

Electrolysis of Fused Anhydrous Aluminium Chloride and Chlorination of Salem Bauxite

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Investigations carried out to determine (i) optimum conditions for the electrolysis of fused anhydrous aluminium chloride to yield aluminium metal and (ii) the optimum conditions for the chlorination of the ferruginous bauxite-ores from Salem District so as to eliminate selectively the chief impurities associated with these and to yield an acceptable grade of bauxite, are described. The electrolysis experiments were carried out using chemically pure salts, to obtain reliable working results. Chlorination experiments yielded encouraging results if carried out on a mixture of the bauxite and powdered charcoal and on initially sulphided bauxite.

DESPITE the pre-eminent position of the Hall-Heroult process for the commercial production of aluminium metal, based on the electrolytic reduction of aluminium oxide, certain disadvantages are nevertheless inherent in it. For example, not considering the large amount of electrical energy required for electrolysis, the process involves a large consumption of costly electrode material and depends upon cryolite for the electrolysis besides a highly corrosive nature for the electrolytic bath and a high temperature of operation. Although the consumption of cryolite per ton of aluminium produced may not exceed about 200 lb., as it has to be almost entirely obtained from Greenland, the lack of an indigenous source of supply is undoubtedly a great disadvantage, which could be potentially critical in times of emergency. The pure aluminium oxide from which alumina is obtained for electrolysis is prepared from natural bauxite ores by the well-known Bayer's process wherein the associated impurities such as the oxides of iron, silicon and titanium are removed. Economic considerations require that the bauxite for the Bayer's process should be rich (not less than about 52%) in alumina and low in the oxides of iron (not more than about 6.5%), silicon (not more than about 5%) and titanium (not more than about 2%). Out of an estimated¹ bauxite reserve in India of about 250 million tons, only about 25 million tons contain more than 50% of alumina and rest are of comparatively low grade. Even these 25 million tons of bauxite are not sufficiently free of the oxides of iron, silicon and titanium to permit direct utilisation by the Bayer's process, the best utilisable grade of bauxite available being somewhat smaller.

The necessity is obvious, therefore, of examining the possibility of the preparation of pure aluminium metal by electrolysis of compounds other than its oxide and of the upgrading of the unutilisable grades of bauxite so as to make them "acceptable" material either for the preparation of pure aluminium oxide by Bayer's process or for the preparation of other salts of aluminium which might permit the preparation of the pure metal.

Preliminary experiments carried out in America and elsewhere have indicated that the electrolysis of the chloride² and the chlorination of the low grade bauxite ores³ offer the greatest promise. In view of the availability of cheap chlorine, as a by-product of the alkali industry, it was considered worthwhile to carry out similar studies on Indian bauxite ores of high alumina content but also of high iron and titanium contents. Accordingly, studies were carried out to determine (i) the optimum conditions for the electrolysis of fused anhydrous aluminium chloride to yield aluminium metal (chemically pure salt has been used to obtain reliable working results), and (ii) the optimum conditions for the chlorination of ferruginous bauxite ores (those from Salem District⁴ were used) so as to eliminate selectively the chief impurities associated with it to yield an "acceptable" grade of bauxite. This scheme of investigation was sponsored by the Council of Scientific & Industrial Research and carried out in the Department of Metallurgy, Indian Institute of Science, Bangalore, by the author when he was on its staff. In presenting briefly the results of these investigations, he wishes to record the assistance of Mr. B. Ramaswami and Mr. M. R. Seshadri, two of his former students and associates.

