Aluminium Electrorefining in Molten Chlorides for the Production of Primary Quality Aluminium from Scrap

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Abstract:

A graphite cell for electrorefining aluminium scrap. was tested on bench scale by continuous operation. Liquid metal anode and cathode are separated by a thin electrolyte-flooded alumina felt diaphragm, which also insolates the graphite shells. The diaphragm thickness was only about 3 mm in order to guarantee low electric cell resistances. The electrolyte was $LiCl/NaCl/AlCl_3$ (34, 51, 15 mol%). The cell has a volume of 500 cm^3/electrode and an effective surface of 300 cm^2. The refining temperature was 700 °C. Sealing problems were solved by liquid/solid (thaw/freeze) sealing. Feeds were aluminium alloys with up to 12 weight% impurities. Primary quality aluminium with a purity grade up to 99.7 wt% was achieved. Energy consumption was kept below 5 kWh kg^{-1} Al, corresponding to a cell voltage lower than 1.0 V at current densities from 0.1 to 0.3 A cm^{-2}.

1 - Introduction

Electrorefining of aluminium scrap from molten chloride melts has been reported by several authors (1, 2, 3). All demonstrated the production of primary quality aluminium from aluminium scrap by using LiCl, $LiAlCl_4$ and the respective sodium salt mixtures as electrolyte. These investigations were confined to small cells, avoiding any difficulties concerning the operation of large scaled electrolytic cells. If this approach is ever to become a feasible technology, it is necessary to construct larger cells of almost technical size and to operate them on long term, to assure that material choice and operation conditions agree to the technological demands.

A cell of narrow gap design was used. The interelectrodes distances of 3 mm had been established by the thickness of an alumina felt diaphragm. An important aim was low energy consumptions, at the most about one third of that required in the well established aluminium production process. Therefore surface specific resistances of the cell should not surmount several tenths of $\Omega\ cm^2$. The specific conductivity of the mentioned electrolyte is roughly 1 $\Omega^{-1}\ cm^{-1}$. One calculates a surface specific resistance of 0.3 $\Omega\ cm^2$ for a 0.3 cm gap.

2 - Theoretical Considerations

The ionic species in the electrolyte are alkali metal cations, chloride anions and tetrachloroaluminate anions. In stagnant electrolytes, which are expected to exist in an alumina felt diaphragm separating the two electrodes, mass transport is only due to ionic migration and molecular diffusion. Figure 1 shows schematically the concentration development of Cl^- and $AlCl_4^-$ with time in molten LiCl/NaCl mixtures containing $AlCl_3$, across the interelectrodic gap. Initially, Fig.1a, there exist equal concentrations. Immediately after imposing current on the cell, the concentration of $AlCl_4^-$ decreases at the cathode and increases at the anode, Fig. 1b. After establishing a steady state distribution, concentrations gradients in the electrolyte layer ($\partial c_i / \partial x$) are the commanding quantity for the diffusive flux density and concentrations c_i, ionic mobility μ_i and electric field E are the quantities commanding migrative flux. Equation (1) describes the ionic fluxes driven by concentration gradients and by the electric field. The current density is coupled to the ionic fluxes by Faraday's law, equation (2), and by the Cl^- and $AlCl_4^-$ total flux balance, equation (3).

$$\dot{n}_i = -D\frac{\partial c_i}{\partial x} + E\mu_i z_i c_i \qquad (1)\,; \qquad i = 3F\dot{n}_{AlCl_4^-} \qquad (2)\,; \qquad \dot{n}_{AlCl_4^-} = -4\dot{n}_{Cl^-} = \dot{n}_{Al^{3+}} \qquad (3)$$

Figure (1c) describes schematically the steady state concentration distribution of Cl^- and $AlCl_4^-$. The chloride ions move under the synergetic effect of the concentration gradient and the electric field, the transport of chloroaluminate anions from the anode to the cathode is hindered by the electric field. The concentration profile at steady state conditions, is characterized by relatively flat concentration gradients of Cl^- as well as $AlCl_4^-$ anions at the cathode and steeper gradients at the anode. The steady state concentration distribuition defines a diffusion limited current density for aluminium deposition at the cathode and this limiting current dendity $i_{\lim}$ is given by equation (4).

$$i_{\lim} = 3FD\left(\frac{\partial c_{AlCl_4^-}}{\partial x}\right)_{cathode}^{c=0,x=d} \qquad (4)$$

Achievable current densities are remarkably lower than estimated by neglecting the influence of migration. However, it must be emphasized that at the onset of the electrolysis, much steeper concentrations gradients are feasible than at steady state. Hence at unsteady state conditions much higher current densities can be imposed on the electrorefining cell. It may be imagined that this mass transfer enhancement can be brought about by gravity driven percolation of the electrolyte through the diaphragm, which would reduce the residence time of the electrolyte considerably below the characteristic time τ_c , for concentration relaxation.

