SHIRAISHI, Y. and SAKURAI, Y. Gliding cylinder method for the viscosity measurement of molten salts, slags and glasses. *VII International Conference on Molten Slags Fluxes and Salts,* The South African Institute of Mining and Metallurgy, 2004.

# Gliding cylinder method for the viscosity measurement of molten salts, slags and glasses

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A new method, the gliding cylinder method, was proposed as a wide range viscometer for the measurements of molten salts, slags, and glasses. The method consists of two coaxial cylinders, cylindrical bob and a vessel containing a liquid sample. There is a narrow gap between bob and vessel. When the vessel moves against the bob, the generated force on the bob consists of three types of resistance: (1) Stokes's resistance on the bob, (2) a capillary flow resistance though an annular gap between vessel and bob, and (3) lubricating resistance in a gap. The last two can be calculated on a theoretical basis but the first cannot be estimated by a simple calculation since a wall effect did not calculate easily. However, it can be assumed that the generated force depends on both the viscosity of a liquid and velocity of the vessel. Thus, the relation between viscosity and a force at desired velocity of the vessel was measured using several standard reference materials including glycerol aqueous solutions and standard reference oils.

The results depended on the magnitude of the gap between the bob and the vessel. For the wider gap, it was shown that the viscosity is a linear function of a gradient of force with respect to a vessel velocity. In contrast, if the gap is small, the viscosity depends on the gradient (of force with respect to velocity). This implies that the non-linear phenomena would occur in Stokes resistance. Though detailed analysis is in a further investigation, a calibration method can be applied to determine the viscosity by this method, because good correlation was obtained among these quantities.

Viscosity of molten salts, such as $NaNO_3$ and $ZnCl_2$ was measured by this method as high temperature demonstration.

Keywords: viscometer, viscosity, sphere pull-up method, fused salts, molten slags, glass melts.

## Introduction

During the past decade, we tried to develop a wide range viscometer which is applied to a viscosity range from glassy state, $10^{10}$ Pa•s, to molten state, $10^{0}$ Pa•s. Fortunately, two methods were achieved for that purpose: (1) sphere indentation and parallel plate creep/rotation method[1] and (2) tube indentation/rotation method[2]. Both methods were compared[3] using the same specimens including NBS standard reference glass. The results showed a good agreement with each other and with the standard value of reference material, except the measurement of tube penetration at its initial stage. However, if we restrict our measuring object to metallurgical melts, the necessary range of measurement must be extended toward a much lower region of $10^{-2}$ ~ $10^{-3}$ Pa•s. Consequently, the necessary range of viscosity may be estimated as $10^{-2}$ ~ $10^{3}$ Pa.s for a metallurgical purpose.

Of course, many methods are known for each kind of melt[4]. For example, the oscillating method or capillary method is well established for measuring fused salts, and a rotating method is widely used for molten slags having a moderate viscosity. For higher viscosity of molten glasses, the falling or pull-up sphere method is frequently applied. This implies that many viscometers must be used when we want to measure the viscosity of these various samples. The purpose of this study is to develop a simple viscometer covering the viscosity range of these melts even though it may be in a less accurate way.

One of the simplest ways to measure the higher and moderate viscosity range is a falling sphere method based on Stokes's law. In another limit of lower viscosity range, a capillary method would be preferable owing to its established principle. Thus, we try to combine these methods to expand a measuring range from lower viscosity of molten salts to the higher viscosity limit of glassy melts.

In this paper, we will describe an outline of a measuring method, experimental apparatus, results of measurements both in room and higher temperatures, and discuss the problems we met.

