

The Measurement of Thermophysical Properties of Molten Slags and Fluxes

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Abstract

Methods for measuring the thermal diffusivity, thermal conductivity, density and viscosity of molten slags and fluxes have been critically reviewed.

The most common method for determining the viscosity of slags is the concentric cylinder method and in particular the rotating bob variant. There is now a well established reference material suitable for high temperatures and two standards for the most common materials investigated i.e. glass and mould powders. For low viscosities (of the order of 5mPa.s) the oscillating vessel method is suitable. The oscillating plate method has been investigated extensively for the measurement of mould fluxes by Japanese workers. A major problem is the containment of the slags to prevent unwanted reactions and the choice of materials used by a selection of workers is reviewed.

Fewer density than viscosity measurements have been made. The most popular methods of determining densities are the maximum bubble pressure (also suitable for determining surface tension); Archimedean and sessile drop methods. There is no corresponding infra structure for density measurements of slags as for their viscosities.

For the thermal diffusivity/conductivity, the most common methods are the laser flash and the transient hot wire techniques. The treatment of the experimental results is complicated, such as including the effects of radiation for translucent materials. It is clear, if the information is industrially important, there are substantial opportunities for further method development including standardisation and understanding the physical processes of heat transfer in these materials.

1. Introduction.

Mathematical modeling is being increasingly used by industry for process and product control and product innovation. The driving force for such modeling is improved productivity through lower energy costs, lower scrap losses, improved product quality, and product consistency. The success of such models is highly dependent on the thermo-physical property data used in the simulation calculations. There are little data available for these models and the data that are available are often of questionable quality. This lack of data is an impediment to fully realising the potential benefits of process modelling.

The principle reasons for the paucity of thermo-physical data for molten slags and fluxes are

- 1) Liquid slags and fluxes are often extremely reactive. This creates problems experimentally as containment materials and gas atmosphere have to be tailored to suit the slag system.
- 2) Slag and flux measurements are invariably high temperature measurements. Most traditional thermal property measurement techniques were designed for ambient or near ambient temperatures. Modifying these methods for high temperature measurements increases the uncertainty in the measurement.

This paper outlines the measurement techniques currently being used to measure some of the more important thermo-physical properties of molten slags and fluxes. These include thermal conductivity/diffusivity; density and viscosity. It is expected that surface tension and interfacial tension will be reviewed by others during this conference. For more information about interfacial and surface tension the reader is referred to references ¹⁻³.

2. Measurement Methods

2.1 Thermal Conductivity / Thermal Diffusivity.

Thermal conductivity mechanisms⁴ in slags are generally accepted to be of three types:

- 1) Lattice; thermal or phonon thermal conductivity (λ_L) where the heat is transferred through the phonons or the lattice vibration. The higher the crystalline perfection of the slag the higher the thermal conductivity of the slag.
- 2) Radiation or photon conduction (λ_R). Slags can be semi-transparent and it is experimentally observed that the thermal conductivity of these types of material increases to a limiting value with increasing thickness, of the specimen at which point the specimen is referred to as optically thick. Empirically it is considered that this condition holds when the product of the absorption coefficient and the thickness of the sample exceeds 3.5. The mechanism involves absorption and emittance of radiant energy by the sections through the specimen.
- 3) Electronic conduction (λ_{el}) is thought to occur when there are high concentrations of Fe^{2+} present. On the basis of electrical resistivity it is concluded that electronic conduction only occurs when there is significant FeO content of the order of 70% or above.

The effective thermal conductivity is expressed as

$$\lambda_{\text{eff}} = \lambda_L + \lambda_R + \lambda_{\text{el}}$$

There are three classes of technique which can be used to measure the thermal conductivity:

- 1) Steady state techniques such as linear heat flow and radial heat flow methods.
- 2) Non-steady state techniques such as radial wave and modulated beam technique.
- 3) Transient methods such as laser flash and line source methods both outlined below.

The most important thermal property measurement techniques with respect to molten slags and fluxes are the laser flash and the line source methods. It is these methods that are detailed below. For steady state methods such as the linear heat flow method or the radial (axial) heat flow techniques see Carslaw and Jaeger⁵ and non-steady modulated techniques refer to the Mills review⁶.

There are little data available for the thermal properties of molten slags and fluxes⁴ much of which is contained in the Slag Atlas data compendium⁴ published in 1995. Most of the thermal property data published since this compendium have been measured using the laser pulse technique⁷⁻¹⁴. In the laser flash technique it is thermal diffusivity that is measured. Thermal diffusivity is related to thermal conductivity by the following equation

$$a = \frac{\lambda}{Cp \cdot \rho}$$

where:

- a is the thermal diffusivity ($\text{m}^2 \text{s}^{-1}$)
 λ is the thermal conductivity ($\text{W m}^{-1} \text{K}^{-1}$)
Cp is the specific heat capacity ($\text{J kg}^{-1} \text{K}^{-1}$)
 ρ is the density (kg m^{-3}).

Of the data published since the compendium, most were measured by workers in Japan⁷⁻¹⁰. Much of this work has been focused on measuring the thermal diffusivity of mould fluxes employed in the steel industry.

