INTERNATIONAL STANDARD

ISO 11599

First edition
1997-12-15

Determination of gas porosity and gas permeability of hydraulic binders containing embedded radioactive waste

Détermination de la porosité et de la perméabilité au gaz de liants hydrauliques contenant des déchets radioactifs

Reference number
ISO 11599:1997(E)

Contents

		Page
1	Scope	**1**
2	Sample preparation	**1**
3	Measurement of open gas porosity	**5**
4	Measurement of gas permeability	**8**

Annexes

A	Gas pycnometer	**12**
B	Bibliography	**16**

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

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.

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.

International Standard ISO 11599 was prepared by Technical Committee ISO/TC 85, *Nuclear energy*, Subcommittee SC 5, *Nuclear fuel technology*.

Annex A forms an integral part of this International Standard. Annex B is for information only.

Introduction

Hydraulic binder-based matrices can be hardened pure cement, mortar or concrete containing embedded wastes; these wastes can be radioactive or non-radioactive.

It has been observed that the durability of these matrices, as well as the leaching rate of immobilized radionuclides in water are very largely dependent on gas open porosity and gas permeability of the matrix. Also, permeability and open porosity can be related to the homogeneity of a hydraulic binder matrix.

The objective of this International Standard is to offer a methodology that allows rapid estimation of the gas porosity and permeability of hydraulic binders. A direct comparison of the results obtained in different laboratories would thus be possible by checking the quality or ageing behaviour of a waste form. The International Standard, once implemented, would reduce discrepancies between laboratories.

Determination of gas porosity and gas permeability of hydraulic binders containing embedded radioactive waste

1 Scope

This International Standard describes the principles and methodologies of measuring both gas open porosity and permeability of hydraulic binder-based matrices used for immobilization of radioactive waste. The measurements can be carried out by using different apparatus designed and constructed on the basis of a few recommended characteristics. The measurements can be performed on samples prepared in a laboratory or taken from industrial production. Samples can be obtained by moulding or by coring a block.

2 Sample preparation

The samples may be obtained either by moulding or by coring of a block. The choice shall be made according to the purpose of the study.

2.1 Moulded samples

The samples are moulded when the hardened cement, mortar or concrete has been prepared either in the laboratory or taken from an industrial or pilot plant.

2.1.1 Sample size

The sample shall be an orthogonal cylinder with square cross-section, or a rectangular parallelepiped. The acceptable sample length is in the range between (40 ± 2) mm and (220 ± 5) mm. The recommended length is (110 ± 3) mm.

The end orthogonalities in relation to the generating line direction shall be (90 ± 1)°. Straight section inherent flatness shall be 0,5 mm.

2.1.2 Mould

The sample is poured into moulds made of steel, plastic or cardboard with an inner sulfurized paper lining.

Mould design shall allow withdrawal of the pattern from the mould without knocking flakes off the solid angle of intersection of the two surfaces. During mould filling, the mixture is stirred with a straight rod to eliminate possible air bubbles. If drum vibration is arranged for an industrial process, the sample is compressed with a vibrating microtable.

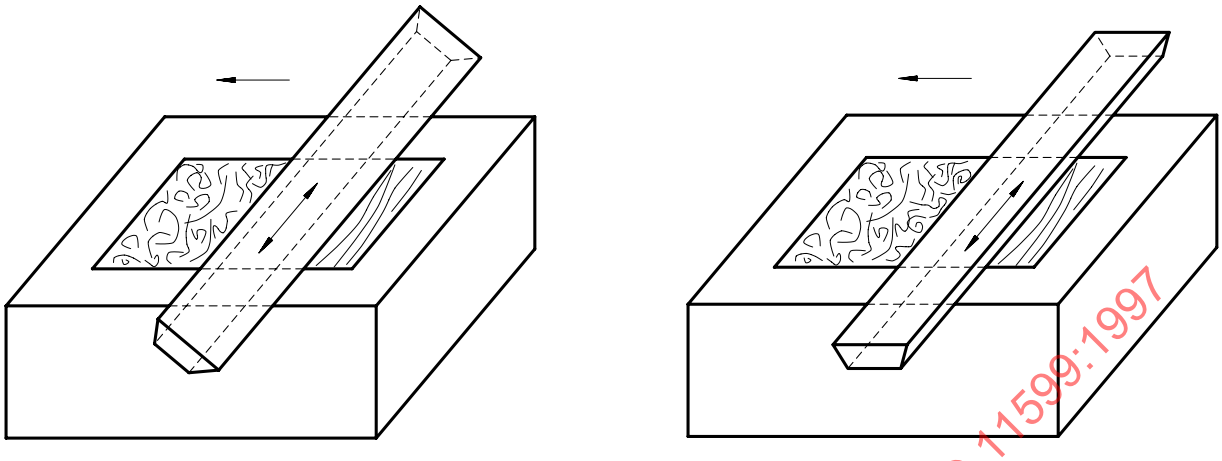
Levelling of the upper surface of the sample is carried out with a steel strip. The cross-section of the strip shall be trapezoidal with a 45° angle. The dimensions of the strip shall be as follows:

— length: 450 mm;

— width of the major base: 60 mm;

— thickness: 15 mm.

