

Some experiences in electro-winning of aluminium from fused chloride bath

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ALTHOUGH the electro-winning of aluminium from a fused chloride bath dates back to 1854, when Bunsen first isolated the metal, the interest in the process since then has been sporadic. Some of the earlier documenters like Mellor¹, Richards², Borches³ and others had taken up the lead, but had been discouraged into branding the approach as impracticable. Patents filed by Aluminium Industrie A.G.⁴, I.G. Farben Industrie, A.G.⁵, Henriques and Thomsen⁶, Brode⁷, Treadwell⁸, Daudonnet⁹ and others during the period 1928 to 1931 indicated a resurgence of the chloride bath, although in the subsequent period the only mentionable patents were by Lovel and Phillips in 1945¹⁰, Electronic Reduction Corporation in 1951,¹¹ Grothe¹² in 1953, and by Slatin¹³ in 1959 and 1963. Some of these were for the declared purpose of electroplating rather than electro-winning. The published investigations are also equally sporadic, and mention may be made of the work of Fink and Solanki¹⁴, Ramachandran¹⁵, and Newalkar and Altekar¹⁶.

The lure of the chloride bath for electro-winning of aluminium lies principally in the following—a lower decomposition voltage; a wider range of operational temperatures from as low as 160°C; negligible anode consumption; regeneration and recycling of chlorine gas; elimination of imported raw materials, and the possibility of obtaining purer metal by the use of pure trichloride. These points have been amply discussed by previous workers^{16,17}. As against the advantages, one has to put up with some disadvantages also. The principal amongst these is the hygroscopicity of the trichloride, its reactivity with moisture resulting in generation of hydrochloric acid fumes; its low sublimation temperature and its high vapour pressure, all leading to loss of AlCl_3 ; its fuming and corrosion by the HCl produced by hydrolysis with moist air.

Whereas Fink and Solanki and Ramachandran had conducted their experimental work in small 30 cc nickel crucibles, Newalkar and Altekar conducted their experiments in 1000 c.c. pyrex beakers using flat electrodes, in the temperature range of 250°C to 500°C. They

SYNOPSIS

Earlier investigations into electrolysis of fused NaCl-AlCl_3 had indicated the feasibility of electro-winning of aluminium at temperatures below its melting point.

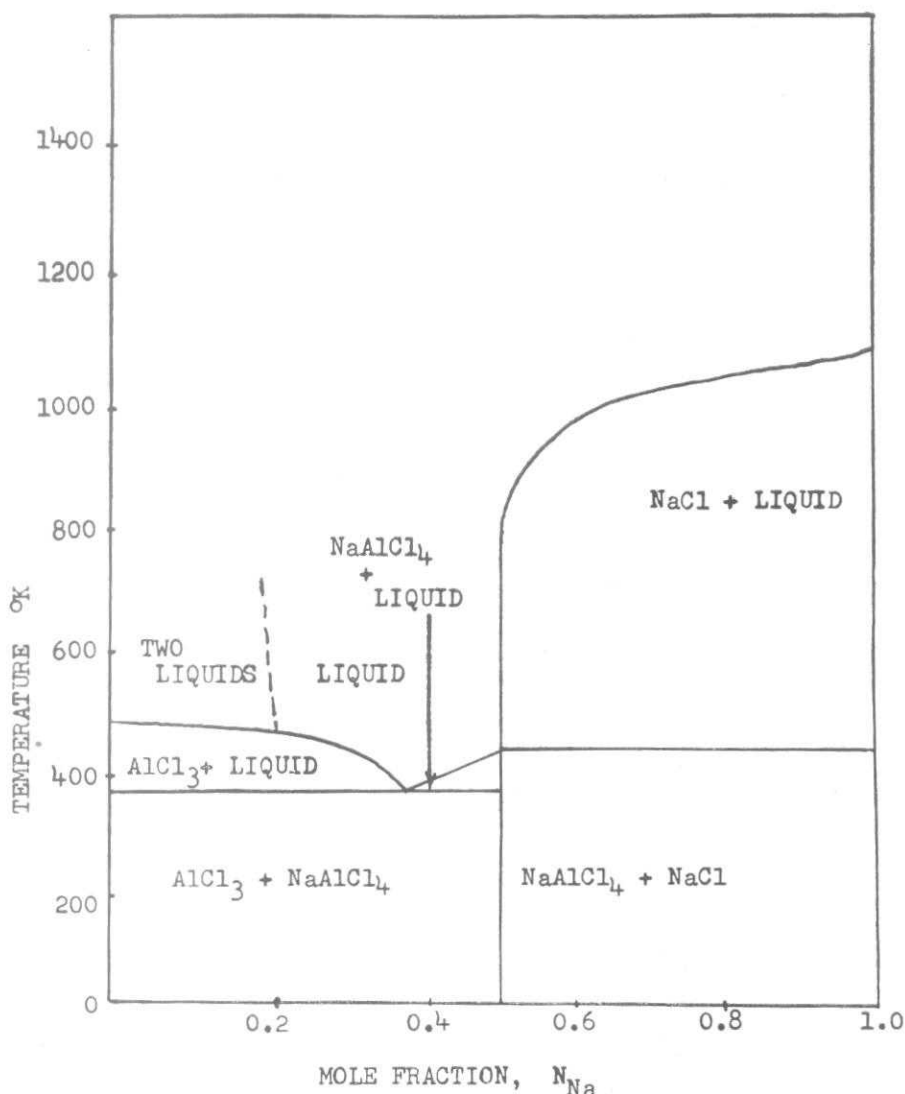
Attempts were made to obtain coherent strippable deposit of aluminium from the fused NaCl-CAlCl_3 bath. The various factors studied include temperature (200°–650°C), cathode materials (Al, Ni, mild steel) cathode current density (1–75 amp/dm²), electrode spacing (1–5 cm), as also pre-electrolysis, neutral gas flushing, rotating cathodes, etc. Although there was no improvement in the adhesion of deposit to the cathode, best results were obtained with Ni cathodes at 400°C, 25 amp/dm² current density obtained at 4V and 3 cm electrode spacing.