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ELECTROLYSIS

The electrolysis experiments were carried out

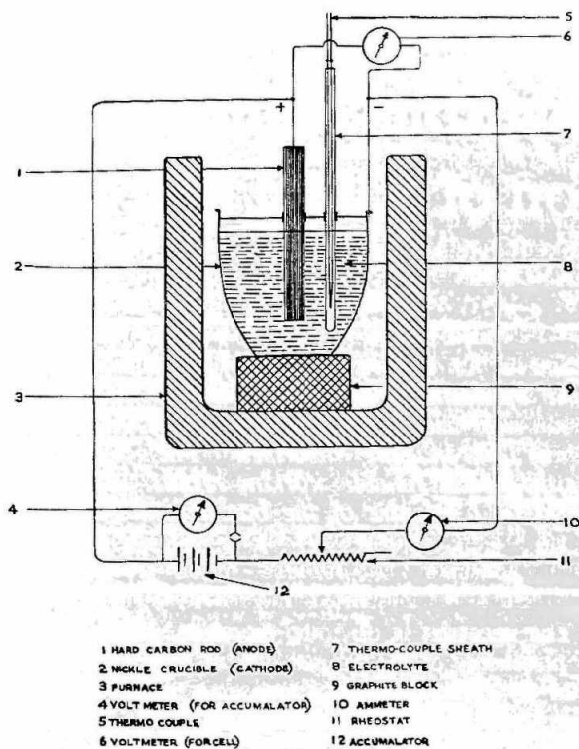


FIG. 1—The experimental set-up

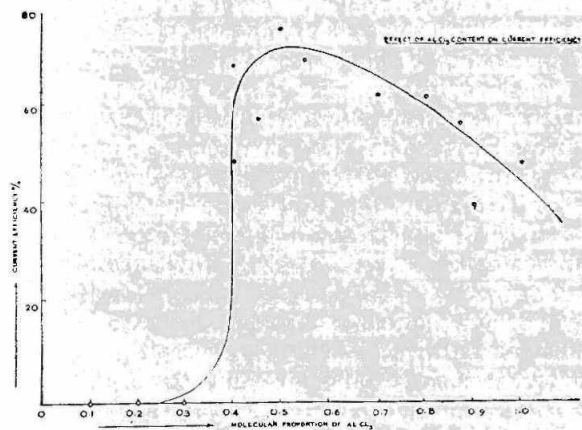


FIG. 2—Effect of $AlCl_3$ content on current efficiency.

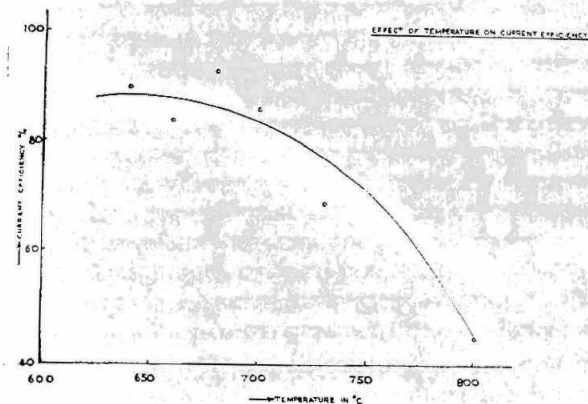


FIG. 3—Effect of temperature on current efficiency.

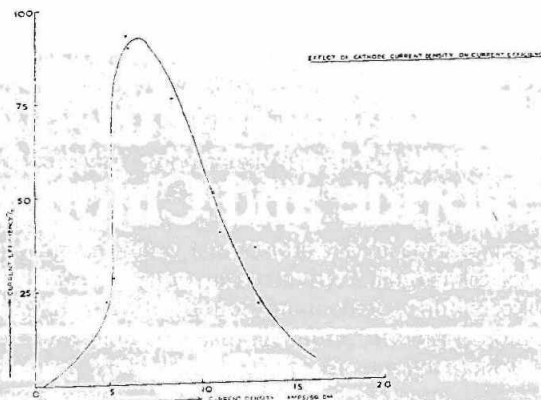


FIG. 4—Effect of cathode current density on current efficiency.

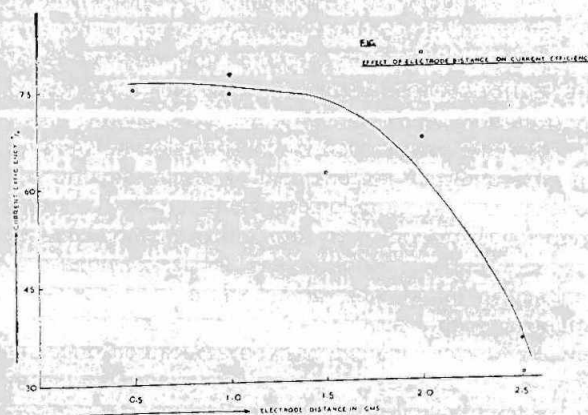


FIG. 5—Effect of electrode distance on current efficiency.

