE BAUXITE.</u> | <u>SWANSEA BAUXITE.</u> |
|----------------------------------|----------------------|-------------------------|
| % SiO ₂ | 3.7 | 9.0 |
| % TiO ₂ | 2.0 | 1.3 |
| % Fe ₂ O ₃ | 26.1 | 27.6 |
| % Al ₂ O ₃ | 43.8 | 38.3 |

Attempted beneficiation of the Ouse ore gave disappointing results.

Digestion of the ground ore with caustic soda solution, at atmospheric pressure, revealed that, at best, 75% of the total alumina could be dissolved from the ore. No doubt the alumina extracted by this process is present in the form of gibbsite, Al₂O₃, 3H₂O while the remainder is combined with silica or present as diaspore, Al₂O₃.H₂O.

It was found that the percentage of extractable alumina rose to 85% when the ground Ouse ore was digested with caustic soda solution under pressure. If the undissolved alumina is considered to be combined with 2Al₂O₃.2Na₂O. 3SiO₂, it can be stated that practically all of the "maximum extractable" alumina has been dissolved in the above process.

70% of the alumina in the sodium aluminate liquor was precipitated as the hydroxide Al₂O₃.3H₂O when the liquor was agitated for 72 hours with a seed charge of gibbsite α -Al₂O₃.3H₂O. Calcination of the precipitated hydroxide gave alumina satisfactory for use in the electrolytic production of aluminium.

Average analysis of the four samples of alumina prepared were.

| | |
|--------------------------------|---------|
| Al ₂ O ₃ | 99.66% |
| Fe ₂ O ₃ | 0.18 |
| SiO ₂ | 0.025 |
| TiO ₂ | <0.007. |
| Na ₂ O | 0.13 |

Roasting of the natural Ouse bauxite, prior to

extraction, improved the percentage alumina extracted by 2.2%.

Percentage extractions of the alumina from Ouse bauxite by the "dry" method (roasting with sodium carbonate and lixiviation with water) did not compare favourably with those given by the "wet" method (extraction with caustic soda solution). Furthermore the alumina obtained from such treatment was of inferior quality.

It is clear that the bauxite from the Ouse district, though not a high grade ore, is amenable to treatment by the Bayer Process and can be made to yield alumina of high purity.

APPENDIX A.

OUTLINE OF METHODS OF ANALYSIS.

In some instances it was found that the standard methods of analysis were inapplicable to the analysis of Tasmanian bauxite and accordingly new methods were adopted or, in some cases, modifications of standard methods applied. Following is an outline of the methods employed.

I. Titanium.

Since the titania content of the samples and residues analysed was never greater than 3.5% i.e. 1.75 mgrms. on a 0.05 gram sample, the colorimetric determination was found to be the quickest and most accurate. The determinations were carried out on the hydrochloric acid solution of the sodium-potassium carbonate fusion. The colour due to the ferric chloride in the solution was bleached with orthophosphoric acid.

Following are the details of the method adopted. To one Nessler tube, add 25 mls of the solution to be analysed, and 25 mls of distilled water to a similar tube. To each added 2 mls. of concentrated sulphuric acid and then from a graduated glass tube, orthophosphoric acid drop by drop until the colour of the solution in the first tube was destroyed. An equal quantity was added to the second tube. In order to ensure complete bleaching, it has been found advisable to allow both solutions to stand over-night, or at least, for 8 hours. Five mls. of 3% hydrogen peroxide were then added to each and then sufficient standard titanium solution to the second tube to approximately match the colours. The exact ratio of the concentrations of the titania in the two tubes was determined by means of an Hilger Duboscq colorimeter.

2. Iron.

The iron was reduced with H_2S in the presence of tartaric acid. Ammonia was added to slight alkalinity, followed by a further treatment of H_2S to completely precipitate the iron sulphide.

The precipitate was filtered, washed, with very dilute and colourless ammonium sulphide, dissolved in dilute HCl and the solution boiled to completely remove the hydrogen sulphide. The iron was oxidized with nitric acid and precipitated with 6N ammonia. Alternative methods were used to complete the determination. The hydroxide either was ignited to the oxide or dissolved in HCl , reduced with stannous chloride and titrated with $N/100$ potassium dichromate using barium disphenylamine sulphonate as indicator.

3. Aluminium.

Several methods were employed for estimation of aluminium but precipitation as the basic succinate (J.I.E.C. Analytical Edn. 9. 357 (1937)) and ignition to the oxide proved for several reasons the most satisfactory. Firstly the precipitate formed is insoluble in water and in excess of the reagent, secondly no preliminary removal of iron is necessary and thirdly the precipitate is small in bulk and easy to wash.

Titanium is also precipitated as the basic succinate at a pH of approximately 4.4 and therefore the ignited precipitate contains the oxides of aluminium and titanium.

