Essential Readings in Light Metals: Electrode Technology for Aluminum Production.
Edited by Alan Tomsett and John Johnson.

2. HALL-HÉROULT CELL CATHODES

A wide range of topics is covered within the cathode section of the book. The selected papers reflect the changing focus of the industry in cell lining materials and performance. The majority of papers were originally published in the 1980s and 1990s. More recent papers are related to graphitized cathode wear and chemical attack of refractories rather than the development of new materials. Many papers were originally published in the Reduction Symposium at the TMS Annual Meeting and have been transferred to this electrode volume to ensure some consistency with the definition of electrodes at the Annual Meeting. When researching cathode performance, this section should be read in conjunction with Volume 2 of *Essential Readings in Light Metals*: *Aluminum Reduction Technology*. That volume contains the papers on cell start up that may be relevant.

Three sub-sections are included: Cell Lining Materials, Cathode Performance, and Spent Pot Lining. The subsections largely reflect the historical progression of papers published, but where possible, review and general papers are included first to provide an introduction to the topic.

ISO STANDARDS FOR TESTING OF CATHODE MATERIALS

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Abstract

ISO/TC 226 (Materials for the Production of Primary Aluminium) recently published a CD with 109 ISO Standards and 2 ISO Technical Specifications, covering the materials: Alumina, Pitch, Coke, Anodes, Cathodes and Ramming Paste. All standards are easily accessed from the CD. In addition to the test procedures for common room temperature properties, methods which characterize the cathode materials at operational conditions, have been developed. Examples are: Sodium expansion of cathodes with and without external pressure, rammability of paste and expansion and shrinkage of ramming paste. Additional studies of cathode property changes as function of temperature and time enable room temperature ISO standards to be extrapolated to operational conditions.

The standards are not only useful for material evaluation and quality control, but also important for development of more reliable mechanical-thermal-electrical models.

Introduction

Aluminium production takes place at 960 °C in an extremely corrosive environment. About 60 % of the production cost is in materials: Alumina, Fluorides, Carbonaceous materials, Refractory and Insulation materials. The quality and consistency of materials are essential for a successful process. These materials are sold freely between suppliers and customers in different countries with test results. Before ISO started its work these test results were based on internal test methods or national standards that could give different results for the same properties dependent on details in the test methods.

The aim of ISO/TC 226 (Materials for the production of primary aluminium) (formerly ISO/TC47/SC7) is to obtain unified and complete standard test methods that suppliers as well as customers have agreed to. ISO/TC 226 is presently responsible for 109 ISO standards and 2 ISO technical specifications, see Appendix.

ISO/TC 226 is organized into 5 working groups each dealing with the following topics: WG 1 Pitch, WG 2 Solid carbonaceous materials, WG 3 Smelter grade alumina, WG 4 Smelter grade fluorides, WG 5 Cryolite resistance of dense refractories.

The test methods are useful for quality control, contracts and for development work. The ISO standards have to a large extent been based on modifications of internal methods and national standards. ISO/TCS 226 has, however, seen it as a special task also to develop international standards that characterize the materials at process conditions. This has been accomplished by involving test laboratories as well as universities in addition to suppliers and aluminium producers.

A clickable CD for all the 109 standards has been published. The standards are organized under the following subtitles: Alumina, Pitch, Coke, Electrodes, Ramming paste, Fluorides, Refractory (only cryolite resistance).

Organization of Standardization Work and Choice of Methods

The development of the ISO standards for cathode materials has been a long struggle. During a 1.5 months sabbatical stay at RDC in Sierre in 1994 the existing standards for carbon materials of interest for the primary aluminium industry was reviewed, especially with respect to ASTM and DIN. At that time ISO had standards for alumina and fluorides, some for pitch and coke, but none for anodes, cathodes and ramming paste. An informal group was called together in Sierre after the review was completed. It consisted of participants from the 3 major cathode producers, 2 Norwegian smelters, RDC and Norwegian University of Science and Technology. This informal group was later incorporated into ISO/TC47/SC7 (later ISO/TC 226) as WG 2 (Solid carbonaceous material).