In a first step, levelling enables a raw surface of a sample to be obtained using the strip's chamfered edge (see operation A in figure 1). In a second step, use the strip's shorter base to obtain the final surface of the sample to be used (see operation B in figure 1).



a) Operation A b) Operation B

Figure 1 — Levelling of moulded sample

Raw and final levellings are made with a sawing movement (an alternating movement). For each levelling, two passes are made with a change in direction of 90°. During levelling, cavities are filled with the same mixture.

All details of this operation shall be noted in the test report.

2.2 Core samples

2.2.1 General

Core drilling is carried out with a tool adapted to the desired final diameter of the sample. During coring, overheating of the tool can be damaging for the material; air or gas cooling shall then be performed. A gas or air cooling filtration system shall be installed to avoid excessive radioactive contamination for tests with actual embedded radioactive or hazardous waste.

The coring material, a cylindrical and tubular muff, is fitted with a diamond abrasive ring. The tool's rotational speed is defined for each manufacturer's specifications. In the absence of specification, a rotational speed of 600 min^{-1} to 800 min^{-1} is recommended. In general, the core is cut into sections with a carborundum plate to obtain samples of a length suitable for tests.

When a matrix with embedded waste is cored, the sample shall be chosen to differentiate homogeneous and heterogeneous parts.

2.2.2 Samples from homogeneous waste forms

Figure 2 shows the procedure used. The cores are obtained in a direction parallel to the container axis, halfway between the centre and the lateral surface of the waste package. The core is then cut as shown in the diagram to obtain five samples.

2.2.3 Samples from heterogeneous waste forms

Figure 3 shows the procedures used for samples from cylindrical or parallelepipedic blocks having a volume $\leqslant 2\ m^3$. One long vertical core and three cross-cores can be obtained to produce five samples.

Figure 4 shows the procedures used for samples from cylindrical or parallelepipedic blocks having a volume $> 2\ m^3$. Two vertical cores and three cross-cores can be obtained. In this case, the number of samples is seven.

If the integrity of the package is not guaranteed during these two procedures, it is possible to sample only on the top of the container. In this case, the statistic sampling representative will not be as accurate as in the procedure recommended above.

