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Carbonaceous materials used in the production of aluminium — Baked anodes and sidewall blocks — Determination of the reactivity to air —

Part 2:
Thermogravimetric method

Produits carbonés utilisés pour la production de l'aluminium — Anodes et blocs de façade cuits — Détermination de la réactivité à l'air —

Partie 2: Méthode thermogravimétrique

Reference number
ISO 12989-2:2004(E)

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Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 12989-2 was prepared by Technical Committee ISO/TC 47, *Chemistry*, Subcommittee SC 7, *Aluminium oxide, cryolite, aluminium fluoride, sodium fluoride, carbonaceous products for the aluminium industry*.

ISO 12989 consists of the following parts, under the general title *Carbonaceous materials used in the production of aluminium — Baked anodes and sidewall blocks — Determination of the reactivity to air*:

- *Part 1: Loss in mass method*
- *Part 2: Thermogravimetric method*

Introduction

Comparison of air reactivities, or air reaction rates, and air dusting rates is useful in selecting raw materials for the manufacture of commercial electrodes for specific smelting technologies in the production of aluminium.

Air reactivities are used to quantify the tendency of a carbon artifact to react with air. Carbon consumed by this unwanted side reaction is unavailable for the primary reaction of reducing alumina to the metal. Air reactivities and the dusting rate are used by some companies to quantify the tendency of the coke aggregate or binder coke of a carbon artifact to selectively react with air. Preferential attack of the binder coke or coke aggregate of a carbon artifact by air causes some carbon to fall off as dust, making the carbon unavailable for the primary reaction of reducing alumina and, more importantly, reducing the efficiency of the reduction cell.

Air reactivities are used for evaluating the effectiveness of beneficiation processes and for research purposes.

Sampling guidelines are under development.

This part of ISO 12989 is based on ASTM D 6559-00.

INTERNATIONAL STANDARD **ISO 12989-2:2004(E)**

Carbonaceous materials used in the production of aluminium — Baked anodes and sidewall blocks — Determination of the reactivity to air —

Part 2
Thermogravimetric method

WARNING — This part of ISO 12989 does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this part of ISO 12989 to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This part of ISO 12989 allows the determination by thermogravimetric analysis (TGA) of air reactivities and dusting of shaped carbon electrodes used in the aluminium-reduction industry. Many types of apparatus are available, with various thermal conditions, sample-size capabilities, materials of construction and procedures for determining the mass loss and subsequent rate of reaction. This test method standardizes the variables of sample dimensions, reaction times and temperatures, and provides a mathematical method to normalize the gas velocity over the exposed surfaces, such that results obtained on different types of apparatus are correlatable.

2 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

2.1
air dusting rate

α_{d}

normalized rate at which carbon falls off the carbon artifact during the test

NOTE The dusting rate is expressed in milligrams per square centimetre per hour.

2.2
final air reactivity

α_{f}

rate of mass loss of the carbon artifact during the final 30 min of exposure to air in the reaction chamber divided by the initial exposed surface area of a sample having the form of a right cylinder

NOTE The final air reactivity is expressed in milligrams per square centimetre per hour.

2.3
initial air reactivity

α_{i}

rate of mass loss of the carbon artifact during the first 30 min of exposure to air in the reaction chamber divided by the initial exposed surface area of a sample having the form of a right cylinder

NOTE The initial air reactivity is expressed in milligrams per square centimetre per hour.

2.4
total air reactivity

α_T

rate of mass loss of the carbon artifact (including dusting) during the total time that the sample is exposed to air (180 min) in the reaction chamber divided by the initial exposed surface area of a sample having the form of a right cylinder

NOTE The total air reactivity is expressed in milligrams per square centimetre per hour.

3 Principle

The air dusting rate and the initial, final and total air reactivities are determined by passing air at a flow rate giving a standard velocity of reactant gas around cylindrically shaped carbon artifacts under nearly isothermal conditions for a specified length of time. The air reactivities are determined by continuously monitoring the mass loss of the sample. The air dusting rate is determined by collecting and determining the mass of the carbon particles that fall off the sample during reaction.

4 Apparatus

4.1 Air reactivity apparatus, as simple as possible and commensurate with the aims of the test.

The principal criterion is that the reaction rate be determined under isothermal conditions and be unaffected by physical and chemical properties inherent in the apparatus (such as gas diffusion patterns, gas temperature, exposed sample surface area, and so forth). A typical apparatus that has been found to be suitable is illustrated in Figure 1.