The carbon producers had most of the competence. They used different methods and wanted their specific method certified as an ISO standard. However, competence was also built up at Norwegian University of Science and Technology as well as in the Norwegian aluminium industry. The wish of the Norwegian aluminium industry had a high impact, as they were large buyers of cathodes and ramming paste material. The main standard test methods at room temperature were, to a large extent, modifications of ASTM, DIN or British standard. A major task was the choice of methods that simulates operating conditions. It was decided that the following methods had to be developed: Sodium expansion of cathode blocks, Rammability of paste and Expansion/Shrinkage of ramming paste. Sample preparation and baking procedures were also important issues.

Sodium expansion is heavily dependent on experimental conditions as bath composition, current density and electrolyte volume. It was necessary that the experimental conditions were described in great detail. As an example the sodium expansion as function of cryolite ratio is shown [1] (Fig. 1).

It was decided to make two standards, sodium expansion without external pressure and sodium expansion with 5 MPa external pressure. The bath composition, current density, temperatures, sample diameter and electrolysis time were the same for both standards.

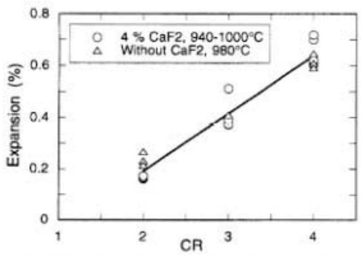

Figure 1: Sodium expansion test of semigraphitic cathode samples as a function of the cryolite ratio (mole NaF/mole AlF_3) [1].

Figure 2 shows the expansion/shrinkage of a ramming paste. A cylindrical ramming paste sample is heated at a rate of 90 °C/h to 950 °C (B), kept at 3 hours at 950 °C (C) and then cooled. The sample is viscous up to point A and the expansion to A is due to formation of vapour within the sample. A former test was to heat the sample to 950 °C, cool it and measure the dimension before and after the experiment. In the present case an expansion will be reported. The ISO/TC 226 opinion was, however, that the relevant property to measure is the shrinkage after the sample is solidified, *i.e.,* between A and C. In this temperature range shrinkage cracks can develop with possible penetration of aluminium.

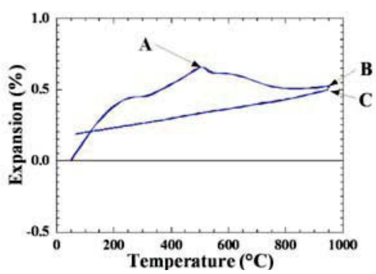

Figure 2: Expansion/shrinkage of ramming paste during continuous heating and cooling (ISO 14428).

An example of a test justification is the cryolite resistance for refractories. A very simple test was developed [2]. A 57 mm diameter hole with depth 40 mm was drilled into the refractory bricks. A salt mixture with 60 % cryolite and 40 % sodium fluoride was heated to 950 °C with a total time of 24 hours. The sample was cooled, cut diagonally through the hole and the penetration measured visually. At the same time the same materials were built into a trial cell which was stopped after 500 days. A very good correlation between test and plant results was found (Fig. 3) [2].

The cup test does not fully simulate the complex reactions taking place in the refractory. Siljan *et al*. [3] give a thorough discussion of the situation. Gaseous SiF_4 and especially Na will also be present, penetrate and react with the refractory. Allaire *et al.* [4] have proposed a test where bath and sodium penetration are determined separately. Nevertheless, the simple cup test is useful for ranking of cathode materials. Figure 4 shows that increased SiO_2 content in the refractory gives increased penetration resistance. This was also found by Brunk *et al.* [5]. These results had a large impact on the industries' choice of refractory materials. The test is being made into an ISO test (20292).

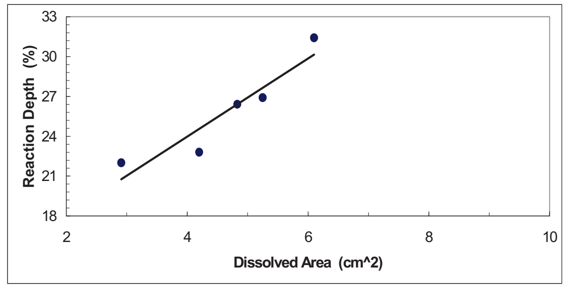

Figure 3: A comparison of laboratory investigation of measured dissolved area (cm^2) versus observed penetration depth in real-life cell linings. Experiments were performed in a 220 kA point-fed prebake cell with lifetime of 500 days. Reaction depth in the cell lining is given as percent of lining thickness reacted [2].

