THE IMPORTANCE AND TESTING OF DENSITY / POROSITY / PERMEABILITY / PORE SIZE FOR REFRACTORIES

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1 Introduction

Refractories are used for demanding conditions and need to be sound, robust and capable. This presentation describes the importance of interactions between density, porosity, permeability and pore size for refractories, and describes how each of these is measured. These properties are an indication of the manufactured quality, and during service they influence strength, slag resistance, flow of gases and liquids, thermal conductivity and thermal shock resistance of the refractory. Understanding these properties and their interactions will help users to understand the performance of these materials better.

2 Refractories

What are refractories, and why do we use them?

2.1 Description

Refractory literally means "Stubborn to withstand not only heat but in many cases chemical attack, abrasion, thermal shock and rough handling" (Hloben, 2000).

2.2 Applications

"The commonest duty of refractories is to contain high temperatures: to erect a solid barrier between hot "inside" and ambient or tolerable "outside". Mechanical loads must be borne … at the service temperature and often through repeated temperature cycles. … in most uses, … as thermal insulator; less frequently, as a conductor of heat. … But the greatest challenge to refractories occurs as they face hot, corrosive fluids. … usually rapidly flowing … erosion … many such fluids carry entrained particulates … abrasion …" (Carniglia & Barna, 1992).

Applications include all forms of metallurgical and heat treatment furnaces, heat exchangers, glass tanks, ceramic kilns, foundry moulds, coke ovens and incinerators.

Important requirements for refractories are:

- Strength at operational temperature
- Thermal shock resistance
- Thermally insulating or conducting
- Gas permeability or not
- Specific heat capacity high or low
- Corrosion resistance at high temperature

The high temperature capabilities required of refractories are governed primarily by chemical composition, and other capabilities required (strength, thermal shock resistance, conductivity, permeability, heat capacity and corrosion resistance) are governed also by physical properties related to density and porosity.

3 Density and Porosity

What is density and porosity, and how are these measured?

3.1 Different types

Density, porosity and volume types are described below:

- Bulk (or Apparent) Density (BD) is mass divided by Bulk Volume
- Bulk Volume is the volume of solid and of open and closed porosity
- Apparent Porosity (% AP) is open pore volume as a percentage of Bulk Volume
- Apparent Solid Density (or ASG) is mass divided by Apparent Solid Volume
- Apparent Solid Volume is the volume of solid and of closed porosity
- Real Density (or SG) is mass divided by Solid Volume only
- Total Porosity (% TP) is total pore volume as a percentage of Bulk Volume

3.2 Archimedes immersion technique

Archimedes Principle states that the buoyant force on a submerged object is equal to the weight of the fluid that is displaced by the object.

One day, while getting into his bath the Greek inventor and mathematician Archimedes noticed water spilling over the sides. In a flash he realised the relationship between the water that had fallen out and the weight of his body - in other words he discovered why some objects float and some sink! Archimedes was so excited with his discovery that he hopped out of the bath, and rushed naked into the street yelling triumphantly, 'Eureka!' 'Eureka!' (Greek word for 'I have found it!), as shown in Figure 1.

Density and porosity (AP, BD and ASG) can be measured of refractory materials using the Archimedes buoyancy technique with dry weights, soaked weights and immersed weights in water (mercury, xylene or denatured alcohol if the refractory is water sensitive) (Figure 2). Various standard test methods are based on this procedure (ISO 5017, ASTM C20, BS 1902-308, and SANS 5905 using mercury).