The method adopted was as follows:- to the solution from the fusion was added 10 mls. of 20% sodium bisulphite solution, diluted to 150 mls. and boiled to reduce ~~the iron~~ to the ferrous state. Next, to the hot solution added 5 grams of succinic acid, 4 grams of urea (C.P.), 10 grams of ammonium chloride and 2 mls. of phenylhydrazine. Diluted to 500 mls, heated to boiling and neutralized to incipient turbidity with 6N ammonia. The solution was boiled gently for two hours maintaining the volume at 500 mls. The precipitate was allowed to settle, then filtered and washed with a 1% solution of succinic acid made neutral to Methyl red with ammonia. The precipitate was then ignited at $1200^\circ C$ to constant weight.

In some cases, it was found that a little of the iron had not been reduced and had precipitated together with the titanium and aluminium. Colorimetric determinations, for iron, carried out on several ignited precipitates, revealed that in no case was the ferric oxide content greater than 0.4 mgrms on 0.1 gram of precipitate i.e. not greater than 0.4%. For very accurate determination of alumina, a colorimetric iron was carried out on the correction made.

For quicker and less accurate determinations of aluminium precipitation as the hydroxide at the colour change of methyl red was used with satisfactory results.

4. Manganese.

The manganese oxide content of the samples was not greater than 0.1% and hence the colorimetric determination of this element was used. This method adopted was to remove chlorides and reducing agents by evaporating with concentrated nitric and sulphuric acids, next the colour due to iron was bleached with a mixture of sulphuric and phosphoric acids and then the manganese was oxidised to permanganate with potassium periodate. A standard manganese solution treated similarly was used for comparison.

5. IRON - COLORIMETRICALLY.

Small quantities of iron were determined as ferric thiocyanate.

The complete oxidation of the iron was accomplished by the addition of 0.02N potassium permanganate and a 50% ammonium thiocyanate solution was used to form the complex.

In determining the iron oxide content of the precipitated alumina, steps were taken to eliminate the fading of the thiocyanate complex. This was accomplished by the use of a 2-methoxy-ethanol as a solution medium instead of distilled water (J.I.E.C. Analytical Edition Vol. 9. p. 453). Except for this particular case water was used as the medium.

4. Silica - Colorimetrically.

It was necessary to determine the percentage of silica, in the precipitated alumina, colorimetrically. For this purpose, the alumina was fused with sodium carbonate to form the sodium silicate and the mass was then extracted with boiling water. The solution was filtered, washed and, if necessary, the volume of the filtrate reduced to less than 50 mls. The solution was then acidulated and the colour developed 30 minutes after the addition of an ammonium molybdate solution, compared with that of a standard potassium chromate solution.

The solutions of ammonium molybdate and potassium chromate were made up as given in Vogel's "A Textbook of Quantitative Inorganic Analysis" 1939 Edition.

7. Sodium.

It was necessary to determine the Na_2O content of the ore and also of the purified alumina. Most of the standard methods for the determination of sodium are time consuming and accordingly the following rapid method was adopted.

For the samples analysed the Na_2O content did not exceed 0.5%. About 5 grams of the sample were boiled with 1 gram of $\text{Ba}(\text{OH})_2$ and CO_2 bubbled into the hot solution until it was colourless to phenolphthalein. The solution was then filtered, washed and the filtrate made up to a given volume. The whole or an aliquot part of this volume was boiled to remove the

bicarbonates and the Na_2CO_3 titrated with N/10 HCl in the presence of a mixed indicator (methyl orange + indigo carmine, $P_T = 4.1$)

8. Silica, Moisture and Combined Water.

These were determined by the usual standard methods. The moisture on all samples was determined at 105°C .

A P P E N D I X . B .

Table 15. gives the analyses of four samples of clay occurring in the vicinity of the bauxite deposits, Ouse.

- No. 1s. - Decomposed dolerite capping the deposits.
 No. 2s. - Yellow clay.
 No. 3s. - Clay underlying the deposits.
 No. 4s. - White clay resembling pipeclay.

T A B L E No. 15.

| | Sample 1s. | Sample 2s. | Sample 3s. | Sample 4s. |
|--------------------------------|---------------|---------------|---------------|---------------|
| T/H ₂ O | 10.0 | 13.5 | 18.7 | 9.2 |
| SiO ₂ | 49.2 | 39.3 | 30.4 | 55.5 |
| TiO ₂ | 1.3 | 1.7 | 2.2 | 0.7 |
| Fe ₂ O ₃ | 10.1 | 9.7 | 5.3 | 2.7 |
| Al ₂ O ₃ | 28.9 | 35.6 | 43.1 | 30.5 |
| | 99.5 | 99.8 | 99.7 | 99.6 |

Table 16 gives the analysis of the same samples on a water-free basis.

T A B L E No. 16.

| | Sample 1s. | Sample 2s. | Sample 3s. | Sample 4s. |
|--------------------------------|---------------|---------------|---------------|---------------|
| SiO ₂ | 54.6 | 45.4 | 37.4 | 62.1 |
| TiO ₂ | 1.5 | 2.0 | 2.7 | 0.8 |
| Fe ₂ O ₃ | 11.2 | 11.2 | 6.5 | 3.0 |
| Al ₂ O ₃ | 32.1 | 41.4 | 53.0 | 33.6 |
| | 99.4 | 99.7 | 99.6 | 99.5 |