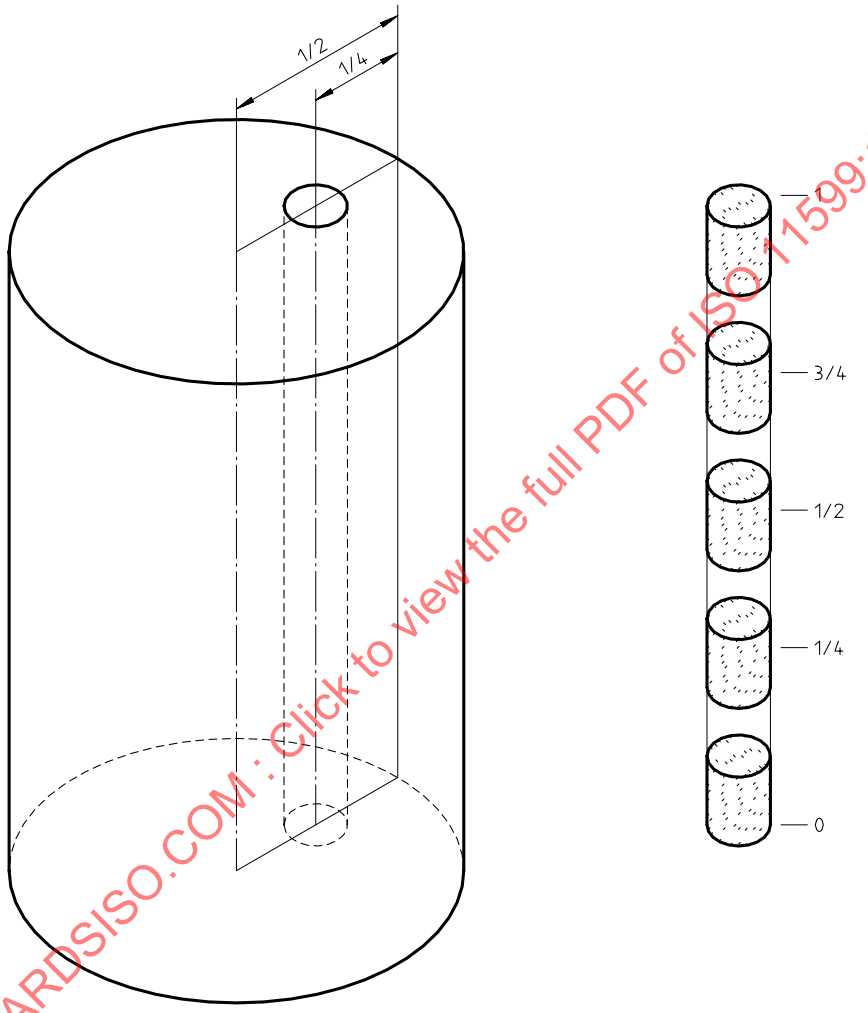


Figure 2 — Sampling of homogeneous waste forms

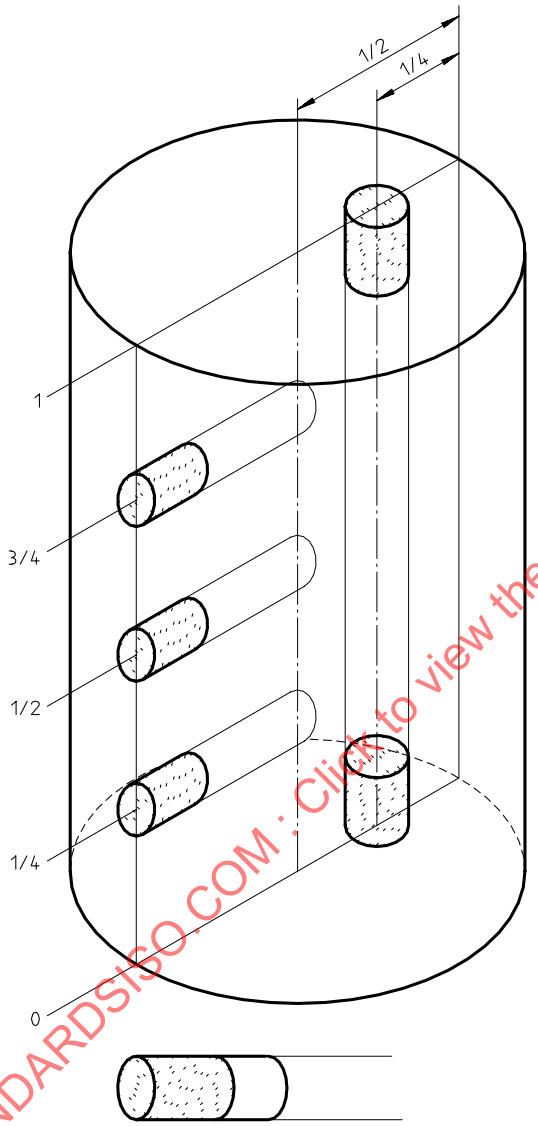


Figure 3 — Sampling of heterogeneous waste forms of block volume ⩽ 2 m³

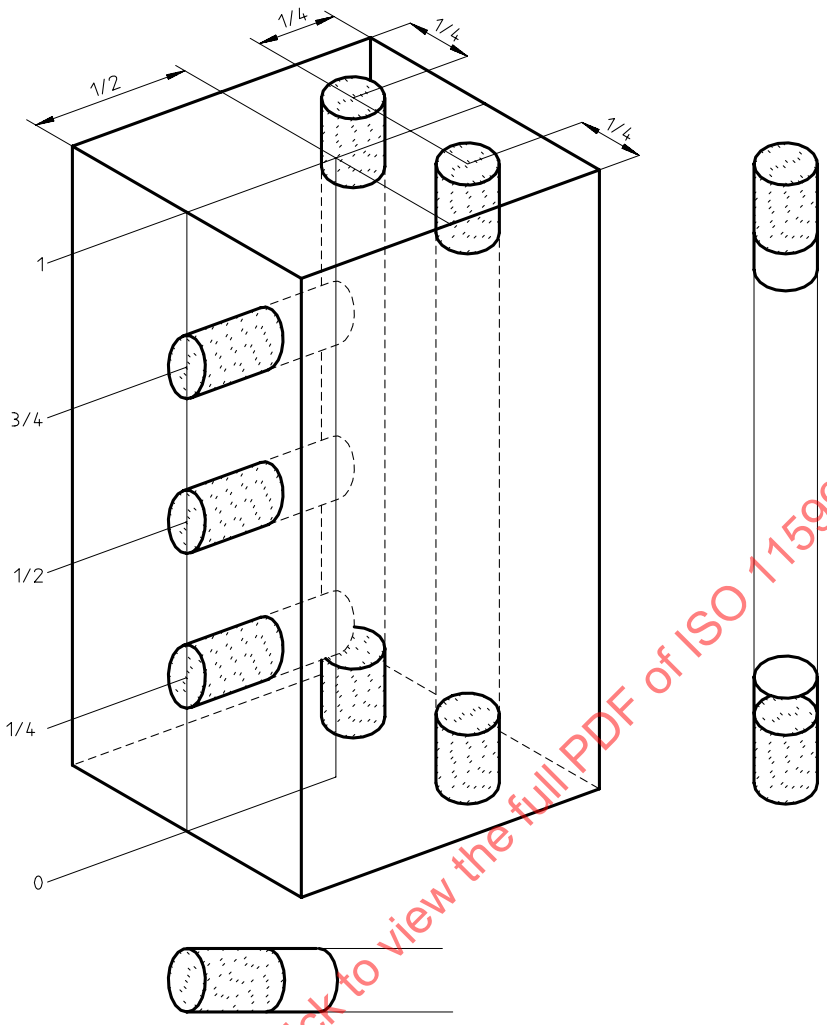


Figure 4 — Sampling of heterogeneous waste forms of block volume > 2 m³

3 Measurement of open gas porosity

3.1 Definition

The sample open gas porosity (P), expressed as a percentage, is the ratio of the open pore volume (V_o) of a sample to the geometrical volume (V_g) (also called the apparent volume). The open pore volume of a sample is also equal to the geometrical volume minus the real volume (V_s) of the sample.

$$P = \frac{V_o}{V_g} \times 100 \quad \ldots(1)$$

$$V_o = V_g - V_s \quad \ldots(2)$$

Thus,

$$P = \frac{V_g - V_s}{V_g} \times 100 \quad \ldots(3)$$

3.2 Principle

The determination of gas porosity is based on the measurement of the real volume of a sample, including the closed pores, by the use of a helium pycnometer.

NOTE — The theory of the gas pycnometer is given in annex A.

The following steps are carried out:

— drying the sample at 60 °C until a constant mass is reached;

— measurement of the geometrical volume of the sample;

— measurement of the real volume of the sample.

3.3 Apparatus

The apparatus necessary for open gas porosity measurement comprises the following.

3.3.1 Oven, for drying the sample at a temperature of (60 ± 2) °C.

3.3.2 Desiccator, for cooling the sample before measuring its mass.

3.3.3 Scale, of capacity 0 to 5 kg and an accuracy of 0,01 %.

3.3.4 Square caliper, of accuracy 0,1 mm, for determining the geometrical volume of the sample.