4.2 Furnace and controller, capable of maintaining the temperature constant to within ± 2 °C in the 100-mm reaction zone in which the sample is centred.

A typical apparatus (Figure 1) employs a three-zone heating element and associated controls to accomplish this, but other types of heaters such as tapered windings or long linear heaters are also suitable. The control thermocouple is a grounded type and shall be located within the reaction chamber near the surface of the test sample. This is to allow the furnace controller to compensate for the exothermic reactions that occur when the furnace is used for air reactivity testing. The control thermocouple shall be positioned 4 mm ± 1 mm from the side surface of the sample and within 5 mm vertically of the centre of the reaction chamber. The furnace shall be large enough to accommodate the reaction chamber.

4.3 Reaction chamber, consisting of a vertical tube constructed of a material capable of withstanding the temperature of the reaction and with a sufficiently large inside diameter to accomodate the sample and sample suspension device while not affecting the gas flow past the sample. An inside diameter of 100 mm ± 25 mm is recommended.

The reaction chamber shall be constructed with a removable dust collection cup at the bottom capable of capturing all the dust that falls off the sample during the test. The most common materials of construction are quartz and Incone(1).

4.4 Sample suspension device, capable of supporting the sample in the reaction chamber for the duration of the test and which should be reusable.

The sample suspension device shall not change in mass during the test, shall not affect the flow pattern of the gas past the sample, shall not limit the gas-accessible surface area of the test sample and shall not interfere with the production of dust by the sample. A typical sample suspension device is illustrated in Figure 2.

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1) Inconel is an example of a suitable product available commercially. This information is given for the convenience of users of this part of ISO 12989 and does not constitute an endorsement by ISO of this product.

4.5 Gas preheat tube, extending into the first heating zone of the reaction chamber, to preheat the gas prior to entering the reaction chamber.

The length and diameter of the tube may vary, as long as the gas leaving the tube is at the same temperature as the reaction chamber. The inlet gas shall leave the preheat tube downward to prevent channelling of the gas through the reaction chamber and to prevent plugging of the preheat tube with carbon dust.

4.6 Balance, capable of measuring the mass (approximately 200 g maximum) of the sample and sample suspension device to the nearest 0,01 g continuously throughout the duration of the test.

4.7 Gas flow meter, capable of measuring the flow rate of the gas entering the reaction chamber.

All gas flow rates shall be maintained at the rate specified for the particular test apparatus.

4.8 Needle valve, to make fine adjustments to the gas flow rate.

4.9 Pressure-reducing valve, to reduce the pressure of the compressed gas to near atmospheric pressure before it enters the gas flow meter.

4.10 Thermocouple(s), (for example, three couples in the same sheath with probes located at the tip, and at 50 mm and 100 mm above the tip; or a packet of thermocouples with tips located at similar known distances) capable of being inserted into the reaction chamber to calibrate the furnace zone controllers. An optional thermocouple may be used to monitor reaction temperatures.

Some users find continuous temperature measurement of the central part of the reaction chamber to be of value.

4.11 Callipers, or other suitable device, capable of measuring the sample diameter and height to within 0,01 mm to calculate the geometric surface area exposed to the test gas.

4.12 Optional equipment, including, but not limited to, automatic control devices, multi-channel line selectors and personal computers to automate data recording, processing, reporting and storage.

5 Reagents

Use only reagents of recognized analytical grade, unless otherwise specified.

5.1 Nitrogen, 99,95 %.

5.2 Air, containing less than 0,1 % by mass of moisture.

6 Sample

6.1 Prepare the sample by coring and then cutting or machining to a right cylinder, 50 mm ± 1,0 mm high and 50 mm ± 1,0 mm in diameter. Most sample suspension devices (4.4) require a hole of about 3 mm in diameter to be drilled vertically through the centre of the cylinder to accommodate a suspension wire.

The sampling plans for anodes and cathode blocks given in ASTM D 6353 and D 6354 may be used if desired.

The finished sample shall be smooth and free of visible cracks and gouges.

