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Coal — Determination of carboxyreactivity

Charbon — Détermination de la carboxyréactivité

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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.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 27, *Coal and Coke,* Subcommittee SC 5, *Methods of analysis*.

Introduction

Coal gasification is an important technology for clean coal conversion, which involves many factors. The chemical reactivity of coal is one of the essential parameters for the gasification industry and its relevant coal trade.

The chemical reactivity of coal with CO_2 (carboxyreactivity of coal) is a measurement of the coal's ability to reduce CO_2 to CO, which is an important parameter of evaluating the coal quality for gasification and combustion industry. The level of carboxyreactivity of coal is directly related to other characteristics of the coal in the gasification or combustion furnace like the reactive extent, the reaction speed and efficiency, the consumption of coal and oxygen, the effective compositions of the coal gas, so it is not only used for evaluating the applicability of coal for gasification, combustion, indirect liquefaction, etc., but also for guiding users to select coal used for above technologies.

This document integrates and modifies GB/T 220[2] to specify a method for determining the reactivity of coal with carbon dioxide (carboxyreactivity). It can also be applied to determine the reactivity of coke for the purpose of gasification and combustion.

Coal — Determination of carboxyreactivity

1 Scope

This document specifies the method for determining the reactivity of coal with carbon dioxide (carboxyreactivity). It can be applied to determine the reactivity of coke for the purpose of gasification and combustion.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1213-2, *Solid mineral fuels — Vocabulary — Part 2: Terms relating to sampling, testing and analysis*

ISO 18283, *Coal and coke — Manual sampling*

ISO 13909-4, *Hard coal and coke — Mechanical sampling — Part 4: Coal — Preparation of test samples*

3 Terms and definitions

For the purposes of this document, the terms and definitions given in ISO 1213-2 apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at https://www.electropedia.org/

4 Principle

A coal sample with the size fraction of 3 mm to 6 mm is carbonized in a dry distillation furnace to remove the volatile matter (this is not necessary for coke samples). Sieve and collect a portion of the carbonized products (coke residue) with the designated size. Put them into the reaction tube and heat to the specified rates. When the required temperature is achieved, pass CO_2 gas through the reaction tube at a uniform flow rate. Determine the volume fraction of residual CO_2 in the gases by a gas analyser at the specified time of passing CO_2 gas. Calculate the ratio α (%) of CO_2 gas being reduced to CO and take it as the index of the carboxyreactivity at the specified temperature.

5 Reagents

Unless otherwise specified, all reagents shall be of analytical reagent grade, and only distilled water, or water of equivalent purity, shall be used.

5.1 Anhydrous calcium chloride.

5.2 Sulfuric acid, relative density, ρ = 1,84.

5.3 Potassium hydroxide or sodium hydroxide solution, 500 g/l.

Dissolve 50 g of potassium hydroxide or sodium hydroxide in 100 ml of distilled water.

5.4 Cylinder CO_2 gas, purity is not lower than 98 %.

6 Apparatus

6.1 Equipment for treating sample, consist of the following parts:

6.1.1 Tube-furnace, with a temperature controller, adequate volume, capable of maintaining a temperature of (900 ± 20) °C.

6.1.2 Dry distillation tube, made of porcelain or corundum capable of withstanding temperatures of 1 000 °C, (550 to 660) mm in length, 30 mm inner diameter and (33 to 35) mm external diameter.

6.2 Reactivity determination apparatus (see Figure 1), consists of the following parts:

6.2.1 Reaction furnace, vertical furnace with 600 mm in chamber length, (28 to 30) mm inner diameter, capable of reaching the maximum temperature of 1 350 °C.

6.2.2 Reaction tube, silicon or corundum tube withstanding temperature of 1 500 °C, (800 to 1 000) mm in length, (21 ± 0,5) mm inner diameter and (25 ± 0,5) mm external diameter.

6.2.3 Temperature controller, capable of heating to 1 300 °C according to a specified program and controlling temperature with an accuracy of ±5 °C.

