



Standard Test Method for Determination of TGA CO₂ Reactivity of Baked Carbon Anodes and Cathode Blocks¹

This standard is issued under the fixed designation D6558; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

^{ε1} NOTE—SI unit formatting was corrected editorially in December 2015.

1. Scope

1.1 This test method covers the thermogravimetric (TGA) determination of CO₂ reactivity and dusting of shaped carbon anodes and cathode blocks used in the aluminum reduction industry. The apparatus selection covers a significant variety of types with various thermal conditions, sample size capability, 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 temperature, gas velocity over the exposed surfaces, and reaction time such that results obtained on different apparatuses are correlatable.

1.2 The values stated in SI units are to be regarded as standard. No other units of measurement are included in this standard.

1.3 *This standard 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 standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 ASTM Standards:²

[D6353 Guide for Sampling Plan and Core Sampling for Prebaked Anodes Used in Aluminum Production](#)

[D6354 Guide for Sampling Plan and Core Sampling of Carbon Cathode Blocks Used in Aluminum Production](#)

[E691 Practice for Conducting an Interlaboratory Study to Determine the Precision of a Test Method](#)

¹ This test method is under the jurisdiction of ASTM Committee D02 on Petroleum Products, Liquid Fuels, and Lubricants and is the direct responsibility of Subcommittee D02.05 on Properties of Fuels, Petroleum Coke and Carbon Material.

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² For referenced ASTM standards, visit the ASTM website, www.astm.org, or contact ASTM Customer Service at service@astm.org. For *Annual Book of ASTM Standards* volume information, refer to the standard's Document Summary page on the ASTM website.

3. Terminology

3.1 Definitions of Terms Specific to This Standard:

3.1.1 *dusting, n*—that quantity of carbon that falls off the carbon artifact while in the reaction chamber and is collected in the container at the bottom of the reaction chamber.

3.1.2 *final CO₂ reactivity, n*—the mass loss of the carbon artifact during the final 30 min of exposure to CO₂ in the reaction chamber divided by the initial geometric (right cylindrical) exposed surface area of the sample, expressed as milligrams per centimetre squared per hour.

3.1.3 *initial CO₂ reactivity, n*—the mass loss of the carbon artifact during the first 30 min of exposure to CO₂ in the reaction chamber divided by the initial geometric (right cylindrical) exposed surface area of the sample, expressed as milligrams per centimetre squared per hour.

3.1.4 *total CO₂ reactivity, n*—the total mass loss of the carbon artifact (including dusting) during the total time that the sample is exposed to CO₂ (420 min) in the reaction chamber divided by the initial geometric (right cylindrical) exposed surface area of the sample, expressed as milligrams per centimetre squared per hour.

4. Summary of Test Method

4.1 Initial, final, and total CO₂ reactivity and dusting are determined by passing carbon dioxide gas at flow rates giving a standard velocity of reactant gas around cylindrically shaped carbon artifacts under isothermal conditions for a specified length of time. The reactivity is determined by continuously monitoring the sample mass loss. The dusting term is determined by collecting and determining the mass of carbon particles that fall off the sample during reaction.

5. Significance and Use

5.1 The CO₂ reactivity rates are used to quantify the tendency of a carbon artifact to react with carbon dioxide. Carbon consumed by these unwanted side reactions is unavailable for the primary reactions of reducing alumina to the primary metal. CO₂ dusting rates are used to quantify the tendency of the coke aggregate or binder coke of a carbon artifact to selectively react with these gases. Preferential attack

of the binder coke or coke aggregate of a carbon artifact by these gases causes some carbon to fall off or *dust*, making the carbon unavailable for the primary reaction of reducing alumina and, more importantly, reducing the efficiency of the aluminum reduction cell.

5.2 Comparison of CO₂ reactivity and dusting rates is useful in selecting raw materials for the manufacture of commercial anodes for specific smelting technologies in the aluminum reduction industry.

