Observing the Cure Processes of Cement Materials based on Static Viscosity Measurements

(Re: Change in State of Various Materials from a Liquid to a Solid Observed with a Tuning-fork Vibration Viscometer)

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Change in State from a Liquid to a Solid of Various Materials Observed with a Tuning-fork Vibration Viscometer

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Abstract

First, the cure processes of several different cement materials were measured using a tuning-fork vibration viscometer. Then, based on the measurement results, the possible influence of the material, temperature, water-cement ratio and the ambient temperature on the cure process of cement are examined. In addition, examinations are conducted and proposals offered regarding the measurement principle of the tuning-fork vibration viscometer and the physical quantity measured by this method is also discussed. At the same time, measurement results concerning the state variation from a liquid to a solid of various materials, which are only obtainable using a tuning-fork vibration viscometer, are also reported.

Keywords: Tuning-fork Vibration Viscometer, Kinetic Viscosity, Viscosity, Static Viscosity, JCSS

Introduction

A&D Company, Limited is a manufacturer specializing in the field of weights and measurements. A&D Company, Limited designs, develops, manufactures and sells weighing and measuring instruments, including electronic balances. Around 20 years ago, the electromagnetically driven, tuning-fork vibration viscometer was introduced in the cement industry. This electromagnetic driving method is comparable in structure to the electromagnetic mass sensor used for electronic precision balances. This characteristic made it possible to perform far more precise viscosity measurements than those conducted by other viscosity measuring methods. For example, with the electromagnetic driving method, continuous measurements can be performed from a low viscosity of approx. 0.30 mPa·s (1/3 the viscosity of purified water) to a high viscosity of 10,000 mPa·s. Moreover, it has recently become possible to perform continuous measurements from 0.30 mPa·s with sample liquid as small as 2ml, or to measure a viscosity of up to 100,000 mPa·s.

Almost all kinds of liquid materials, including composite (multicomponent) materials, are measurable. Although the initial purpose of the product was the measurement of the viscosity of cement, its application has since been expanded to include lubricants such as engine oils, abrasives for semiconductors, water & oil-based inks, etching solutions for metals such as ferric oxide, liquid crystal solutions for flat panels, adhesives and molding materials needed in the production of electronic parts, measurement of the change in the state from a liquid to a solid of materials such as adhesives, and more recently, soft drinks, human blood, bile and the cloud points of nonionic surface-active agents.

The present study centers on the discussion of measurement technologies from the perspective of a weighing and measuring instruments manufacturer, rather than on a discussion of cement materials themselves. Data showing the cure processes of materials that change from a liquid to a solid over time and data for materials whose states vary due to temperature changes are provided as actual measurement examples. Changes in the physical properties that may be inferred from the viscosity measurements are also examined.

Tuning-fork Vibration Viscometer

In the field of liquid viscosity measurements, the capillary viscometer and the rotational viscometer have a long history and are widely recognized throughout the industry. This article provides a brief explanation of the vibration viscometer, which is relatively new as a method for viscosity measurements.

- Principle: The principle for the vibration viscometer itself was proposed many years ago. However, it was only about 20 years ago that the theory was put into actual practice because of various difficulties involved in the practical realization. Initially, the characteristics of the damped vibration were the focus of measurements based on the idea that the damped vibration of the spring in a liquid would be influenced by the viscous resistance of the liquid. The formula that expresses this principle is a linear motion equation involving the inertial force due to the mass, the restorative force of the spring and the damping force due to the viscous resistance. Based on the solution of the equation, it could be deduced that the product of viscosity and density governs damping.

When the oscillator vibrates at the frequency *f*, the mechanical impedance R_z that the oscillator receives from the liquid will be $R_z = A\sqrt{\pi f \eta \rho}$ where, *f* is vibration frequency (Hz), *A* is planar dimensions of the both sides of the oscillator plate, η is the viscosity of the liquid, and ρ is the density of the liquid. Then if the force of the constant vibration velocity $Ve^{i\omega t}$ that the electromagnetic driving unit exerts to the oscillator plate is *F*, the equation $R_z = \frac{F}{Ve^{iwt}} = A\sqrt{\pi f \eta \rho}$ is valid. Therefore, it is evident that the force generated by the electromagnetic driving unit to maintain constant amplitude is proportional to the static viscosity, the product of the viscosity η and the density ρ.