Electrolysis in the range of 660–800°C yielded aluminium in molten form, easy to collect and recover. These experiments were conducted in a 2-litre graphite cell in a stainless steel container heated externally. Graphite anodes and cathodes were used. In some experiments the graphite cell itself was used as a cathode. Variables studied were current density (2–110 A/dm²), NaF addition to molten bath (2.5–10%) electrode spacing (1–5 cm) in the temperature range of 660–800°C. A peak cathode current efficiency of 88% was obtained at 750°C, 50 amp/dm² and 3 cm spacing between graphite cathodes and anodes.

reported¹⁷ the working of a one-litre cell under the optimum conditions obtained in their earlier 100 cc cell. Although a current efficiency of over 85% was achieved with a power consumption of 17 watt-hrs per gram of metal, there was one important difficulty observed in these experiments. The recovery of the metal deposited at temperatures below its melting point was extremely problematical, since the deposits tended to be flaky, fluffy, loosely adherent and tending to drop off into the electrolyte.

The work reported here had as its main aim to ensure complete recovery of the deposited metal either by converting the fluffy flakes into a strippable sheet, or if this could not be achieved, to conduct the electrolysis at above the melting point of the metal so that the deposited metal could be collected in a pool.

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1 Phase diagram—NaCl-AlCl₃

It was decided that after a quick confirmation of the optimum conditions obtained earlier, the scale of operation be maintained in 1 to 2 litres range.

Thermodynamics and electrochemistry

Study of the phase equilibrium diagram of the NaCl-AlCl₃ system (Fig. 1) shows the formation of a compound NaAlCl₄ at equimolecular proportions; there is a eutectic formation with excess trichloride. The compound melts without decomposition and is rather indistinguishably close to the eutectic point. The steepness of the liquidus indicates a rapid loss of activity of NaCl as the compound composition is reached from the NaCl side. According to Lumsden¹⁸, the two components NaCl and Na·AlCl₄ mix with pronounced positive departure from ideality.

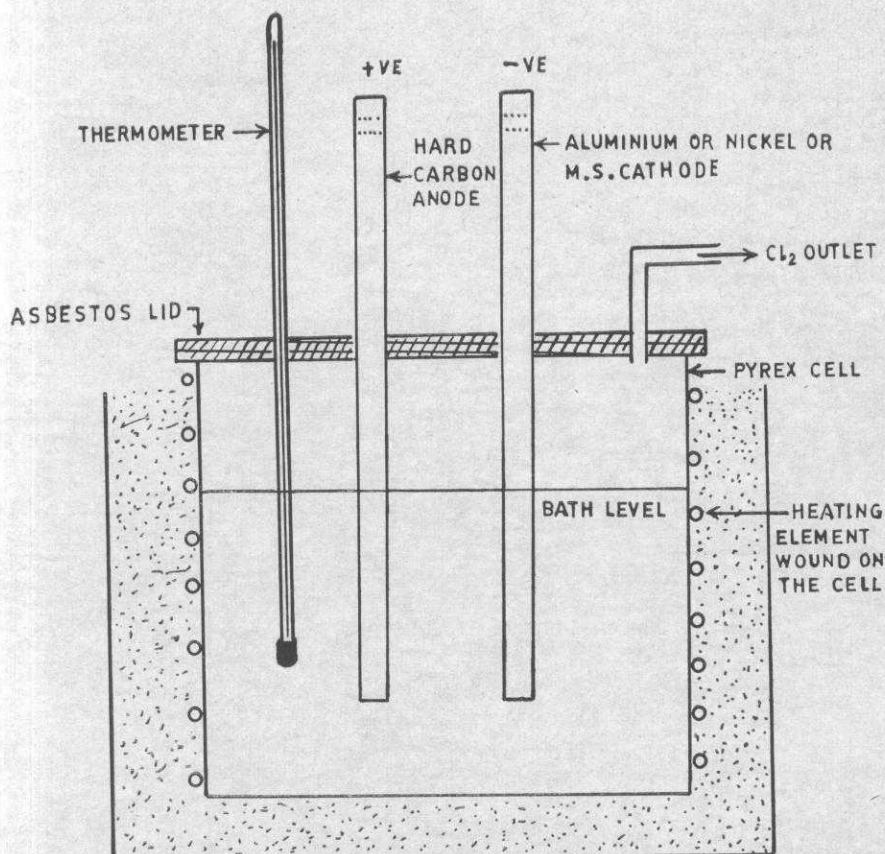
The AlCl₃ side of the phase equilibrium diagram is substantially as determined by Kendall and coworkers¹⁹. The pronounced non-ionic nature of the AlCl₃ results

