TC 102

International Standard ISO 4695

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Iron ores — Determination of reducibility

Minerais de fer — Détermination de la réductibilité

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Foreword

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Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council.

International Standard ISO 4695 was developed by Technical Committee ISO/TC 102, *Iron ores*, and was circulated to the member bodies in November 1982.

It has been approved by the member bodies of the following countries:

Australia	Italy	Sweden
Canada	Japan	United Kingdom
China	Korea, Dem. P. Rep. of	USA
Czechoslovakia	Poland	USSR
Egypt, Arab Rep. of	Portugal	Venezuela
France	Romania	
Germany, F.R.	South Africa, Rep. of	

The member body of the following country expressed disapproval of the document on technical grounds:

India

Iron ores — Determination of reducibility

0 Introduction

The reducibility test method is one of several procedures used to evaluate the behaviour of natural and processed iron ores under specific conditions. The specific conditions involved in this test are: isothermal reduction; reduction in a fixed bed; reduction by means of carbon monoxide; and a sample having a specified size range.

The results of this test should be considered in conjunction with the results of other tests, particularly those showing the physical behaviour of materials during reduction.

The mathematical derivation of formulae for reducibility is included for information only in the annex.

1 Scope and field of application

This International Standard specifies a method for determining the reducibility expressed as reduction rate of natural iron ores and agglomerates such as pellets or sinters.

2 References

ISO 2597, *Iron ores — Determination of total iron content — Titrimetric methods.*[1]

ISO 3081, *Iron ores — Increment sampling — Manual method.*[2]

ISO 3082, *Iron ores — Increment sampling and sample preparation — Mechanical method.*[3]

ISO 3083, *Iron ores — Preparation of samples — Manual method.*[4]

3 Definition

For the purpose of this International Standard the following definition applies:

3.1 reducibility: A measure of the ease with which oxygen combined with iron can be removed from natural or processed iron ores by a reducing gas, which is expressed as the rate of reduction at an atomic ratio O/Fe = 0,9, relative to the iron(III) state.

4 Principle

Isothermal reduction of the test portion at a specified size range in a fixed bed, at a temperature of 950 °C using a reducing gas consisting of CO and N_2.

Weighing of the test portion at specified time intervals.

Calculation of the degree of reduction relative to the iron(III) state and calculation of the rate of reduction at the oxygen/iron ratio of 0,9.

5 Reducing gas

Gas volumes and flow rates used in this International Standard are as measured at a temperature of 0 °C and at atmospheric pressure (101,325 kPa).[5]

The reducing gas shall consist of

CO	40 ± 0,5 % (V/V)
N_2	60 ± 0,5 % (V/V)

1) At present at the stage of draft. (Revision of ISO 2597-1973.)

2) At present at the stage of draft. (Revision of ISO 3081-1973.)

3) At present at the stage of draft.

4) At present at the stage of draft. (Revision of ISO 3083-1973.)

5) 1 mmHg ≈ 0,133 3 kPa; 1 atm = 0,101 325 MPa

Impurities in the reducing gas shall not exceed

H_2 0,2 % (*V*/*V*)
CO_2 0,2 % (*V*/*V*)
O_2 0,1 % (*V*/*V*)
H_2O 0,2 % (*V*/*V*)

6 Apparatus

The apparatus shall consist of the following

a) a system to supply and regulate the gases;

b) a reduction tube;

c) a weighing device to determine the oxygen loss at regular intervals;

d) an electrically heated furnace to heat the test portion to the specified temperature;

e) test sieves.

Figure 1 shows an arrangement of the reduction tube and the furnace.

6.1 Reduction tube, made of non-scaling, heat resisting metal to withstand temperatures of higher than 950 °C. The perforated plate is mounted in the reduction tube for supporting the test portion. The diameter of the sample bed shall be 75 ± 1 mm.

Figure 2 shows an example of the reduction tube.

6.2 Furnace, having a heating capacity sufficient to maintain the entire test portion and the gas entering the bed at 950 ± 10 °C.

6.3 Weighing device, capable of weighing the load to an accuracy of 1 g. The weighing device shall be checked for sensitivity at regular intervals.

6.4 Test sieves, conforming to test sieve standard specifications and having square mesh apertures of the following nominal sizes:

16,0 mm, 12,5 mm and 10,0 mm.