6.2 Dry the finished sample in an oven at 105 °C ± 5 °C to constant mass.

6.3 Free the finished sample from loose carbon dust and impurities from the shaping process by blowing with dry air.

7 Calibration

7.1 The purpose of this procedure is to establish a relationship between the controller settings for the three-zone furnace and the actual temperature inside the reaction chamber in the region of the sample. The length of the calibrated zone shall be 100 mm.

7.2 Insert a multi-probe thermocouple (4.10) into the zone where the sample will be located. Align the middle probe of the multi-probe thermocouple with the sample position.

7.3 Connect the middle thermocouple (4.10) to the main controller, set at 525 °C.

7.4 Connect the other two thermocouples to any temperature-indicating device. A recording temperature indicator is required to determine the actual temperature profile.

7.5 Allow 4 h for the furnace to reach equilibrium under nitrogen purge (at a rate of gas flow in accordance with 7.7).

7.6 Adjust the zone temperature controllers until all three temperature indicators are within ± 2 °C of each other.

7.7 The gas flow rate for the reference analysis is based on 250 l/h ± 5 l/h (at ambient temperature) for a sample diameter of 50 mm in a reaction chamber with an inside diameter of 100 mm. Reactivities determined with this test method are affected by the velocity of the gas sweeping the reaction surfaces during the test. This requires gas flow rates to be such that the velocity through the annular space between the sample and reaction-chamber wall is constant for various sizes of reaction chambers. The flow rate for other annular cross-sectional areas is determined by multiplying the reference flow rate (250 l/h) by the ratio of the annular area of the test system to the annular area of the reference system, in accordance with Equations (1) and (2):

$$A_{\mathrm{R}} = \left(\frac{D_{\mathrm{i,t}}{}^{2} - D_{\mathrm{s}}{}^{2}}{D_{\mathrm{i,rt}}{}^{2} - D_{\mathrm{rs}}{}^{2}} \right) \qquad (1)$$

where

A_{R} is the ratio of the annular area of the test system to that of the reference system;

$D_{\mathrm{i,t}}$ is the internal diameter of the test reaction chamber;

$D_{\mathrm{i,rt}}$ is the internal diameter of the reference reaction chamber;

D_{s} is the outside diameter of test sample;

D_{rs} is the outside diameter of the reference sample;

and

$$q_{\mathrm{v},G} = \left(q_{v,rG} \right) \times A_{\mathrm{R}} \qquad (2)$$

where

$q_{\mathrm{v},G}$ is the volume flow rate, expressed in litres per hour, calibrated to the annular area of the test system;

$q_{\mathrm{v},rG}$ is the volume flow rate, expressed in litres per hour, for the reference annular area;

A_{R} is the ratio of the annular area of the test system to that of the reference system.

EXAMPLE The volume flow rate for a test system using a test sample with a diameter of 50,8 mm in a reaction chamber with an internal diameter of 75 mm is calculated as

$$A_\mathrm{R} = \left(\frac{75^2 - 50{,}8^2}{100^2 - 50^2} \right) = \frac{3\,044}{7\,500} = 0{,}406$$

where

$D_{\mathrm{i,t}}$ is 75 mm;

$D_{\mathrm{i,rt}}$ is 100 mm;

D_s is 50,8 mm;

D_rs is 50 mm;

and

$$q_{\mathrm{v},G} = 250 \times 0{,}406 = 102$$

where

$q_{\mathrm{v},G}$ is the volume flow rate, equal to 102 l/h, calculated for the test system;

$q_{\mathrm{v},rG}$ is equal to 250 l/h;

A_R is equal to 406.

8 Procedure

8.1 Preheat the reactor tube to 525 °C ± 2 °C.

8.2 Purge the reaction chamber with nitrogen at the flow rate determined in 7.7.

8.3 Weigh and record the mass m_i of the sample to the nearest 0,01 g.

8.4 Measure the sample diameter (D_s), sample height (h_s), and diameter of the centre hole (D_H) to an accuracy of ± 0,01 mm to calculate surface area for the reaction in accordance with Equation (3) in 9.1.

8.5 Insert the sample into the reaction chamber by placing the sample in the sample suspension device and suspend the sample from the balance.

8.6 Preheat the sample under nitrogen purge for 30 min.

8.7 Tare the balance according to the balance manufacturer's instructions.

8.8 Switch the gas introduced to the reaction chamber from nitrogen to air after 30 min in the nitrogen preheat, and maintain the flow rate as specified in 7.7.