in only very slight solubility of NaCl in molten AlCl₃. The result is a miscibility gap. There is good reason to believe that the liquid AlCl₃ really consists of Al₂Cl₆ molecules. Since the Al ion is so small, it is reasonable to suppose that *if* aluminium chloride formed as *ionic* liquid each Al³⁺ ion would be in contact with only four chloride ions; this implies that each chloride ion would, on the average, be in contact with 1 1/3 Al³⁺ ions. With most of the chloride ions attached to only one cation, the structure of the melt is pronouncedly different from that of the NaCl melt.

The decomposition potential of the aluminium trichloride has been calculated from the Thomson's equation:

$$E = -\frac{J \times F^\circ}{nF}$$

J = Joule's constant (4.182)



2 Cell diagram (section A)

n = Valency,
 F = Faraday number 96,494 coulombs
 F° = Free energy of reaction (-138,160 cal)
 E = Decomposition potential

Thus for $AlCl_3$

$$E = - \frac{4 \cdot 128 \times (-138,160)}{3 \times 96,494} = 1.99 \text{ volts.}$$

The decomposition potential of sodium chloride at 720°C is 2.75 volts, which is higher than that of aluminium chloride (1.4 volts at 720°C) according to C.L. Mantell.²⁰ The sodium chloride, therefore, possesses greater electrical stability than the aluminium chloride.

The Gibbs-Hemoltz equation takes into account the temperature dependence of the E_{DP} by inserting a $T \frac{DE}{dT}$ component. At 400°C the E_{DP} values have been determined to be 1.89 volts; whereas at 750°C it dips down to 1.66 volts.

