

## Viscosity of Fluxes for the Continuous Casting of Steel

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Mold fluxes are routinely used in both continuous casting and bottom pouring of steel. These fluxes are generally calcium-silicate based compositions with alkali oxides [(Li, Na, K)<sub>2</sub>O] and fluorides [CaF<sub>2</sub>, NaF] added as fluidizers. The compositions are sometimes based on the blast furnace slag [Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>] system, but the fly ash [CaO-SiO<sub>2</sub>] system is more common.

A variety of properties of the flux must be controlled, including fusion characteristics (fusion temperature range and sintering characteristics, flow properties of the powder, viscosity of the molten flux, and non-metallic absorption ability. The viscosity influences the consumption rate of flux, heat transfer in the mold, and non-metallic dissolution rate, and has been the subject of a great deal of published and unpublished work over the last ten years. The purpose of this paper is to discuss the expression of viscosity as a function of composition and temperature in separate relations.

In a previously published work (1), fluxes based on the CaO-SiO<sub>2</sub> system were examined to determine the effects of basicity ratio and alkali oxide and fluoride additions on the viscosity of oxide melts in the mold flux composition range. Those results showed that for that range of compositions, the viscosity at a given temperature could be expressed as a function of the silica content squared. In this work, an expression for viscosity as a function of temperature is derived from the Claussius-Clapeyron equation.

### Previous Work - Viscosity vs. Composition

The viscosity of twenty controlled composition fluxes was measured as a function of temperature. The compositions, given in Table 1, were selected to fit a second order statistical design in the variables V-ratio, %Na<sub>2</sub>O and %CaF<sub>2</sub>. The V-ratio [wt%CaO/wt%SiO<sub>2</sub>] was varied from 0.6 to 1.3, Na<sub>2</sub>O from 4 to 19wt%, and CaF<sub>2</sub> from 2 to 12wt%. Al<sub>2</sub>O<sub>3</sub> was kept constant at 10wt%. The viscosity was measured using a rotating type viscometer with a molybdenum spindle in an argon atmosphere. Details of the experimental technique were reported earlier (1).

A summary of the experimental results is given in Table 2. Viscosity decreased with increasing V-ratio, CaF<sub>2</sub> content and Na<sub>2</sub>O content as shown in Figures 1, 2 and 3, respectively. A plot of viscosity vs. silica content, Figure 4, shows that silica has a predominating effect on viscosity. A simple quadratic relation of viscosity with wt% silica or mole fraction of silicon cations produced a better fit of the data than a model containing the design variables. The best fit of data was obtained with a quadratic relation of the ratio of network forming cations [Si, Al and Zr] to total anion concentration [O and F]. Specifically,

$$\eta_{1500^{\circ}\text{C}} = 6.338 - 43.44K + 75.03K^2$$

where

$$K = \frac{X_{\text{Si}} + X_{\text{Al}} + X_{\text{Zr}}}{X_{\text{O}} X_{\text{F}}}$$

The log of viscosity versus reciprocal absolute temperature showed a distinct non-linearity as evidenced by the typical results shown in Figure 5. This is not a complete surprise, but a simple Arrhenius type equation is not adequate to describe the viscosity/temperature relationship.

#### Viscosity vs. Temperature

Viscosity can be considered as a measure of the ease of movement of molecules in a liquid undergoing shear. Several factors may influence this ease of movement including molecule size and intermolecular attraction, but a major factor is the amount of space available between the molecules, hence, the variety of models incorporating a free volume term.

The Claussius-Clapeyron equation relates pressure with temperature, enthalpy, and volume, and has been used to develop semi-theoretical expressions of vapor pressure (2). Many properties, including viscosity, can be related to an energy barrier, free volume and temperature. The attempt here is to express viscosity in the form of the Claussius-Clapeyron equation.

The Claussius-Clapeyron equation can be written

$$\frac{dP}{dT} = \frac{H}{T \Delta V} = \frac{\Delta H}{T(V-V_0)} \quad 1)$$

where P, T, and  $\Delta H$  have their usual meaning. For this discussion,  $\Delta V$  is a measure of free volume or the difference between the volume at temperature and the volume at some standard state, e.g., at absolute zero.