There is a large uncertainty associated with the thermal property data available for slags. The scatter is often so large that only order of magnitude values can be assumed. In addition to the general containment problems that dealing with molten slags and fluxes bring, reliable thermal property data are difficult to obtain because

- 1) the heat transfer in slags and fluxes is complex, involving phonon (thermal diffusion) and photon (radiation) conduction. It is difficult separate the radiation component of heat conduction from the thermal diffusivity measurements.
- 2) at the high temperatures encountered when dealing with liquid slags and fluxes, it is difficult to obtain the thermal stability in order to avoid convective (mass) flow in a sample. This can lead to apparently high measured thermal diffusivities.

In order to overcome some of the containment problems experienced when dealing with molten slags and fluxes researches are being undertaken into minimal contact photo-thermal techniques such as photo-acoustic¹⁵; photo-deflection¹⁶; mirage effect¹⁷ and radiometry¹⁸, as well as Rayleigh Scattering¹⁹ type measurements. At present these techniques still require some development before confidence in the data generated from them is secured.

2.1.1 Thermal Diffusivity by Laser Flash.

A typical laser flash thermal diffusivity measurement involves heating the front face of a disc-shaped sample using a high intensity laser and monitoring the temperature rise on the back face²⁰. A schematic of a laser flash technique is given in Figure 1¹¹. From the temperature transient the thermal diffusivity can be calculated²⁰⁻²⁴. For liquid slag or flux measurements the sample is usually held (sandwiched) in a platinum cell. The effect of this cell on the temperature transient must be accounted for. The sandwich (platinum-sample-platinum) thermal diffusivity measurement is treated as three layer system^{7-11,25}. The unknown thermal diffusivity of the sample can be determined if the thermal properties (thermal diffusivity, heat capacity and density) of the cell are known.

This technique is similar to the method referred to as the stepwise heating technique (SHT) in the literature^{26,27}. The main differences being that the heat source in the SHT is often electrical, not laser, and the temperature response to the heat pulse is not necessarily made on the face of the sample.

The principle advantages:

- 1) The transient measurement times are short ~1 s. The short transient times minimise effects of convection on the heat transfer measurement and enable thermal diffusivity measurements to be carried out over large temperature ranges in a day.
- 2) There is minimal contact of the material, reducing the risk of contamination of the sample by the apparatus.

Disadvantages:

- 1) The samples are small and may not be representative of the bulk material.
- 2) Due to the small sample size, bubble formation in the sample will cause large errors in the measurement.

2.1.2 Line Source Method.

In the line source technique, a current is pulsed through a wire²⁸. The temperature response (ΔT) of the wire to the pulse is monitored. This magnitude of this temperature response is inversely proportional to the immersion medium (sample) of the wire. The thermal conductivity of the immersion medium can be calculated from the following equation,

$$\Delta T = \frac{q}{4\pi\lambda} \ln \left(\frac{4at}{r^2 \exp \gamma} \right)$$

where q is the heat input per unit length of wire, r is the radius of the wire, a is the thermal diffusivity of the liquid, Euler's constant and t is time. A schematic of a line source method is given in Figure 2²⁹.

This equation only applies when $(r^2/4at) \ll 1$. The thermal conductivity is obtained from the reciprocal of the slope of a plot of ΔT as a function of \ln time. The onset of convection is observed as a departure from linearity of the ΔT versus \ln time plot. The temperature of the wire may be obtained directly from a knowledge of its resistivity-temperature characteristics or measured using a thermocouple²⁹.

This method is also referred to as the transient hot wire method. The plane source technique^{30,31} is essentially the same as the line source, where the metallic wire is replaced by a strip. The wire can be shielded³² or coated³³ to protect it from electrical leakage to the immersion liquid (sample).

The principle advantages:

- 1) The measurement times are short ~ 1 s. The short transient times minimise effects of convection on the heat transfer measurement and enable thermal conductivity measurements to be carried out over large temperature ranges in a day.
- 2) The onset of convection in the measurement can be identified and its effects excluded.

Disadvantages:

- 1) The measurement wire is not robust and may break when inserted in the liquid.
- 2) Measurements on low thermal conductivity materials, such as slags, are sensitive to electrode end effect errors which are a result of a distortion of the heat pulse in the immersion medium due to heat losses through the connecting electrodes.
- 3) It is an immersion method and the wire may contaminate or be contaminated by the sample.

2.2 Density.

Although density is an important parameter for the modelling of slag behaviour and required in the measurement of viscosity by some techniques e.g. oscillating plate, there is less available data than for viscosity. This is partly because it is thought that densities can be modelled more easily than viscosity. The models for calculating density are reviewed elsewhere^{34,36}. In general an additive model is most widely used, adopted for its relative simplicity. Some workers have modified this model³⁵ to allow for structural changes in the slag. Tokuda et al⁴⁹ employed an excess volume on mixing with an interaction parameter for determining densities of slags used in viscosity measurements.

The density of slags can be measured with a wide variety of techniques³⁶ including weighing methods (pycnometry); buoyancy or displacement methods including the Archimedean method; dilatometry; pressure methods both manometer and maximum bubble pressure; droplet methods and suspension methods.

Although many of the measurement methods have been used in the past, the high reactivity of slags combined with the difficulty of accurately determining the increase in volume of containers with increasing temperature has led to the adoption of the maximum bubble pressure method. The other common techniques are the Archimedean and sessile drop methods.

2.2.1 Density by Displacement.

The apparent change in mass of an inert probe of known dimensions, immersed in a liquid provides a measurement of density. When stationary, the classic Archimedean method is used, but dynamic measurements may also be made as the probe is driven into the liquid at a constant rate. Once the surface forces have been overcome the density of the liquid is derived from the slope of the plot of mass against displacement. Figure 3 shows a schematic of a system which has been constructed at NPL.