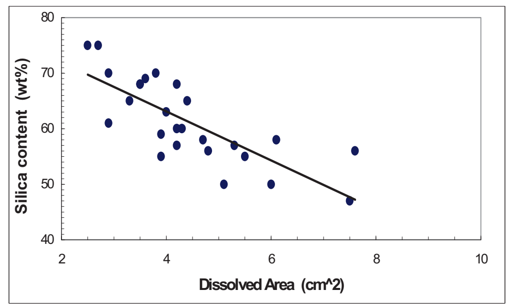

Figure 4: The effect of silica content on a measured dissolved area in alumino-silicate bricks. Linear regression trend-line determined by least-square analysis is included [2].

Developed Standards for Ramming Paste and Cathodes

The developed ISO methods are given in Tables 1 and 2.

Table 1. Test methods for ramming paste.

Method	ISO no.	Comments
UNBAKED PASTE		
Binder and aggregate content	14423	General characterization.
Loss of volatile matter	14425	A measure of carbon yield.
Baking loss	20202	A measure of carbon yield.
Apparent green density	14427	Used to calculate density change during baking.
Rammability	17544	Important to establish temperature window for ramming.
Expansion/shrinkage during baking	14428	Very important property. Too high shrinkage after solidification may give crack opening in cathode.
BAKED PASTE		
Electrical resistivity	11713	Not important.
Compressive strength	18515	Too high or too low strength is not wanted.
Open porosity	12985-2	Pore distribution more important than porosity.
Thermal expansion	14420	Not important.
Thermal conductivity	12987	Not important.
Baked density	20202	Should not be too low.
Ash content	8005	Not important but gives information about raw materials

Table 2. Test methods for carbon cathodes

Method	ISO no.	Comments
Bulk density, geometric	12985-1	Density is not directly relevant, but changes may indicate change of raw materials.
Bulk density, hydrostatic	12985-2	
Real density, xylene	9088	Indication of degree of graphitization.
Real density, helium	21687	Indication of degree of graphitization.
Open porosity	12985-2	Pore distribution more important than porosity.
Total porosity	12985 9088 21687	
Air permeability	15906	More important for anodes than for cathodes, but gives information about pore structure.
Compressive strength	18515	Less important than bending strength, but easy to measure.
Bending strength, 3 point	12986-1	The most important strength property.
Bending strength, 4 point	12986-2	The most important strength property.
Youngs (E) modulus		Important property, the dynamic E-modulus is easiest to measure.
Electrical resistivity	11713	Very important property, but note temperature and time coefficient.
Thermal conductivity	12987	Important design parameter, but note temperature and time coefficient.
Thermal exp.	14420	Not important as quality parameter.
Ash content	8005	Unimportant, but changes may indicate change of raw materials.
Sodium exp. with pressure	15379-1	Very important property. Expansion decreases with graphitization
Sodium exp. without pressure	15379-2	

A smelter's approval of a material is usually a major undertaking. In addition to evaluation of standard properties, extra testing is performed as well as performance test in trial cells. It is, however, important that the properties of an approved material stay constant, *i.e.*, no change in raw materials or production procedure. Such quality insurance is performed by using some easily performed tests which not necessarily is very relevant for the performance. Examples on such quality control procedures are given below.

Quality control of ramming paste (ISO number in parenthesis):

Apparent green density (20202)
Apparent baked density (14427)
Compressive strength of baked sample (18515)
Dilation / shrinkage (14428)

In addition storage durability should be checked by the rammability test (17544).

Quality control of cathode blocks (ISO number in parenthesis):

1. Real density (9088, 21687)
2. Apparent density (12988, 1-2).
3. Compressive strength (18515).
4. Electrical resistivity (both ⊥ and II) (11713)
5. Bending / shear strength (both ⊥ and II (12986, 1-2)
6. Ash content (8005).
7. Specification of slot cutting (for vibrated blocks).