7 Preparation of test sample

7.1 General

In case of commercial test, the test sample shall be prepared according to ISO 3082[1)] or ISO 3083,[1)] from the sample for physical testing which has been taken in accordance with ISO 3081 or ISO 3082.[1)] The test sample shall be oven dried at 105 ± 5 °C and cooled to room temperature before testing.

7.2 Sample for reducibility test

A quantity of test sample sufficient to provide at least five 500 g test portions shall be prepared as follows:

a) Pellets

The test sample in the size range of 10,0 mm to 12,5 mm shall be obtained by sieving and, after sieving, only pellets taken at random shall be used for the test.

b) Ore or sinters

The test sample in the size range of 10,0 mm to 12,5 mm shall be prepared as follows:

Screen the sample on a 12,5 mm sieve and carefully crush the plus 12,5 mm material until it all passes the 16,0 mm sieve. Combine all fractions and remove by sieving the plus 12,5 mm and the minus 10,0 mm material from the sample.

NOTE — The reducibility of iron ores is a function of the size range of the particles so that results obtained with this International Standard will relate only to material in the size range 10,0 mm to 12,5 mm. If the reducibility of an iron ore of a different size range is required, it shall be obtained by a separate reducibility test or by other means. Using the apparatus specified in this International Standard, iron ores with a maximum diameter greater than 16,0 mm shall not be tested.

7.3 Sample for chemical analysis

A 500 g test portion shall be reserved for the determination of total iron content and Fe(II) content.

8 Test conditions

8.1 Flow rate of reducing gas

The reducing gas (clause 5) flow rate shall, during the test period, be maintained at 50 ± 0,5 l/min.

8.2 Temperature of test

The test portion is reduced at a temperature of 950 °C.

The reducing gas shall be preheated before entering the test portion to maintain the test portion at 950 ± 10 °C during the entire test period.

1) At present these International Standard do not specify any requirements applicable to this International Standard. An annex will be prepared for the purpose in due course.

9 Procedure

9.1 Number of determinations

Carry out the test generally in duplicate on one ore sample.

9.2 Other determinations

Simultaneously with the test, determine the Fe(II)[1] and, in accordance with ISO 2597, the total iron content.

9.3 Test portion

Weigh, to the nearest 1 g, approximately 500 g (± 1 particle) of the test sample (mass m_0).

9.4 Reduction

Place the test portion (9.3) in the reduction tube (6.1) so that the surface is even. In order to achieve a more uniform gas flow, a two-layer bed of porcelain pellets having a size range of 10,0 mm to 12,5 mm may be placed between the perforated plate and the test portion.

Close the top of the reduction tube. Insert the reduction tube into the furnace (6.2) and suspend it centrally from the weighing device (6.3) ensuring that there is no contact with the furnace or heating elements.

Pass a flow of inert gas through the reduction tube at a flow rate of approximately 25 l/min and commence the heating. When the temperature of the test portion approaches 950 °C increase the flow rate of the inert gas to 50 l/min. Continue the heating maintaining the flow of the inert gas until the mass of the test portion is constant (mass m_1) and the temperature is constant at 950 ± 10 °C.

CAUTION — Carbon monoxide and the reducing gas which contains carbon monoxide are toxic and therefore hazardous. During the following procedure, the testing shall be carried out in a well ventilated area or under a hood. Precautions, according to the safety codes of each country, should be taken for the safety of the operator.

Introduce the reducing gas to replace the inert gas at a flow rate of 50 l/min. Record the mass of the test portion at least every three minutes for the first 15 min and thereafter at 10 min intervals.

Terminate the reduction when the oxygen loss reaches 65 %. If, after 4 h, this has not been achieved, the test may be stopped.

NOTE — If so desired, the test portion may then be cooled under a flow of inert gas to enable sample examination to be carried out.

10 Expression of results

10.1 Calculation of degree of reduction

Calculate the degree of reduction after time t, R_t, relative to the iron(III) state, as a percentage, by the following formula:[2]

$$\left[\frac{0{,}111\, w_1\,(\%)}{0{,}430\, w_2\,(\%)} + \frac{m_1 - m_t}{m_0 \times 0{,}430\, w_2\,(\%)} \times 100 \right] \times 100$$

where

m_0 is the mass, in grams, of the test portion;

m_1 is the mass, in grams, of the test portion immediately before starting the reduction;

m_t is the mass, in grams, of the test portion after reduction time t;

w_1 (%)[3] is the iron(II) oxide content, as a percentage by mass, of the test sample prior to the test and is calculated from the iron(II) content by multiplying it by a factor of 1,286;[4]

w_2 (%)[3] is the total iron content, as a percentage by mass, of the test sample prior to the test, determined in accordance with ISO 2597.