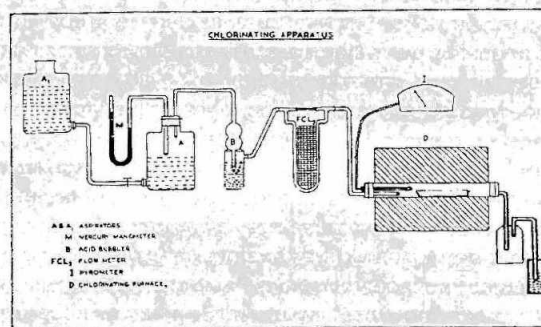
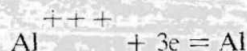


FIG. 6—Chlorinating apparatus.

using the experimental set up shown in Fig. 1. The power supply was from a 12 volt storage battery and nickel crucibles of approximately 100 c.c. capacity were used as the container as well as cathode and a hard carbon rod as anode. The electrolyte used was a mixture of sodium chloride, potassium chloride, sodium fluoride and aluminium chloride. The first three salts were previously well mixed in known proportions (usually equimolecular⁵) and aluminium chloride was added to this mixture, which was after thorough mixing quickly transferred to a nickel crucible already heated to a

temperature of about 800°C. As this temperature was about 200°C higher than the melting point of the electrolytic mixture, the volatilisation loss of aluminium chloride during melting was kept to a minimum. The crucible with the electrolyte was placed inside the furnace whose operating temperature could be adjusted and maintained constant, and the electrolysis carried out carefully, with all the usual precautions being taken. The aluminium produced was carefully estimated in the usual fashion and the current efficiency for the electrolysis calculated on the basis of the following reaction:



The influence of the following factors on the efficiency of the electrolysis was studied: (i) container material, (ii) anode material, (iii) aluminium chloride content of the bath, (iv) temperature of the bath, (v) cathode current density, (vi) vertical electrode distance, and (vii) duration of the electrolysis.

The results of the experiments are given in Tables I to V and graphically in Figs. 2 to 6.

The experimental results given in the tables indicate that the optimum conditions for the most efficient deposition of aluminium in the electrolytic system Al/AlCl₃, NaCl, KCl, NaF/Cl₂ are as under:—

1. Composition of the Bath:
NaCl: KCl: NaF: AlCl₃ = 1:1:1:0.5 to 0.8 (Molecular proportion)
2. Container: Nickel crucibles are found to

TABLE I—EFFECT OF VARIATION OF AlCl₃ IN THE ELECTROLYTE ON CURRENT EFFICIENCY

[Equimolecular proportions of NaCl, KCl and NaF; Cathode current density = 6.2 to 6.8 amps. sq. dm.; temperature of electrolysis : 720°C–750°C]

Sl No.	Molecular Proportion of AlCl ₃	Duration in minutes	Weight of Al in gms	Current efficiency (%)	Anode effect observed after
1	0.10	2	No deposit	—	½ min.
2	0.20	43	—	—	43 "
3	0.35	55	very small	—	55 "
4	0.40	30	0.59	69	Not observed
5	0.50	60	1.18	76	"
6	0.55	60	1.10	70	"
7	0.70	60	1.02	63	"
8	0.80	60	1.02	62	"
9	0.90	60	0.78	40	"
10	1.00	60	0.85	49	"

TABLE II—EFFECT OF TEMPERATURE OF THE ELECTROLYTE ON CURRENT EFFICIENCY

[Composition of the electrolyte : NaCl : KCl : NaF : AlCl₃ = 1 : 1 : 1 : 0.5 (molecular proportion); cathode current density : 6.7 amps./sq.dm.]