3.3.5 Gas pycnometer, for measurement of the real sample volume, with a pressure accuracy of not less than 10 Pa.

3.4 Sample preparation

The samples shall be obtained either by moulding or by coring and cutting. Several examples of sample preparation are given in clause 2. Samples shall have a parallelepipedic or cylindrical configuration.

3.5 Procedure

3.5.1 Sample drying and weighing

Dry the samples at (60 ± 2) °C in the oven (3.3.1) until constant mass is achieved. Constant mass is considered achieved when the difference between two mass values measured using the scale (3.3.3) at a 24 h interval is lower than 0,1 % of the value in the previous measurement. Before any measurement of mass, cool the samples to ambient temperature in the desiccator (3.3.2).

3.5.2 Determination of geometrical volume

Determine the geometrical volume (V_g) immediately after the mass measurement.

3.5.2.1 Cylinder diameter measurement

Use the square caliper (3.3.4) for the diameter measurement. Make four measurements at each end and in the middle for the sample, turning the sample 45° after each measurement. The average diameter ($\overline{D}$) is the arithmetical mean of the twelve measured values.

3.5.2.2 Linear measurements

For linear measurements, measure the cylinder height (H) or the sides of the parallelepiped (H_1, H_2, H_3). Make four measurements with the square caliper for each side of the parallelepiped and for the cylinder height, turning the sample 45° after each measurement. The average height ($\overline{H}$) is the arithmetic mean of the four measured values.

3.5.2.3 Geometrical volume, V_g

Determine the geometrical volume of the sample from the following mathematical expressions:

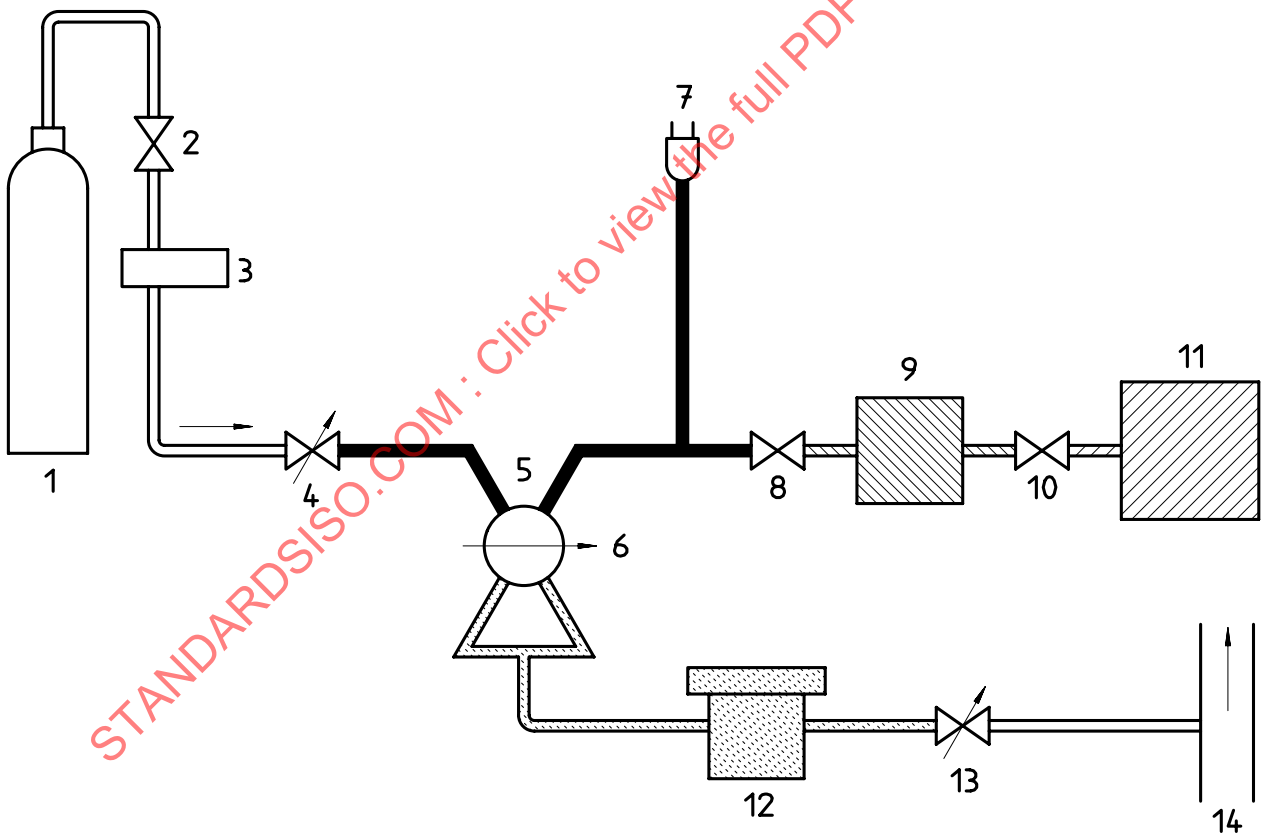
Cylinder volume: $$V_g = \frac{\pi \cdot \overline{D}^2 \cdot \overline{H}}{4} \quad \ldots(4)$$

Rectangular parallelepiped volume: $$V_g = \overline{H}_1 \cdot \overline{H}_2 \cdot \overline{H}_3 \quad \ldots(5)$$

3.5.3 Determination of real volume

Determine the real volume (V_s) using a gas pycnometer immediately after determining the geometrical volume.

The gas pycnometer is shown in figure 5; the theoretical basis for its use and calibration procedures are explained in annex A.



Key

1	High-pressure gas (He or N_2) bottle with reducing valve	6	Selector valve	11	Large reference cell V_{rg}
2	Connection and isolation valve	7	Pressure transducer	12	Sample cell V_c
3	Relief valve 0 to 117,2 kPa	8	Valve 1	13	Gas-out toggle valve
4	Gas-in toggle valve	9	Small reference cell V_{rp}	14	Vent
5	Micro reference cell V_{rm}	10	Valve 2		

Figure 5 — Gas pycnometer

Select the sample cell volume of the pycnometer so that the geometrical sample volume represents about 75 % of the total volume of the sample cell. Select the volume of the pycnometer reference cell so that the residual volume of the sample cell represent about 15 % to 30 % of the total volume. The reference cells are generally filled with helium at normal pressure. If this is not the case, flush with helium, using an amount not less than twice the volume of the reference cell selected.

Carry out helium flushing of the sample positioned in the sample cell at low gas flow for 15 min. Regulate the gas flow such that slow-rising single bubbles are observed in a beaker filled with water. Then stop the gas flow and isolate the sample cell from the atmosphere. Set the pressure pick-up at zero level.

Now introduce helium gas into the reference cell and pressurize at 100 kPa to 120 kPa. Wait 20 s for pressure stabilization. Record this pressure as P_1. Do not wait any longer for pressure stabilization because every 30 s a pressure change of about 7 Pa occurs due to temperature influence. Slowly turn the selector valve to connect the reference cell with the sample cell. Wait 20 s for pressure stabilization and record this pressure as P_2.