Figure 3 shows the makeup of a porous body with solid, open pores and closed pores, and how water absorbed into the open porosity (by vacuum or boiling) presents when weighed either suspended or soaked. The Apparent Porosity, Bulk Density and Apparent Specific Gravity are calculated from the Dry, Soaked and Suspended weights as follows:

- % AP = (Soaked Weight - Dry Weight) x 100 / (Soaked Weight – Suspended Weight)
- BD = Dry Weight / (Soaked Weight – Suspended Weight)
- ASG = Dry Weight / (Dry Weight – Suspended Weight)

Figure 1: Archimedes and his bath time discovery (www.pitara.com)

Figure 2: Laboratory Archimedes setup

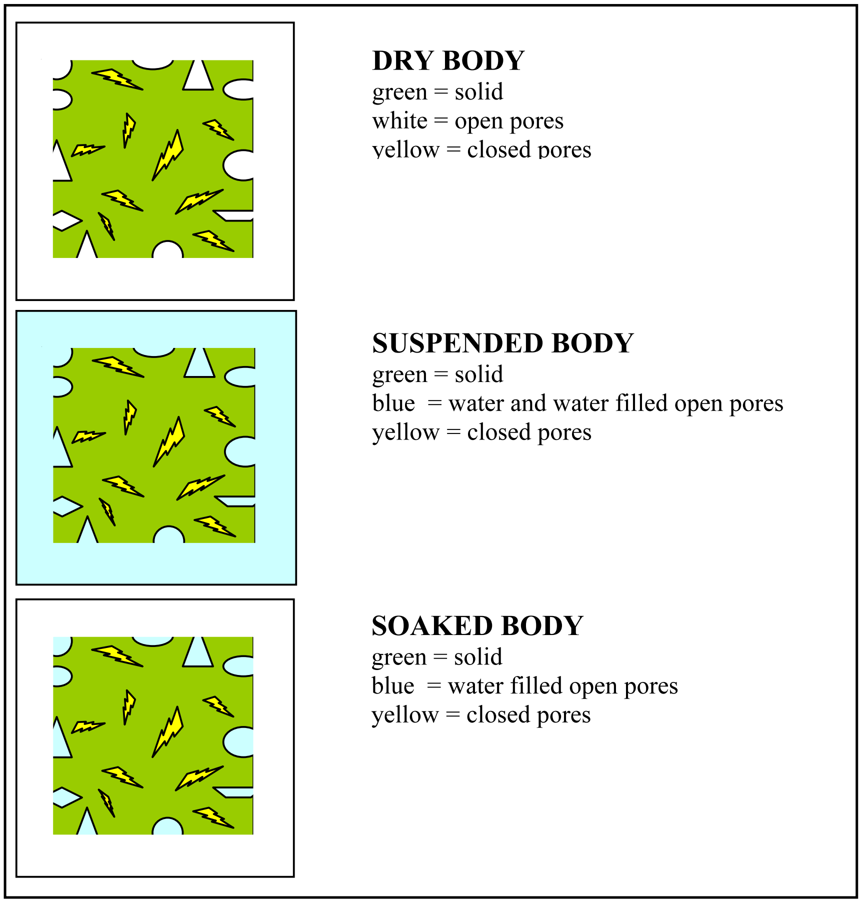

Figure 3: Dry, soaked and suspended bodies

3.3 Bulk Density by measurement

For uniform rectangular refractory shapes the simplest way of measuring Bulk Density is by dividing Dry Weight by Bulk Volume which is calculated from measured dimensions. This is the recommended procedure for measuring Bulk Density of insulation bricks (containing >40 % true porosity) (ISO 5016 and ASTM C134).

3.4 Specific Gravity (or Real Density) and Total Porosity

In order to measure Specific Gravity (SG) (or Real Density), a refractory should first be finely milled (sub 62 micrometres) to open up all its closed porosity. A known weight of this fine powder can then be used to displace liquid within a pycnometer to determine its True Volume, and thereby it's Real Density (ISO 5018 and SANS 5902). Total Porosity can then be calculated from Bulk Density and True Density (ISO 5016 and BS 1902-308).

- SG = Powder Dry Weight / True Volume
- % TP = (SG – BD) x 100 / SG

3.5 Pycnometers

Pycnometers are vessels with accurate volumes which can be used to measure liquid (or gas) volume displaced by a solid material (in powder, granular or bulk form), and thereby the density of the material.