For the Archimedean method the density is given by:

$$\rho = (\Delta w + s)/g(V + v)$$

$$s = 2\pi r \gamma \cos\theta$$

where g is the gravitational acceleration; V is the volume of the sinker; v is the volume of the immersed suspension wire; s is the surface tension correction i.e. the force acting against the suspension wire of radius r in a liquid of surface tension γ and the contact angle between the wire and liquid is θ . The volume of the sinker and the wire must be corrected for expansion with temperature. The double sinker method can be used to eliminate the effects of surface tension of the suspension by using two sinkers of different size.

The main disadvantage of this technique is the possible reaction between the sinker and the slag including changing wetting characteristics during the experiment.

An uncertainty of approximately $\pm 2\%$ may be achieved for molten slags and fluxes with these displacement techniques.

2.2.2 Maximum Bubble Pressure (MBP).

In the MBP technique the maximum pressures required to detach bubbles at the end of a capillary tube, at two or more known depths in the liquid, is used to determine the density of the liquid.

$$\rho = \Delta P / g \cdot \Delta h$$

where ΔP is the pressure difference between two heights (Δh) and g is the gravitational acceleration (see Figure 4). Frequently the densities are calculated from the slope of the immersion depth against maximum bubble pressure obtained from several depths.

Historically the maximum pressure corresponding to the detachment of the bubble was measured with a manometer but it is now more common to use a digital pressure gauge. The digital pressure gauge also allows the pressure build up during bubble formation to be followed.

The MBP technique has been used to measure the densities of Al_2O_3 and Ti_2O_3 ³⁷. The crucible and capillary tube were made from molybdenum and the gas was Ar-10% H. Induction heating was employed. Their results for Al_2O_3 were in reasonable agreement with three other independent investigations using the Archimedean technique^{85,86} and the MBP⁸⁷ method. The

results by a sessile drop method with a graphite substrate were lower and it was postulated that this lower value was influenced by a reaction between the substrate and the Al_2O_3 .

The densities of a Cu_xO and Cu_xO - SiO_2 slags were measured³⁸ in air at 1300°C using a platinum crucible. The density decreased as the SiO_2 concentration increased.

The main advantages of the MBP technique are that a new surface is exposed for each bubble so it is less susceptible to contamination and there is no mass measurement. The disadvantages are that it can be difficult to detect the surface to measure the depth of immersion; the equilibrium bubble shape is easily distorted; there is a danger of capillary/sample reactions including blocking of the capillary and the accurate measurement of the radius tube.

Ikemiya et al³⁷ list their experimental errors for their MBP apparatus for density measurement. They estimate their largest error is the pressure measurement; followed by the temperature and the immersion height of the capillary giving a total of about <1.7%.

Vaislurd et al⁸⁹ have constructed a combined unit capable of measuring viscosity, surface tension and density of oxide melts. The density and surface tension are incorporated in a MBP apparatus.

2.2.3 Droplet Methods.

These methods involve the imaging of a drop of slag at temperature and measuring the dimensions of the drop to determine its volume. If the mass is known the density can be determined. Although very simple in principal the method presents the challenge of determining the drop's shape; ensuring it is symmetric and measuring the correct dimensions.

The sessile drop is used for slags by resting the slag on a plate or substrate of a smooth horizontal surface (see Figure 5). The volume of the drop is calculated from the tables of Bashforth and Adams³⁹ or more recently by digital image analysis.

Levitation methods are now becoming available for the measurement of density. This eliminates contamination problems associated with the melt/crucible reactions. The levitation methods suitable for measuring non-electrically conducting materials have been reviewed by Weber⁹⁰. The density of superheated and under-cooled alumina⁹¹ was measured by levitation using an aerodynamic device. The sample was heated by a CO_2 laser. Levitation techniques are only at an early stage of development and their use limited. This is likely to change as confidence in the application of levitation techniques to slags and fluxes for measurements of density and surface tension increases.

2.3 Viscosity.

The rheological properties of slags are important for the modelling and control of industrial processes. Different industrial slags display a wide range of viscosity values ranging from about 5 mPa.s for CaF_2 based slags to several thousand Pa.s. No viscosity technique can measure over such a wide property range and therefore a technique suitable for the viscosity range of interest must be chosen. At the lower viscosities, the oscillating cylinder can be used although most work has been performed with concentric cylinder (rotation) viscometer. The concentric

cylinder is limited to the measurement of slags in the viscosity range of ~100 mPa.s to a maximum of about 200 Pa.s.

During the last ten years more attention has been paid to the calibration of viscometers so that data from different laboratories can be compared. Generally the performance of a viscometer is checked at room temperature with several certified reference materials (oils) which have viscosities corresponding to the range of viscosities to be measured. There are a number of standard reference glasses (such as NBS 710; 711 and 717) available for testing at high temperature and recently a lithia-alumina-silicate slag was developed for calibration⁴⁰ around relevant to metallurgical slags (~1-10 Pa.s).