8.9 Record the mass of the sample every minute for the duration of the test. The test duration for air reactivity is 3 h (180 min).

8.10 Remove the sample from the reaction chamber as soon as possible after the test time has expired, as the dusting parameter will be affected. Exercise care so the sample does not strike the sides of the reaction chamber upon removal, which could result in dislodging particles and adding to the mass of dust.

8.11 Remove the dust collection cup from the bottom of the reaction chamber and place in a desiccator until cool.

8.12 Weigh the dust collected in the dust collection cup and record as m_d.

9 Calculation of results

9.1 Exposed surface area of the sample

Calculate the total exposed surface area of the finished sample by adding the calculated area of the top surface minus the centre hole to the calculated area of the bottom surface minus the centre hole, in accordance with Equation (3):

$$A_E = (\pi D_s h_s + \frac{2\pi}{4}\left[D_s{}^2 - D_H{}^2\right])/100 \qquad (3)$$

where

A_E is the exposed surface area, expressed in cubic centimetres;

D_s is the sample diameter, expressed in millimetres;

D_H is the diameter, expressed in millimetres, of central hole (if any);

h_s is the sample height, expressed in millimetres.

9.2 Total air reactivity

Calculate the total air reactivity, α_T, in accordance with Equation (4):

$$\alpha_T = \frac{1\,000\,(m_i - m_f)}{3A_E} \qquad (4)$$

where

α_T is the total air reactivity, expressed in milligrams per square centimetre per hour;

m_i is the initial sample mass, expressed in grams;

m_f is the final sample mass, expressed in grams;

A_E is the exposed surface area, expressed in square centimetres.

9.3 Initial air reactivity

Calculate the initial air reactivity, α_i, in accordance with Equation (5):

$$\alpha_i = \frac{2\,000\,(m_i - m_{30})}{A_E} \qquad (5)$$

where

α_i is the initial air reactivity, expressed in milligrams per square centimetre per hour;

m_{30} is the sample mass, expressed in grams, after 30 min of test exposure;

A_E is the exposed surface area, expressed in square centimetres.

9.4 Final air reactivity

Calculate the final air reactivity, α_f, in accordance with Equation (6):

$$\alpha_f = \frac{2\,000(m_{150} - m_f)}{A_E} \tag{6}$$

where

α_f is the final air reactivity, expressed in milligrams per square centimetre per hour;

m_{150} is the sample mass, expressed in grams, after 150 min of test exposure.

9.5 Air dusting rate

Calculate the air dusting rate, (α_d), in accordance with Equation (7):

$$\alpha_d = \frac{1\,000\,m_d}{3A_E} \tag{7}$$

where

α_d is the dusting rate, expressed in milligrams per square centimetre per hour, during 3 h of test exposure;

m_d is the mass, expressed in grams, of dust collected during test;

A_E is the exposed surface area, expressed in square centimetres.

10 Precision and bias

10.1 Precision

The precision was determined by an inter-laboratory study conducted in accordance with ASTM Practice E 691. Six laboratories tested nine materials (seven anodes and two cathodes). The linear regression of the results showed that the repeatability and reproducibility are dependent on the average value of the measured reactivity or rate. Consequently, a regression equation is used in the precision statements. Based on this study, the criteria in 10.2 and 10.3 shall be used for judging the acceptability of results (95 % probability).

10.2 Repeatability

10.2.1 Repeatability limits

Duplicate values, expressed in milligrams per square centimetre per hour, by the same operator using the same equipment shall not be considered suspect unless the determined values differ by more than the r value given by the following equations.

10.2.2 Total air reactivity

The repeatability of the total air reactivity is calculated according to the equation

$$r_{\alpha\mathrm{T}} = (0{,}203\,2 \times \bar{\alpha}_{\mathrm{T}}) + 8{,}023\,1$$

where

$r_{\alpha\mathrm{T}}$ is the repeatability of the total air reactivity;

$\bar{\alpha}_{\mathrm{T}}$ is the average of duplicate total air reactivity values [applicable between 13 mg/(cm^2·h) and 62 mg/(cm^2·h) total air reactivity].