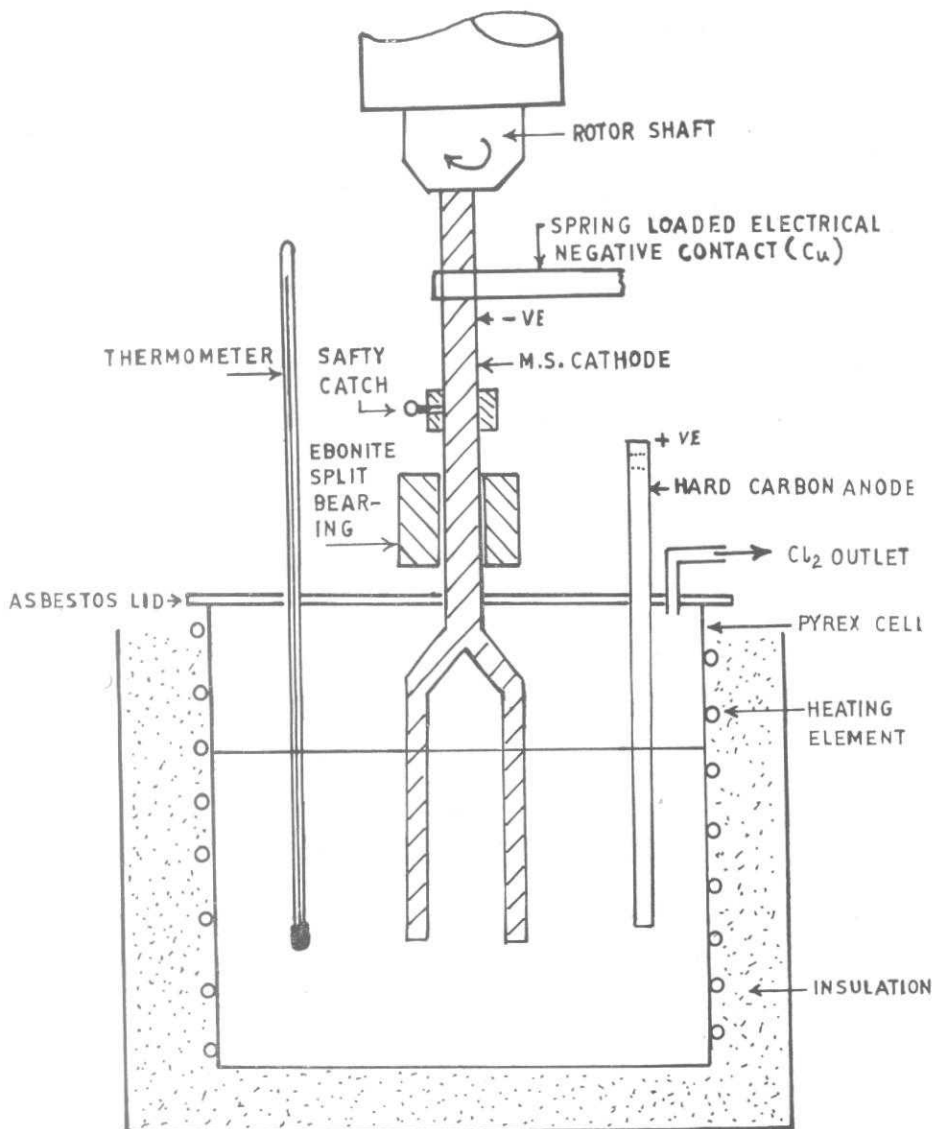
For complex-electrolytes comprising mixtures of salts, as used in the present work, the decomposition values are higher at various temperatures compared to those of single fused salts. This is explained, not only

in terms of concentration change, but also by a possible chemical interaction between the components of the melt. Since there is no theoretical method for calculation of E_{DP} of complex mixtures a practical approach is always preferred. The E_{DP} of a fused mixture of $AlCl_3$ at various temperatures and concentrations have been determined by Delinmarskii and Markov²¹; Abramov and coworkers²²; and Kher and Mene.²³ The values reported by the various workers are at variance. The reported values, however, seem to lie in a range of 1.7 to 2.2 volts for Al. The corresponding E_{DP} for Na in the fused mix at 700°C is reported to be 3.332 volts. This shows that unless the cell voltage is too high, there is no possible chance of codeposition of Na along with Al. In some of the experiments by Newalkar and Altekar, the codeposited sodium gave rise to a series of troubles, like very low current efficiency and loss of deposited aluminium during washing.

The codeposited sodium may lead to the production of metallothermic aluminium, by the following reaction:



However, the reduced aluminium produced in this manner is known to be very finely divided, in fact



3 Cell diagram—with rotating cathode

produces a metallic cloud and spongy metal not at the cathode, but throughout the body of the electrolyte.

The total impressed voltage of the system is a sum total of the $E_{DP} + E_{RV} + E_{OV} + E_{contact}$ where ohmic resistance of the cell (E_{RV}) the over voltage (E_{OV}) and the contact resistance are taken into account. The conductance of the melts of this system under various conditions of temperature and composition have been determined by Yamaguti and Sisido²⁴ and others.

The solubility of the metal is of great significance in the fused salt electrolysis. The solvent power of the salt for the metal increases generally with the temperature. Decrease in the temperatures results in precipitation of the metal in the form of clouds or fog. Even 0.1% metal in the colloidal dispersion can cause a fog and colour the melt.

Earlier work in this laboratory^{16,17} had not only confirmed the results reported in the literature, but had gone a step ahead in proposing and conducting electrolysis on extended time schedule with periodic addi-

tions of the trichloride. It, however, was conducted at an optimum temperature of 400°C i.e. below the melting point of the metal. The deposit, however, was obtained mostly as loosely adherent flakes. The recovery of such a deposit had been problematical and the cell operation had to be interrupted because the fluffy deposit would soon accumulate to short circuit the electrodes. Further, it would drop off the cathode while the same was being removed, thus further complicating the procedure. This work which was in the nature of continuation of the previously reported work set up its aims in overcoming this draw-back. It sought to maintain the scale of operation between 1 and 2 litres of cell volume in trying to obtain continuous runs.