## Method of measurement

Suppose a cylindrical bob immersed into a cylindrical vessel containing a liquid as shown in Figure 1. When the vessel is moved up or down, a force exerted on the bob, $F$, may consist of three terms, Stokes's resistance, $F_S$; capillary tube resistance for flow through an annular part of the gap between bob and vessel, $F_C$; and lubricating resistance for relative motion of the bob against the vessel, $F_L$.

$$F = F_S + F_C + F_L \qquad [1]$$

The last two terms can be expressed[5] as follows:

$$F_c = 8\pi / V\left[\left(b^4 - a^4 - \left(b^2 - a^2\right)^2\right) / 1n(b/a)\right] \qquad [2]$$

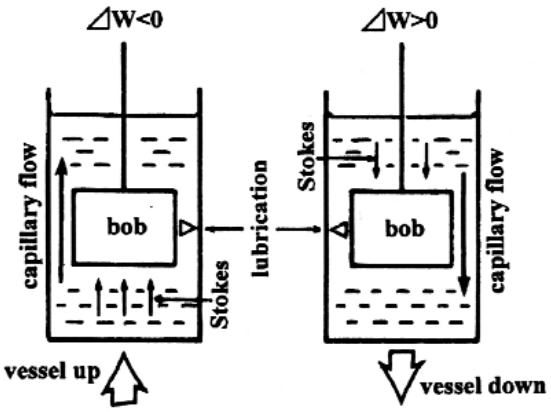


**Figure 1. Principle of measuring method**

$$F_L = 2\pi a^3 l/(b-a)^2(b+a), \qquad [3]$$

where, $b$ and $a$ are the radius of the bob and vessel, respectively, $V$ is a volumetric flow rate through the gap and $l$ is the length of the bob.

On the other hand, Stokes's term cannot be estimated easily, because Stokes's law is only valid in an infinite medium. In this case, the gap between bob and vessel is narrow. There are many proposals for the correction of Stokes's equation to include a wall effect. However, such improvement is limited within a value of a/b being less than 0.3 at most. Since the ratio a/b approaches 0.9 or more in this experiment, we have no good correction of Stokes's term.

However, it can be safely assumed that the force exerting on the bob is linearly related to the velocity of the vessel and the viscosity of the liquid, at least as a first approximation. This assumption may be equivalent to a phenomenological relation. When we differentiate $F$ with respect to $v$, we obtained the viscosity coefficient at once,

$$\eta = const \times (dF/dv) \qquad [4]$$

This equation means that if we measure the forces with the changing velocity of the vessel, then we can determine the viscosity eliminating the effect of an additional term, if any.

From this point of view, we measured the force exerted on the bob with the changing velocity of vessel motion in several levels, and took a linear regression between forces and velocities to determine a gradient of force with respect to velocity.

## Experiment

A schematic diagram of an experimental apparatus is shown in Figure 2. The main body of the apparatus originates from another experiment. As a result, the speed range of the reciprocating mechanism, 0.1~ 1mm/s, is not sufficient for this experiment.

The force exerting on the bob is measured by means of a load cell, whose capacity is 100 g with a resolution of 0.05 g, located on top of the apparatus. In a preliminary experiment, the force exerted on the vessel is also measured by another load cell placed on a reciprocating plate. Since

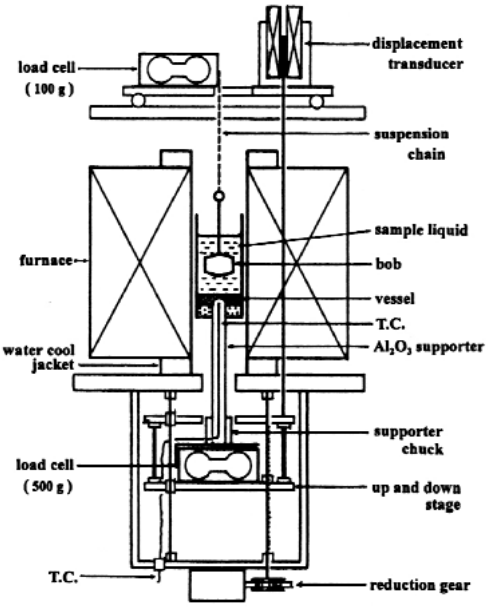


**Figure 2. Experimental apparatus**

both measurements gave almost the same values, we measured only with the upper load cell having a higher sensitivity. The velocity of the vessel is determined from a distance travelled between successive sampling times as recorded by a data logger. The distance travelled by the vessel is determined by means of a displacement transducer. All the output of the load cell and displacement transformer are gathered into a data logger and treated by a personal computer with temperature data.