- Structure of the tuning-fork vibration viscometer: The tuning-fork vibration viscometer utilizes the same measurement principle as the vibration method, which was proposed a long time ago. However, the difference is that with the tuning-fork vibration viscometer, the vibromotive force generated due to the vibration—a problem inherent in the vibration method—has been successfully eliminated by the adoption of a tuning-fork structure with two oscillator plates. The tuning fork and two oscillators function as a resonance system that is a highly sensitive viscosity sensor. Moreover, the viscous resistance of the liquid and the driving force generated in the electromagnetic unit are balanced because the amplitude of the oscillators is always kept constant. By adopting the same measuring system as the electromagnetic weighing sensor of a balance (called the “null method”), it is now possible to perform a wide, dynamic range of highly sensitive viscosity measurements.

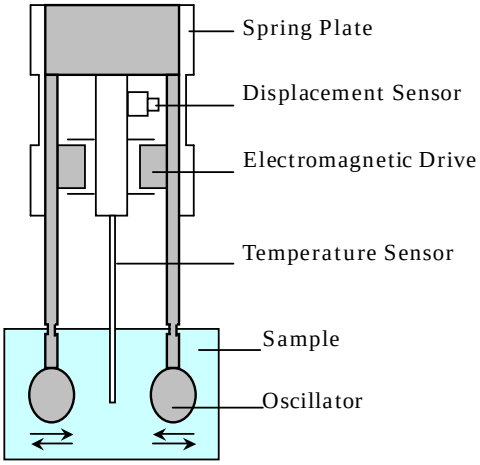

Fig 1. Structure of Viscosity Detection Unit

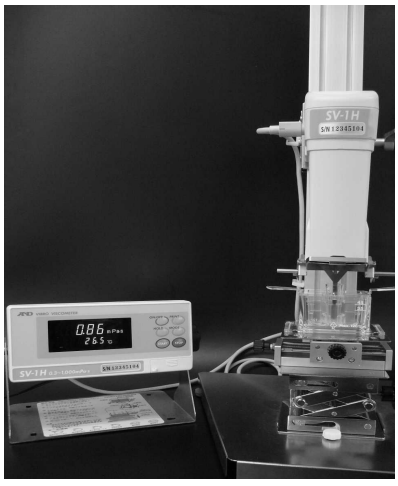

Fig 2. Tuning-fork Vibration Viscometer SV-A

○ Physical quantity (static viscosity) to be measured: As illustrated in the solution of the above-mentioned motion equation, the physical quantity measured by the vibration viscometer is viscous resistance, and this viscous resistance consists of "viscosity × density." If we define "viscosity × density" as "static viscosity,"[1] the relationships between each viscosity measuring method and physical quantity to be measured will be the "kinetic viscosity" (viscosity / density) for the capillary viscometer, the "viscosity" for the rotational viscometer, and the "static viscosity" (viscosity × density) for the vibration viscometer. The following is a brief summary of each viscometry device, its features and unit system:

(1) Kinetic viscosity is determined by measuring the time taken by a liquid to go through a flow channel in accordance with gravity.

(2) Viscosity is determined directly from the difference in the rotational torque generated within a liquid in accordance with rotational movement.

(3) Static viscosity is determined based on the driving force torque loaded on the oscillator within a liquid.

Terms	Kinetic Viscosity	Viscosity	Static Viscosity
Definition	Viscosity / Density	Viscosity	Viscosity × Density
SI Unit	m^2/sec	Pa·s	Pa·s × kg/m^3
Dimension	L^2/T	$ML^{-1}T^{-1}$	$M^2L^{-4}T^{-1}$
CGS Unit	St	cP	cP × g/cm^3 = sv
Unit Conversion	1 $m^2/sec = 10^6$ cSt	1 Pa·s = 10^3 cP	1 Pa·s × kg/m^3 = 1 sv
Measurement Method	Capillary method, etc.	Rotational method	Vibration method
Conversion to Viscosity	Density correction required	——	Density correction required