Experimental

In view of the aims set forth for this investigation, the approach was divided into two sections: (i) To operate at a temperature below the melting point of Al, and

TABLE I Influence of cathode material

Electrode material	Sr. No.	Current amps.	Current density amp/dm ²	Voltage volts	Temp. °C	Weight Al deposited g	Current efficiency %	Cathode deposit
Nickel	1	1.5	5	5	350	0.355	47	Al deposited was flaky, bright, shining and crystalline Duration 1 hr.
	2	2.5	8.3	3.5	375	0.813	65	
	3	3.5	12	4	375	1.348	77	
	4	5	16.7	4	400	1.975	79	
	5	8	27	5	400	3.28	82	
	6	12	40	6.5	400	3.30	82.5	
Aluminium	7	1.5	5	2.9	375	0.322	43	non-adherent, flaky, shining and brilliant Duration 1 hr.
	8	2.5	8	3.5	380	0.826	66	
	9	3.5	12.5	3.8	380	1.312	75	
	10	5	17.2	4	400	1.985	79.3	
	11	8	29	4.5	380	3.260	81.5	
	12	12	45	5.5	400	3.280	82	
Mild Steel	13	1.5	5	3.5	400	0.305	40	Ash like and powdery Flaky, shining and non-adherent Duration 1 hr.
	14	2.5	8	3.8	380	0.750	60	
	15	3.5	12	4	400	1.260	72	
	16	5	17.5	5	400	1.875	75	
	17	8	25	5.5	380	3.110	77.7	
	18	12	48	6	400	3.120	78	

to manipulate conditions of electrolysis so as to obtain a coherent and yet strippable deposit on the cathodes; and (ii) to operate at higher temperatures above the melting point of Al with arrangement for periodic collection of the molten metal. Certain procedures were commonly followed throughout the investigations and these are outlined here. Deviations or additional features appear at appropriate places.

Materials

These investigations mainly pertained to the NaCl-AlCl₃ system. In the initial stages of the project non-availability of pure anhydrous AlCl₃ in small quantities compelled the authors to produce anhydrous AlCl₃ by

a fluidized bed technique.²⁵ This consisted of chlorinating a fluidized aluminium powder bed above the sublimation point of AlCl₃ and condensing the AlCl₃ vapours. However, in the later investigations almost all the AlCl₃ was supplied by a local manufacturing firm. The salt was supplied in widemouthed glass bottles sealed with paraffin wax. Opened bottles were stored in chambers desiccated with CaCl₂ or the bottles were resealed with paraffin wax. Sodium chloride was of A. R. grade of B. D. H. and Merk makes.

Electrical circuit

The electrical circuit consisted of the cell with suitably selected electrodes; ammeter 0-50 amps/0-500 amps;

voltmeter 0–10 V; rheostats; potential divider; D. C. generators capable of producing 50/500 amps current at any desired voltage etc. Suitable electric resistance furnaces were built and the energy input was varied by using appropriately matched dimmerstats. Temperatures were read by adequately protected chromel-alumel thermocouples.

Cell material and construction

It was found that Pyrex glass beakers could be conveniently used as cell materials for temperatures below 650°C. Evidently, this being below the melting point of aluminium, aluminium was obtained in the solid form. However, when the necessity arose for liquid metal production, Pyrex was obviously unsuitable. Graphite containers, encased into stainless steel containers for mechanical stability were used. The cells were closed by closely fitting asbestos lids with provisions to insert electrodes, pyrometers, thermometers, stirrers and chlorine outlets. The care and maintenance of the graphite cells were similar to those of graphite electrodes, described later.

The chlorine evolved at the anode was led out of the system with the help of a water ejector, through a series of absorption towers containing NaOH. In order to avoid contact of the bath with the moist air, dry nitrogen was used as a flushing gas under the cell lid.

Electrodes

Mild steel, aluminium and nickel plates were tested as cathodes in the early stages. Modifications like rotating cathode, made of mild steel were also tried. Hard carbon anodes were found to be most suitable for low temperature electrolysis. However, for high temperature electrolysis, graphite electrodes showed better integrity.

Procedure

Electrolyte preparation

Hygroscopicity and subliming nature of AlCl_3 caused a good deal of difficulty in its handling. Weights were taken quickly, and by difference wherever possible. Making the electrolyte was very difficult. A convenient method of making the electrolyte was to spread alternate layers of AlCl_3 and NaCl, keeping the top most layer of NaCl to seal off any vapours of escaping AlCl_3 . NaCl also had to be preheated to 200°C to drive away any moisture and was stored in a desiccator before use. The melting pot, generally of Pyrex glass, was gradually heated till the components fused into a homogeneous melt. For larger volumes of electrolytes, the electrolyte was prepared in the cell itself.