Additional Non-standardized Studies

The ISO/TC 226 committee participants did also carry out additional tests which were not standardized, but which were of importance for thermo-electric-strain-stress modelling. Examples are Thermal expansion to 950 °C, Thermal and electrical conductivities to 950 °C, Static E-modulus, Sodium expansion as function of experimental parameters (pressure, bath composition, current density), Pore characterization by image analysis. Thermal and electrical conductivities are prime examples of such studies (Fig. 5) [6].

Note the very different temperature coefficients. The properties of non-graphitic materials also change with time due to graphitization (Fig. 6). With such data it is possible to extrapolate ISO standardized room temperature data.

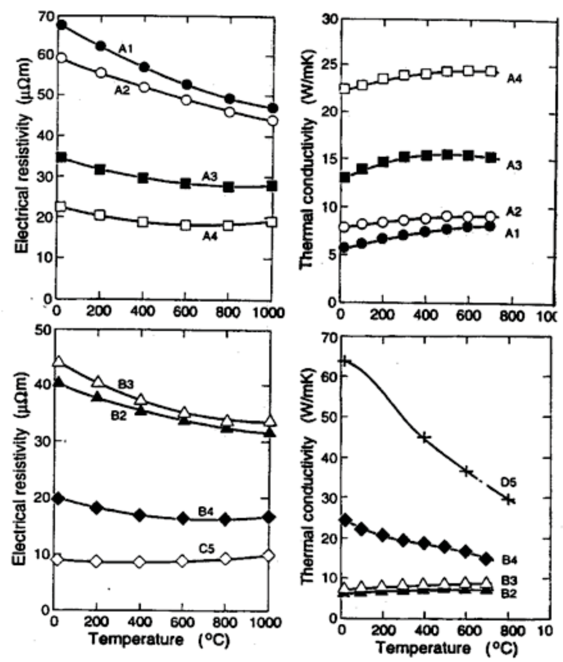

Figure 5: Electrical and thermal conductivity as function of temperature [6].

Figure 7 shows a strain stress modelling based on extrapolated room temperature ISO data. Sodium penetrates downward into the bottom of the cathode carbon block with time. The stress in the bottom of the cathode block increases while the stress on the top of the cathode block decreases due to the bottom expansion. The maximum stress on the surface of the cathode block is at arrow (12.2 MPa). The object of this modelling work was strengthening of the pot shell.

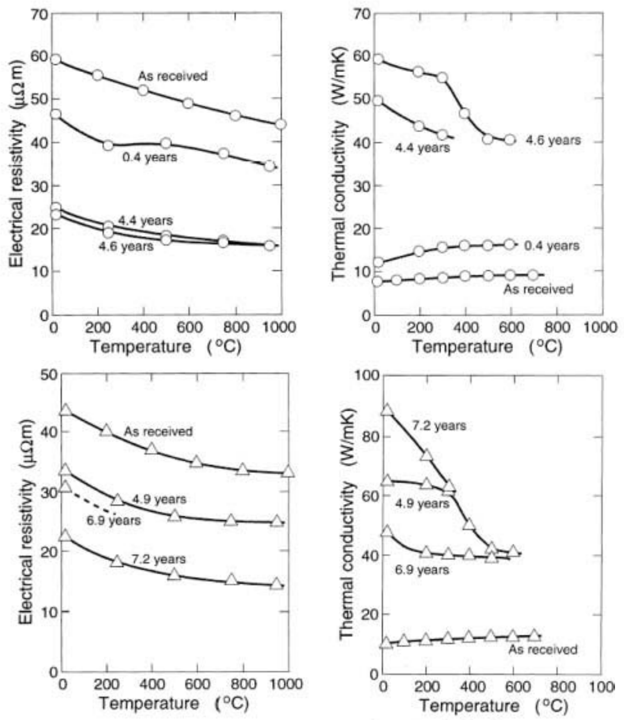

Figure 6: Electrical and thermal expansion as function of time. Changes with time are due to graphitization [6].