Equation 1 can be rewritten as

$$\frac{d(\ln P)}{d(1/T)} = - \frac{\Delta H}{R \Delta z} \quad 2)$$

where  $\Delta z = PV/RT - PV_0/RT$

Expanding  $\Delta H$  to the Taylor series form and integrating with respect to  $1/T$  yields

$$\ln P = \frac{1}{R} \left( a - \frac{\Delta H_0}{T} + b \ln T + dT + \frac{e}{2} T^2 + \dots \right) \quad 3)$$

If the higher order terms are ignored, the expression reduces to

$$\ln P = A - \frac{B}{T} + C \ln T \quad 4)$$

Such a derivation was originally developed and used by Kirchoff [1858] and Rankine [1849] (2) to express the temperature dependence of vapor pressure. It was also successfully used by Brostow (3) to express the temperature dependence of the isothermal compressibility of a wide variety of organic liquids, some metallic liquids and water. By a similar analogy, we have used it to express the viscosity of liquid mold fluxes.

#### Regression Analysis

The flux viscosity data was fitted to the Kirchoff-Rankine equation as,

$$\eta = \exp(C_1 + \frac{C_2}{T} + C_3 \ln T) \quad 5)$$

and to the Andrade-Arrhenius equation

$$\eta = A \exp(E/RT) \quad 6)$$

using the Marquardt method of non-linear least squares regression in the Statistical Analysis Systems [SAS] program package (4). The results of the regression are given in Table 3. The standard deviation and an average difference between calculated and measured values are given in Table 4.

In some cases, viz., Fluxes 5, 6 and 13 in Table 3, the signs of the coefficients are reversed, and a concave downward curve is generated. This is most likely caused by the regression being trapped at a local minimum in the data and assuming convergence at that point. It is required for these cases that the size of the regression step should be increased to avoid the local minima, which SAS does not allow. Also, there may not be enough data points to expand the regression step as is probably true for Fluxes 6 and 13.

For the majority of fluxes evaluated, the standard deviation,  $s$ , and the average percent variation,  $\Delta\bar{\eta}$ , is lower for the Kirchoff-Rankine fitted equation vs. the Andrade-Arrhenius model, indicating a better fit of the experimental data. The average percent variation between calculated and experimental values is lower for the Kirchoff-Rankine equation, and the difference is most pronounced for those fluxes where the non-linearity of the experimental  $\ln \eta$  vs.  $1/T$  data is greatest.

#### Discussion

When the non-linearity of the log viscosity vs. reciprocal temperature data was first observed, tests were made to insure that the curvature was real and not an artifact of the experimental apparatus. Hysteresis curves and constant temperature for extended time tests showed that the non-linearity was not caused by volatilization of alkali or fluoride constituents or from thermal deviations in the furnace setup. The observed curvature of the data was not an artifact and represented the true physical behavior of the materials. The application of the Kirchoff-Rankine equation produced a more accurate description of the temperature dependence of viscosity.

Additional work on liquid metals, simple chloride salts and some small molecule organic liquids (5) indicates that the advantage of the Kirchoff-Rankine equation over the Andrade-Arrhenius equation improves as the size of the melt species increases. The improvement in the description of viscosity vs. temperature for metals and simple salts [e.g., NaCl and BiCl<sub>2</sub>] is not great, but for materials with larger melt species, there is a distinct improvement.

#### References

- (1) W. L. McCauley and D. Apelian, *Canadian Metallurgical Quarterly*, 20(2) 1984, pp. 247-262.
- (2) G. W. Thomson, *Chemical Review*, 38, February 1946.
- (3) W. Brostow and P. Maynadier, *High Temperature Science*, 11 1979, pp. 7-21.

- (4) SAS User's Guide, SAS Institute, Inc., Cary, North Carolina, 1979.
- (5) W. L. McCauley and D. Apelian, "Temperature Dependence of the Viscosity of Liquids," to be presented at the International Symposium on Slags and Fluxes, TMS-AIME Fall Meeting, Lake Tahoe, NV, November 1984; to be published.