5.3 CO₂ reactivity rates are used for evaluating effectiveness and beneficiation processes or for research purposes.

6. Apparatus

6.1 The apparatus to be used should be as simple as possible and be commensurate with what is to be achieved, the principal criteria being that the reaction rate is to be determined under isothermal conditions and unaffected by physical and chemical properties inherent to 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 Fig. 1.

6.1.1 *Furnace and Controller*, capable of maintaining constant temperature, within $\pm 2\text{ }^\circ\text{C}$ in the 100 mm region centered on the specimen. The example apparatus of Fig. 1 employs a three zone heating element and associated controls to accomplish this, but other methods 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 to allow the furnace controller to adjust to exothermic reactions, which occur during air reactivity tests, if the furnace is also used for air reactivity testing. The control thermocouple shall be positioned $4\text{ mm} \pm 1\text{ mm}$ from the side sample surface and centered vertically within 5 mm of the center. The furnace shall be large enough to accept the reaction chamber.

6.1.1.1 *Reaction Chamber*, consisting of a vertical tube constructed of a material capable of withstanding the temperature of the reaction ($960\text{ }^\circ\text{C} \pm 2\text{ }^\circ\text{C}$) with sufficient inside diameter (ID) to accept the sample and sample holder while not affecting the gas flow to and from the sample ($100\text{ mm} \pm 25\text{ mm}$ ID is recommended). The reaction chamber is to be constructed with a dust collection cup at the bottom that is removable and capable of capturing all the dust that falls off the sample during the test. The most common materials of construction are quartz and Inconel.

6.1.1.2 *Sample Holders*, capable of supporting the sample in the reaction chamber for the duration of the test and should be capable of being reusable. The sample holder shall not change in mass during the test, affect the diffusion pattern of the gases to or from the sample, limit the gas accessible surface area of the test sample, or interfere with the free fall of dust from the sample. A typical sample holder is illustrated in Fig. 2.

6.1.1.3 *Gas Preheat Tube*, extending into the first heat zone of the reaction chamber to preheat the gases prior to entering the reaction chamber. The length and diameter of the tube can vary as long as the gases exiting the tube are the same