6.3 Gas analyser, Aus-gas analyser or other CO_2 gas analyser (IR spectrometer or gas chromatograph), measuring range of 0 % to 100 %, accuracy of ±2 %.

6.4 Pt10 %Rh-Pt thermocouple, measures the temperature of reaction tube (6.2.2).

6.5 NiCr-NiSi, NiCrSi-NiSi or NiCr-NiAl thermocouple, measures the temperature of dry distillation tube (6.1.2).

6.6 Thermocouple well, two, made of corundum with (500 to 600) mm length, (5 to 6) mm inner diameter and (7 to 8) mm external diameter.

6.7 Flowmeter, measuring range of (0 to 700) ml/min [a flow meter with wider range should be used at the location where the atmosphere pressure is lower than 799,9 hPa (600 mmHg)].

6.8 Round hole sieves, 3 mm and 6 mm aperture size respectively, 200 mm in diameter, less than 3 mm thickness of the sieve plate, with a cover and a bottom.

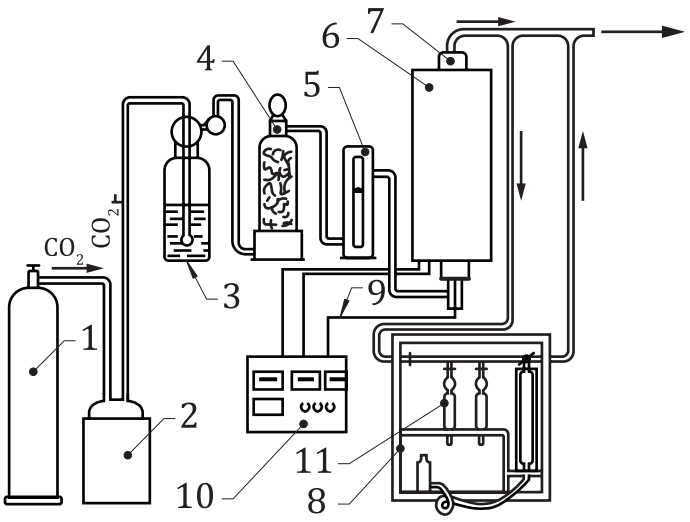
6.9 Sample vessel, column with 21 mm inner diameter and 100 mm high, open at one end and closed at the other for taking test sample.

6.10 Gas washing bottle, filled with concentrated sulfuric acid.

6.11 Drying tower, packed with anhydrous calcium chloride.

6.12 Barometer, measuring range of (799,9 to 1 066,6) hPa with an accuracy of 0,13 hPa and a graduation of 1,33 hPa, working temperature of (-15 to 45) °C.

6.13 Top-loading balance, with a resolution of 0,01 g.



Key

1	cylinder of CO_2	6	reaction furnace
2	bucket of gas storing	7	reaction tube
3	gas washing bottle	8	gas analyser (aus-gas analyser or IR spectrometer or gas chromatograph)
4	drying tower	9	Pt10 %Rh-Pt thermocouple
5	flowmeter	10	temperature controller
11	gas absorbers (fill with potassium hydroxide solution or sodium hydroxide solution (5.3))		

Figure 1 — Schematic for determination of carboxyactivity

7 Preparation of test sample

7.1 Prepare the test sample with the top size of (3 to 6) mm about 300 g by the method specified in ISO 13909-4 and ISO 18283.

7.2 Fix the thermocouple well (6.6) in the dry distillation tube (6.1.2) with a silicon rubber stopper and have the tip of the thermocouple located in the centre of the dry distillation tube. Hold the dry distillation tube upright and fill it with porcelain or corundum pieces of (6 to 8) mm until the bed is 100 mm distance from the tip of the thermocouple well (6.6). Add the test sample into the dry distillation tube to a 200 mm thickness. Fill the remaining space of the dry distillation tube with porcelain or corundum pieces.