3 - Experimental

Refining experiments were carried out in a vertical devided cell of outer dimensions 440x420x80 mm. An alumina felt separates the molten metal anode and cathode, both being contained between graphite shells, as shown in the figure 2. The cell volume was 500 cm^3, with an effective electrode area of 300 cm^2. The graphite was stabilized against atmospheric oxidation by inbibing it with a proprietory inhibitor (Stockum Mechanik, Breuberg, Germany), whose presence did not impair the quality of the refined aluminium, although it contained considerable concentrations of chromium. This procedure also prohibited the diffusion of the electrolyte through the graphite shells, damaging the heating plates. The cell was kept under dry argon. A 99,7 % pure alumina felt, 80 % porous (product number 300, from Cotronics Corp, USA), with a maximun working temperature of 1260 °C was used. Impregnating the felt with Al_2O_3 powder (0.05 g per cm^2, product number 901, Cotronics Corp, USA) stabilized the felt mechanically a lot. The refining temperature was set to 700 °C, slightly above the melting point of aluminium (660 °C).

Melts composed of 51 mol% NaCl, 34 mol% LiCl (T_f=660 °C) and 15 mol% $AlCl_3$ were used, because the relatively high melting point of 660 °C enabled to seal the cell by a thaw/freeze sealing at the air-cooled fringe of the cell. The eletrolyte was prepared in a glove box under dried argon with less than 2 % relative humidity. The electrolyte was pre-melted and devided in little pieces, which facilitated cell feeding. The cell was heated by two flat heating elements (VF812A18S, Watlow, USA), each of max. 2.2 kW, pressed against the outer surface of the shells. After melting of the anode and cathode metals the chosen current density was applied to the cell and kept constant (galvanostatic mode). Cell current potential curves were taken after a given operating time, varying from 3 to 8 h, to determine the cell resistance and metal samples were collected for analysis by X-ray fluorescence for Cu, Cr, Si, Fe, Ni, Zn, V, Zr, Sr, Pb, Li, Mn, Ti, Na and Mg. Anodic and cathodic current efficiencies were determined gravimetrically after quenching and dissassembling the cell. Scrap anodes were obtained from typical cast alloys with up to 12 weight% impurities.

4 - Results

(1) Due to impregnation with the stabilizer, the carbon shell surface, whose oxidation in air amounted otherwise to approximetly 1 mm per hour, became so stable, that after 24 h the mass loss was not detectable (< 0.05 mm). The cell can be operated safely over more than 100 h. A series of five experiments had been performed with one single cell without serious deterioration of the carbon shell. Only the diaphragm was exchanged after each experiment, because it was destroyed by dissassembling the cell.

(2) Surface specific resistances of the cell are much higher than calculated from melt conductivities and amounted to between 3 and 4 Ω cm^2. Accordingly, current densities were kept below 0.3 A cm^{-2} in order to sustain a cell voltage of less than 1 V, usually 0.8 V. The energy consumption was approximately 3 kWh/kg Al.

(3) Mechanical and electrical cell performance on long term kept steady, with almost no variation with time of cell resistance and continuous flux of refined aluminium from the cathode chamber through a vertical channel separated from the molten cathode by a weir (see fig. 2).

(4) The refining effect was as good as expected from small-scale experiments (3). In particular the initial iron concentration of 0.46 wt% was decreased by a factor of approximately 9 to 0.047 wt% and the Si content from 8.15 to 0.37 wt%. 99.7 wt% purity was achieved. In the case of electrorefining of Al 99.7 wt%, purity grades up to 99.99 wt% were acchieved.

(5) Anodic and cathodic current efficiencies were significantly lower than unity. Particularly the cathodic current efficiency, which amounts to 60 % at low current densities, figure 3, decreases to as little as 35 % at higher current densities. The anodic current efficiency, which begins at close to 90 % at low current densities also decreases to 30 % at current densities approaching 1 A cm^{-2}.

5 - Conclusions

The high cell resistance and low current efficiency at higher current densities, which were also detected by Nagayama and coworkers (2), are contraproductive for electrorefining on large scale. High cell resistances are likely due to some type of passivation of anode and cathode surfaces, i. e., their coverage by Al_2O_3 , which might be counteracted by adding AlF_3 , whose solubility in chloride melts is low but close to 10^{-2} M. AlF_3 could dissolve or etch away Al_2O_3 - coatings by formation of AlO_yF_x - complexes. In particular low anodic and cathodic current efficiencies are certainly caused by concentration polarisation and correspondingly cathodic generation of dissolved or dispersed alkali metals in the melt, leading to a type of electrochemical shorting by anodic reoxidation of the alkali metal. Similar effect had been reported elsewhere (4). Percolating the electrolyte through the diaphragm would allow for higher current efficiencies and densities. The transition time to approach zero concentration of $AlCl_4^-$ at the cathode comes close to 10 s at 1 A cm^{-2} and 1000 s at 0.1 A cm^{-2}. If electrolyte percolation through the diaphragm would allow for less than a quarter of an hour residence time, a current density of 0.1 A cm^{-2} could be applied safely, avoiding cathodic alkali metal reduction. The results show clearly that still a lot of R & D work would be necessary to come closer to the aims, using chloride melts for electrorefining of aluminium scrap.