Table1: Comparison between Kinetic Viscosity, Viscosity & Static Viscosity

○ JCSS standardization: The JCSS requirements for the standardization of viscosity were established and made public in April 2006. Four devices are listed as JCSS standard devices for viscosity measurements. These are the standard (calibration) liquids of viscosity, the capillary viscometer, the rotational viscometer and the vibration viscometer. The validation of the principle by "model equation" and

[1] For a more detailed discussion on static viscosity, see N. Izumo (2006). Physical Quantity Measured by a Vibration Viscometer (Re: JCSS Standardization of Viscosity). *23rd Sensing Forum*. http://www.aandd.jp/support/materials/23rd_sensing_forum_sv.pdf

"uncertainty" related to viscosity measurements have already been completed for each of these devices[2]

Measurement Results

Now, let us examine various measurement results obtained using a tuning-fork vibration viscometer. The graphs principally show static viscosity changes along a time axis. Unless specifically mentioned, the terms "static viscosity" and "viscosity" will not be distinguished and shall collectively be called "viscosity," "viscosity value," etc. Since it would create confusion to use a unit system that has not been officially recognized, the unit of viscosity Pa·s or mPa·s will be used, assuming that the densities of the samples are all 1g/cm^3.

(1) The cure processes of cements were observed by measuring changes in viscosity over time with a vibration viscometer. Based on viscosity measurements that use different types of cement and curing conditions as parameters, the initial fluidity and the cure processes of each material are examined.

a) Cure processes of various ready-mixed mortars and cement pastes (see Fig.3 & 4)

Instant cement (generic name), quick-drying cement, flash-set cement, waterproof cement and raw cement (all available in retail stores) were obtained, mixed with the amount of water recommended for each cement material, and then measured for their respective cure processes at room temperature. Sand, resinous bonding materials, etc. were previously mixed into the cement materials, and significant differences in the cure processes of the cement materials were discovered. The viscometer used here is capable of continuous measurements from 0.30 to 10,000 mPa·s. When graphed, the X-axis indicated the viscosity values between a value just after being mixed with water and near the maximum displayable value of 12,000 mPa·s, whereas the Y-axis indicated time. The cure process of each cement material is largely different. For example, it can be determined from the graph that the curing speed of Mortar No.1 is very high just as it is labeled "flash set." The data shows that from the moment the measurement started (133 mPa·s) the viscosity value rapidly increased, and there was such a significant change in fluidity in just 7-8 minutes that the

[2] For further details on JCSS standardization, please visit the National Institute of Technology and Evaluation website: http://www.nite.go.jp/index-e.html

viscosity exceeded 10,000 mPa·s, which is the upper limit of the measurable range for present viscometers. However, on the other hand it was demonstrated that Mortars No. 2, 3 & 4 did not become solid easily and they required more than 30 minutes. As for the cement pastes, the initial fluidity was found to differ depending on the water-cement ratio.