Prepare the reduction curve by plotting the degree of reduction R_t against time t.

10.2 Calculation of reducibility index

Read out from the reduction curve the time in minutes to attain degrees of reduction of 30 % and 60 %.

The reducibility index, expressed as the rate of reduction at the atomic ratio of O/Fe of 0,9[5], in per cent per minute, is calculated from the following formula:[2]

$$\frac{dR}{dt}\,(\mathrm{O/Fe} = 0{,}9) = \frac{33{,}6}{t_{60} - t_{30}}$$

where

t_{30} is the time, in minutes, to attain a degree of reduction of 30 %;

t_{60} is the time, in minutes, to attain a degree of reduction of 60 %;

33,6 is the constant.

Express the result to two decimal places.

1) An International Standard for the determination of Fe(II) content is now in preparation, and until its publication the authentic standard in each country can apply.

2) The derivation of the formula is given in the annex.

3) In the case of a commercial test, it is preferable to adopt w_1 (%) and w_2 (%) not for the 500 g test portion (7.3) but for consignment.

4) Oxide conversion factor FeO/Fe(II) = 1,286.

5) The atomic ratio O/Fe = 0,9 means 40 % degree of reduction.

NOTE — In certain instances, a degree of reduction of 60 % is not attained in the test. In such cases, lower values may be accommodated by the following formula:

$$\frac{dR}{dt}(O/Fe = 0{,}9) = \frac{K}{t_y - t_{30}}$$

where

t_y is the time, in minutes, to attain a degree of reduction of y %;

K is the constant depending on y %:

If y = 50 % then the value of K = 20,2;

If y = 55 % then the value of K = 26,5.

10.3 Permissible tolerance and acceptance of test results

For a paired result, the two individual results shall be within ± 2,5 % of the mean value of the pair of results. The reducibility index reported shall be the arithmetic mean of a paired result rounded off to the nearest 0,01 %/min.

If the difference between the paired results does not meet the permissible tolerance, another duplicate test shall be carried out. The reducibility index reported shall be the arithmetic mean of the four results rounded off to the nearest 0,01 %/min.

11 Test report

The test report shall include the following information:

a) reference to this International Standard;

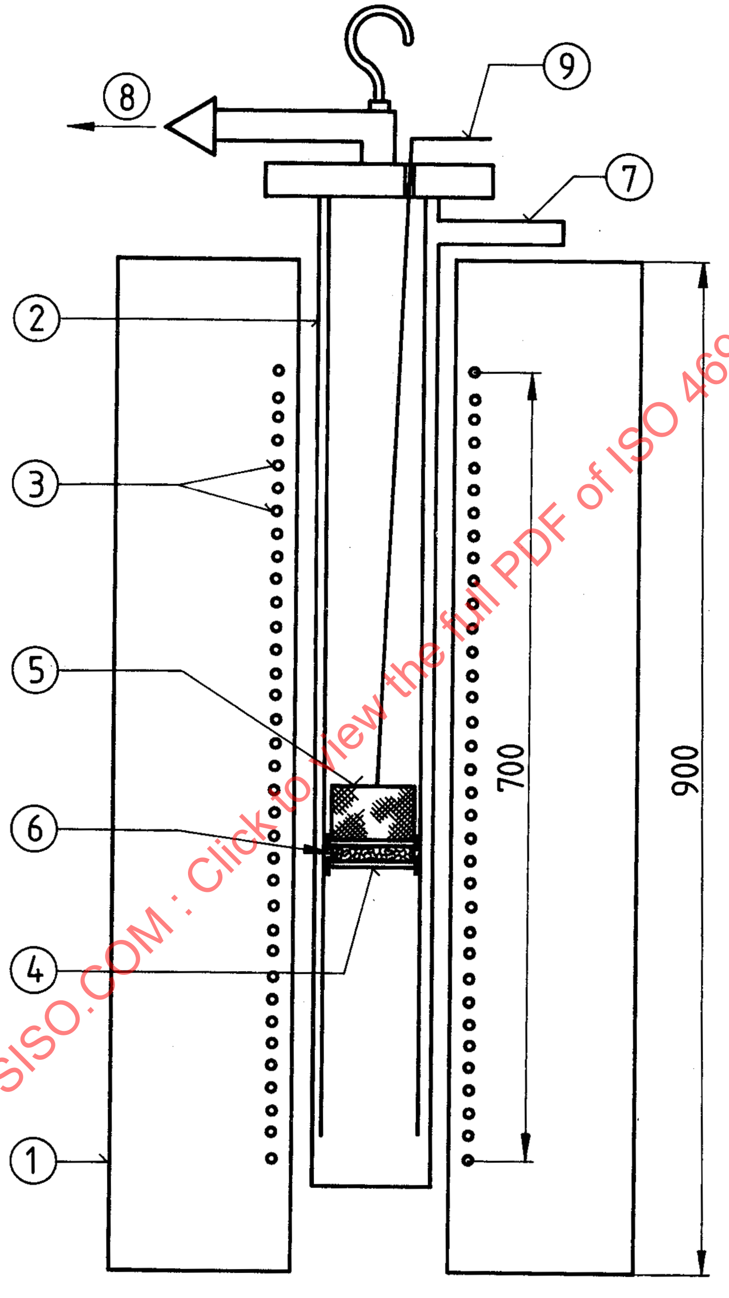
b) description of the test sample;