That study⁴⁰ also demonstrated the importance of the composition of the container materials in affecting the measured viscosity values, recommending that molybdenum rather than graphite is used for containment. Both molybdenum and graphite require an inert atmosphere. Graphite appears to be more reactive with the standard reference glasses used for the calibration. It's reaction results in an increased viscosity. Also there is discussion of the effects of the contact angle between the slag and graphite on the measurement. This contact angle is very sensitive to the grade of graphite used. Therefore great care needs to be exercised in choosing the materials for containment of the slag to prevent unwanted reactions.

The other factor which can affect the composition of certain slags is the composition of the atmosphere surrounding the slag and in particular the oxygen potential. This requires good atmosphere control.

Changes in the composition of the slag during the measurement highlights the importance of pre and post chemical analysis of the measured slag to check for any composition changes.

There are a wide variety methods used to measure the viscosities⁴¹⁻⁴³ of slags and glasses.

2.3.1 Capillary.

The time (t) required for the liquid to flow through a capillary tube is substituted in the Poiseuille formula:

$$\eta = \pi r^4 \Delta P t / 8 V L$$

where r is the capillary radius; L the capillary length; ΔP the pressure difference along the capillary and V is the discharged volume of liquid. There are a number of corrections to be applied for its accurate application including allowing for the retained kinetic energy of the liquid at the bottom of the tube.

The method is considered as a suitable for intermediate temperatures⁴³. Above 1200°C there are problems in the choice of tube material and dimensional stability especially of the radius which is to the fourth power, therefore critical. It is an absolute method.

2.3.2 Falling Body or Counter Balanced Sphere.

In this method a body (normally a sphere) is either allowed to drop due to gravity or dragged upwards through the liquid. The viscosity is calculated using Stoke's Law:

$$\eta = 2.g.r^2 (\rho_k - \rho_{liq}) / 9S$$

where g is the gravitational constant; r is the radius of the sphere and ρ_k and ρ_{liq} are the density of the sphere and the liquid respectively and S is the velocity of descent or ascent of the sphere. It is normal to correct for the expansion of the ball⁴⁴ and the diameter of the ball should be less than 1/10 of the diameter of the crucible⁴⁵.

This is not an absolute method requiring an apparatus constant to be derived from calibration curves with liquids of known viscosity. The method was successfully demonstrated by Endell et al.^{46,47} for slag and glasses by the time taken to pull a ball from a melt at a constant measured force.

Hara et al.⁴⁸ used the counter balance sphere of Pt-20%Rh to determine the viscosity of CaO-SiO₂-Al₂O₂-Fe₂O₃ to study the effect of changes in the alumina content. The experiments were performed in air. For melts with a low viscosity (Reynolds number $Re < 0.1$) Stoke's Law does not hold therefore, they used a modified equation based. Hara et al.⁴⁸ showed the melt viscosity increased with increasing Al₂O₂ and a corresponding decrease in Fe₂O₃. The perceived disadvantages of the counter balance sphere compared to the concentric cylinder method are tabulated by Terada et al.⁵⁹

The major advantages of the concentric cylinder over the counter balanced sphere method are the greater viscosity measurement range; the speed of measurement; the potential for automation; the shorter furnace with associated temperature control and the smaller amount of material required for the concentric cylinder method compared to the counter balanced sphere.

The combined viscosity, surface tension and density measurement apparatus⁸⁹ incorporates a rotating bob for the measurement of viscosity.

2.3.4 Oscillating Plate.

This method⁴⁹⁻⁵¹ relies on vibrating a flat plate in a liquid with a constant driving force. The amplitude of motion will be dependent on the viscosity of the liquid. The amplitude of the plate oscillations are measured in air and in the liquid and the following relationships have been derived^{52,53}:

$$\rho\eta = (R_M^2 / \pi f A^2) \cdot (f_a \cdot E_a / f \cdot E - 1)^2 = K \cdot \theta_0$$

where ρ is the density; E_a and E are the amplitudes of oscillation in air and the liquid respectively; f_a and f are the frequency of the oscillation in air and the liquid; A is the area of the plate and R_M is the real component of the mechanical impedance.

The assumptions of the method are:

- 1) The liquid is a Newtonian Fluid.
- 2) Turbulent flow does not occur.
- 3) There is no slippage between the plate and the fluid.
- 4) The size of the oscillating plate must be larger than one wavelength of the oscillation wave and is planer.
- 5) The end effects of the plate on damping of the amplitude are negligible.
- 6) The size of the vessel is large enough that the effects of the reflected waves from the walls are negligible.

It has been shown that the resonant frequency in air and in the liquid can be considered to be the same for all practical purposes so that:

$$\rho\eta = (R_M^2 / \pi f A^2) \cdot ((E_a / E) - 1)^2 = K \cdot \theta$$

$\theta = (R_M^2 / \pi f A^2)$ is the damping factor and $K = (E_a / E) - 1$ is determined experimentally using viscosity reference materials.

The later designs have an improved vibration system which may explain why the earlier comparisons⁴⁰ of the viscosities measured by concentric cylinder systems and the oscillating plate are not as good as more recent comparisons⁵⁴. Typically the claimed reproducibility of the measurements were within $\pm 7\%$ of measured values⁴⁹.

2.3.5 Concentric Cylinder.

Viscometers of this type consist of two concentric cylinders i.e. a bob and a crucible. The viscosity is determined from measurements of the torque generated on the rotor arm of the rotating cylinder. When rotating the cylinder at a constant speed the viscosity can be obtained from the following equation

$$\eta = (1/r_1^2 - 1/r_0^2) \cdot M / 8\pi^4 nh$$

where M is the torque; n is the number of revolutions per second; r_1 is the radius of the bob; r_0 is the radius of the crucible; and h the height of the bob. The theory is applicable to infinitely long cylinders and it is normal to calibrate the system with reference materials using the equation:

$$\eta = G = S/n$$

where S is the scale deflection and G is the apparatus constant.