Pycnometers come in many types, the most common being the SG Bottle which is often used for measuring SG of finely milled powders. These are also used for measuring Relative Density of liquids whereby a liquid weight is divided by the weight of an equal volume (using the same vessel) of water. Liquids other than water can be used in these pycnometers when water is a problem, the most common being xylene. Figure 4 shows SG Bottles on the right and a large Bulk Pycnometer on the left. The Bulk Pycnometer can be used for measuring BD, ASG or SG of larger pieces or chips using a similar procedure to that of the SG Bottle.

Figure 4: Bulk Pycnometer (left) and SG Bottles (right)

The Rees Hugill flask shown in Figure 5 is another type of pycnometer which uses xylene generally to displace a set weight (normally 100 g) of fine powder, and allows one to read off SG which is inscribed in a corresponding range onto the elongated neck (SANS 5902). Xylene is used because it has low surface tension with most powders, and for this has good penetration of fine open porosity. Different powder weights can be used with mathematical corrections for those powders with SG values which fall outside of the inscribed range. These flasks can be used with water to measure Grain (Bulk) Density of water soaked chips or grains.

Figure 5: Rees Hugill flasks

The Beckmann pycnometer shown in Figure 6 works on a similar principle to SG Bottles, but displaces helium gas instead of water or xylene. The advantage of using helium is that its molecules are extremely small and can more completely enter even the tiniest of open pores. Similar gas pycnometer apparatuses use nitrogen gas as the displacement medium.

Figure 6: Beckmann pycnometer

The mercury pycnometer shown in Figure 7 works on a similar principle to SG Bottles, but displaces mercury around the Bulk Volume of a solid lump or of chips to measure Bulk Density or Grain Density (ISO 8840 and SANS 5904). This can also be used to measure Bulk Density of green clay body chips which would with other techniques break down under water or xylene.