c) reducibility index;

d) total iron content and iron(II) content in the sample before reduction;

e) loss in mass versus time data, if required.

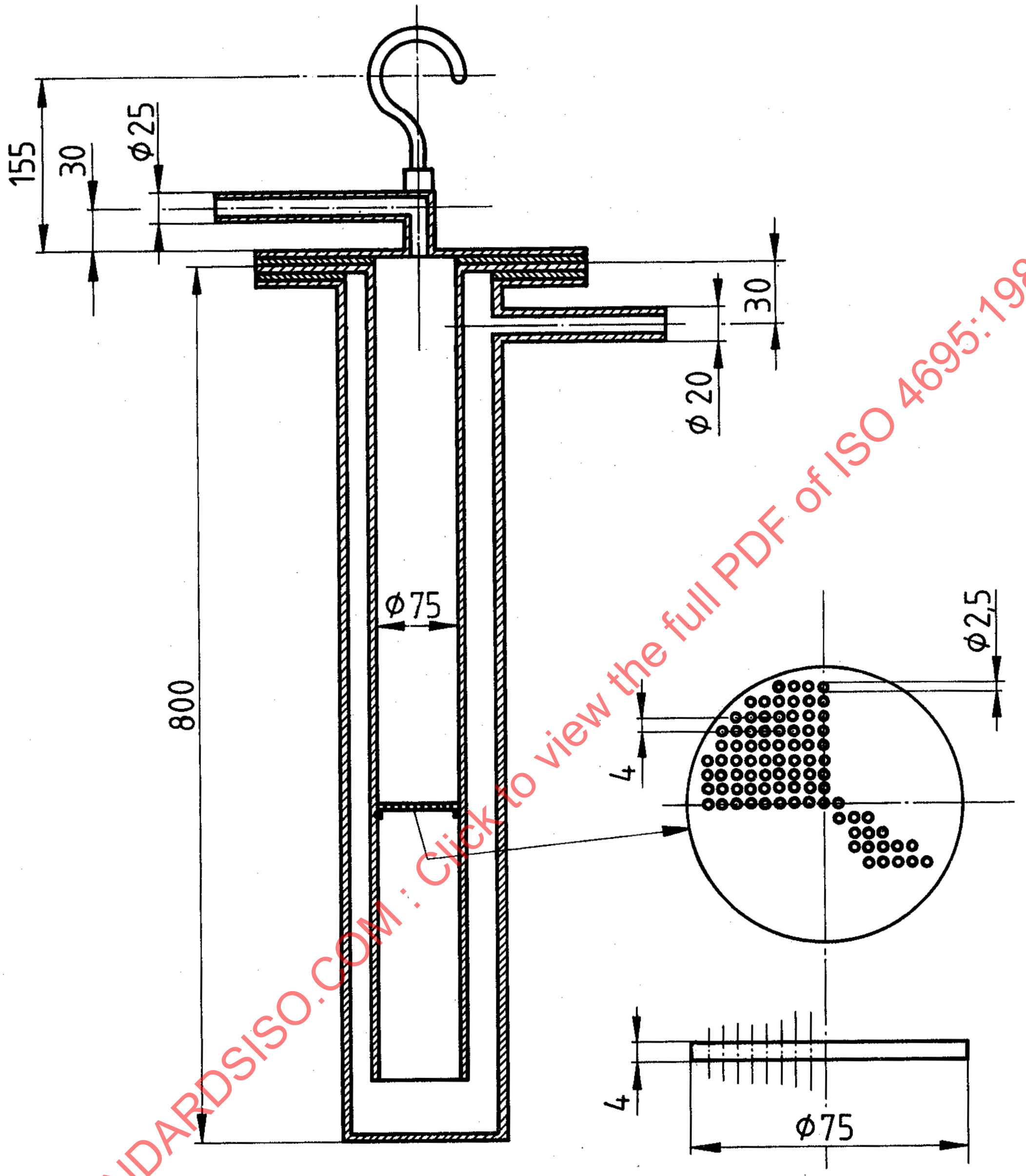
Dimensions in millimetres (for information only)