Sl No.	Temperature °C	Duration in minutes	Weight of Al in gms	Current efficiency %
1	640	58	0.97	90
2	660	60	1.12	84
3	680	94	1.95	93
4	700	60	1.44	86
5	730	60	1.37	69
6	760	60	0.61	40
7	800	60	0.67	45

TABLE III—EFFECT OF CATHODE CURRENT DENSITY ON CURRENT EFFICIENCY

(Temperature of Electrolysis : 640°C–680°C)
[(a) Composition of the electrolyte : NaCl : KCl : NaF : AlCl₃ = 1 : 1 : 1 : 0.5 (molecular proportion)]

Sl No.	Current density amps/sq. dm.	Duration in minutes	Cell voltage (in volts)	Weight of Al (in gms)	Current efficiency (%)
1	0.8	57	2.0	No deposit	—
2	4.8	60	3.3	0.23	22
3	5.3	31	3.2	0.15	29
4	6.0	94	4.0	0.95	93
5	6.1	58	4.2	0.97	90
6	7.8	60	4.0	1.44	86
7	8.5	60	4.0	1.02	76
8	10.6	60	3.6	0.83	50
9	11.1	20	4.8	0.35	40
10	13.1	20	3.8	0.20	21

[(b) Composition of the electrolyte : NaCl : KCl : NaF : AlCl₃ = 1 : 1 : 1 : 0.8 (molecular proportion)]

1	4.5	60	3.2	0.46	55
2	5.4	63	3.6	0.91	63
3	6.3	30	3.3	0.48	71
4	6.8	60	3.4	0.98	74
5	10.6	60	4.0	0.85	51

TABLE IV—EFFECT OF VERTICAL ELECTRODE DISTANCE ON CURRENT EFFICIENCY

[Composition of the electrolyte NaCl : KCl : NaF : AlCl₃ = 1 : 1 : 1 : 0.5 (molecular proportion)]

Sl No.	Vertical distance in cms.	Duration in minutes	Weight of Al in gms	Current efficiency (%)
1	0.5	60	1.20	75
2	1.0	60	0.98	74
3	1.6	60	1.20	62
4	2.0	60	1.07	62
5	2.5	60	0.60	36

TABLE V—EFFECT OF DURATION OF ELECTROLYSIS
CURRENT EFFICIENCY

[Composition of the electrolyte : NaCl : KCl : NaF
AlCl₃ = 1 : 1 : 1 : 0.5 (molecular proportion); cathode
current density : 6.0 to 6.6 amps./sq. dm.; temperature
of the electrolyte : 680°C.—720°C]

Sl No.	Duration in minutes	Weight of Al in gms.	Current efficiency
1	30	0.48	71
2	60	1.10	75
3	69	1.19	77
4	94	1.95	93
5	120	1.60	51

give a better performance. That of graphite crucibles are not however unsatisfactory.

3. Cathode: the container can serve as cathode
4. Anode: hard carbon or graphite.
5. Cell voltage: 4.0 to 8.0 volts
6. Current density at the cathode: 6.0 to 8.0 amps/sq. dm.
7. Temperature: 640 to 720 deg.C.
8. Current efficiency: about 80.0%
9. Purity of product: 99% (minimum)

CHLORINATION

Bauxite ore for chlorination was obtained from Messrs. Shevaroy Bauxite Products Ltd., Shevaroy, Salem Dist., Madras State. The ore was in the form of porous lumps, brick-red in colour. Representative samples were obtained and analysed using standard methods. Compositions of the two grades of bauxite used for subsequent investigations are given below:—

	Sample No. 1	Sample No. 2
Al ₂ O ₃	63.8%	60.7%
Fe ₂ O ₃	21.2%	29.5%
SiO ₂	8.4%	3.4%
TiO ₂	3.2%	3.0%
Balance	3.4%	3.4%

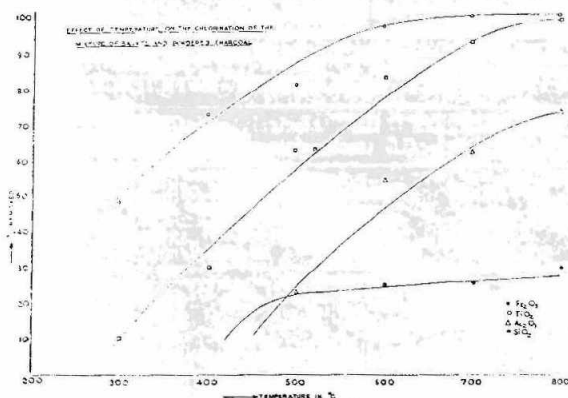


FIG. 7—Effect of temperature on the chlorination of the mixture of bauxite and powdered charcoal.