This is the most common method for the measurement of slag viscosity and for several practical reasons it is more customary to rotate the bob rather than the crucible. Probably the most important reason is that the rotating bob viscometer is based upon readily available and cheap commercial instruments. It is also easier to centre the bob but the viscosity range is less than for a rotating crucible instrument. Nakashima et al.⁶³ show a modern example of a rotating crucible method.

Table 1 includes a list of rotor and crucible materials used with various slags and glasses by a selection of workers with rotating bob viscometers. Some industrial slags are aggressive towards the crucible and the bob and there is a change in the composition of the melt. For example coal⁶⁷ slags with high K and S attack Mo and slags containing high concentrations of FeO⁷² or Cu₂O are usually measured with iron crucibles and bobs. The maximum temperature is limited to about 1450°C when using iron crucibles.

Industrial slags may show non-Newtonian behaviour, usually indicating the presence of high melting point solids. The use of calculated phase diagrams⁵⁵, which are becoming increasingly available, helps in the interpretation of the results. The control of atmosphere composition is essential for FeO/Fe₂O₃ containing slags. The suspension system entry point can be a cause of unwanted oxygen ingress. This can be overcome by bellows⁵⁷ or a sliding system⁵⁶ at the top of the apparatus. CaF₂ based slags are unstable at measurement temperatures and fluorine emissions (NaF, SiF₄, AlF₃ and HF) can be a problem. Finally, hydrolysis of the slag/flux, by exposure to moisture, can affect the results.

For a description of one modern concentric cylinder designed instrument with atmosphere control the reader is referred to the work of Seetharaman et al.⁵⁷. This instrument has been used to measure viscosity of a wide variety of systems (Table 2). This data has been used to develop their viscosity model. Figure 6 shows a schematic of the system used in the authors' laboratory.

An interesting application⁵⁸ of the variation of viscosity for CaO-SiO₂ and complex silicates with temperature, is the estimation of liquidus temperatures from the activation energies for viscous flow. The second derivative of the activation energy for viscous flow with respect to temperature, when plotted as a function of temperature, was found to exhibit a break at the liquidus point.

For a non-reactive slag and with careful calibration, it is estimated that a measurement uncertainty of less than ±10% can be achieved using a rotating cylinder instrument.

2.3.6 Oscillating Vessel Method (OVM).

In the OVM a cylinder of molten material is contained in a crucible supported on a thin wire forming a torsional pendulum. To start the measurement an oscillation is initiated in the pendulum. The decay in the amplitude of the oscillation (logarithmic decrement) with time is measured to obtain the viscosity. The OVM has a measurement range of between approximately 0.5 mPa.s to 100 mPa.s. These type of instruments have been used extensively in the measurement of the viscosities of molten salts⁷⁴, metals⁷⁵⁻⁷⁷ and are applicable to slags with low viscosities.

The main problems with the method are

- 1) the analytical method used to analyse the data. Iida and Guthrie⁷⁸ review this aspect in detail and recommend the Roscoe equation⁷⁹.
- 2) The wetting characteristics of the container can affect the result. It is preferred that a non-wetting container is used.
- 3) The corrections to the measured viscosity to account for the thermal expansion of the crucible can be large. Also the density of the sample (often unknown) is required to make the expansion correction.

In a recent design an optical pointer using a laser and a 40 diode array for detection has been developed⁷⁷ and it is claimed this gives higher repeatability of the measurements compared with the more normal three diode system. A schematic of this apparatus is shown in figure 7.

The method has been used successfully for a wide range of metal alloys up to temperatures of about 1650°C but the reactivity of some alloys with the crucible material can limit the technique. For extreme cases, uncertainties of the viscosity data by the OVM technique are of the order of +/- 10%.

2.3.7. Spiked Parallel Plate Creep/ Rotational Viscometer.⁸⁰

An elegant design to measure a wide range of viscosities from about 10^{12} to 10^1 Pa.s has been successfully demonstrated with various glasses to a temperature of 1200°C. The instrument combines an indentation method for the highest viscosities; a creep parallel plate method for the intermediate range, 10^7 to 10^4 Pa.s, and a rotating plate method for the lower range. It is claimed that because the principles and mechanism of this viscometer are simple, the absolute values of sample viscosity can be determined, at least to the right order, without any calibration using standard reference samples.

2.3.8. Industrial Viscometers.

Several simple viscometers have been developed for “on plant” determination of slag viscosities and quality assurance exercises. Examples are the Herty viscometer⁸¹ where the viscosity is determined by the length of the slag ribbon formed, and the Krabiell immersion viscometer^{82,83}.

In recent years the inclined plane method has been investigated in more detail⁸⁴. The molten slag is poured from a crucible onto an inclined steel plate plane with a “V” section (see Figure 7). The viscosity can be related to the length of the slag ribbon obtained. Mills et al⁸⁴ claim that measurement uncertainties of $\pm 15\%$, for slags with viscosities in the range of 0.1 to 1 Pa.s, are possible.

The oscillating plate method has also been proposed as an in-situ measurement.