1 Furnace (10 kVA) (6.2)
2 Reduction tube (6.1)
3 Heating element
4 Perforated plate
5 Test portion
6 Layer of porcelain pellets
7 Gas inlet
8 Gas outlet
9 Thermocouple

Figure 1 — Example of test apparatus

Dimensions in millimetres



Perforated plate

Hole diameter: 2,5 mm

Pitch between holes: 4 mm

Number of holes: 241

Total hole area: 1 180 mm²

Thickness of plate: 4 mm

NOTE — Dimensions not specified in clause 6 are shown for information only.

Figure 2 — Example of reduction tube (6.1)

Annex

Derivation of formula for reducibility

(For information only.)

"Degree of reduction" describes the extent to which oxygen has been removed from iron oxides, and is defined generally as shown below:

$$\text{Degree of reduction} = \frac{\text{oxygen removed from iron oxide}}{\text{original oxygen combined with iron}} \qquad \text{... (A1)}$$

The formula in 8.5 is derived on the assumption that all oxygen combined with iron is present in the form of hematite (Fe_2O_3) whereas, for most iron ore materials, some magnetite (Fe_3O_4), wustite (FeO), and metallic iron are also present. Therefore, the degree of reduction is estimated from the loss in mass of the test portion during reduction plus the difference between the theoretical oxygen content of the original sample, based on all iron being associated as Fe_2O_3, and the true oxygen content based on actual amounts of Fe_2O_3, Fe_3O_4 and FeO in the sample.

$$R_t = \frac{m_0\, w_1 \times \dfrac{8}{71{,}85}}{m_0 w_2 \times \dfrac{48}{111{,}7}} \times 100 + \frac{m_1 - m_t}{m_0 \times \dfrac{w_2}{100} \times \dfrac{48}{111{,}7}} \times 100 \qquad \text{... (A2)}$$

The formula in 9.1 is derived on the assumption that the rate of oxygen removed from iron ores is a first-order reaction with respect to the prevailing oxygen concentration.

$$-\frac{dO}{dt} = k \times O_v \qquad \text{... (A3)}$$

$$dO = -dR \times \frac{O_{total}}{100} \qquad \text{... (A4)}$$

$$\frac{O_v}{O_{total}} = 1 - \frac{R}{100} \qquad \text{... (A5)}$$

where

O_v is the prevailing oxygen content;

O_{total} is the total oxygen combined with iron (as Fe_2O_3);

R is the degree of reduction.

From equations (A3), (A4) and (A5), the rate of reduction is derived:

$$\frac{dR}{dt} = k \times \left(1 - \frac{R}{100}\right) \times 100 \qquad \text{... (A6)}$$

Integration of equation (A3) gives

$$\log_{10}\left(1 - \frac{R}{100}\right) = -\,0{,}434\, kt + C$$

For R between 30 and 60 %,

$$k = \frac{-\log_{10}(1 - 60/100) + \log_{10}(1 - 30/100)}{0{,}434\,(t_{60} - t_{30})} = \frac{0{,}56}{t_{60} - t_{30}} \qquad \text{... (A7)}$$

In the case of hematite, the oxygen/iron ratio of 0,9 has the same meaning as R = 40 %. By substituting R = 40 % and equation (A7) into equation (A6), the value of dR/dt (at O/Fe = 0,9) is obtained, i.e.

$$\frac{dR}{dt}\,(O/Fe = 0{,}9) = \frac{33{,}6}{t_{60} - t_{30}}$$