

Viscosity Measurements of Ceramic Oxides by Aerodynamic Levitation¹

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The aerodynamic levitation technique has been used to achieve contactless surface tension and viscosity measurements of oxide liquids at high temperature ($T > 2000$ K). An analytical approach (hydrodynamic equations) and a new recent approach, the energetic approach, are presented. The energetic approach is interesting because it can be applied to all cases, including ceramic oxides, even for droplets far from spherical shape. A device (VITI: Viscosity Temperature Installation) has been developed to perform viscosity measurements on corium using the aerodynamic levitation method. Specific experimental setups for the preparation and for the heating of the sample have been developed. This device has been successfully tested up to 1950 K for viscosity measurements and up to 2900 K without sample. These steps are indispensable to accomplish the final goal of VITI device: the measurement of rheological properties on oxides corium in this field of temperature. Viscosity models at high temperature for molten oxides are presented and compared.

KEY WORDS: aerodynamic levitation; corium; high temperature; oxides; viscosity.

1. INTRODUCTION

Safety studies are required under accident and severe accident conditions for current and future water-cooled nuclear reactors. In a hypothetical case of a severe accident, a very high temperature could be reached (up to 2800 K)

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and the materials of the nuclear reactor (ceramic oxides, cladding, metallic alloys, structural materials, concrete, etc.) could melt to form complex and aggressive mixtures called "corium." In the framework of severe accident studies, accurate thermophysical properties data are necessary to model the corium behavior (thermo-hydraulics, physico-chemistry, etc.) and for the calculation with severe accidents codes. Corium viscosity is a key property both for predicting corium spreading and convective heat transfers.

High temperature (> 2000 K) thermophysical properties measurements of molten oxides are constrained by difficulties in achieving and controlling high temperatures, and in preventing physical and chemical inertness between the oxides and its container. Among the existing levitation techniques, the aerodynamic levitation of a droplet by a gas is interesting for thermophysical measurements of ceramic molten oxides, such as the corium. For these reasons, the French Atomic Energy Commission (CEA) has developed for the rheological properties of the corium two complementary approaches: viscosity models, especially for calculations of spreading experiments [1–4] and a specific experimental device for the measurements of rheological properties [5, 6].

The current corium viscosity models are consistent with many spreading experiments, but some experimental viscosity data are still missing, especially for the liquid state of some compounds of the corium. Very few characterization techniques can be used to measure rheological properties because of the high temperatures and the great reactivity of the corium [7]. Contactless measurements avoid these technological problems, especially the levitation techniques. Among the levitation techniques, the gas-film levitation technique is well adapted to insulating liquid materials, such as the corium [8, 9]. At CEA-Cadarache, a device, called VITI (VISCOSITY TEMPERATURE INSTALLATION), has been developed to perform viscosity measurements on prototypic corium (mixture with uranium dioxide) using the aerodynamic levitation method. The specific experimental setup for the preparation and the heating of the sample are presented and the first results on a nuclear glass are discussed.

2. MODELING OF THE CORIUM VISCOSITY

Within the scope of severe accident studies, the corium rheological behavior plays an important role in many phenomena such as the relocation of the core materials, the spreading of the corium, and the interactions with vessel pit structural materials. Predictions of corium mixture viscosities are needed to study scenario evolutions.

A general methodology has been developed by CEA to calculate the corium viscosity for temperatures above the liquidus temperature and for

temperatures between the liquidus and solidus temperatures of the mixture (both for the liquid phase viscosities and the apparent viscosities) [1–3]. From an estimation of the mass and the composition of the liquid and solid phases at a given temperature (e.g., by thermodynamic calculations), different models must be applied to estimate the apparent viscosity according to the nature of the corium. The starting point of all these models is a knowledge of the liquid-phase viscosity.

Two main types of liquid phases can be distinguished according to the composition [3]:

- Liquid with silica: Urbain's [11] or Seetharaman [13] model.
- Liquid without silica: Andrade's model modified by Nazaré [14].