3. Conclusions.

This paper reviews some of the methods available for measuring the density, viscosity and thermal conductivity/diffusion of molten slags and fluxes. There are a number of experimental difficulties in performing the measurements associated with the chemical reactivity of molten

slags and fluxes. Due to this reactivity and the need for high temperatures, furnace environment (gas/containment) is critical.

It is clear that the measurement of viscosity is the most developed property area, with a sound measurement infrastructure, including a well characterised reference material and measurement standards for the more common materials i.e. glass and mould fluxes. The concentric cylinder method is the most popular method, spanning the common range of viscosity values. The rotating bob variant is based upon relatively cheap commercial instruments. For a non-reactive slag and careful calibration, it is estimated that uncertainties of measurement of less than $\pm 10\%$ can be achieved with a rotating cylinder instrument.

Substantially less work has been carried out on the determination of density of slags than viscosity. This can either be interpreted as that density can be estimated more easily than viscosity or the property is of less industrial interest than viscosity. The maximum bubble pressure has been used most frequently in recent years but there are limitations for this method associated with the wetting behaviour of the capillary and the slag.

True thermal conductivity/diffusivity data on molten slags and fluxes are hard to come by. Invariably the data available in the literature has a radiation component associated with it. The treatment of radiation conduction for translucent materials is complex. Its solution will require the high temperature optical properties of the molten slag or flux. These data are not readily available. If thermal data for molten slags and fluxes are needed with greater precision there are substantial opportunities in method development, including standardisation and understanding of the physical processes involved in the measurement.

In an attempt to overcome the contamination problems associated with holding molten slags and fluxes, it is to be expected that future measurement developments will focus on the application of non-contact and levitation methods to make measurements

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Table 1 A: Selection of work which shows the rotor and crucible materials used in the measurement of viscosity of a wide range of slags.

Crucible Material	Material of Rotor	Slag Type	Comment	Ref.
Pt or Pt-Rh ⁵⁹	Pt	Mould powders	Suitable for oxidising but fails under reducing conditions.	61
90% Pt-10%Rh; 80%Pt-20%Rh	90% Pt-10%Rh; 80%Pt-20%Rh	Glasses	Attacked by S in melts. ⁶⁰ “Crucible should be preferably Pt alloy but a refractory material may be used provided it does not contaminate the glass”	62
	80%Pt-20%Rh	R ₂ O-SiO ₂ -B ₂ O ₃ R=Na or K RO-SiO ₂ -B ₂ O ₃ R=Ba or Ca		63
	17%Pt-13%Rh	Effect of CaO on viscosity of PbO-SiO ₂		64
Mo	Mo	Blast furnace	Require inert atmosphere. Cold inert gas can affect thermal profile of furnace.	66 65 67
		LF Mould powders Fluxed coal slags.	Sacrificial graphite liner to remove oxygen from nitrogen gas. No control of pO ₂ with graphite. High S containing slags form FeS and Fe-Mo-.S. Danger of crucible leaks.	
Graphite	Graphite	Na ₂ O-SiO ₂ -B ₂ O ₃		
Mo	Graphite	Copper based slags	Purified nitrogen atmosphere.	69
Alumina	Fe-23%Cr; 5%Al	Copper based slags	Argon atmosphere. Rotor more resistant to S attack than Pt	60
Alumina	Mo	Lead Smelting slags	Purified nitrogen atmosphere. Induction heating to speed experiments and minimise reaction time.	70
Ag-Pd alloy	Ag-Pd alloy	Iron bearing system	Diminish loss of iron to crucible below 1150°C	71
Fe	Fe	Iron bearing systems CaO-Fe _n O-SiO ₂	Maximum temperature 1450°C	72
Stainless Steel	Stainless Steel	Mould fluxes with additions of Al ₂ O ₃ and TiO ₂	Maximum Temperature 1300°C	73

Table 2: Systems under study to generate experimental data required for viscosity prediction model. ⁵⁷

Binary	CaO-SiO ₂
	Fe _n O- SiO ₂
	MnO-SiO ₂
Ternary	Al ₂ O ₃ - Fe _n O- SiO ₂
	CaO- Fe _n O- SiO ₂
	CaO-MnO-SiO ₂
	Fe _n O- MgO-SiO ₂
	Fe _n O- MnO-SiO ₂
Quarternary	Al ₂ O ₃ - CaO-MgO-SiO ₂
	CaO- Fe _n O- MgO-SiO ₂
	CaO- Fe _n O- MnO-SiO ₂
	CaO-MgO-MnO-SiO ₂
	Fe _n O- MgO-MnO-SiO ₂
Quinary	CaO- Fe _n O- MgO-MnO-SiO ₂