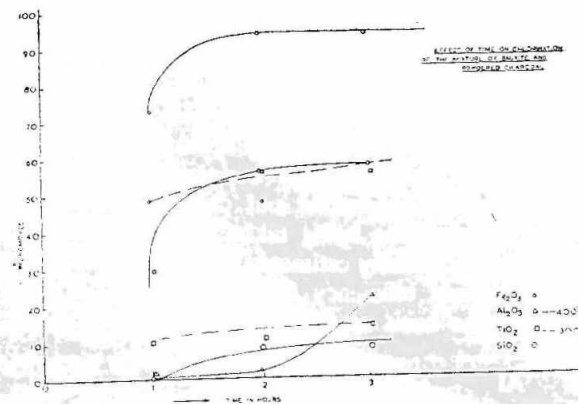


FIG. 8—Effect of time on chlorination of the mixture of bauxite and powdered charcoal.

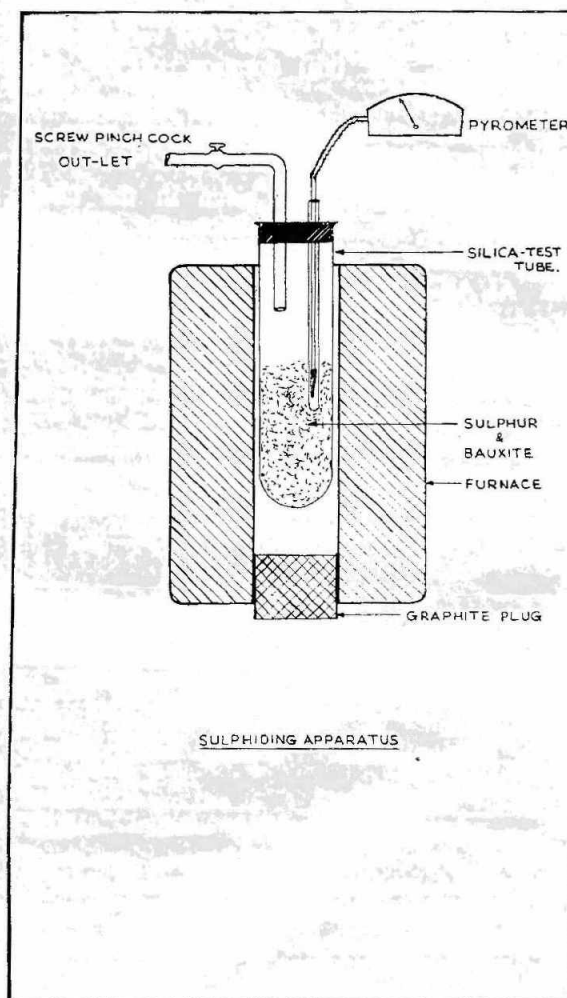


FIG. 9—Sulphiding apparatus.

The experimental set up for carrying out chlorination is given in Fig. 6. The chlorination was carried out at various temperatures, rates of flow of chlorine and durations in a nichrome wound silica-tube furnace, whose operating temperature could be regulated suitably. The bauxite to be chlorinated

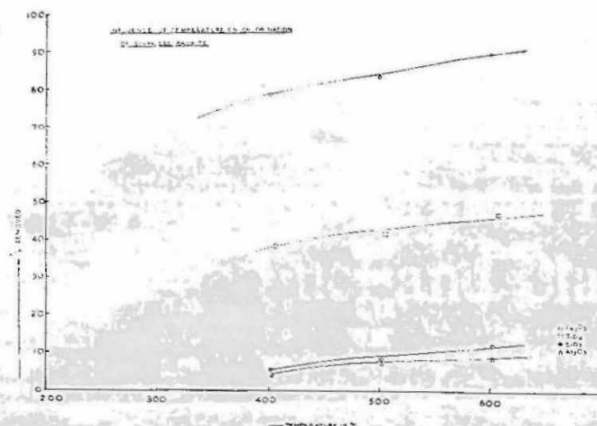


FIG. 10—Influence of temperature on chlorination of sulphidated bauxite.