10.2.3 Initial air reactivity

The repeatability of the initial air reactivity is calculated according to the equation

$$r_{\alpha\mathrm{i}} = (0{,}738\,1 \times \bar{\alpha}_{\mathrm{i}}) + 1{,}264\,3$$

where

$r_{\alpha\mathrm{i}}$ is the repeatability of the initial air reactivity;

$\bar{\alpha}_{\mathrm{i}}$ is the average of duplicate initial air reactivity values [applicable between 4 mg/(cm^2·h) and 16 mg/(cm^2·h) initial air reactivity].

10.2.4 Final air reactivity

The repeatability of the final air reactivity is calculated according to the equation

$$r_{\alpha\mathrm{f}} = (0{,}177\,1 \times \bar{\alpha}_{\mathrm{f}}) + 6{,}580\,9$$

where

$r_{\alpha\mathrm{f}}$ is the repeatability of the final air reactivity;

$\bar{\alpha}_{\mathrm{f}}$ is the average of duplicate final air reactivity values [applicable between 21 mg/(cm^2·h) and 89 mg/(cm^2·h) final air reactivity].

10.2.5 Air dusting rate

The repeatability of the air dusting rate is calculated according to the equation

$$r_{\alpha\mathrm{d}} = (1{,}221\,6 \times \bar{\alpha}_{\mathrm{d}}) + 0{,}991\,3$$

where

$r_{\alpha\mathrm{d}}$ is the repeatability of the air dusting rate;

$\bar{\alpha}_{d}$ is the average of duplicate air dusting rate values [applicable between 0 mg/(cm^2·h) and 2,5 mg/(cm^2·h) air dusting rate].

10.3 Reproducibility limits

10.3.1 General

The values, expressed in milligrams per square centimetre per hour, reported by each of two laboratories, representing the arithmetic average of duplicate determinations, shall not be considered suspect unless the reported values differ by more than the R value given by the following equations.

10.3.2 Total air reactivity

The reproducibility of the total air reactivity is calculated according to the equation

$$R_{\alpha\mathrm{T}} = (0{,}520\,7 \times \bar{\alpha}_{\mathrm{T}} + 1{,}724\,2$$

where

$R_{\alpha\mathrm{T}}$ is the reproducibility of the total air reactivity;

$\bar{\alpha}_{\mathrm{T}}$ is the average of duplicate total air reactivity values [applicable between 13 mg/(cm^2·h) and 62 mg/(cm^2·h) total air reactivity].

10.3.3 Initial air reactivity

The reproducibility of the initial air reactivity is calculated according to the equation

$$R_{\alpha\mathrm{i}} = (0{,}700\,7 \times \bar{\alpha}_{\mathrm{i}} + 4{,}176\,2$$

where

$\mathrm{R}_{\alpha\mathrm{i}}$ is the reproducibility of the initial air reactivity;

$\bar{\alpha}_{\mathrm{i}}$ is the average of duplicate initial air reactivity values [applicable between 4 mg/(cm^2·h) and 16 mg/(cm^2·h) initial air reactivity].

10.3.4 Final air reactivity

The reproducibility of the final air reactivity is calculated according to the equation

$$R_{\alpha\mathrm{f}} = (0{,}669\,4 \times \bar{\alpha}_{\mathrm{f}}) + 3{,}715\,4$$

where

$R_{\alpha\mathrm{f}}$ is the reproducibility of the final air reactivity;

$\bar{\alpha}_{\mathrm{f}}$ is the average of duplicate final air reactivity values [applicable between 21 mg/(cm^2·h) and 89 mg/(cm^2·h) final air reactivity].

10.3.5 Air dusting rate

The reproducibility of the air dusting rate is calculated according to the equation

$$R_{\alpha\mathrm{d}} = (2{,}812 \times \bar{\alpha}_{d}) + 0{,}690\,6$$

where

$R_{\alpha\mathrm{d}}$ is the reproducibility of the air dusting rate;

$\overline{\alpha}_d$ is the average of duplicate air dusting rate values [applicable between 0 mg/(cm^2·h) and 2,5 mg/(cm^2·h) air dusting rate].

10.4 Bias

This procedure has no bias because the values of air reactivity are defined in terms of this test method.