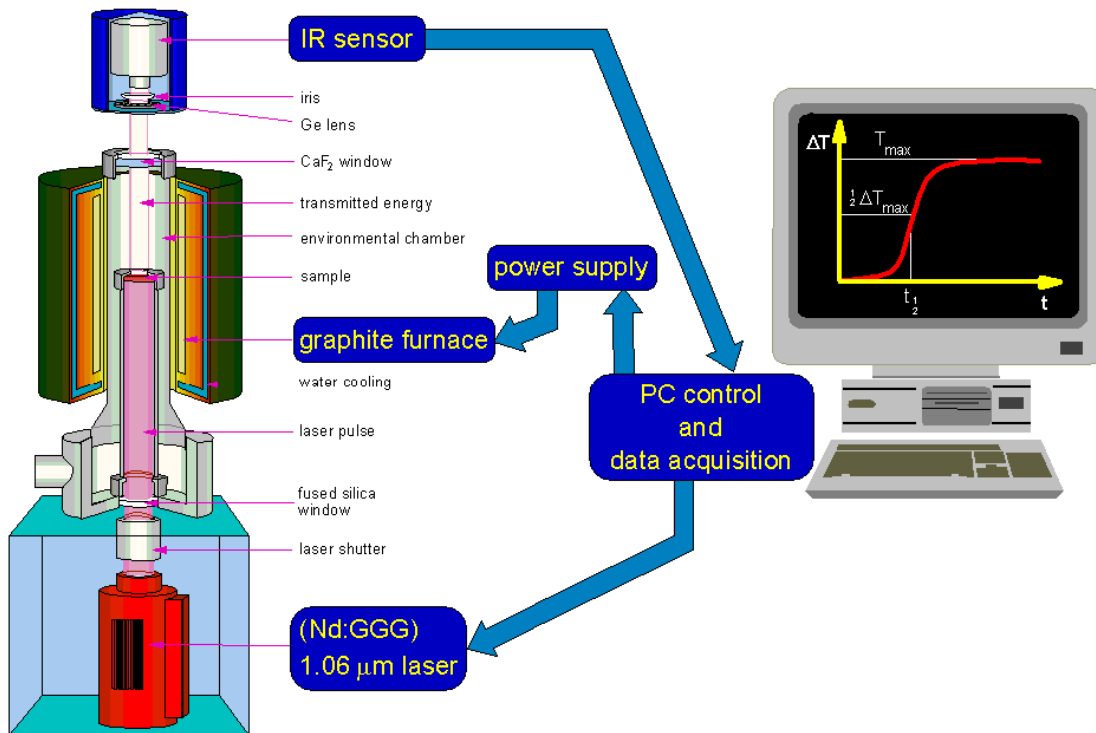


Figure 1: A schematic of a laser flash apparatus for measuring thermal diffusivity

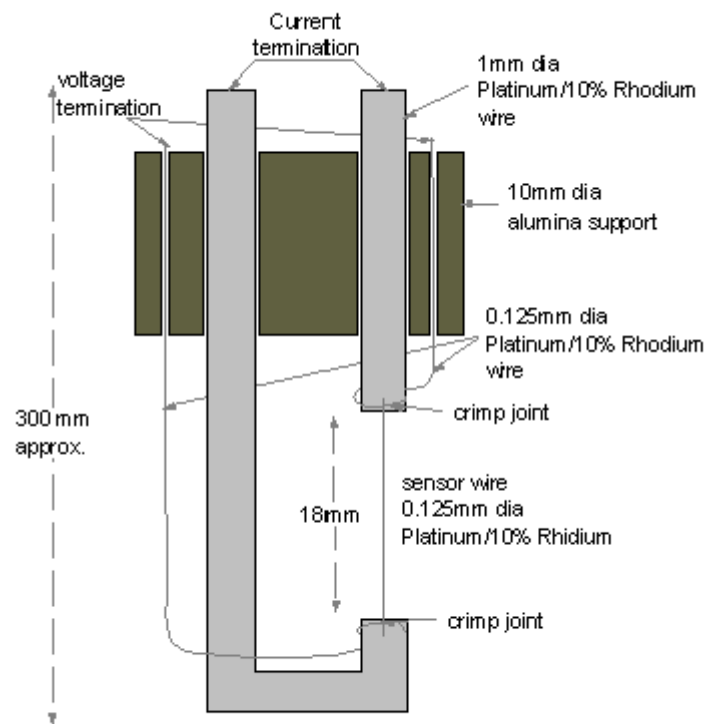


Figure 2: A schematic of the NPL line source method for measuring thermal conductivity.

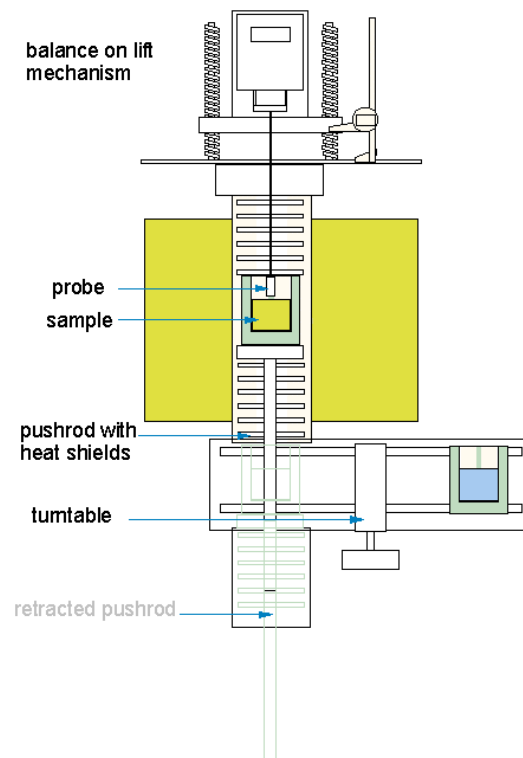


Figure 3: A schematic of an hydrostatic probe for measuring density.