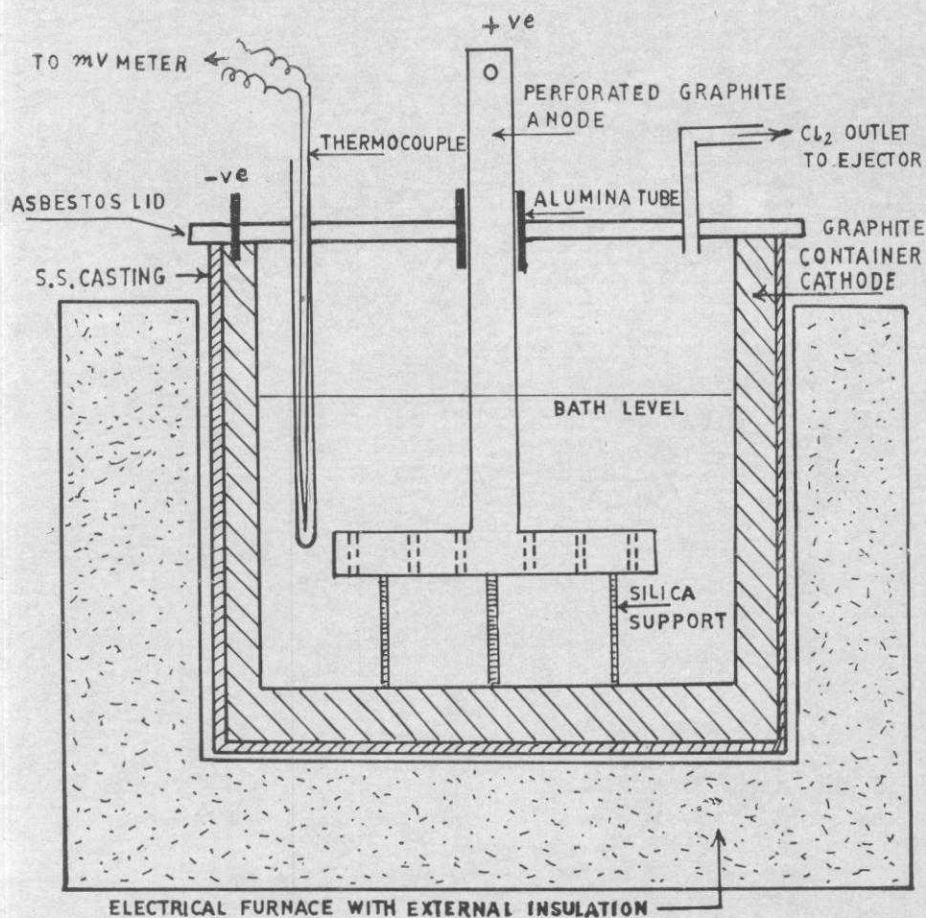
Care and use of electrodes

The electrodes had to be cleaned properly before use.

TABLE II Electrolysis with rotating cathode

m. s. cathode, 2.5 cm dia. × 5.5 cm long
Duration—One hour

Sr. No.	Voltage volts	Current amps	Depth of cathode in batch cm	Current density amps/dm ²	Temp. °C	Weight Al deposited g	Current efficiency %	Remarks
1	4-5	5	4	16	250	1.015	61	Powdery grey
2	4-5	5	4	16	300	1.075	64.4	Coarser and bright
3	4-5	5	4	16	350	1.150	68.7	Bright, shiny and flaky
4	4-5	5	4	16	400	1.210	72.5	
5	4-5	5	4	16	450	1.203	72	
6	3	5	4	16	400	1.210	72.5	Brilliant, lustrous and flaky deposits
7	4-5	10	5	25	400	2.480	74.5	
8	4-5	10	4	32	400	2.426	74.1	
9	5-6	12	3	51	400	2.953	73.8	
10	5-6	15	3	75	400	3.520	70.5	



4 Cell diagram—with container acting as a cathode

Any traces of moisture in the dense graphite or hard carbon electrodes caused violent spurring of the molten bath. A standard practice of initially washing the electrodes with water and drying them was followed. They were then cleaned with alcohol to remove greasy matter and then dried in an oven and kept in a desiccator. Before using they were preheated at about 200°C for at least half an hour to remove gas, moisture, etc. and then immersed into the electrolyte for the electrolysis. Even after the electrolysis, the electrodes required a meticulous but routine care for longevity. This comprised an immediate washing after use, leaching out the chlorides in boiling water, alcohol wash and oven drying. Any laxity in this routine resulted in swelling, flaking and general disintegration of the electrodes.