11 Test report

The test report shall include the following information:

a) an identification of the sample;

b) the method used by reference to this part of ISO 12989, i.e.12989-2:2004;

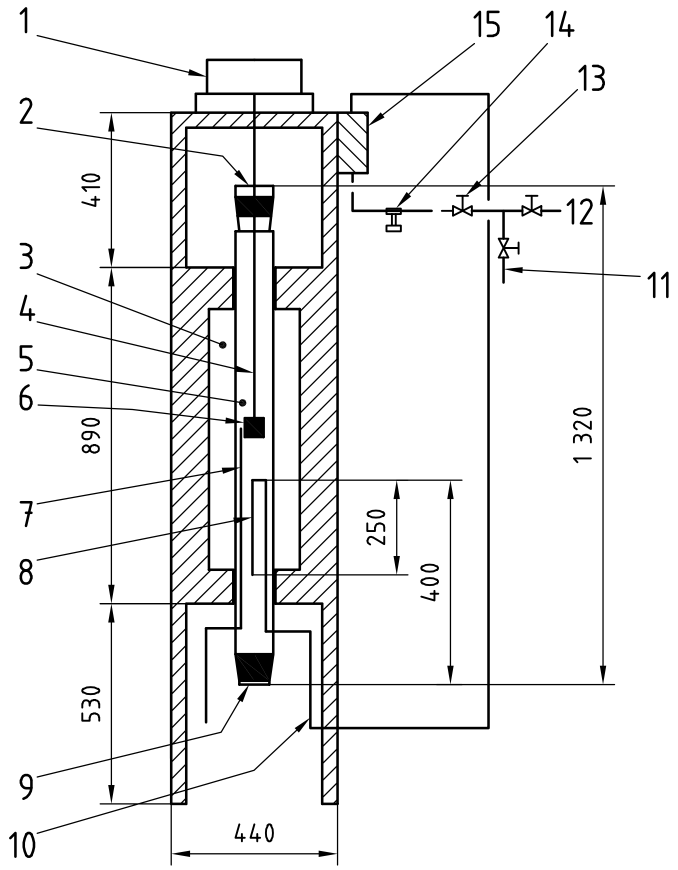
c) the date of the test;

d) the results of reactivity, expressed to the nearest 0,1 mg/(cm^2·h);

e) any unusual features noted during the determination;

f) any operation not included in this part of ISO 12989.

Dimensions in millimetres

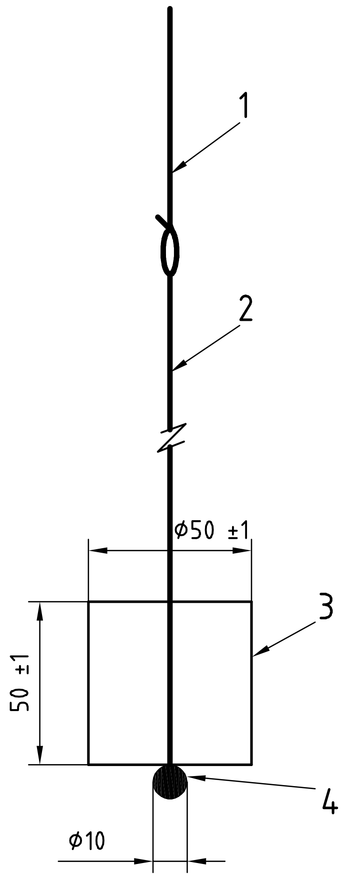


Key

1	balance	9	dust-collection cup
2	gas outlet (10 mm hole)	10	gas inlet
3	three-zone furnace	11	air or CO_2
4	connecting wire (see Figure 2)	12	N_2
5	reaction chamber	13	pressure-reducing valve
6	sample	14	needle valve
7	control thermocouple	15	flow meter
8	preheat tube		

Figure 1 — Typical air reactivity apparatus

Dimensions in millimetres



Key

1 suspension wire (Nichrome[2])

2 sample support wire (platinum, 1 mm diameter)

3 cylindrical sample

4 stainless steel ball

Figure 2 — Typical sample suspension arrangement

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[2] Nichrome is an example of a suitable product available commercially.This information is given for the convenience of users of this part of ISO 12989 and does not constitute an endorsement by ISO of this product.

Bibliography

[1] ASTM D 6353, *Standard Guide for Sampling Plan and Core Sampling for Prebaked Anodes Used in Aluminum Production*

[2] ASTM D 6354, *Standard Guide for Sampling Plan and Core Sampling of Carbon Cathode Blocks Used in Aluminum Production*

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