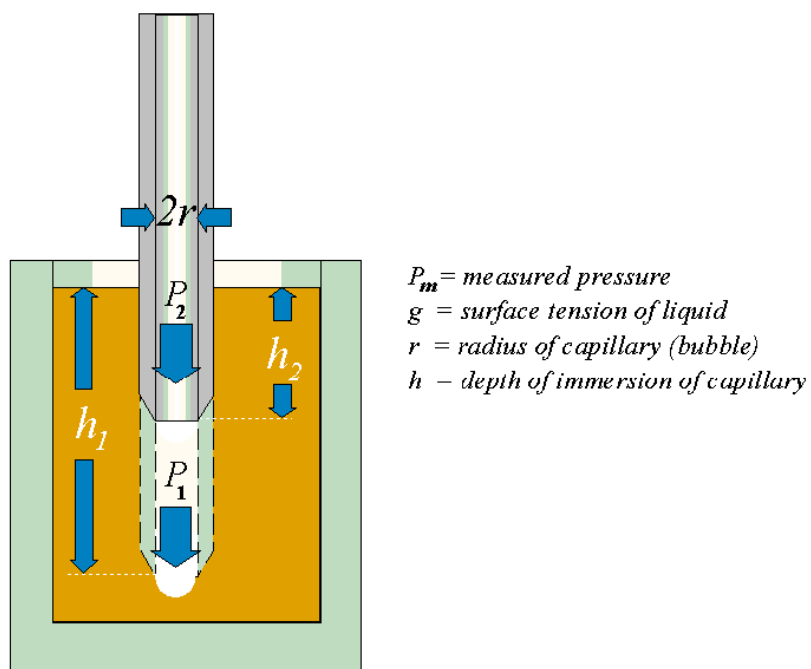


Figure 4: A schematic of a maximum bubble apparatus for measuring density.

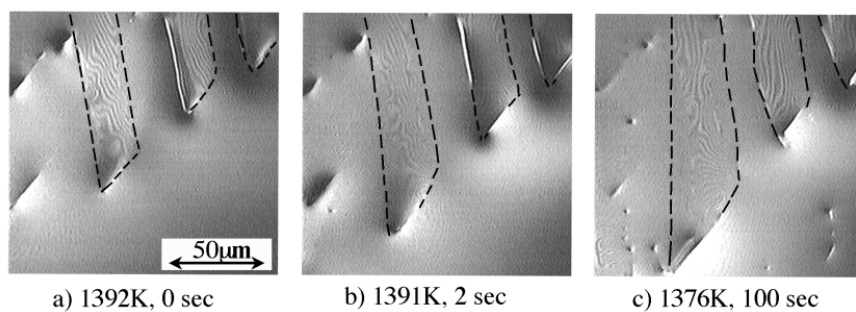


Figure 5: A schematic of a sessile drop apparatus for measuring density.

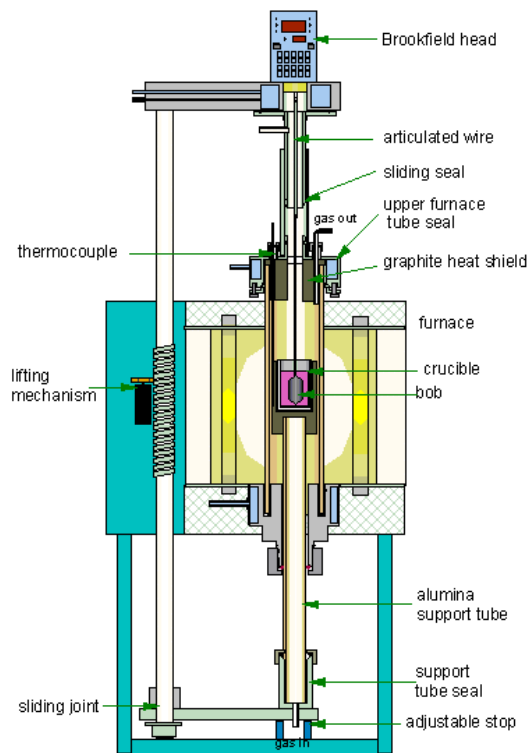


Figure 6: A schematic of a rotating bob apparatus for measuring viscosity.

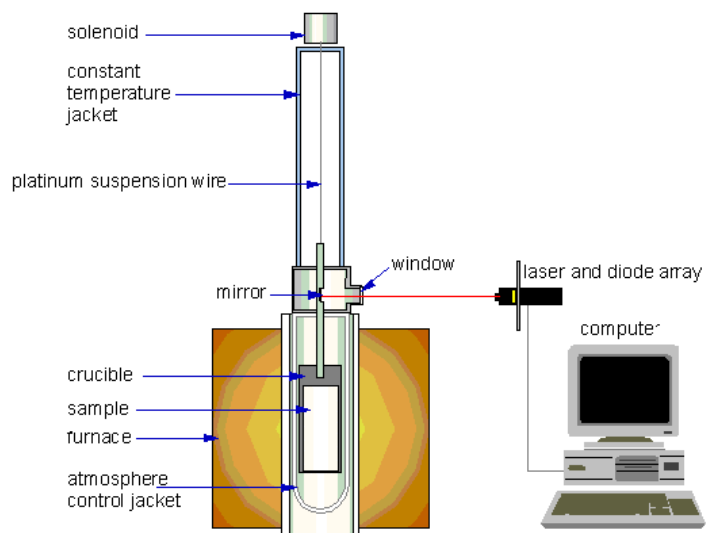


Figure 7: A schematic of a oscillating viscometer.