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(a) Initial. (b) Onset of electrorefining. (c) Steady state.

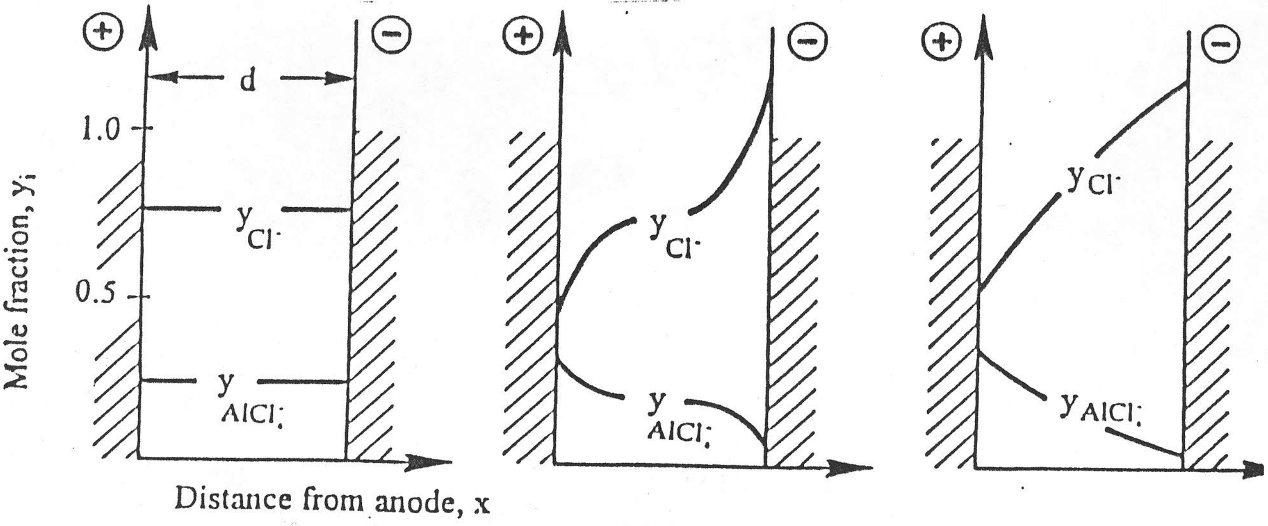

Fig. 1 a,b,c: Concentration distribution of Cl^- and $AlCl_4^-$ in the interelectrodic gap.

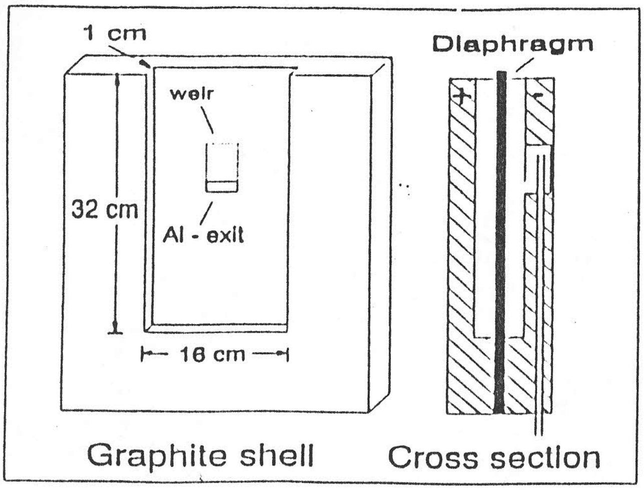

Fig. 2: Schematic of the refining cell.

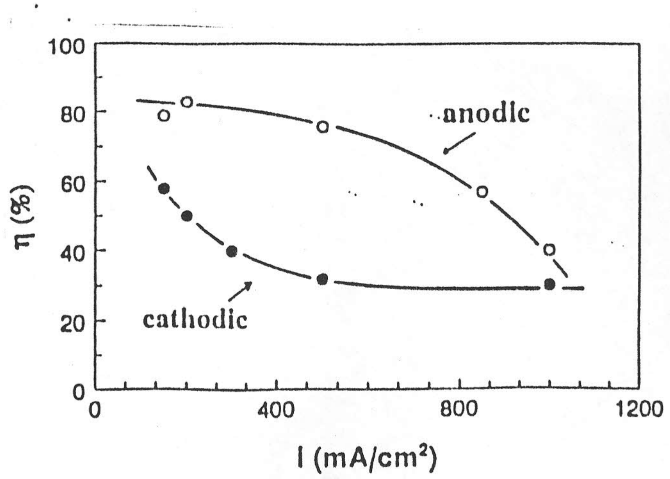

Fig. 3: Current efficiencies vs. current densities.

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