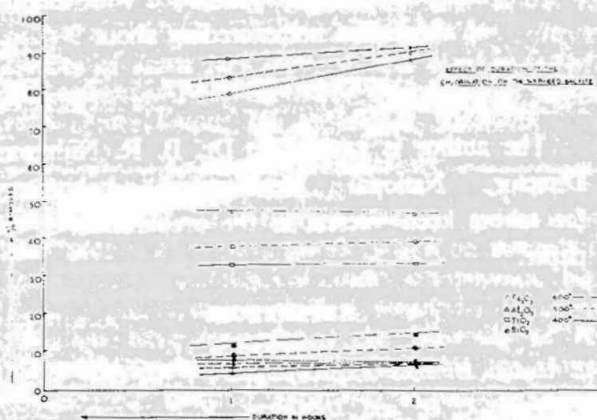


FIG. 11—Effect of duration of the chlorination on the sulphidated bauxite.

was carried in a small boat and residue after chlorination was calcined and analysed using standard methods.

Initially, the chlorination of bauxite only was carried out at various temperatures and rates of flow of chlorine. Although a substantial amount of iron oxide (upto 85%) can be removed when chlorinating at 950°C, the accompanying loss of alumina is also quite appreciable and is quite serious at 950°C. On the other hand when chlorinated with addition agents, it has been found, as the following Tables show, that even at much lower temperatures, there is a substantial removal of iron oxide, the loss of alumina however remaining negligible. The experimental results obtained are summarized in Tables VI to XI and indicated in Figs. 7 to 11.

The results of the chlorination experiments given in the tables indicate that the optimum conditions for the most effective removal of the chief impurities from the ferruginous Salem bauxite ores may be stated as follows :—

1. Bauxite and charcoal mixture: By chlorinating a mixture of bauxite and powdered

charcoal (1:1 by volume) at 400°C for 2 hours with a rate of flow of chlorine of 30 c.c./min., as high as 93% of iron oxide and 56% of titanium oxide can be removed from the bauxite with a negligible loss of alumina (1.5%).

2. Sulphidated bauxite: By chlorinating the sulphidated bauxite (10:3 ratio by weight between bauxite and sulphur and sulphidated at 700°C for ½ hr.) at 600°C for 1 hour with

TABLE VI—EFFECT OF TEMPERATURE ON THE CHLORINATION OF THE MIXTURE OF BAUXITE AND POWDERED CHARCOAL

[Bauxite : Carbon = 1 : 1 (by vol.); duration of chlorination—1 hr. rate of flow of chlorine—30 c.c. min.]

Sl No.	Temperature °C	% Removal			
		Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂
1	300	47.6	—	10.5	—
2	400	71.2	—	29.5	—
3	500	80.0	23.3	60.2	—
4	600	96.3	53.7	82.3	24.0
5	700	99.6	61.6	94.0	25.4
6	800	99.6	70.3	98.4	29.6

TABLE VII—EFFECT OF DURATION OF CHLORINATION ON THE CHLORINATION OF THE MIXTURE OF BAUXITE AND POWDERED CHARCOAL

[Bauxite : carbon = 1 : 1 (by vol.); rate of flow of chlorine 30 c.c. min.]