Record the volumes of the sample cell V_c and reference cell V_r on a data card.

Calculate the real volume of the sample V_s using the working equation (see annex A):

$$V_s = V_c - V_r \left(\frac{P_1}{P_2} - 1 \right) \quad \ldots(6)$$

Carefully open the toggle valve “gas out” to release the pressure from the cells and repeat the measurement process a second and third time to confirm the test reproducibility.

4 Measurement of gas permeability

4.1 Principle

The following steps are carried out:

— placing the sample holder with a sealing gasket,

— placing the sample holder onto the apparatus and pressurizing the permeameter,

— measuring and recording the time-dependent pressure; measurements may be duplicated,

— data calculation and permeability determination.

The value of the gas permeability can be found by studying the fluid flow through a sample. If a quasi-continuous and isothermal flow is assumed, and if the gas used is a perfect gas, the gas flow is governed by Darcy's Law given below:

$$Q = \frac{KA_s}{\eta H} \left(P - P_0 \right) \quad \ldots(7)$$

where

Q is the gas flow, in cubic metres per second ($m^3 \cdot s^{-1}$);

K is the permeability, in square metres (m^2);

A_s is the surface area, in square metres (m^2), perpendicular to the flow direction;

P_0 is the atmospheric pressure, in pascals (Pa);

η is the gas viscosity, in pascal seconds (Pa·s);

H is the thickness of the sample, in metres (m).

Moreover, the flow of a perfect gas, at an average pressure $(P + P_0)/2$ and when the flow is isothermal can be determined as:

$$Q = \frac{2V}{(P + P_0)} \frac{dP}{dt}$$

where

V is the volume of the permeameter, in cubic metres (m^3);

$\frac{dP}{dt}$ is the slope of the $P = f(t)$ curve;

P is the pressure, in pascals (Pa);

t is the time, in seconds (s).

Setting equation (7) equal to equation (8) we obtain equation (9):

$$K = \frac{2V\eta H}{A_s(P^2 - P_0^2)} \frac{dP}{dt} \quad \ldots(9)$$

The mean permeability of the sample can be obtained in two ways:

— from a curve by the measurement of slope at different pressures;

— from curves of $P = f(t)$ at a given pressure, by the measurement of different slopes.

A geometric permeability of $K = 1\ m^2$ is typical for a fluid, with 1 Pa·s of viscosity, flowing through this substance with a velocity of 1 $m \cdot s^{-1}$ when the pressure gradient is 1 $Pa \cdot m^{-1}$.

4.2 Apparatus

Figure 6 shows a diagram of the equipment for gas permeability measurement which includes the following.

4.2.1 High-pressure gas bottle with a reducing valve system to control permeameter pressure in the range 0 to 5 MPa.

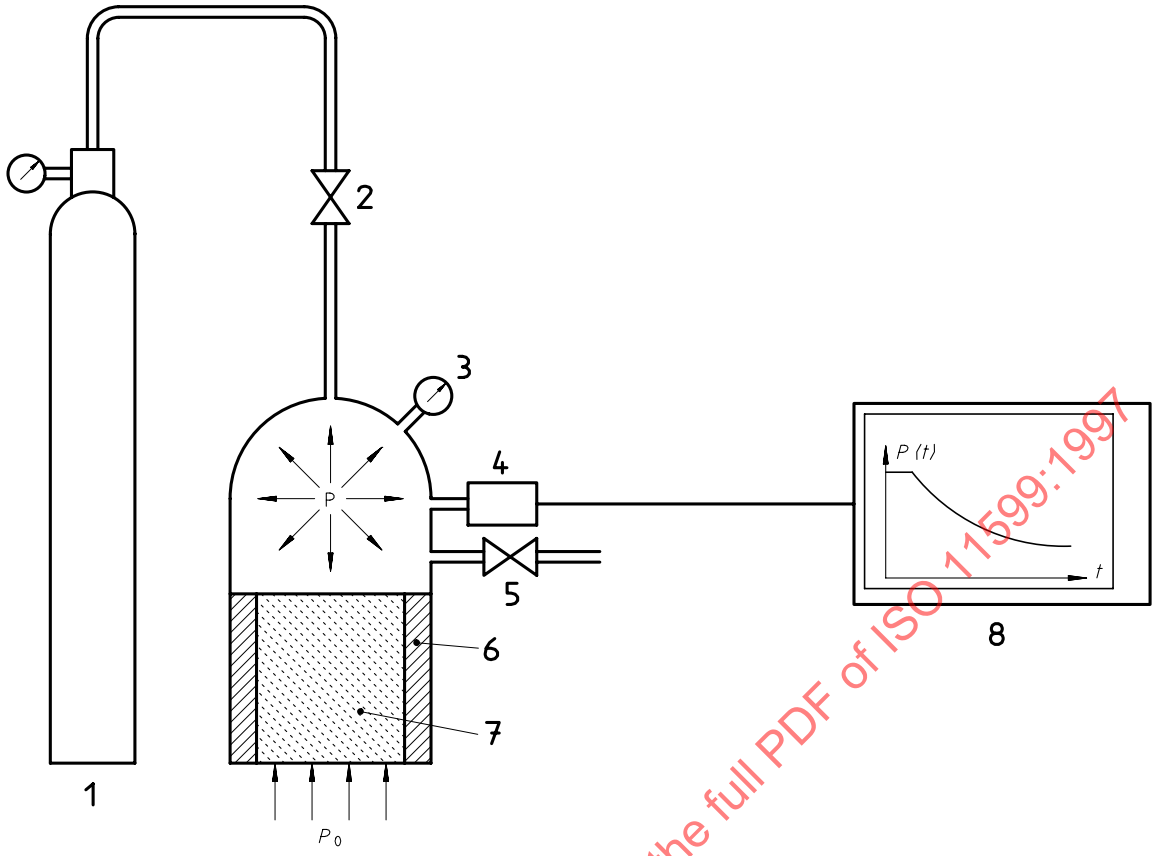
4.2.2 Cylindrical stainless steel cell in which the sample with a resin gasket should be set up.