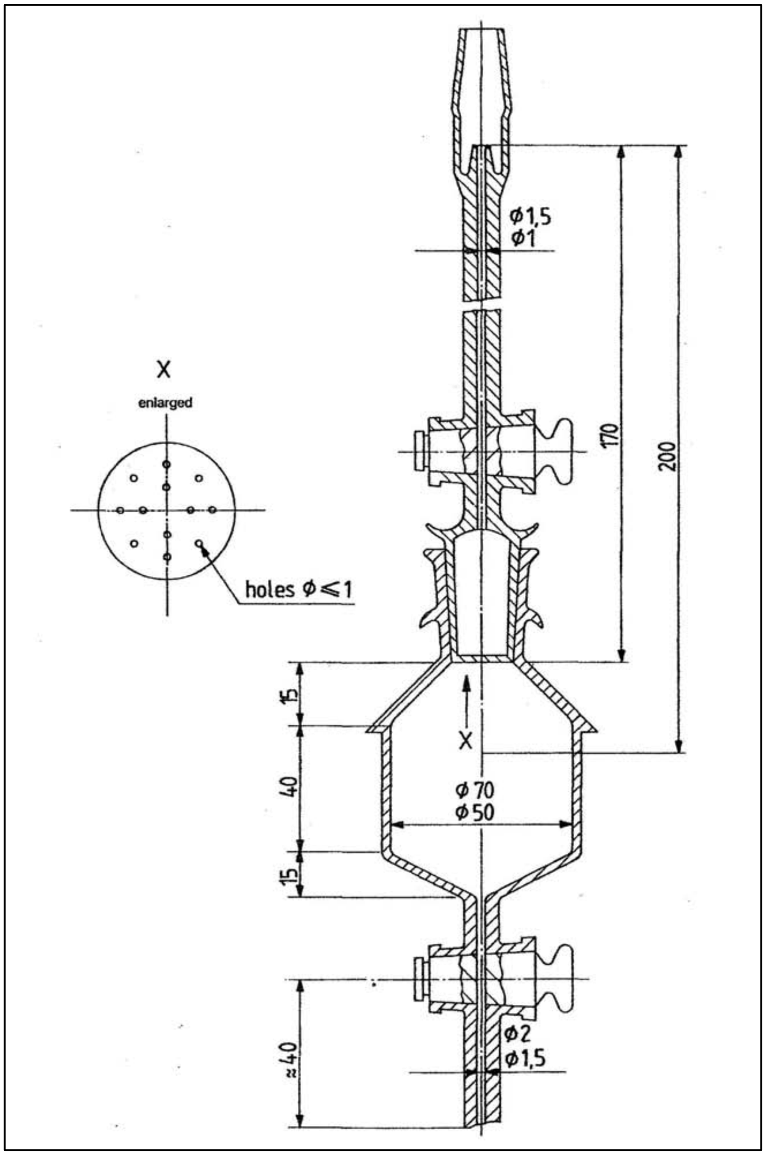

Figure 7: Mercury pycnometer

The Tap Density apparatus shown in Figure 8 is used to measure Tap Density of aggregate, grain or powder. This allows measurement of the settled Bulk Density of such materials which are often important measures affecting performance, and which relate to packaging and transport volumes. This involves measuring the final settled volume of a known weight of such material, and from this the calculation of its Tap Density (ASTM D1895).

Figure 8: Grain or powder Tap Density apparatus

3.6 Pore size distribution

Pore size distribution is measured either by mercury intrusion porisometry or by nitrogen porisometry. Mercury intrusion porisometry involves submersing a body in mercury under vacuum and then pressurising this to force mercury into the open pores. This generates a pore size distribution profile which shows pore surface area and pore volume in different pore size ranges. Figure 9 shows the pore sizes within a porous body A fall predominately in the range of 50 to 90 micrometres.

Nitrogen porisometry works in a similar way by measuring the adsorption of nitrogen onto the surfaces of open pores.

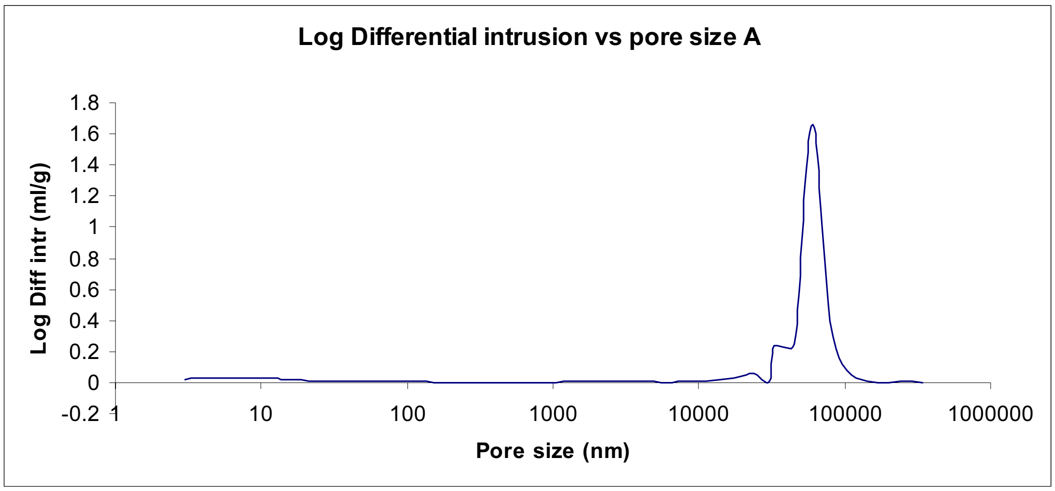

Figure 9: Mercury pore size distribution plot

3.7 Permeability

Permeability is the measure of flow through porosity within a body, and in the case of refractories is measured as the flow of either air or nitrogen. Permeability measured of dense refractories gives an indication of how well that refractory will stand up to slag, melt or gas penetration during service (low permeability = better slag, melt or gas penetration resistance).