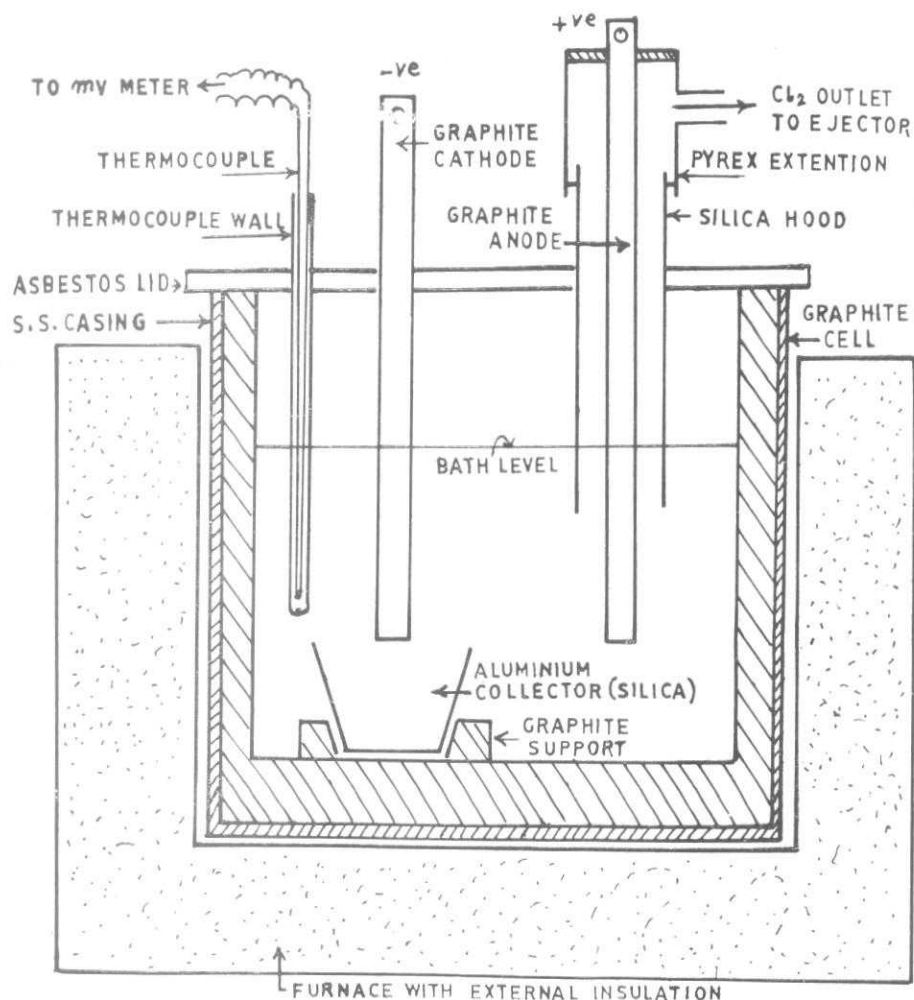
Phase I: Low temperature electrolysis

Investigations in this phase were conducted to obtain data on optimum conditions involving compositions, temperatures, voltages, current densities and inter-electrode spacings. Attempts were then made to prolong the electrolysis under constant cell conditions by periodic removal of the cathodes for removal of the deposited metal.

Another series of experiments were conducted to investigate the possibility of internal heat generation due to the passage of the electrolyzing current through the electrolyte. It was concluded that external heating of the cell would be essential.

Since the adhesivity of the aluminium to the cathode greatly depends upon the type of bond between the two, different cathode materials were tried. For identical set of conditions nickel cathodes gave the best results, aluminium next and mild steel last. As the temperature of the electrolysis approached the melting point of aluminium, sheet aluminium cathodes tended to warp and non-strippable intermetallic compounds appeared to have formed with nickel and steel.

It was also felt that a lack of adequate stirring on the proximity of the cathode produced a concentration gradient, concentration of AlCl_3 decreasing with decreasing distance towards the cathode. Such conditions, as observed earlier, could lead to codeposition of sodium and thus prevent the adhesion of the liberated aluminium. It was decided to take advantage of a rotating cathode, which could offset such concentration gradients. Fig. 3 indicates an electrolytical cell with such an attachment. The cathode consisted of mild steel, 1" diameter by 2" long, hollowed out so as to reduce its dead weight. The cathode was attached to a rotating



5 Cell diagram

shaft of a low H. P. stirrer motor. In order to avoid heavy vibrations and wobbling, it was necessary to provide an additional support, through an ebonite split bearing. The electrical contact was made through a spring loaded copper strip. The tabulated values of the current efficiency show a much lower peak value of 74% (Table II) as against the peak efficiency of 82.5% obtained with stationary Nickel cathode (Table I). The deposit continued to be non-adherent and non-cohesive, though bright and lustrous. It was surmised that instead of producing the desired adhesion and a coherent deposit the rotary action of the cathode perhaps threw away the deposited metal due to the centrifugal action.

For the above set of conditions best result were obtained at 400°C, 2.5 cm inter-electrode spacing, current density of 30 amp/dm² at 4 volts with a NaCl : AlCl₃ ratio of 1 : 2.5. The only major drawback was the non-adhesivity of the aluminium to the cathode. It, therefore, became necessary to investigate higher operating cell temperatures, where aluminium could be obtained in the molten form.