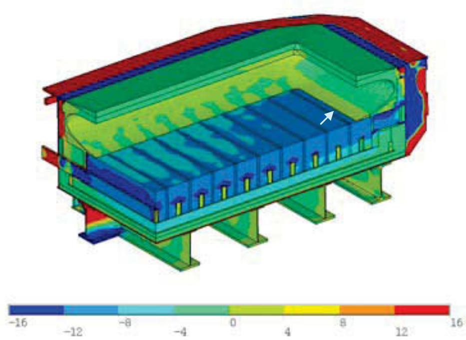

Figure 7: X-direction stress with thermal and sodium expansion, 400 days after start up (MPa)

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6. M. Sørlie, H. Gran and H.A. Øye, "Property Changes of Cathode Lining Materials during Cell Operation", Light Metals 1995, 497-506.

APPENDIX: The List of all the ISO/TC 226 Standards Included on the CD-Rom

Alumina	**Aluminium oxide primarily used for the production of aluminium**
ISO 802:1976	Preparation and storage of test samples
ISO 804:1976	Preparation of solution for analysis -- Method by alkaline fusion
ISO 805:1976	Determination of iron content -- 1,10-Phenanthroline photometric method
ISO 806:2004	Determination of loss of mass at 300 degrees C and 1 000 degrees C
ISO 900:1977	Determination of titanium content -- Diantipyrylmethane photometric method
ISO 901:1976	Determination of absolute density -- Pyknometer method
ISO 902:1976	Measurement of the angle of repose
ISO 903:1976	Determination of untamped density
ISO 1232:1976	Determination of silica content -- Reduced molybdosilicate spectrophotometric method
ISO 1617:1976	Determination of sodium content -- Flame emission spectrophotometric method
ISO 1618:1976	Determination of vanadium content -- N-Benzoyl-N-phenylhydroxylamine photometric method
ISO 2069:1976	Determination of calcium content -- Flame atomic absorption method
ISO 2070:1997	Determination of calcium content
ISO 2071:1976	Determination of zinc content -- Flame atomic absorption method
ISO 2072:1981	Determination of zinc content -- PAN photometric method
ISO 2073:1976	Preparation of solution for analysis -- Method by hydrochloric acid attack under pressure
ISO 2828:1973	Determination of fluorine content -- Alizarin complexone and lanthanum chloride spectrophotometric method
ISO 2829:1973	Determination of phosphorus content -- Reduced phosphomolybdate spectro-photometric method
ISO 2865:1973	Determination of boron content -- Curcumin spectrophotometric method
ISO 2865:1973 / Cor 1:1991	
ISO 2926:2005	Particle size analysis for the range 45 µm to 150 µm -- Method using electroformed sieves
ISO 2927:1973	Sampling
ISO 2961:1974	Determination of an adsorption index
ISO 3390:1976	Determination of manganese content -- Flame atomic absorption method
ISO 8008:2005	Determination of specific surface area by nitrogen adsorption
ISO 8220:1986	Determination of the fine particle size distribution (less than 60 µm) -- Method using electroformed sieves
ISO 17500:2006	Determination of attrition index
ISO 23202:2006	Determination of particles passing a 20 micrometre aperture sieve