Urbain's model considers three types of species: the formers, the modifiers, and the amphoteric. This classification of the species was proposed by Carron [10] and can be used to account for the effect of each constituent of the oxide mixtures. The Urbain model [11] was proposed for estimation of the liquid viscosity in the ternary system $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ as a function of the composition at a given temperature. This model describes the viscosity using the Weymann relation, which is expressed as

$$\eta = 0.1A \exp\left(\frac{1000B}{T}\right) \quad (1)$$

where η is the viscosity, A and B are two empirical parameters correlated to the relative fractions of formers, modifiers and amphoteric, and T is the absolute temperature. This model has been extended to the mixtures of corium and concrete decomposition products. Presently, the qualification of such a model for corium-concrete mixture is limited because of the lack of direct measurements on this system. Furthermore, the classification of the corium constituents is not definitively established: ZrO_2 is considered by some authors as a modifier without qualitative studies; by analogy, UO_2 is considered as a modifier. Very few data are available to validate this model. The missing data, which are absolutely necessary for the validation of this model, is represented on the Urbain diagram (Fig. 1).

More recently, Seetharaman et al. [13] have proposed a model linking viscosity to the excess Gibbs energies found in thermodynamic modeling. Since there is a thermodynamic database for corium [15, 16] enabling the estimation of Gibbs energy for multicomponent corium melts, we have also tested this technique for UO_2 containing melts.

Figure 2 presents the viscosity measured by Leibowitz et al. [17] for a mixture of 18wt% UO_2 in molten Columbia River Basalt (52wt% SiO_2 , 16wt% Al_2O_3 , 11wt% FeO_x , 10wt% CaO , 3wt% NaO , 7wt% MgO).

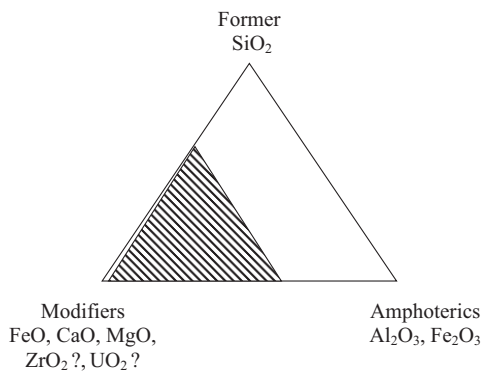


Fig. 1. Identification of the zone in Urbain's diagram with missing liquid viscosity data for corium (▨).

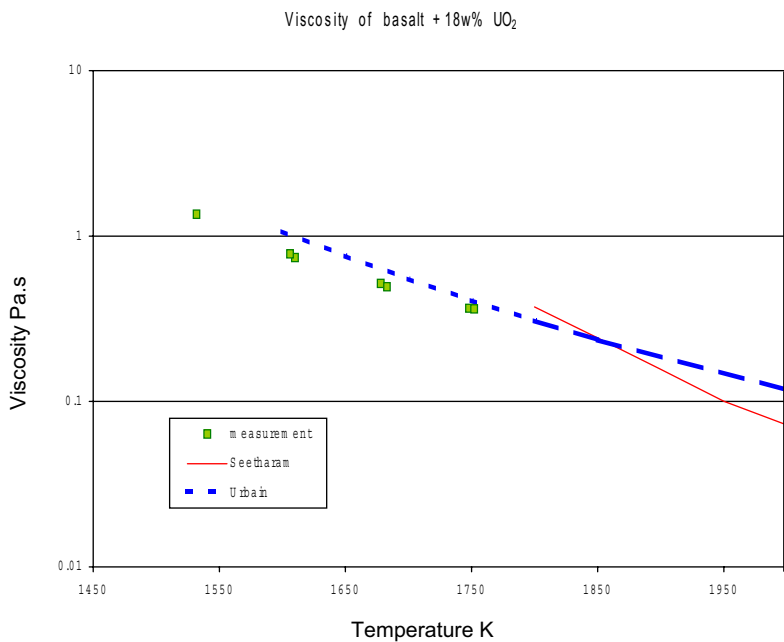


Fig. 2. Comparison of experimental viscosity on basalt + 18w% UO_2 with estimations using Urbain's and Seetharaman models from Leibowitz data [17].