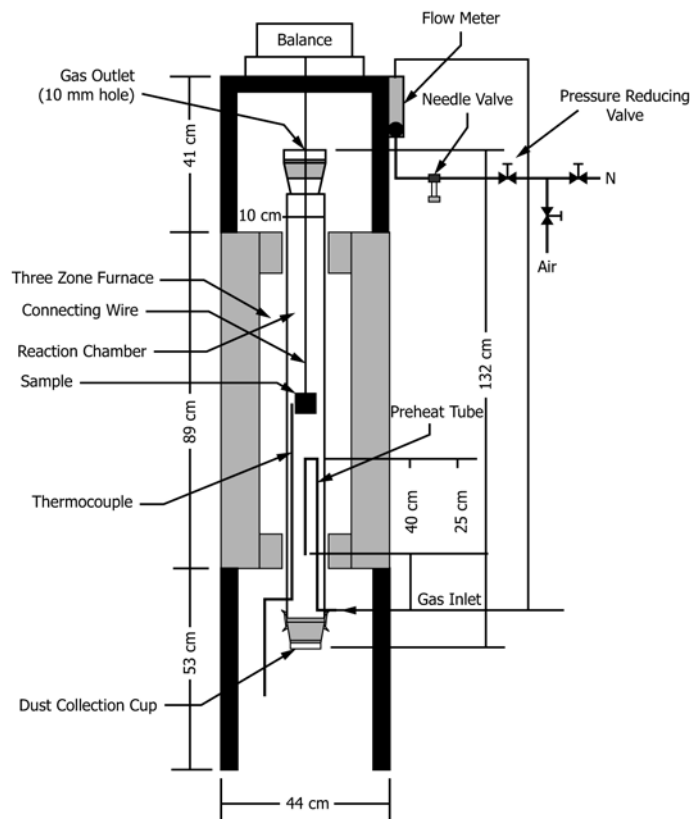


FIG. 1 Typical CO₂ Reactivity Apparatus

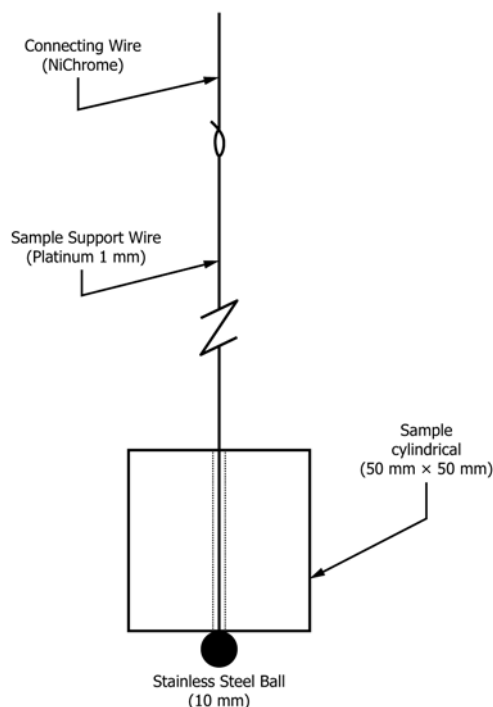


FIG. 2 Typical Sample Holder

temperature as the reaction chamber. The inlet gas shall exit the preheat tube downward to prevent channeling of the gas through the reaction chamber and to prevent plugging of the preheat tube with carbon dust.

6.1.1.4 *Balance*, capable of measuring the mass of the sample and sample holder (a maximum of approximately 200 g) continuously throughout the duration of the test to the nearest 0.01 g.

6.1.1.5 *Gas Flow Meter*, capable of monitoring the gas flow rate into the reaction chamber. All gas flow rates are to be maintained at the rate determined for the particular test apparatus.

6.1.1.6 *Needle Valve*, to make fine adjustments to the gas flow rate.

6.1.1.7 *Pressure Reducing Valve*, to reduce the pressure of the compressed gases to near atmospheric pressure prior to entering the gas flow meter through the needle valve.

6.1.1.8 *Thermocouple(s)*, 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 internal reaction chamber to be of value.

6.1.1.9 *Calipers*, or other suitable device, capable of measuring to within 0.01 mm for determining the sample diameter and height to calculate geometric surface area exposed to the test gases.

6.1.1.10 *Optional Equipment*, including, but not limited to, automatic control devices, multichannel line selector, and personal computer to automate data gathering, manipulation, reporting, and storage.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade, conforming to the specifications of the Committee on Analytical Reagents of the American Chemical Society.

7.1.1 *Nitrogen*—99.95 %.

7.1.2 *Carbon Dioxide*—99.95 %.

8. Sampling

8.1 Shape the carbon specimen by coring and cutting or machining to a right cylindrical geometry, with a length of $50 \text{ mm} \pm 1.0 \text{ mm}$ and diameter of $50 \text{ mm} \pm 1.0 \text{ mm}$. Most sample holders require a hole of about 3 mm diameter to be drilled vertically through the center of the cylinder to accommodate a hanger. The shaped specimen is to be smooth and free of visible cracks and gouges. Sampling plans for anodes and cathode blocks given in Guides D6353 and D6354 may be used if desired.

8.2 Dry the shaped specimen in an oven at $105 \text{ }^\circ\text{C} \pm 5 \text{ }^\circ\text{C}$ to constant weight.

8.3 Make the sample free of loose carbon dust and impurities from the shaping process by blowing with dry air.

9. Calibration

9.1 The purpose of this procedure is to establish a relationship between the controller settings for three zone furnaces and the actual temperatures inside the reaction chamber in the region of the specimen. The length of the zone to be calibrated is 100 mm (4 in.).

NOTE 1—For single zone furnaces, the calibration probe shall be placed in center of where sample will be placed and confirm that the zone of 100 mm is within $\pm 2 \text{ }^\circ\text{C}$.

