CATHODE WEAR DURING ALUMINIUM ELECTROLYSIS

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Graphitic instead of anthracitic bottom blocks are increasingly used in modern aluminium cells. Graphitic blocks have lower sodium expansion, and the higher electrical conductivity allows current increase which improves the profitability of the electrolysis. Graphitic blocks generally are, however, subject to an increased wear. Cathode wear then often becomes the life-determining factor. The possible wear mechanisms can be summarized as follows:

Chemical

$$4\,Al + 3\,C \xrightarrow{\text{cryolite}} Al_4C_3$$

Galvanic

$$3\,C + 4\,Al^{3+} + 12\,e^- = 4\,Al_4C_3$$
$$4\,Al = 4\,Al^{3+} + 3\,e^-$$

Electrochemical

$$3\,C + 4\,Al^{3+} + 12\,e^- = Al_4C_3$$

Physical

Detachment of C-particles due to abrasive forces from particles in the moving electrolyte.

Oxidation of Al_4C_3

Al_4C_3 dissolves in the electrolyte and get oxidized at the anode

$$Al_4C_3 + 9\,CO_2 = 2\,Al_2O_3 + 12\,CO$$

Table 1 gives typical wear rates:

Table 1. Cathode Wear Rates Observed in Operating Cells.

Block Type and Zone	Approx. Rate (cm/y)
Anthracitic	
Typical range	0.5-1.5
High velocity zone	1.5-2.5
Taphole (Low Range)	0.5-1.5
Taphole (Highest)	3.5
During tapping	150-1,000
Graphitic /Semigraphitic	
Typical range under anode	1.5-2.5
High velocity zone	2.5-4.0
Taphole (Low Range)	1.2-3.0
Taphole (Highest)	4.5
During tapping	250-1,000

The following set-up was used for laboratory study of wear rates in Fig. 1.

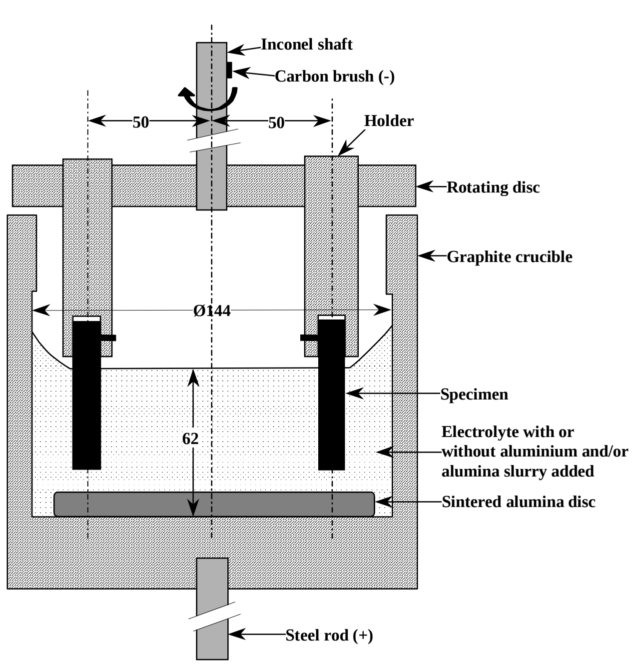

Fig. 1. Set-up for wear study of carbon cathode materials with or without aluminium electrolysis. Temperature 960 - 1015°C.

The experimental conditions were as follows:

No Current Flow
- Fluoride + excess Al_2O_3 slurry
- Aluminium metal only
- Fluoride saturated with Al
- Fluoride + Al + Excess Al_2O_3 slurry

Cathodic Current Flow:
- Electrolyte only
- Electrolyte + excess Al_2O_3 slurry
- Electrolyte + 3 wt% Al_4C_3 excess.

The following results were found:
1. The wear rate by electrolysis increases with increasing current density but levels off at current densities above 0.8 A/cm^2.
2. With electrolyte and aluminium present without electrolysis galvanic wear was observed.
3. Electrolytic or galvanic wear was much higher than physical wear.
4. Electrolytic wear rates were the same for graphitic and anthracitic materials.
5. Presence of alumina slurry suppresses the electro-chemical wear.
6. The physical wear rate increases strongly with velocity and increased concentration of an alumina slurry.
7. Physical wear rate of graphite is about 5 times the physical wear of anthracitic carbon.
8. The physical wear ratio graphite/anthracite is about the same in room temperature abrasion tests and in cryolitic melts.
9. The mechanisms of wear in industrial cells are a combination of physical and chemical wear in spite of that the physical wear is much smaller.