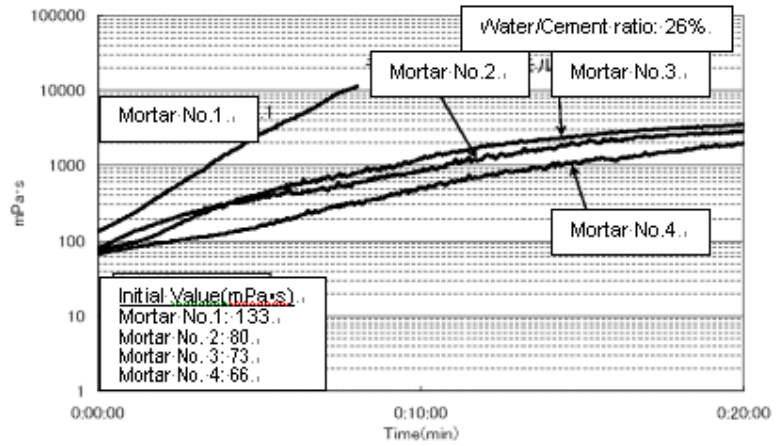

Fig 3. Viscosity Change of Various Mortars

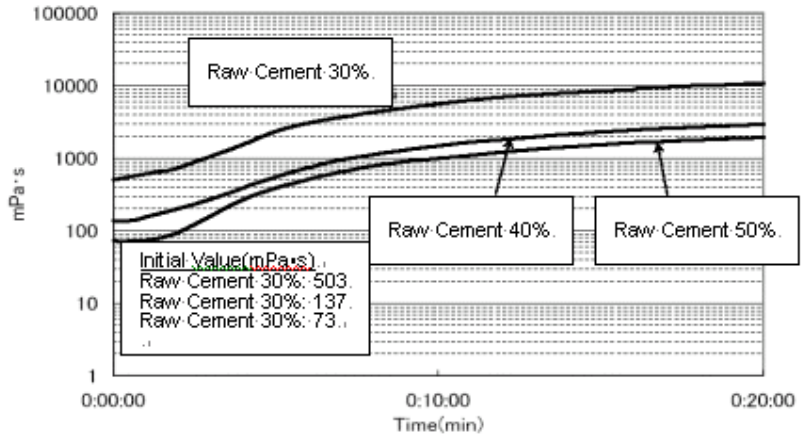

Fig 4. Viscosity Change of Cement Pastes

b) Differences in the curing process due to different mixing ratios with water (see Fig.5)

In Mortar No.1, the influence of differences in water-cement ratio on the cure process was measured. It was demonstrated that the larger the water content,

the lower the initial viscosity and consequently, the longer it took for curing to begin. In particular, when the water content was 26% or below, the mortar increased its solidness rapidly, resulting in poor fluidity. From the “20% curve,” several peaks for viscosity were observed during the same cure process. These are sudden viscosity changes apparently caused by slipping between the cement material and the sensor oscillators that were in direct contact with the sample.

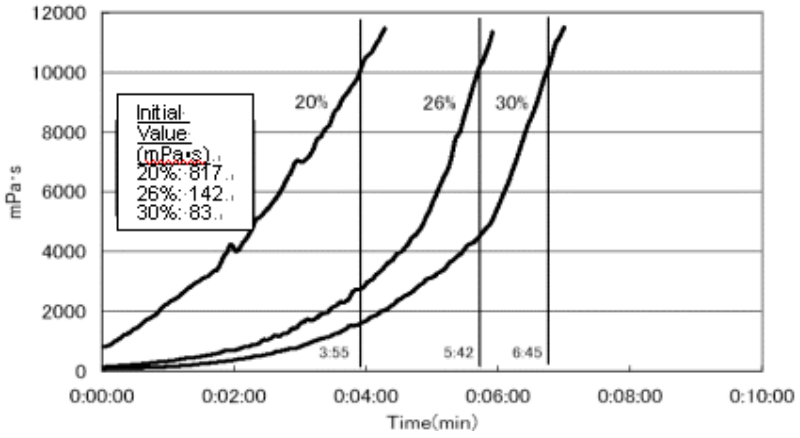

Fig 5. Cure Processes of Mortars with Different Water Content

c) Influence of ambient temperature on the cure process (see Fig.6)

Mortar No.1 was once again used for the experiment. The viscometer and the material were placed inside a temperature-controlled room, where water and the mortar were mixed under different temperatures in order to measure the influence of differences in ambient temperature on curing. Consistent with what is already known, the graph shows that curing is slow at a low temperature (10˚C) and fast at a high temperature (40˚C). In the case of Mortar No.1, it is deduced that changes in the curing speed of areas that change in temperature were determined to have a low progressivity. In addition, when the cure process is under a temperature of 40˚C, there exists a viscosity variation around 8000 mPa·s supposedly due to slipping between the sample and the oscillators.

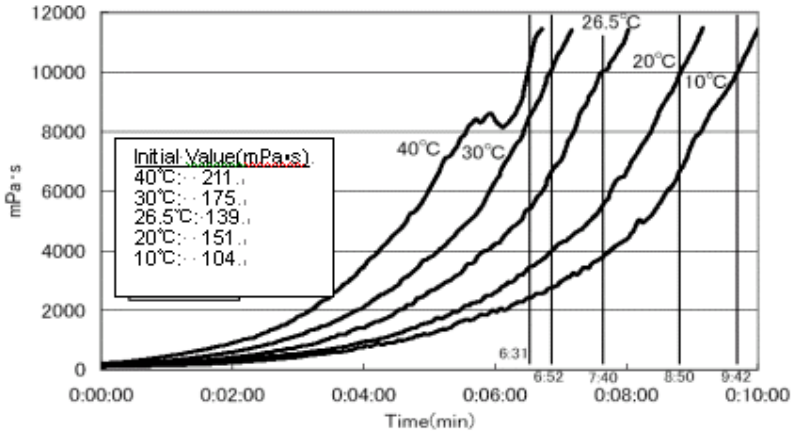

Fig 6. Cure Processes of Mortars under Different Ambient Temperatures

(2) The Cure processes of materials other than cement

a) Cure process of plaster (see Fig.7)