GEMINI2 thermodynamic computations with the TDBCRO01 thermodynamic database have been made for this composition (in which sodium—not included in the database—is replaced molewise by calcium) liquidus temperature of 2100 K. Urbain's and Seetharaman models have been used to estimate the above-liquidus viscosity. As it can be noted, there is a good agreement between the experimental measurement and both models.

For mixtures without network-forming molecules (in our case without silica), Sudreau and Cognet [1] have shown that the general Andrade formula fits satisfactorily measurements made on urania and urania-zirconia mixtures:

$$\eta = K \frac{(AT_m)^{1/2}}{V_A^{2/3}} \exp \left[\frac{Q_n}{R} \left(\frac{1}{T} - \frac{1}{T_m} \right) \right] \quad (2)$$

where K is a constant equal to $0.194 \times 10^{-6} \text{ kg}^{1/2} \cdot \text{m} \cdot \text{K}^{-1/2} \cdot \text{s}^{-1}$, A is the mean molecular weight (kg), V_A is the mean molecular volume (m^3), T_m is the liquidus temperature (K), R is the perfect gas constant, Q_n is the average of the activation energies for each constituent. Nevertheless, we have not found any experimental data on the activation energy for liquid zirconium dioxide.

3. CHANDRASEKHAR-ENERGETIC APPROACH

In order to obtain experimental viscosity data, the aerodynamic levitation technique is a well adapted solution for radioactive materials such as uranium dioxide or for mixtures containing corrosive materials such as iron oxide. The advantages of this technique include rapid heating up to high temperature ($T > 2000 \text{ K}$), no contamination/reaction with a crucible, and accurate measurement of the surface tension (surface tension is very sensitive to impurities or contamination).

A droplet is levitated by a gas film and a subsequent damping is induced by a perturbation. The oscillation damping time constant is directly related to the droplet viscosity whereas its shape at rest is controlled by its surface tension. Two kinds of perturbations are possible according to the range of droplet viscosity and can be written for $n = 2$ (oscillation mode) as [12]:

- Periodic perturbation ($\Omega < 0.767$): $\omega^2 = \frac{8\sigma}{\rho R^3}$ (3)

$$\tau = \frac{\rho R^2}{5\eta} \quad (4)$$

- A-periodic perturbation ($\Omega > 0.767$): $\tau = \frac{38 R\eta}{40 \sigma}$ (5)

Here, σ is the surface tension, R is the equatorial radius, τ is the damping constant, ρ is the density, and Ω is the Ohnesorge number. This is a dimensionless viscosity: ratio between the viscous strengths and the inertial strengths and the surface tension:

$$\Omega = \frac{\eta}{(\sigma\rho R)^{0.5}} \quad (6)$$

First of all, it is important to notice that the viscosity data are particularly sensitive to flows in liquids caused by external forces such as those forces due to the gravitational field or electromagnetic fields.

The analytical approach of Chandrasekhar [12] considers an ideal case, incompressible spherical droplet at equilibrium with no influence of the gravitational field. For very small deformations, it is possible to easily formulate damping constants and relaxation frequencies of the droplet for each relaxation mode. These hypotheses mean that, for correct viscosity measurement on a levitated droplet, it is necessary to follow these criteria: nearly spherical droplet, droplet radius < capillary length, and droplet deformation < 10%.

Using the same approach to determine the viscosity of some well-known liquids such as water or silicon oil with aerodynamic levitation, Perez [6] did not find the expected value for the viscosity. He explained the differences by the flat shape of the droplet (effect of gravity) and the consequent mixing of oscillating mode ($n = 2$) and translating mode ($n = 1$). So he proposed another approach, called the “energetic approach,” to describe this system. General principles are described in Ref. 6. In this paper, we will only summarise the main results of this interesting work.