4.2.3 Hydraulic press to extract the sample.

4.2.4 Permeameter, including a stainless steel bell-jar fitted with a pressure pick-up and data acquisition capability.

4.2.5 Thermosetting epoxy resin, for setting up the sample.

All this equipment shall be located in a room which is temperature-controlled at (20 ± 2) °C to improve measurement accuracy.



Key

1	High-pressure gas (He or N_2) bottle with reducing valve	5	Gas-out valve
2	Connection and isolation valve	6	High adherence sealing gasket
3	Pressure pick-up for visual monitoring	7	Sample
4	Pressure pick-up for recording	8	Continuous recording of pressure vs. time

Figure 6 — Gas permeameter

4.3 Sample preparation

Samples can be obtained either by moulding or by coring and cutting. Several examples of sample preparation are given in clause 2. Generally, the samples are conditioned at (20 ± 2) °C with a relative humidity of (65 ± 5) %.

4.4 Procedure

4.4.1 Sample setting

Clamp and join the samples in the cylindrical cell with a thermosetting resin. The thickness of the resin joint around the sample should be ⩽ 1 cm. The permeability of the thermosetting resin shall be ⩽ 10^{-22} m^2 in the same operating conditions.

In order to obtain good height stability of the sample in the cylindrical cell during the test, the internal part of this cell should be shaped like a truncated cone. The narrowest part of the cell should be positioned toward the bottom.

4.4.2 Permeameter preparation and pressure recording

The cylindrical cell is considered to be set up on the permeameter when resin polymerization is close to 99 % complete. Replace the air atmosphere of the permeameter by nitrogen or helium using a gas flowrate of 10 $l \cdot h^{-1}$ for 2 h. In any case, sweep with a volume of gas at least 20 times the volume of the permeameter.

Then turn off the “gas out” valve and introduce a relative pressure of 1,0 MPa to 1,5 MPa in the cell. Maintain this pressure constant for 2 d to 4 d so as to obtain a continuous gas flow.

Start the data acquisition device (recorder). Verify that the pressure is constant. Isolate the gas bottle and maintain this state while the pressure drops. Stop the recording when the pressure falls lower than 0,9 MPa.

In any case, the period of time when the pressure is maintained constant should be shorter than when the permeameter pressure drops from 1,0 MPa to 0,9 MPa. If this is not the case, due to very low sample permeability, a new continuous gas flow through the sample should be set up. Only in this case can the measurement be considered valid.

It is possible to obtain a second curve using the same sample by providing beforehand a continuous gas flow for 24 h beyond the normal period of time for obtaining continuous gas flow.

4.4.3 Calculation of results

At the relative pressure of 1 MPa, the slope of the curve $P = f(t)$ must be considered. Calculate the value $\mathrm{d}P/\mathrm{d}t$ in the range 1,0 MPa to 0,9 MPa as function of time.

The permeability at the relative pressure of 1 MPa will be given by equation (9):

$$K = \frac{2\,V\eta H}{A_s\left(P^2 - P_0^2\right)} \frac{\mathrm{d}P}{\mathrm{d}t}$$

where all values are known.

The reproducibility of this test is always good and it is unnecessary to draw many curves from one sample. When an exact value of a certain material is required, it is better to test several samples of this material.