Fig.7 shows the cure processes when the water-plaster ratio was 67, 60 and 50%. Here, it is easy to understand how plaster hardens rapidly and that curing speed varies greatly depending on the water-plaster ratio.

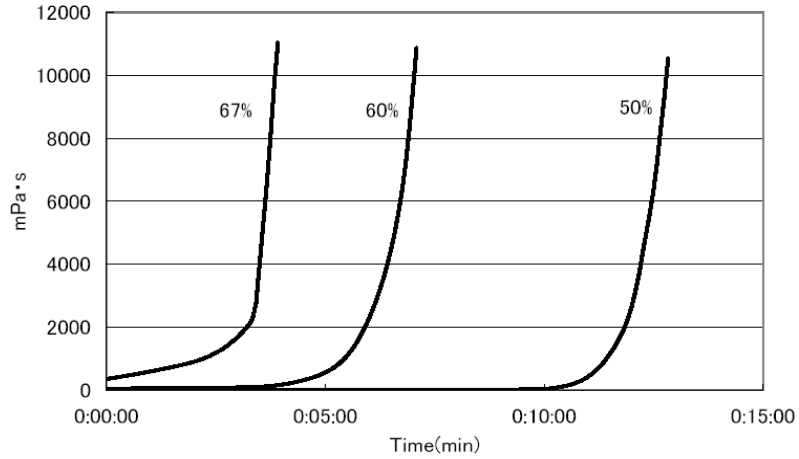

Fig 7. Cure Process of Plaster

b) Cure process of a silicon adhesive agent (see Fig.8)

In general, silicon adhesive agents require a long time for curing. As shown in the example in Fig.8, the sample measured took 22 hours for its slow curing. This and other measurement examples of a long curing process are very rare, but these kinds of measurements are important for examining the physical

properties of an adhesive agent during its cure process and for designing its adhesion characteristics.

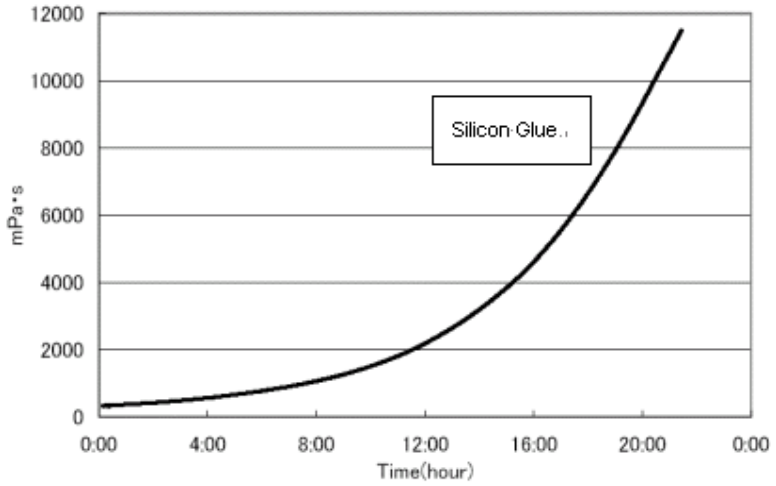

Fig 8. Cure Process of a Silicon Adhesive Agent

c) Curing of egg whites due to temperature (see Fig.9)
The process in which protein becomes irreversibly hardened was measured by heating egg whites. Based on the thermal history of the graph (the horizontal axis indicates temperature and the vertical axis viscosity), the process can be described as (1) softening due to heat until 60˚C, (2) starting to harden suddenly from 60˚C, (3) passing a small peak around 68˚C, and then (4) fully hardening. The peak around 68˚C indicates that the egg white contains several kinds of proteins with different curing characteristics.