The total energy of a levitated droplet approximated by an ellipsoid of revolution, can be calculated as the sum of the gravitational potential and the surface energy:

$$E(R_{po}) = \sigma S(R_{po}) + \rho V g R_{po} \quad (7)$$

where g is the acceleration due to gravity, S is the surface of the ellipsoid of revolution, V is the volume, and R_{po} is the polar radius of the free droplet.

Deriving Navier–Stokes’ equations, it is possible to evaluate the viscosity with periodic perturbation and a-periodic perturbation knowing the resonance peak and Δf , the relaxation time τ of the aperiodic decay.

$$\eta_{\text{periodic}} = \frac{2\pi}{3} R_{po}^2 \rho \Delta f \quad (8)$$

$$\eta_{\text{a-periodic}} = \frac{1}{3} R_{po}^2 \omega_o^2 \tau \quad (9)$$

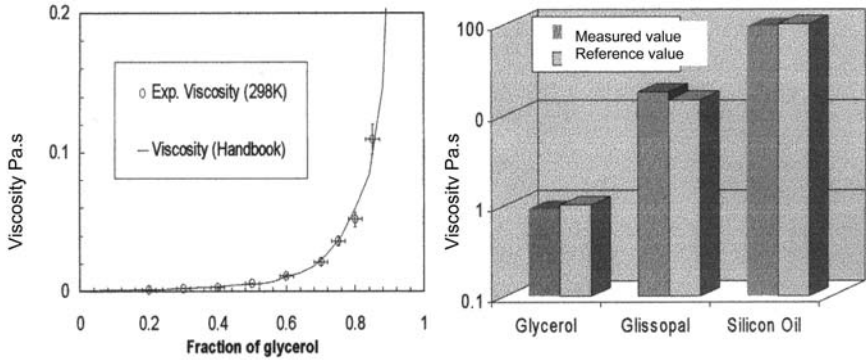


Fig. 3. Comparison between measured and reference values of viscosity for calibrated liquids (glycerol, glissopal, silicon oil) [6]. (1) periodic mode. (2) a-periodic mode.

As it can be seen in Fig. 3, there is good agreement for both perturbations (periodic or a-periodic modes) with the energetic approach using Eqs. (8) and (9).

4. EXPERIMENTAL PROCEDURE

At CEA-Cadarache, a device called VITI (Viscosity Temperature Installation) has been developed to perform viscosity and surface tension measurements on corium by aerodynamic levitation within the PLINIUS European corium experimental platform. A schematic of the experimental VITI device is presented on Fig. 4.

Today, VITI operates only according to the a-periodic mode (“high” viscosity). The liquid droplet stands on a thin gas film ($< 100 \mu\text{m}$) passing through a pressurized porous membrane (diffuser) (see an example on Fig 5). A second membrane (pressing membrane) stands above the droplet and is moved to reach the required pressing amplitude. It is stressed that there is no contact between the droplet and the pressing membrane due to the presence of the gas film. The droplet is then relaxed, and the relaxation time constant to the equilibrium state is measured. No contact occurs between the drop and both membranes.

To obtain high temperatures up to 2800 K, a radio frequency generator is coupled with the diffuser and the pressing membrane (made from graphite). The oxide sample is heated at low temperature by thermal radiation of the diffuser and pressing membranes. At higher temperature, the droplet is heated directly (volume heating) with the increasing of the current induced inside the oxide materials (dramatic increase of electrical