Pitch	**Carbonaceous materials for the production of aluminium**
ISO 5939:1980	Pitch for electrodes -- Determination of water content -- Azeotropic distillation (Dean and Stark) method
ISO 5940:1981	Pitch for electrodes -- Determination of softening point by the ring-and-ball method
ISO 5940-2:2007	Pitch for electrodes -- Part 2: Determination of the softening point (Mettler softening point method)
ISO 6257:2002	Pitch for electrodes -- Sampling
ISO 6376:1980	Pitch for electrodes -- Determination of content of toluene-insoluble material
ISO 6791:1981	Pitch for electrodes -- Determination of contents of quinoline-insoluble material
ISO 6998:1997	Pitch for electrodes -- Determination of coking value
ISO 6998:1997 / Cor 1:1999	
ISO 6999:1983	Pitch for electrodes -- Determination of density -- Pycnometric method
ISO 8003:1985	Pitch for electrodes -- Measurement of dynamic viscosity
ISO 8006:1985	Pitch for electrodes -- Determination of ash
ISO 9055:1988	Pitch for electrodes -- Determination of sulfur content by the bomb method
ISO 10238:1999	Pitch for electrodes -- Determination of sulfur content by an instrumental method
ISO 12977:1999	Pitch for electrodes -- Determination of volatile matter content
ISO 12979:1999	Pitch for electrodes -- Determination of C/H ratio in the quinoline-insoluble fraction
ISO 21687:2007	Calcined coke – Determination of real density by helium pyknometry (can be used)
Coke	**Carbonaceous materials used in the production of aluminium**
ISO 5931:2000	Calcined coke and calcined carbon products -- Determination of total sulfur by the Eschka method
ISO 6375:1980	Coke for electrodes -- Sampling
ISO 6997:1985	Calcined coke -- Determination of apparent oil content -- Heating method
ISO 8004:1985	Calcined coke and calcined carbon products -- Determination of the density in xylene – Pyknometric method
ISO 8005:2005	Green and calcined coke -- Determination of ash content
ISO 8658:1997	Green and calcined coke -- Determination of trace elements by flame atomic absorption spectrometry (without precision)
ISO 8723:1986	Calcined coke -- Determination of oil content -- Method by solvent extraction
ISO 9406:1995	Green coke -- Determination of volatile matter content by gravimetric analysis
ISO 10142:1996	Calcined coke -- Determination of grain stability using a laboratory vibration mill
ISO 10143:1995	Calcined coke for electrodes -- Determination of the electrical resistivity of granules
ISO 10236:1995	Green coke and calcined coke for electrodes -- Determination of bulk density (tapped)
ISO 10237:1997	Calcined coke -- Determination of residual-hydrogen content
ISO 11412:1998	Calcined coke -- Determination of water content
ISO 12980:2000	Green coke and calcined coke for electrodes -- Analysis using an X-ray fluorescence method
ISO 12981-1:2000	Calcined coke -- Determination of the reactivity to carbon dioxide -- Part 1: Loss in mass method
ISO 12982-1:2000	Calcined coke -- Determination of the reactivity to air -- Part 1: Ignition temperature method
ISO 12984:2000	Calcined coke -- Determination of particle size distribution
ISO 14435:2005	Petroleum coke -- Determination of trace metals by inductively coupled plasma atomic emission spectrometry
ISO 20203:2005	Calcined coke -- Determination of crystallite size of calcined petroleum coke by X-ray diffraction
ISO 21687:2007	Calcined coke -- Determination of real density by helium pyknometry
Electrodes	**Carbonaceous materials used in the production of aluminium**
ISO 8007-1:1999	Sampling plans and sampling from individual units -- Part 1: Cathode blocks
ISO 8007-2:1999	Sampling plans and sampling from individual units -- Part 2: Prebaked anodes
ISO 8007-3:2003	Sampling plans and sampling from individual units -- Part 3: Sidewall blocks
ISO 9088:1997	Cathode blocks and prebaked anodes -- Determination of the density in xylene by a pyknometric method
ISO 11713:2000	Cathode blocks and baked anodes -- Determination of electrical resistivity at ambient temperature
ISO 12985-1:2000	Baked anodes and cathode blocks -- Part 1: Determination of apparent density using a dimensions method
ISO 12985-2:2000	Baked anodes and cathode blocks -- Part 2: Determination of apparent density and of open porosity using a hydrostatic method
ISO 12986-1:2000	Prebaked anodes and cathode blocks -- Part 1: Determination of bending/shear strength by a three-point method
ISO 12986-2:2005	Prebaked anodes and cathode blocks -- Part 2: Determination of flexural strength by the four-point method (without precision)
ISO 12987:2004	Anodes, cathodes blocks, sidewall blocks and baked ramming pastes -- Determination of the thermal conductivity using a comparative method
ISO 12988-1:2000	Baked anodes -- Determination of the reactivity to carbon dioxide -- Part 1: Loss in mass method