9.1.1 Insert a multiprobe thermocouple (for example, three couples in same sheath with probes located at the tip, and at 50 mm and 100 mm (2 in. and 4 in.) above the tip; or a packet of thermocouples with tips located at similar known distances) into the zone where the sample will be located. The multiprobe thermocouple center probe shall be located where the center of the sample will be located.

9.1.2 The center thermocouple is connected to the main controller setting, that is, $960 \text{ }^\circ\text{C}$ for CO_2 reactivity.

9.1.3 Connect the other two (2) thermocouples to any temperature indicating device. For determining actual temperature profile, a recording temperature indicator is required.

9.1.4 Allow 4 h for furnace to reach equilibrium under nitrogen purge (rate per 9.2).

9.1.5 Adjust zones until all three (3) temperature indicators are $\pm 2 \text{ }^\circ\text{C}$.

9.2 *Gas Flow Rates*, for this test are based on $250 \text{ L/h} \pm 5 \text{ L/h}$ (ambient temperature) for a sample diameter of 50 mm and a reaction tube with an ID of 100 mm. Reactivities determined with this test method are affected by the gas velocity 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 tube wall is constant for various size reaction tubes. The proper flow rate for other geometries is determined by multiplying the reference flow rate (250 L/h) by the ratio of annular area of the system

to the annular area of the reference system. For example, a tube with ID of 75 mm and sample diameter of 50.8 mm would have a flow rate calculated by:

$$\text{Ratio} = \quad (1)$$

$$\left[\frac{\text{Tube ID}^2 - \text{Sample OD}^2}{\text{Ref Tube ID}^2 - \text{Ref Sample OD}^2} \right] = \left[\frac{75^2 - 50.8^2}{100^2 - 50^2} \right] = \frac{3044}{7500} = 0.406$$

$$\text{Flow Rate} = [250 \text{ L/h}] \cdot [0.406] = 102 \text{ L/h} \quad (2)$$

10. Procedure

10.1 Preheat the reactor tube to $960 \text{ }^\circ\text{C} \pm 2 \text{ }^\circ\text{C}$ for CO_2 reactivity.

10.2 Purge the reaction chamber with nitrogen at the flow rate determined in 9.2.

10.3 Weigh and record the mass of the sample to the nearest 0.01 g as W_i .

10.4 Measure the sample diameter (d_s), sample height (h), and diameter of the center hole (d_h) to ± 0.01 mm to calculate geometric surface area for the reaction as given in 11.1.

10.5 Insert the sample into the reaction chamber by placing the sample in the sample holder and suspending the sample holder from the balance.

10.6 Preheat the sample under nitrogen purge for 30 min.

10.7 Tare the balance in accordance with the balance manufacturer's instructions.

10.8 Switch the gas introduced to the reaction chamber from nitrogen to CO_2 after 30 min in the nitrogen preheat, and maintain the flow rate as determined in 9.2.

10.9 Record the mass of the sample every minute for the duration of the test. The test duration for CO_2 reactivity is 7 h (420 min).

10.10 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 that 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.

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

10.12 Weigh the dust collected in the dust collection cup, and record as W_d .

11. Calculation

11.1 Calculate the exposed surface area of the shaped sample as follows:

$$A = \text{Area of} \quad (3)$$

{circumference + top and bottom (surfaces – center hole)}, or

$$A = \left\{ \pi d_s h + \frac{2\pi}{4} (d_s^2 - d_h^2) \right\} / 100 \quad (4)$$

where:

A = exposed surface area, cm^2 ,

d_s = sample diameter, mm,

d_h = diameter of central hole (if any), mm, and

h = sample height, mm.

11.2 Calculate total CO_2 reactivity rate (TR_c) as follows:

$$TR_c = \frac{1000(W_i - W_f)}{7A} \quad (5)$$

where:

TR_c = total CO_2 reactivity rate, $\text{mg}/\text{cm}^2\text{-h}$,

W_i = initial sample mass, g, and

W_f = final sample mass, g.

11.3 Calculate initial CO_2 reactivity rate (IR_c) as follows:

$$IR_c = \frac{2000(W_i - W_{30})}{A} \quad (6)$$

where:

IR_c = initial CO_2 reactivity rate, $\text{mg}/\text{cm}^2\text{-h}$, and

W_{30} = sample mass after 30 min of test, g.