Figure 10 shows a Ridsdale permeability apparatus, which is used for measuring the flow of air through preformed foundry green sand samples.

- Permeability P = v x h / p x a x t

Figure 10: Ridsdale permeability apparatus

Foundry green sand has relatively high air flow for low pressures (<10 cm of water pressure), and permeability of refractories requires higher pressures to obtain more meaningful results. Figure 11 shows such an apparatus which measures the flow of nitrogen gas at pressures of up to 6 bar (EN 993-4).

Figure 11: Refractories permeability tester

3.8 The influence of density and porosity on performance of refractories

Why do we measure density, porosity, pore size distribution and permeability of refractories?

Figure 12 shows the different stages of sintering (from loose powder, through initial stage and intermediate stage to the final dense product), and Figure 13 shows the microstructure of a fully dense alumina body. Density and porosity measurements show a manufacturer whether his product has densified correctly (not in the intermediate stage for example), and they show a user whether the product he has purchased matches with its specification.

Density, porosity and permeability measurements show whether a body is fully dense (as in Figure 13), and whether therefore it can be expected to stand up to aggressive slag attack and/or penetration by process gases. The type of porosity present in a body (closed or open) has also an influence because a small amount of closed porosity will not translate into permeability as would open porosity.

Density and porosity measurements can indicate whether a refractory is likely to be strong in service (higher density = higher [strength / Young's Modulus / abrasion resistance / knock resistance]). High temperature creep is reduced / RUL is increased with higher density.

A degree of porosity can influence the thermal shock resistance of a refractory (more porosity = better thermal shock resistance).

The density, porosity and pore size distribution of a refractory will influence its thermal conductivity (more porous = more insulating), (finer closed porosity = more insulating) and (fully dense = more conducting).

The density, porosity and pore size distribution of a refractory will influence its electrical resistivity (higher porosity = higher electrical resistivity).

The density and porosity of a refractory will influence its heat capacity (higher density = higher heat capacity) and (highly porous insulating = low heat capacity).

The density and porosity of a refractory will influence its PLC at high temperatures (higher porosity refractory = higher PLC).

Some fine porosity can increase the toughness of a refractory by terminating propagating cracks.

Balanced (or Zoned) furnace linings use different grades of the same refractory with more or less density (less or more porosity) for use in areas of greater or lesser (hence cheaper) requirements respectively.