7.3 Place the dry distillation tube (6.1.2) with the test sample in tube-furnace (6.1.1) and test sample should be located within the uniform temperature zone. Insert the NiCr - NiSi, NiCrSi-NiSi or NiCr-NiAl thermocouple (6.5) into the thermocouple well (6.6).

7.4 Heat the tube-furnace (6.1.1) to 900 °C at a rate of (15 to 20) °C/min and maintain the temperature of 900 °C for 1 h. Remove the dry distillation tube from the tube-furnace and allow the sample (coke residues) to cool to room temperature. Sieve the sample using a combined sieve of 3 mm and 6 mm aperture. Retain the fraction of 3 mm to 6 mm size for testing. For the caking coal, the coke residue pieces larger than 6 mm should be crushed to pass a 6 mm sieve totally.

NOTE Coal sample can also be treated using 100 ml crucibles with lids in a furnace (see ISO 562) according to the procedure in 7.4.

8 Procedure

8.1 As shown in Figure 1, connect all of the parts and ensure no leakage of gas.

8.2 Insert the thermocouple well (6.6) in the reaction tube (6.2.2) from the bottom until its tip is located in the central position of the uniform temperature zone, then fix it with a silicon rubber stopper. Hold the reaction tube upright and pack it with porcelain or corundum pieces of (6 to 8) mm until the tip of the thermocouple well is positioned at 50 mm above the pieces bed.

8.3 Fill the reaction tube to 100 mm thickness with the treated test sample of 3 mm to 6 mm by using the sample vessel (6.9) and ensure the top of the thermocouple located vertically in the centre of the test sample bed. Fill any remaining space of the reaction tube with either porcelain or corundum pieces. For duplicate determinations, the mass difference of test sample should not differ by more than 0,1 g.

8.4 Put the reaction tube into the reaction furnace (6.1.1). Block the upper end of the reaction tube tightly by using a silicon rubber stopper with a gas-guide tube. Insert the Pt 10 %Rh-Pt thermocouple (6.4) into the thermocouple well (6.6).

8.5 Pass CO_2 through the system to check for leaks. After confirming the reaction tube is air-tight, Continue CO_2 flow at a rate of 500 ml/min for 3 min to remove air, then stop the flow of CO_2.

8.6 Switch on the power. Raise the temperature of the reaction furnace, at a rate of (20 to 25) °C / min, up to 750 °C (for brown coals and lignites) or 800 °C (for bituminous and anthracite). Maintain this temperature for 5 min. Flow CO_2 gas through the test sample at a flow rate of 500 ml/min under the atmosphere pressure of (1 013,3 ± 13,3) hPa and the room temperature of (12 to 28) °C. If the atmosphere pressure or room temperature (or both) are out of the above ranges, the flow rate shall be corrected in accordance with Annex A.

8.7 Draw the gas from the reaction tube with a gas analyser (6.3) once CO_2 has been inlet for 2,5 min and finish both process of purging the measuring system and collecting the gas sample within 1 min. Stop the flow of CO_2 gas and analyse the CO_2 volume fraction of the gas sample with a gas analyser (6.3). If an automatic CO_2 analyser is used like an IR spectrometer or gas chromatograph (6.3), read the CO_2 volume fraction at the point of 3 min of passing through the CO_2.

8.8 Continue the gas analysis at increasing increment of 50 °C. Raise the temperature of the furnace at a rate of (20 to 25) °C/min. For every rise of 50 °C, maintain the temperature, purge the measuring system with CO_2 and then collect the gas sample. Determine the CO_2 volume fraction according to the procedure described in 8.6 and 8.7, until the temperature rises to 1 100 °C (or to 1 300 °C if there is a special requirement).

9 Expression of result

9.1 Calculate the ratio α (%) of CO_2 gas reduced to CO based on the CO_2 volume fraction in the gas after reaction by the following Formula (1):

$$\alpha = \frac{100(100-x-v)}{(100-x)(100+v)} \times 100 \quad (1)$$

where

α is ratio of CO_2 reduced to CO, as a volume fraction, in %;

x is the volume fraction of impurity in CO_2 gas, in %;