Sl No.	Temperature °C	Duration in hours	% Removal			
			Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂
1	300	1	47.6	—	10.5	—
2	300	2	48.3	—	10.2	—
3	300	3	56.8	—	13.2	—
4	400	1	71.2	—	29.5	—
5	400	2	93.0	1.5	55.6	8.3
6	400	3	92.6	20.9	55.3	8.2

TABLE VIII—EFFECT OF RATE OF FLOW OF CHLORINE ON THE CHLORINATION OF THE MIXTURE OF BAUXITE AND POWDERED CHARCOAL

[Bauxite : Carbon = 1 : 1 (by vol.); duration of chlorination 2 hrs.; temperature of chlorination—400°C]

Sl No.	Rate of flow of chlorine c.c./min.	% Removal			
		Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂
1	30	93.0	1.5	55.6	8.3
2	90	86.7	—	33.0	4.0
3	300	63.0	—	18.2	—
4	600	47.6	—	10.5	—

TABLE IX—CHLORINATION OF SULPHIDED SAMPLES

[Temperature of chlorination : 600°C; duration of chlorination—1 hr.; rate of flow of chlorine—30 c.c./min.]

Sample No.	Bauxite : Sulphur (by weight)	Temperature of sulphiding. (°C)	Duration of sulphiding (minutes)	%Removal			
				Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂
1	10 : 3	700	30	88.5	9.9	46.3	12.3
2	10 : 3	600	30	83.8	9.7	41.8	12.3
3	10 : 2.5	700	30	80.8	9.9	43.5	12.4
4	10 : 2.5	600	30	81.2	9.6	40.0	11.4
5	10 : 2	700	30	78.0	9.7	41.4	12.3
6	10 : 2	600	30	77.3	9.5	40.2	12.0

TABLE X—EFFECT OF TEMPERATURE ON THE CHLORINATION OF SULPHIDED BAUXITE

[Sample No. 1; duration of chlorination : 1 hour; rate of flow of chlorine : 30 c.c./min.]

Sl No.	Temperature °C	% Removal			
		Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂
1	400	78.7	4.6	33.7	5.4
2	500	83.3	7.7	40.0	8.0
3	600	88.8	9.9	46.9	12.3

TABLE XI—EFFECT OF DURATION OF CHLORINATION ON THE CHLORINATION OF SULPHIDED BAUXITE

[Sample No. 1; rate of flow of chlorine : 30 c.c./min.]

Sl No.	Temperature °C	Duration in hours	% Removal			
			Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	SiO ₂
1	400	One	79.1	4.6	33.1	5.4
2	400	Two	87.3	7.1	33.4	7.1
3	500	One	83.6	7.6	7.9	7.8
4	500	Two	89.0	6.1	39.1	10.8
5	500	One	89.1	9.8	47.5	12.4
6	600	Two	90.2	7.2	47.0	15.1

BAYER PROCESS IN THE MANUFACTURE OF ALUMINA . . . *Continued from page 158*

the reactive silica in bauxite, which forms a complex sodium aluminium silicate, presumably, having the structure 3(Na₂O·AlO₃·2SiO₂) Na₂X. Some soda is lost with calcined alumina in the red mud pond. The soda loss is made up by addition of fresh caustic to the system.

This brief paper should make it amply clear that although the chemistry of Bayer process is quite simple and can be represented by a couple of equations, its application for the manufacture of alumina presents formidable technical problems.

APPENDIX
DEFINITION OF TERMS

CAUSTIC—The amount of free uncombined sodium

a rate of flow of chlorine of 30 c.c./min., nearly 89% of iron oxide and 46% of titanium oxide can be eliminated with the loss of aluminium not exceeding about 9%.

ACKNOWLEDGMENT

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hydroxide plus the amount of sodium hydroxide tied up with alumina in the form of sodium aluminate. Unless otherwise stated, caustic concentration throughout this paper is expressed at Na₂CO₃.

TOTAL SODA—The sum of the quantity of caustic and free sodium carbonate, expressed as Na₂CO₃.

RATIO—The ratio of the concentration of alumina to caustic (expressed as Na₂CO₃) in a solution, both expressed as grammes per litre. Ratio is a pure number.

European practice is to report molar ratio, Na₂O to AlO₃.

PREGNANT LIQUOR—Liquor rich in dissolved alumina, going to precipitators.

SPENT LIQUOR—Pregnant liquor after precipitating out as hydrate bulk of its dissolved alumina.