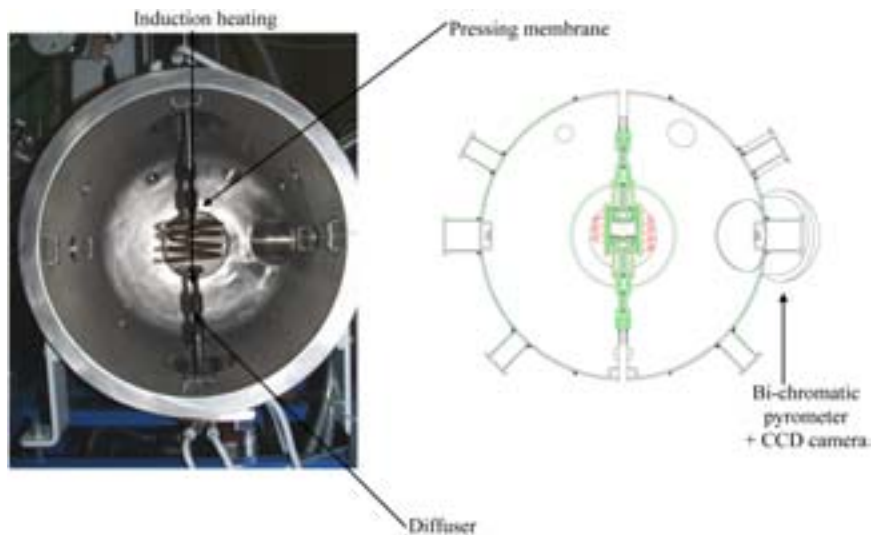


Fig. 4. Experimental setup of VITI: (VIscosity Temperature Installation).

conductivity of oxides at high temperature) and always indirectly with the thermal radiation (surface heating) from the membranes. The coupling of these 2 heating sources limits thermal gradients inside the droplet. Furthermore, even the thermal gradients inside the droplet are also reduced by a special thermal and reflector barrier installed just behind the membranes with only a small window to measure the surface temperature of the droplet.

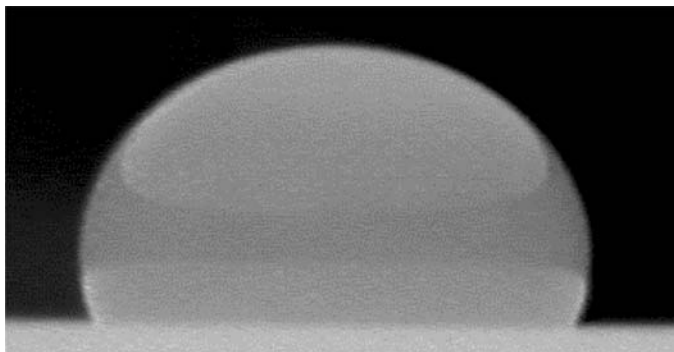


Fig. 5. Photo of a droplet (AR-glass) in aerodynamic levitation at 1215°C.

A bi-chromatic pyrometer ($\lambda_1 = 0.92$ and $\lambda_2 = 1.04$ μm) is used to measure the surface temperature of the droplet between 1300 and 2800 K. Two video cameras allow the precise measurement of the size of the droplet. A video recorder is used during each test. Then, a specific image analysis software evaluates the main geometric characteristics of the droplet (polar, equatorial radii, etc.) and a second software estimates the viscosity and the surface tension of the materials according to Chandrasekhar's approach or the energetic approach, knowing the density in the liquid state.

5. RESULTS AND DISCUSSION

The VITI device has been tested with success for the measurement of the liquid viscosity on a range of different materials and viscosity: standard materials (water and standard oils), organic compounds, metallic alloys, glasses and ceramic oxides. To validate the ability of the experimental device to reach high temperature ($T > 2500$ K) with an appropriate instrumentation, VITI membranes have been successfully heated at 2900 K-30 minutes without any levitated material.

A series of experimental tests has been conducted to establish a general optimized experimental procedure from the preparation of the sample to the continuous aerodynamic levitation during the experiment. So, some general rules can be given: before the levitation and the heating of the solid material, the sample must be prepared by a specific polishing procedure in order to obtain a pre-form of the sample with the same radius of curvature as the diffuser. To guarantee the levitation, it is necessary to use a homogeneous and nonporous material at the beginning; that means that samples of corium (multiphase materials) must be first of all melted ($T > T_{\text{liquidus}}$) and homogenized before levitation experiment.