ISO 12988-2:2004	Baked anodes -- Determination of the reactivity to carbon dioxide -- Part 2: Thermogravimetric method
ISO 12989-1:2000	Baked anodes and sidewall blocks -- Determination of the reactivity to air -- Part 1: Loss in mass method
ISO 12989-2:2004	Baked anodes and sidewall blocks -- Determination of the reactivity to air -- Part 2: Thermogravimetric method
ISO 14420:2005	Baked anodes and shaped carbon products -- Determination of the coefficient of linear thermal expansion
ISO 15379-1:2004	Cathode block materials -- Part 1: Determination of the expansion due to sodium penetration with application of pressure
ISO 15379-2:2004	Cathode block materials -- Part 2: Determination of the expansion due to sodium penetration without application of pressure
ISO 15906:2007	Baked anodes -- Determination of the air permeability
ISO 17499:2006	Baked anodes -- Determination of baking level expressed by equivalent temperature
ISO 18515:2007	Cathode blocks and baked anodes -- Determination of compressive strength
ISO 21687:2007	Calcined coke -- Determination of real density by helium pyknometry (can be used)
Ramming paste	**Carbonaceous materials used in the production of aluminium**
ISO 8005: 2005	Green and calcined coke -- Determination of ash content (can be used)
ISO 11713:2000	Cathode blocks and baked anodes -- Determination of electrical resistivity at ambient temperature (can be used)
ISO 12985-2:2000	Baked anodes and cathode blocks -- Part 2: Determination of apparent density and of open porosity using a hydrostatic method (can be used)
ISO 12987: 2004	Anodes, cathodes blocks, sidewall blocks and baked ramming pastes -- Determination of the thermal conductivity using a comparative method (can be used)
ISO 14420:2005	Baked anodes and shaped carbon products -- Determination of the coefficient of linear thermal expansion
ISO 14422:1999	Cold-ramming pastes -- Methods of sampling
ISO/TS 14423:1999	Cold-ramming pastes -- Determination of effective binder content and aggregate content by extraction with quinoline, and determination of aggregate size distribution
ISO/TS 14425:1999	Cold-ramming pastes -- Determination of volatile-matter content of unbaked pastes
ISO 14427:2004	Cold and tepid ramming pastes -- Preparation of unbaked test specimens and determination of apparent density after compaction
ISO 14428:2005	Cold and tepid ramming pastes -- Expansion/shrinkage during baking

ISO 17544:2004	Cold and tepid ramming pastes -- Determination of rammability of unbaked pastes
ISO 18515:2007	Cathode blocks and baked anodes -- Determination of compressive strength (can be used)
ISO 20202:2004	Cold and tepid ramming pastes -- Preparation of baked test pieces and determination of loss on baking
Fluorides	**Cryolite, natural and artificial**
ISO 1619:1976	Preparation and storage of test samples
ISO 1620:1976	Determination of silica content -- Reduced molybdosilicate spectrophotometric method
ISO 1693:1976	Determination of fluorine content -- Modified Willard-Winter method
ISO 1694:1976	Determination of iron content -- 1,10-Phenanthroline photometric method
ISO 2366:1974	Determination of sodium content -- Flame emission and atomic absorption spectrophotometric methods
ISO 2367:1972	Determination of aluminium content -- 8-Hydroxyquinoline gravimetric method
ISO 3391:1976	Determination of calcium content -- Flame atomic absorption method
ISO 3393:1976	Determination of moisture content -- Gravimetric method
	Sodium fluoride primarily used for the production of aluminium
ISO 3429:1976	Determination of iron content -- 1,10-Phenanthroline photometric method
ISO 3430:1976	Determination of silica content -- Reduced molybdosilicate spectrophotometric method
ISO 3431:1976	Determination of soluble sulphates content -- Turbidimetric method
ISO 3566:1976	Determination of chlorides content -- Turbidimetric method
	Anhydrous hydrogen fluoride for industrial use
ISO 3699:1976	Determination of water content -- Karl Fischer method
	Cryolite, natural and artificial, and aluminium fluoride for industrial use
ISO 2830:1973	Determination of aluminium content -- Atomic absorption method
ISO 4280:1977	Determination of sulphate content -- Barium sulphate gravimetric method
ISO 5930:1979	Determination of phosphorus content -- Reduced molybdophosphate photometric method
ISO 5938:1979	Determination of sulphur content -- X-ray fluorescence spectrometric method
ISO 6374:1981	Determination of phosphorus content - Atomic absorption spectrometric method after extraction
Refractory	**Materials for the production of primary aluminium**
ISO CD 20292	Dense refractory bricks –Determination of cryolite resistance