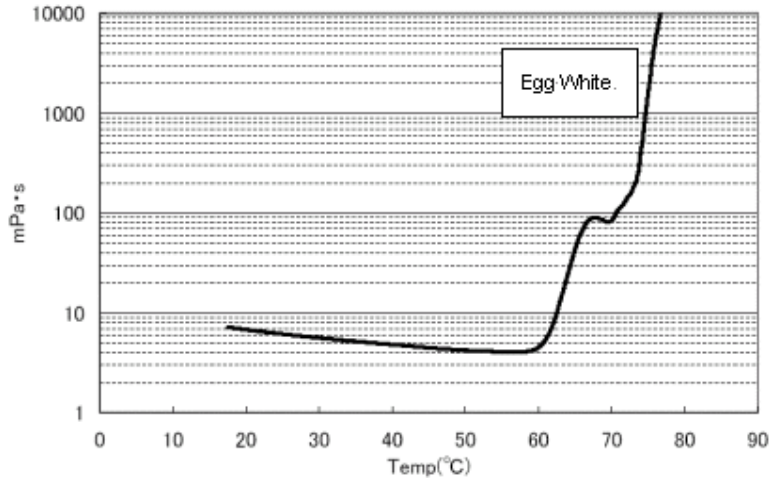

Fig 9. Increase in Viscosity of Egg White along with Rise in Temperature

d) Measurement of the gelation point of a soldering flux due to heat. (Fig.10)
In the graph in Fig.10, the horizontal and vertical axes indicate temperature and viscosity respectively. At around 70˚C there is an inflection point where viscosity changes drastically. It can be inferred that a soldering flux also has a phase transition point due to temperature.

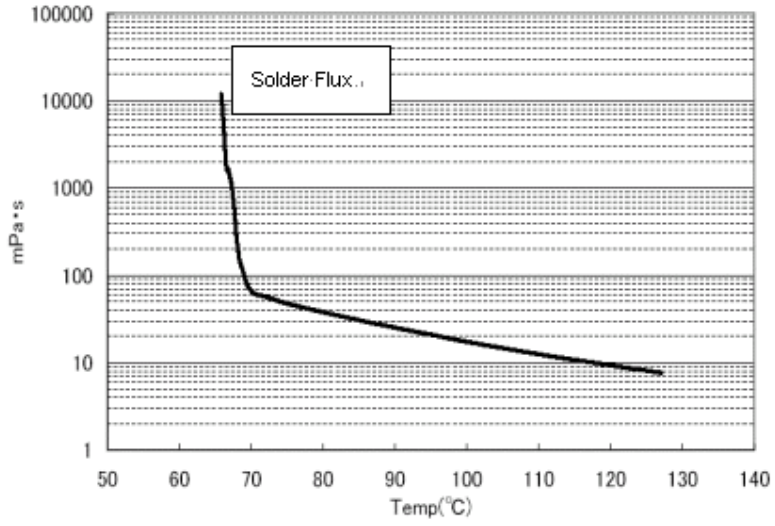

Fig 10. Measurement of the gelation point of a soldering flux due to heat

Summary and Discussion

Based on observed changes in viscosity, the characteristics of each material during the cure process from a liquid to solid can be summarized as follows:

- By measuring static viscosities with a tuning-fork vibration viscometer, it was confirmed that there were large differences in viscosity values (which determine the curing time and the initial fluidity) depending on the kind of the cement, the water-cement ratio and the difference in ambient temperature during curing. Since the viscosity value makes it possible to evaluate the initial fluidity of a cement material, it is also possible to ascertain possible feedback regarding the cure process of measurements to material design.
- By comparing the cure processes of cements with other materials, it has become evident that in the case of ordinary cement, the cure process will be gradual, and slipping is likely to occur between the sample and the oscillators because the material consists of multiple components and is slow to follow the movement of the oscillators. By minimizing the kinetic energy of the oscillators (making the amplitude smaller), this problem can be solved and thus a wider range of static viscosity measurements for cements should be possible.
- Even though vibration viscometers are presently available commercially, the shear rate is not changeable by users. Although the potential market size is still unknown, if, for the purposes of viscoelasticity analysis, a viscometer is developed whose shear rate is changeable by varying the amplitude of the oscillators, it will then become possible to perform more detailed viscoelesticity analyses of non-Newtonian fluids.