Table 1. Experimental Fluxes - Frit Composition, wt%

Flux	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	CaF <sub>2</sub>	MgO	ZrO <sub>2</sub>	Total	V-ratio
1	34.8	10.2	32.7	10.7	7.6	0.9	0.6	97.5	0.94
2	34.4	9.8	32.1	10.9	8.4	0.7	0.6	96.9	0.93
3	34.5	10.0	32.7	11.0	7.6	0.7	0.7	97.2	0.95
4	34.6	10.1	32.5	10.8	7.8	0.6	0.6	97.0	0.94
5	34.6	10.3	32.3	10.9	8.0	0.7	0.5	97.3	0.93
6	34.7	10.1	33.0	10.8	7.2	0.6	0.6	97.0	0.95
7	26.7	9.8	31.8	14.4	11.7	0.6	1.9	96.9	1.19
8	30.7	8.9	32.6	12.9	2.3	0.7	8.8	96.9	1.06
9	31.2	10.4	40.3	5.7	7.6	0.8	0.7	96.7	1.29
10	35.2	10.3	40.8	5.7	3.3	0.9	0.8	97.0	1.16
11	33.5	10.4	24.9	15.1	11.5	0.5	0.4	96.3	0.77
12	38.8	10.4	26.2	15.1	3.5	0.7	0.9	95.6	0.67
13	41.9	10.6	29.5	6.8	7.8	0.7	0.9	98.2	0.77
14	48.0	10.6	28.6	6.5	3.3	0.8	1.4	99.2	0.60
15	46.8	10.4	22.2	10.7	5.5	0.6	2.7	98.9	0.47
16	30.6	10.0	36.2	10.3	7.0	1.0	2.1	97.2	1.18
17	30.0	10.2	27.8	18.6	8.2	0.8	1.6	97.2	0.93
18	39.6	10.4	35.7	4.0	4.7	1.0	1.3	96.7	0.90
19	32.4	10.4	30.4	10.8	11.7	0.7	1.1	97.5	0.94
20	39.1	10.4	32.6	11.3	1.7	0.9	1.2	97.2	0.83

Table 2. Summary of Flux Viscosities

Flux	Viscosity at 1300°C, Ns m <sup>-2</sup>	Viscosity at 1400°C, Ns m <sup>-2</sup>	Viscosity at 1500°C, Ns m <sup>-2</sup>
1	0.395	0.230	0.135
2	0.310	0.175	0.112
3	0.340	0.205	0.128
4	0.485	0.235	0.125
5	0.290	0.190	0.088
6	0.510	0.230	0.122
7	0.110	0.065	0.035
8	NA*	NA*	NA*
9	0.280	0.160	0.080
10	6.00	0.360	0.180
11	0.270	0.150	0.114
12	0.930	0.460	0.270
13	1.15	0.530	0.280
14	2.80	1.30	0.710
15	2.40	1.30	0.725
16	7.00	0.170	0.090
17	0.160	0.115	0.059
18	1.40	0.670	0.380
19	0.250	0.130	0.094
20	1.40	0.720	0.410

\*Not available

Table 3. Regression Analysis Results

Flux	Andrade-Arrhenius Equation				Kirchoff-Rankine Equation					
	A (Pa s)	E (cal/mole)	s <sup>†</sup>	$\overline{\Delta\%}^{++}$	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	s	$\overline{\Delta\%}^{+++}$	n <sup>+++</sup>
1	8.831E-6	33783	7.03E-3	2.40	-184.35	51341	20.502	6.36E-3	1.94	12
2	2.704E-6	36304	1.99E-2	7.98	-282.59	68183	32.337	1.27E-2	3.47	6
3	2.332E-6	30095	8.92E-3	2.08	-184.30	47516	20.792	5.68E-3	1.42	6
4	8.016E-7	41748	1.82E-2	2.73	-278.11	71633	31.502	1.67E-2	3.20	6
5	2.528E-5	29493	2.15E-2	4.14	132.94	-10764	-17.290	2.10E-2	3.91	14
6	8.079E-7	41814	2.33E-2	5.41	123.80	-5309	-16.447	2.29E-2	5.68	7
7	1.963E-7	41439	1.31E-2	7.01	-1511.91	297516	179.394	5.72E-3	3.91	5
9	1.496E-5	30736	1.22E-2	3.15	-1626.10	321853	192.942	1.11E-2	3.62	6
10	7.5E-3	36000*	-	-	-8603.16	1735752	1019.0	2.83E-2	3.97	18
11	7.820E-6	32510	1.43E-2	3.15	-276.14	63473	31.935	5.81E-3	1.52	7
12	4.828E-7	45110	6.00E-2	2.95	-239.51	62253	27.155	3.35E-2	1.10	12
13	2.661E-6	40700	5.19E-2	4.69	169.80	-13879	-21.843	5.00E-2	3.89	8
14	5.488E-8	48579	2.26E-1	13.00	-987.72	212141	116.012	9.85E-2	5.30	11
15	5.761E-6	40568	1.32E-1	5.57	-233.90	60668	26.660	6.26E-2	3.07	10
16	2.0E-2	30000*	-	-	-42701.6	8456727	5071.8	8.69E-2	15.8	17
17	5.469E-6	32981	8.65E-3	5.05	-483.18	105664	56.221	1.60E-3	0.84	5
18	4.126E-6	39880	2.66E-2	3.01	-200.79	56382	22.457	1.66E-2	1.84	6
19	7.393E-6	32313	1.48E-2	7.39	-377.12	85334	43.656	8.69E-3	4.89	7
20	1.493E-7	50240	1.62E-1	16.46	-517.30	116706	60.246	5.32E-2	4.46	8