Phase II : high temperature electrolysis

Temperatures were now varied between 660 and 800°C.

Materials of construction now became a problem ; glass beakers, earlier used as cell materials, could not withstand the temperature and the hard carbon anodes disintegrated. A 2-litre graphite container, encased in a stainless container, for mechanical stability, was now used as a cell. Dense graphite was used as the electrode material. Initially, attempts were made to use the container as a cathode (Fig. 4) but this design had to be rejected as the anode and the cathode tended to shortcircuit at the sides. This, however, brought to our notice a very important point, i.e. within the intended electrolyzing area, the inter-electrode distance within the electrolyte should be an optimum. In the later designs (as in Fig. 5) plate electrodes were used. Suitable containers, mostly of silica, were placed under the graphite cathode plate to collect the molten aluminium. An anode hood was also used to remove the liberated chlorine at the anode. At higher temperatures, bath compositions found appropriate for low temperatures, were found to fume profusely of AlCl₃ vapours. Several bath compositions were tried to obtain a stable bath in which, neither NaCl remained behind as a residue nor did the bath fume of AlCl₃. Table III indicates baths with NaCl : AlCl₃ = 5 : 9 to 1 : 2 to be the best. Within

TABLE III Selection of bath composition

Sr. No.	Initial weight of			Weight NaCl : AlCl ₃	Weight of mixture after heating g	Remarks
	NaCl g	AlCl ₃ g	NaCl+ AlCl ₃ g			
1	600	600	1200	1 : 1	1187	Clear electrolyte but lot of free NaCl as residue
2	500	800	1300	1 : 1.6	1290	„ „ with lesser free NaCl as residue
3	500	900	1400	1 : 1.8 or 5 : 9	1386	Clear electrolyte with no residue
4	500	1000	1500	1 : 2	1492	„ „
5	500	1200	1700	1 : 2.4	1610	No residue but AlCl ₃ fuming continuously
6	500	1500	2000	1 : 3	1820	Excessive fuming

this composition range, the bath produced no fuming over prolonged periods of holding between 660 and 800°C.

Temperatures were varied between 660 and 800°C without finding any appreciable change in the current efficiency. It thus became necessary to choose the lowest practical temperature. A temperature of 750-760°C was found to be most ideal as this left sufficient superheat of about 100°C to prevent the metal from solidifying during subsequent handling.

The voltage was varied between 2 and 8 volts and a voltage of 4 volts was found to be the best. The current density was also varied between 2 and 110 amps/dm². The current deficiency was found to level off at 50 amps/dm².

The effect of salt additions towards betterment in electrolytical characteristics was investigated. NaF, KCl and LiCl were added separately up to 10% by weight. However, none of these additions showed any encouraging results, as all of them tended to decrease the conductivity of the bath.

Since the main purpose of this investigation was towards a continuous aluminium producing unit, larger cells than 2-litre capacity were designed. A higher current of 500 amp was used. However, it was found that much larger currents than 500 amp would be necessary to produce sizable amounts of aluminium, so that it could be either tapped out or siphoned out.

Conclusions

Low temperature electrolysis of fused AlCl₃-NaCl melts indicates that but for the non-adhesivity of aluminium to the cathode, the electrolytical parameters are attractive. Optimum conditions for high temperature electrolysis are encouraging. However, the difficulty in making the process continuous due to the depletion of AlCl₃ during the electrolysis, was overcome in the following manner. Direct additions of AlCl₃ to the bath, to maintain the compositions is not economical as there is a tremendous loss of AlCl₃ as it sublimes away. On the experimental scale, the bath compositions were maintained by replacing a part of the electrolyte by a highly concentrated electrolyte in its AlCl₃ content, made separately in another melting pot. This idea may be exploited on a larger scale by inter-connecting several electrolytical cells through a mixer containing concentrated AlCl₃ electrolyte.

In the conventional Hall-Heroult process heat is generated internally largely due to the ohmic resistance and to some extent by an exothermic oxidation of the carbon anodes, whereas the chloride process requires additional heating. Though cells lined with dense graphite are satisfactory, any porosity in the lining can allow the electrolyte to percolate through the lining and corrode the external lining.

So far as the electrical energy consumption is concerned, both the processes seem to require just the same amount of power. The experiments conducted so far, were restricted to a few litres. This size is too small to assess the proper thermal balance of the process. It is quite likely that, if the process be scaled up to a capacity where a few kiloamps of electrolysing currents could be used, it is likely that the thermal balance may be more favourable and the heat generated by the ohmic drop may be sufficient to maintain the cell at the working temperature.

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