11.4 Calculate final CO_2 reactivity rate (FR_c) as follows:

$$FR_c = \frac{2000(W_{390} - W_f)}{A} \quad (7)$$

where:

FR_c = final CO_2 reactivity rate, $\text{mg}/\text{cm}^2\text{-h}$, and

W_{390} = sample mass after 390 min of test, g.

11.5 Calculate CO_2 dusting rate (DR_c) as follows:

$$DR_c = \frac{1000W_d}{7A} \quad (8)$$

where:

DR_c = dusting rate during 7 h test, $\text{mg}/\text{cm}^2\text{-h}$, and

W_d = mass of dust collected during test, g.

12. Report

12.1 Report reactivity results to the nearest $0.1 \text{ mg}/\text{cm}^2\text{-h}$.

13. Precision and Bias³

13.1 *Precision*—The precision was determined by an inter-laboratory study conducted in accordance with Practice E691. Six laboratories tested nine materials (seven anodes and two cathodes). It was found, by linear regression, that the repeatability and reproducibility are dependent on the average value of the measured rate. Consequently, the regression equation is used in the precision statements. Based on this study, the criteria in 13.1.1 and 13.1.2 shall be used for judging the acceptability of results (95 % probability):

13.1.1 *Repeatability Limits*—Duplicate values (milligrams per centimetre squared 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:

13.1.1.1 *Total CO_2 Rate*: $r = (0.4977 \times x) + 3.1512$ x = average of duplicate total CO_2 rate values [Applicable between $11 \text{ mg}/\text{cm}^2\text{-h}$ and $42 \text{ mg}/\text{cm}^2\text{-h}$ total CO_2 rate]

³ Supporting data have been filed at ASTM International Headquarters and may be obtained by requesting Research Report RR:D02-1494.

13.1.1.2 *Initial CO₂ Rate*: $r = (-0.1804 \times x) + 6.9468$ $x =$ average of duplicate initial CO₂ rate values [Applicable between 5 mg/cm²-h and 17 mg/cm²-h initial CO₂ rate]

13.1.1.3 *Final CO₂ Rate*: $r = (0.4918 \times x) - 1.5454$ $x =$ average of duplicate final CO₂ rate values [Applicable between 14 mg/cm²-h and 57 mg/cm²-h final CO₂ rate]

13.1.1.4 *CO₂ Dusting Rate*: $r = (0.919 \times x) + 0.4796$ $x =$ average of duplicate CO₂ dusting rate values [Applicable between 0.3 mg/cm²-h and 5 mg/cm²-h CO₂ dusting rate]

13.1.2 *Reproducibility Limits*—The values (milligrams per centimetre squared 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:

13.1.2.1 *Total CO₂ Rate*: $R = (1.0706 \times x) - 9.2078$ $x =$ average of duplicate total CO₂ rate values [Applicable between 11 mg/cm²-h and 42 mg/cm²-h total CO₂ rate]

13.1.2.2 *Initial CO₂ Rate*: $R = (-0.1101 \times x) + 9.9455$ $x =$ average of duplicate initial CO₂ rate values [Applicable between 5 mg/cm²-h and 17 mg/cm²-h initial CO₂ rate]

13.1.2.3 *Final CO₂ Rate*: $R = (0.8985 \times x) - 5.6199$ $x =$ average of duplicate final CO₂ rate values [Applicable between 14 mg/cm²-h and 57 mg/cm²-h final CO₂ rate]

13.1.2.4 *CO₂ Dusting Rate*: $R = (2.2671 \times x) + 0.8844$ $x =$ average of duplicate CO₂ dusting rate values [Applicable between 0.3 mg/cm²-h and 5 mg/cm²-h CO₂ dusting rate]

13.2 *Bias*—This test method has no bias because the values of CO₂ reactivity are defined in terms of this test method.

14. Keywords

14.1 anode; cathode block; CO₂ reactivity; dusting

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