Figure 3 shows the dimensions of a vessel and bobs as examples. They are made of SUS 304 stainless steel. Traveling distance of the bob is about 20 mm. Spacers keep a clearance between bob and vessel. Otherwise, holding the bob in the centre of the vessel is difficult. Of course, these spacers make an additional force on the bob when the vessel moves. But, it does not have a serious effect on the viscosity measurement because the velocity dependence of a frictional force is negligible compared with viscous resistance.

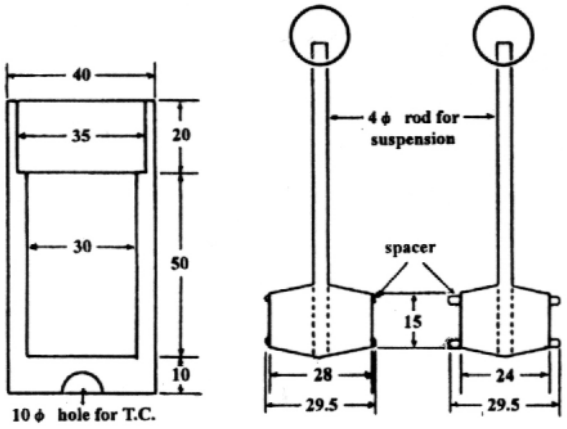


**Figure 3. Example of vessel and bobs (unit:mm)**

**Table I**
**Logarithmic regression between the viscosity and a gradient of the force with respect to the velocity of the bob**

| Diameter of bob/vessel | $\log \eta = A \log (dF/dv) + B$ $A$ | $B$ | Correlation factor, $R$ | Viscosity range |
|---|---|---|---|---|
| 20/30 | 1.0077 | -0.0148 | 0.9989 | 1 ~ 10 |
| 24/30 | 0.9479 | -0.5583 | 0.9943 | 0.615 ~ 10 |
| 27/30 | 1.1835 | -1.6308 | 0.9941 | 0.017 ~ 6.7 |
| 28/30 | 1.2489 | -2.315 | 0.9972 | 0.005 ~ 0.86 |

**diameter / mm, $\eta$ / Pa•s, d $F$ / gf d $v$ / mm.s$^{-1}$, viscosity range / Pa•s.**

**Table II**
**Viscosity of molten $NaNO_3$ and $ZnCl_2$**

| $NaNO_3$ | Temp./ °C | d $F$/ d $v$ | $\eta$ / mPa•s | Temp./ °C | $\eta$ / mPa•s *) |
|---|---|---|---|---|---|
| | 330 ~ 350 | 0.579 | 2.4 | 350 | 2.4 |
| | 370 ~ 380 | 0.295 | 1.1 | 380 | 1.8 |
| $ZnCl_2$ | 270 ~ 280 | 56.0 ~ 58.4 | 3.52 ~ 3.57 | 318 | 3.72 |
| | 280 ~ 290 | 24.4 ~ 26.9 | 1.26 ~ 1.43 | 350 | 1.125 |
| | 290 ~ 300 | 10.6 ~ 12.5 | 0.48 ~ 0.55 | 375 | 0.515 |
| | 300 ~ 310 | 9.76 ~ 12.3 | 0.40 ~ 0.54 | | |
| | 310 ~ 315 | 8.59 ~ 9.32 | 0.30 ~ 0.33 | 400 | 0.260 |

*) : reference value [6]

The purpose of this measurement is to prove the validity of the new method. Thus, we chose standard reference materials, such as glycerin and its aqueous solution, and standard reference oils for measuring samples. Fused $NaNO_3$ and $ZnCl_2$ are also used as a sample for high temperature measurement.