The most important aspect for the experiments with oxides samples is to guarantee continuously the levitation of the sample during induction heating. If there is a single contact point between the diffuser or pressing membranes and the oxide sample, there are irreversible chemical reactions, the levitation fails, and the diffuser membrane is fatally damaged. For these reasons, the induction heating must be conducted with a specific heating procedure. Below the solidus temperature of the oxide sample, it is recommended to heat slowly in order to homogenize the sample temperature. But above the solidus temperature (according to the corium compositions, the solidus temperature ranges between 1300 and 2800 K), it is absolutely necessary to heat quickly the oxide sample because of its change of the state. The solid-liquid mixture has different properties than those of the solid: these differences of behavior can lead to the destabilization of the

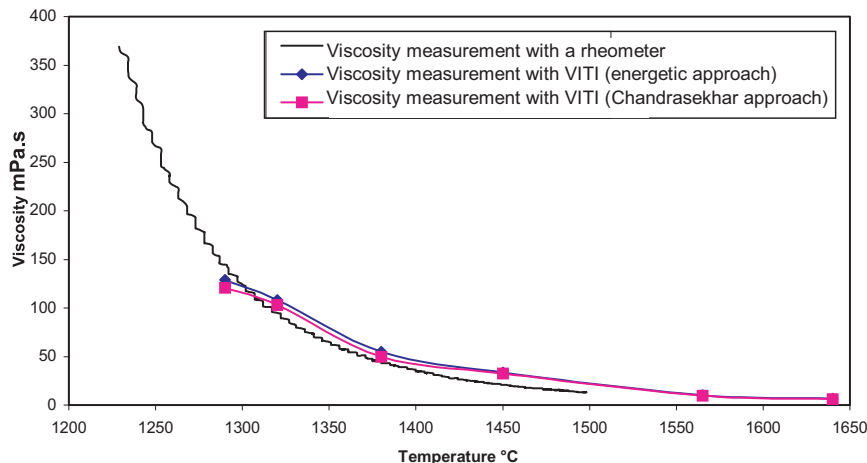


Fig. 6. Viscosity measurement on a nuclear glass with VITI device.

sample, and the termination of the levitation, and to the failure of the experiment. In this range of temperature, it is necessary to reach the liquid state as quick as possible (according to the corium compositions, the liquidus temperature ranges between 2000 and 3100 K), since the liquid state is the stable state for the aerodynamic levitation.

As an example, viscosity measurements of a nuclear glass between 1200 and 1650°C is presented in Fig. 6. VITI experimental results (Chandrasekhar and energetic approach) are compared with experimental results from a classical co-axial cylinder rheometer. As can be seen, there is a good agreement between VITI's results and a classical rheometer. This important results allows to validate the experimental device VITI and the models used to calculate the viscosity of the oxides mixtures. Furthermore, it can be noted that the values of the viscosities are closed between the Chandrasekhar's approach and the energetic approach. This result was foreseeable on this nuclear glass because the main conditions of the Chandrasekhar's approach are respected: small deformations, "quasi" spherical form.

6. CONCLUSIONS

Rheological properties measurements of oxides materials have been obtained with the aerodynamic levitation of a droplet on a specific device (VITI: Viscosity Temperature Installation) up to 1950 K. Technological qualification was tested successfully up to 2900 K. In order to calculate

the viscosity, two models are used: the classical analytical approach of Chandrasekhar when the droplet is close to the ideal case (incompressible spherical droplet at equilibrium with no influence of the gravitational field) and a new approach, the energetic approach, when the droplet is close to a flat form. These two approaches have been successfully applied on a range of materials with different viscosities. This intermediate development of the VITI device is an indispensable step to successful rheological measurements on corium up to 2800 K. Up to now, different models have been used to estimate the viscosity of the corium (liquid with silica: Urbain's or Seetharaman model, and liquid without silica: Andrade's model), but to validate these models, it is necessary to measure experimental viscosities of some corium compositions.

In the near future, this device will be used to perform physical measurements on corium mixtures with uranium dioxide (in- or ex-vessel corium) containing corrosive materials such as iron oxide. Viscosity will be evaluated using Chandrasekhar or energetic approaches according to the influence of the gravity on the droplet. Finally, it is also planned to adapt the VITI device to the periodic perturbation (ohnesorge number less than 0.767) in order to deal with less viscous mixtures.

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