+ s =  $\sqrt{c(n_{exp}^2 - n_{calc}^2)/(n-1)}$

\* estimated

++  $\overline{\Delta\%} = \frac{1}{n} \left( \frac{n_{exp} - n_{calc}}{n_{exp}} \right) \times 100$

+++ n = number of observations

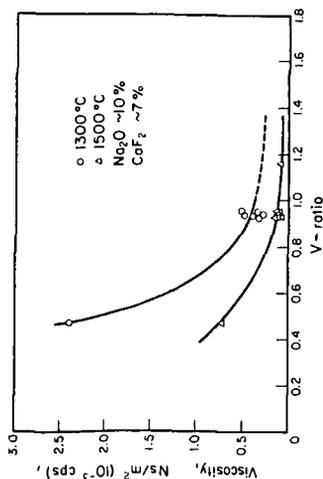


Figure 1. Viscosity vs. V-ratio

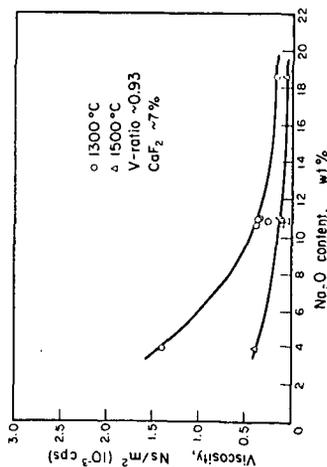


Figure 2. Viscosity vs. Na<sub>2</sub>O Content

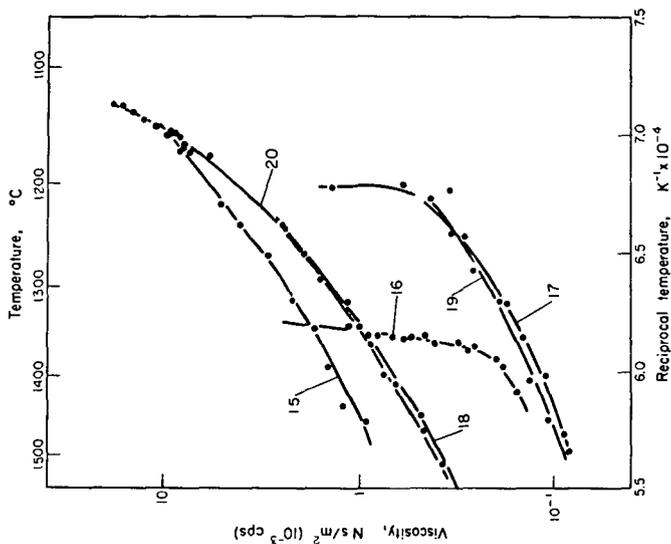


Figure 5. Typical viscosity results vs. reciprocal temperature

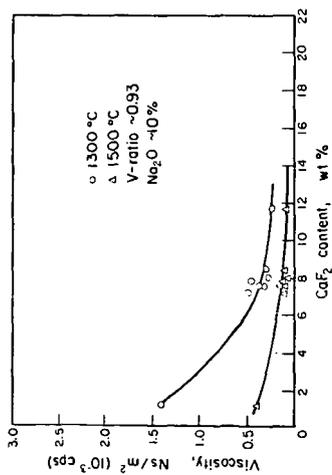


Figure 3. Viscosity vs. CaF<sub>2</sub> Content

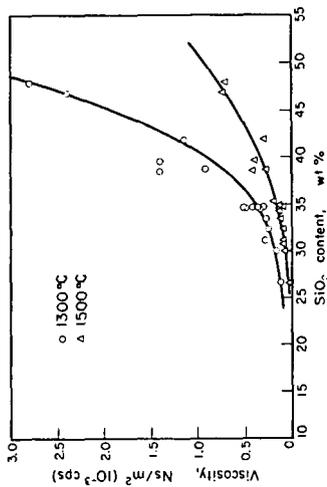


Figure 4. Viscosity vs. SiO<sub>2</sub> Content