A vessel containing a sample is set on the alumina support connected to the lower load cell and a bob is immersed in a sample. The vessel is moved up and down several times, usually 8 or 10 times, at different velocities. At each velocity, the force is measured at a suitable time interval, 2 to 18 s, during vessel movement upward or downward. To eliminate the effect of buoyancy acting on the bob, the force was measured at a constant vertical position. At the desired velocity of the vessel, the correlation between the force and the height of the bob in the vessel was determined, to obtain a reliable value of the force at a standard bob position. The forces at the standard positions were regressed against the velocities and, finally, the gradient of the force with respect to the velocity is obtained. Viscosity values are correlated by these measured gradient values.

All these correlations are taken among the same direction of the vessel motion. Small discrepancies were observed between the direction of up and down motion. The force generated by down motion is always larger than that of upward motion of the vessel. Since the differences of these forces are not so large, we ignore the difference and plot them together on the correlation diagram.

## Results

Correlation between the viscosity against a gradient of the force with respect to the vessel velocity is shown in Figure 4 in logarithmic scale. Each line corresponds to the fixed geometry of bob/vessel diameter ratio. Correlation is well expressed in linear form in the cases of 20/30 and 24/30 of bob/vessel dimension. This means that Equation [4] is valid for a wider clearance between bob and vessel, such as 5 or 3 mm on one side against 30 mm of a vessel diameter. However, for a narrow gap, such as 27/30 or 28/30 of bob/vessel diameter Equation [4] must be corrected to higher than first order correlation as shown in Figure 4. This implies that the nonlinear wall effect will appear in Stokes's resistance term.

Details of regression values are summarized in Table I with correlation coefficients and a regressed region of viscosity. At this moment, we have no empirical equation which can generally express the viscosity with the parameters used in the measurement, such as diameters of bob and vessel, velocity and force etc. However, the correlation between the viscosity and the gradient of the force has been well established as shown in Table 1 and Figure 4. Thus, we can use them to determine the viscosity of an unknown sample under the fixed condition of vessel and bob dimension used here.

As a demonstration of the use of these regressions, high temperature measurements of molten salts were carried out. The procedure of measurement is almost the same as that at room temperatures. A vessel containing a premelted sample is placed on the top of the alumina support and is put in a furnace. After the sample is melted, the bob is immersed in a melt and the force is measured for several values of vessel velocity in the same way as at room temperature. The results obtained using the relations in Table I are shown in Table II and compared with reference values[6].

Fused $NaNO_3$ was quite stable in the molten state and the measurement could be carried out smoothly. Thus, we obtained reasonable values as shown in Table II, even though the viscosity is so low and is beyond the lower limit of the regression range. On the contrary, $ZnCl_2$ was very hygroscopic and has high vapour pressure. We had serious bubbling on melting and had heavy fuming at higher temperatures in the molten state. Thus, the measurement was not uniformly carried out and the results were not so reliable. Especially, to save measuring time, we sped up the measurement at the expense of the reliability of temperature measurement. When we compare our data with previous data, there are large discrepancies in temperatures at the same viscosity level. However, the temperature dependence of the viscosity is qualitatively similar to that of the reference values. These results encourage us to further improve of the system for higher temperature measurement.