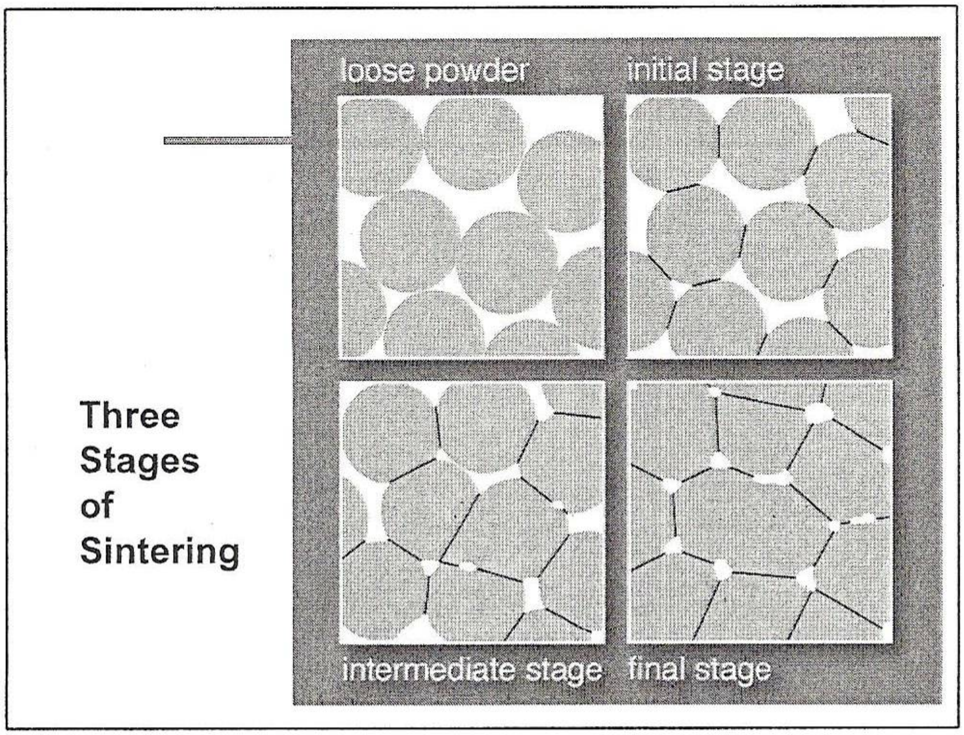

Figure 12: The different stages of sintering

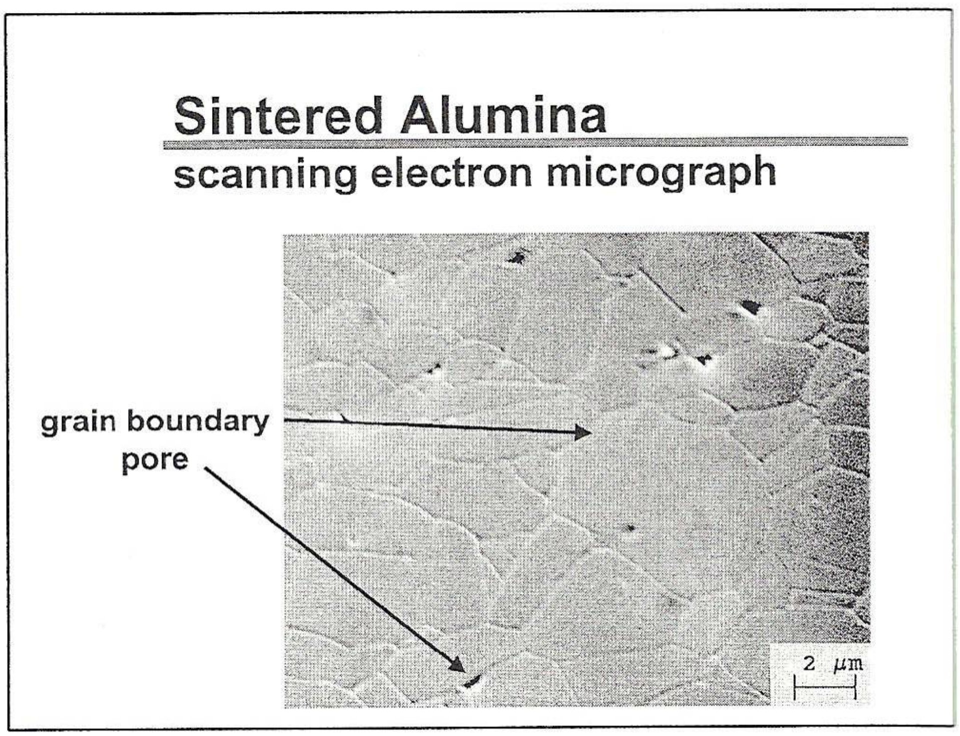

Figure 13: Microstructure of nearly fully dense alumina body

4 Conclusions

In conclusion, this presentation describes:

- refractories, their applications and requirements
- different types of density and porosity
- Archimedes principle
- the Archimedes bouyancy technique for measuring density and porosity
- Bulk Density by measurement
- measurement of Real Density
- Pycnometer types
- measuring Pore size distribution
- measurement of Permeability
- the influence of density and porosity on the performance of refractories

This presentation shows how important density, porosity, pore size distribution and permeability are to the performance of refractories of various types, and why it is necessary always to measure these of a refractory.

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