For example, from a sample of 11 cm diameter and height, the time interval for pressure drop between 1,0 MPa and 0,9 MPa varies between 40 h and 48 h when the permeability is about 1×10^{-20} m^2, and 12 h and 15 h when the permeability is about 1×10^{-17} m^2.

Annex A
(normative)

Gas pycnometer

A.1 Theoretical use

The gas pycnometer is a specific instrument for measuring the true volume of various quantities of solid materials. The technique uses the Archimedes principle of fluid displacement to determine the volume. The displaced fluid is a gas which penetrates the finest pores to ensure maximum accuracy. For this reason, helium is recommended since its small atomic dimension ensures penetration into crevices and pores approaching 1 Å (1×10^{-10} m). Its behaviour as an ideal gas is also desirable. Other gases such as nitrogen can be used, often with no measurable difference.

The pycnometer determines the true volumic mass, in fact the true volume, of solid or powder samples by measuring the pressure difference when a known volume of helium under pressure in a reference cell V_r, is allowed to flow into a precisely known sample cell volume V_c containing the solid or powdered material.

The shaded areas in figure 4 of the main text represent the known reference cell volume V_r (micro V_{rm}, small V_{rp} and large V_{rg}) and the known sample cell volume V_c. After the system is purged with helium, the selector valve is turned to "cell", the "gas out" toggle valve opened, and the "gas in" toggle valve closed. The system is now at ambient pressure P_a and the state of the sample cell with the sample is defined by:

$$(P + P_a)\,(V_c - V_s) = n_a R T_a \qquad \text{…(A.1)}$$

where

$(P + P_a)$ is the absolute pressure;

n_a is the number of moles of gas occupying the sample cell volume V_c, including the sample volume V_s;

R is the gas constant;

T_a is the ambient temperature.

When the reference cell is pressurized to approximately 100 kPa to 120 kPa above ambient, the state of the reference cell volume V_r can be expressed as:

$$(P + P_1)\,V_r = n_1 R T_a \qquad \text{…(A.2)}$$

where

P_1 is the pressure above ambient;

$(P + P_1)$ is the absolute pressure;

n_1 is the total number of moles of gas in the reference cell volume V_r.

When the selector valve is turned to connect the sample cell, the pressure will fall to a lower pressure P_2, given by:

$$(P + P_2)\,(V_c - V_s + V_r) = n_a\,R T_a + n_1 R T_a \qquad \text{…(A.3)}$$

Substituting into equation (A.3) $(P + P_a)(V_c - V_s)$ and $(P + P_1)\,V_r$ for $n_a RT_a$ and $n_1 RT_a$ respectively, gives:

$$(P + P_2)(V_c - V_s + V_r) = (P + P_a)(V_c - V_s) + (P + P_1)\,V_r \quad \ldots(A.4)$$

or

$$(P_2 - P_a)(V_c - V_s) = (P_1 - P_2)\,V_r \quad \ldots(A.5)$$

Then

$$V_c - V_s = \frac{P_1 - P_2}{P_2 - P_a} V_r \quad \ldots(A.6)$$

Since P_a is set at zero on the digital meter, that is to say, all pressure measurements are then relative to P_a, equation (A.6) becomes:

$$V_c - V_s = \frac{P_1 - P_2}{P_2} V_r \quad \ldots(A.7)$$

or

$$V_s = V_c - V_r \left(\frac{P_1}{P_2} - 1 \right) \quad \ldots(A.8)$$

Equation (A.8) is the working equation used in the pycnometer.

A.2 Calibration

Calibration of the pycnometer should be carried out each time it is used at a temperature differing more than 4 °C from the temperature at which it was calibrated. Moreover, the different cells should be checked regularly, as a change in their volume cannot be dismissed following either variations in temperature, or deposition of powders or fines from samples or previous experiments.

Calibrated spheres are supplied with the pycnometer to check the volumes of the reference and measurement cells of large, small and micro sizes.

The calibration is to be carried out according to the steps in A.2.1 to A.2.9.

A.2.1 Put the large reference cell and the large measurement cell into place. Keep valves 1 and 2 open.

A.2.2 Flush the measurement cell with helium for about 5 min under a pressure of 7 kPa.

A.2.3 Stop the helium input after pressure equilibrium and adjust the pressure recorder to zero.

A.2.4 Isolate the pycnometer from the outside atmosphere and fill the reference cell with helium at about 117,2 kPa. Note the pressure P_1 after stabilization.

A.2.5 Connect the reference and measurement cells to each other. Note the pressure P_2 after stabilization.

By applying equation (A.8), and since V_s is zero, we obtain:

$$V_{cg} = V_{rg} \left(\frac{P_1}{P_2} - 1 \right) \quad \ldots(A.9)$$

in which the subscript (g) indicates that we are working with the large cells.