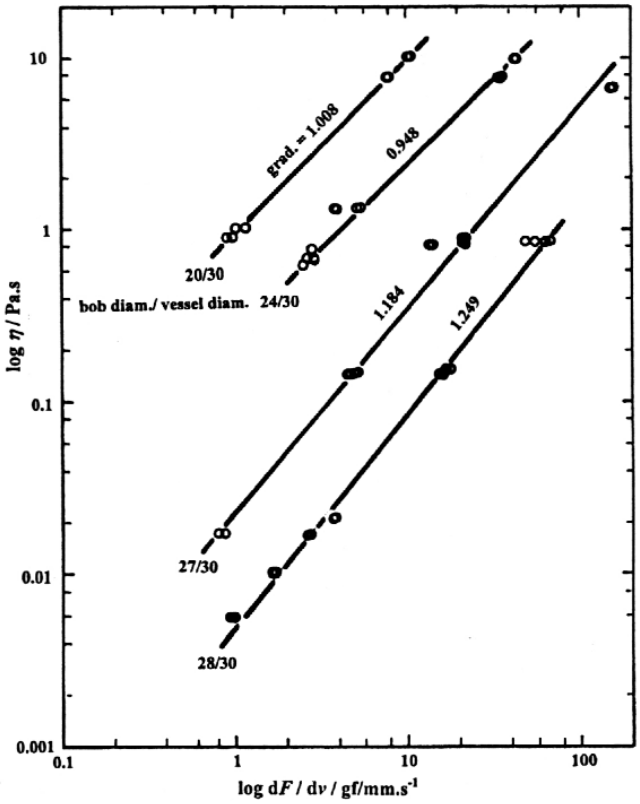


**Figure 4. Logarithmic correlation between viscosity and gradient of force with respect to velocity**

## Discussion

As shown in Figure 4 and Table I, the results of narrow gap measurements do not show the first order relation between viscosity and a gradient of force with respect to velocity. The reason fot this phenomenon is not clear but could be attributed to the non-linear relation in Stokes's term in Equation [1]. In the falling sphere method, several equations are proposed for the correction of the wall effect[7]. All of these corrections are limited in their validity for a radius ratio of bob/vessel less than 0.3. For example, the simplest one is as follows:

$$F_S = 16a(1 + 2.4\ \ a/b), \qquad [5]$$

where a and b indicate a radius of bob and vessel, respectively. This is a case of a flat disc[5] (not a sphere) moving through a finite medium having a ratio of a/b less than 0.1. When we combin e this equation with Equations [2] and [3] and apply it to the data obtained by 20/30 geometry measurements, calculated viscosity values were about twice the the regressed values. The data of 24/30 gave much larger differences between the viscosity and the regressed values. However, these deviations could be corrected by an additional term in Equation [5]. Data of 27/30 and 28/30 should be treated another way in which a factor depending on the sample viscosity itself may be taken into consideration. It should be solved in a further study.

For the high temperature measurement, we chose $NaNO_3$ as an example of a lower viscosity sample, and $ZnCl_2$ as a typical sample having a large viscosity change near its melting point. Since our target for the lower limit of viscosity is around 0.001 Pa•s where the viscosity of most fused salts falls, fused $NaNO_3$ is a suitable sample whose viscosity is 0.002 Pa•s at its melting point, 350ºC. The measured results shown in Table II agree remarkably with previous data[6]. However, the measured results of water were severely scattered and could not be included in regression data. When we take into consideration this fact, it does not mean that the viscosity value measured on fused $NaNO_3$ is in good agreement with the previous value. What we can safely say is that our measurement gave the right order of the viscosity value on fused $NaNO_3$. On the measurement of $ZnCl_2$, it is clear that the problem is in the temperature, both in control and measurement. Obviously, this is a problem of the measuring system and there is no need to discuss it here any more. Currently we use stainless steel as materials for the vessel and bob. This means that the experimental temperature is restricted to less than 500°C. This temperature limit makes a selection of the sample limited. Another possibility for testing sample selection for high viscosity is in PbO glass, which has high viscosity, about $10^2$ Pa•s around 500ºC and will be measured to test the method.

## Conclusion

The gliding cylinder method, which consists of a cylindrical bob and a vessel with a narrow gap, is described.

Using standard substances of known viscosity, the correlation was measured between the sample viscosity and the gradient of the force exerted on the bob with respect to the velocity of the vessel.

In a wider gap arrangement between bob and vessel, whose diameter ratio (mm) is 20/30 or 24/30, the viscosity is proportional to the gradient of the force with respect to velocity. However, in a narrow gap arrangement, where diameter ratio is 27/30 or 28/30, the viscosity depends on the gradient raised to a power larger than one.

In a narrow gap arrangement, the end effect of the bob moving through the vessel becomes serious and the wall effect causes the resistance on the bob to be non-linear.

In order to test the high temperature applicability, viscosities of fused $NaNO_3$ and $ZnC1_2$ were measured. Both measurements showed the applicability of this method to a high temperature use.

It is concluded that the possibility for developing a wide range viscometer from 0.05 to 100 Pa•s is established by this experiment. This range of measurements may cover the slag viscosity of any kinds.

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