Evaluation of Melter Performance: Behavior of Noble Metal Sludge

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EVALUATION OF MELTER PERFORMANCE:
BEHAVIOR OF NOBLE METAL SLUDGE

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Summary and Conclusions

Velocities in a flat bottom, two electrode melter are 0.03 to 0.3 cm/s and are lowest on the cavity bottom where noble metals would tend to accumulate. Velocities in 45° sloped bottom, three-electrode design are estimated to be from 0.1 to 0.4 cm/s and are highest near the bottom of the cavity. The terminal velocity of 100 micron-sized Pd in molten glass is about $1 \times 10^{-3}$ cm/s, which is far slower than normal convection currents. Accumulation of noble metals is thus attributed to trapping inside boundary layers where fluid is nearly motionless. In a flat bottom melter, the boundary layer near the cavity floor could be large due to low bulk fluid motion.

Once a sludge layer forms, it takes on distinct rheological properties having a higher viscosity with pseudo-plastic behavior. The critical velocity for resuspension, calculated from a correlation for flow in a pipe, is 1000 times higher than convection currents in the LFCM. It is thus important to keep noble metals suspended and prevent sludge formation. Gravity could play a role in directing sludge to a bottom drain. The calculated steady state velocity of a falling film of sludge is sufficient to keep a 45° sloped bottom free from major accumulations if it is a Newtonian fluid.

Introduction

This paper examines the possible liquid momentum forces in the LFCM and their influence on noble metals sludge which may accumulate. The analyses involve simplifying assumptions in order to isolate the effects of gravity and glass convection currents in the cavity. The purpose is to better understand these forces and this in turn will help to interpret physical model results and guide in design of the melter cavity.

Characteristic Velocities in Molten Glass

There are no available velocity measurements of glass flow in the LFCM. This information is obtained by computer or physical modeling. Physical modeling studies by Quigley and Kreid (1979) indicate model liquid velocities in a flat-bottom, two-electrode configuration of 0.01 to 0.1 cm/s. The
velocity scaling factor in their work was about 0.3, so the corresponding LFCM velocities would be about 0.03 to 0.3 cm/s. The bottom portion had the lowest velocities.

In the ongoing HWVP modeling effort, model liquid velocities of 0.05 to 0.25 cm/s are measured in a 45° sloped-bottom cavity with three electrodes. The scaling factor is about 0.6 so the corresponding LFCM velocities would be about 0.1 to 0.4 cm/s. In contrast to the flat-bottom model, some of the highest velocities occur near the bottom of the cavity. Low bulk velocities occur at the center or vortex of convection cells but these are well away from the bottom.

Terminal Velocity of Metal Particles

The relationship for terminal velocity of particles (assume spheres) in a Newtonian fluid is (Bird et al 1960):

$$ V_t = \frac{d^2 g (\rho_1 - \rho)}{18 \mu} $$(1)

where:

- $V_t$ = terminal velocity of particle in molten glass
- $d$ = particle diameter
- $g$ = gravity constant = 980 cm/s$^2$
- $\mu$ = glass viscosity = 45 poise
- $\rho$ = molten glass density at 1150°C = 2.1 g/cc
- $\rho_1$ = density of noble metal particle

Calculated terminal velocities of Pd in molten glass (with properties as used in Equation 1) are as follows:

<table>
<thead>
<tr>
<th>Diameter, micron</th>
<th>Terminal velocity, cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>1.2 E-5</td>
</tr>
<tr>
<td>50</td>
<td>3.0 E-4</td>
</tr>
<tr>
<td>100</td>
<td>1.2 E-3</td>
</tr>
</tbody>
</table>

These velocities are very low compared to the normal convection currents in the LFCM cavity which are 0.01 to 0.3 cm/s. It would seem that noble metal settling could not occur due to these low velocities, yet it is an observed
effect in the PAMELA and other melters. The phenomena may be due to particles being propelled towards regions in the melter where glass is not moving or stagnant.

Near any solid surface there is a boundary layer where the average liquid velocity is lower than in the bulk fluid; velocity approaches zero at the surface. Noble metals could accumulate inside this layer. The size of the layer is inversely related to the bulk stream velocity. The higher the bulk velocity, the smaller the boundary layer. Just outside the layer, velocities are high and noble metals would tend to be swept away. Thus higher bulk velocities would tend to result in smaller accumulations of noble metals than low-bulk velocity conditions.

Properties of Glass Sludge

There has been limited characterization of waste glass sludge. Investigators in FRG have measured viscosity of HEWC glass and reported findings in a technical exchange. At 1150°C, sludge-free glass viscosity was 50 poise, while the "bottom glass" was reported to have viscosity of 130 - 250 poise. Plodinec (1986) measured viscosity versus shear rate for glass melts containing insoluble crystals. Results for 35 wt% sludge glass are shown in Figure 1.

![Figure 1. Apparent Viscosity of Simulated Waste Glass Containing 35 wt% Crystalline Sludge.](image)
The apparent viscosity decreases with increasing shear rate indicating pseudo-plastic behavior.

**Falling Film Velocity**

To gain perspective on the ability of a sloped bottom to promote movement of sludge towards the bottom drain, an analysis of flow of a falling film was done. It is assumed that a layer of thickness \( T \) has accumulated on the sloped cavity floor. Gravity will exert a downward force on this sludge. A characteristic velocity associated with this flow can be readily calculated based on steady velocity of a falling film. It is assumed that there is no shear force at the outer film boundary, i.e., the molten glass does not impede or aid downward motion of the sludge film. The analysis thus isolates the effect of gravity. Also, the sludge is taken to be Newtonian. The average velocity of the sludge (Bird et al 1960) is:

\[
\langle v \rangle = \frac{(\rho_s - \rho)gT^2 \sin \theta}{3 \mu_s} \tag{2}
\]

where \( \rho_s \) is bulk sludge density, \( \theta \) is inclination angle from horizontal, and \( \mu_s \) is bulk sludge viscosity. The effective density in equation (2) has been adjusted to account for the buoyant effect of the molten glass.

The density of the noble metals is 7 g/cc for RuO₂ and 12 g/cc for Rh and Pd. The density of glass is about 2.2 g/cc at molten temperature. To calculate the sludge density it is assumed to consist of about 40 vol\% metal and 60 vol\% molten glass. These proportions are roughly based on close-packed spheres. The metal portion is assumed to be half with density 7 g/cc (RuO₂) and the other half 12 g/cc (Pd and Rh). These considerations result in the following sludge density:

\[
\rho_s = (0.6 \times 2.2) + 0.4 \times (12 + 7)/2 = 5.1 \text{ g/cc} = 5100 \text{ kg/m}^3
\]

The sludge viscosity is derived from measurements made on HEWC-Glass from the bottom of the PAMELA melter. At 1150°C, a value of around 200 poise was reported in technical exchange discussions with FRG investigators.
The thickness of the layer is calculated from the total amount of noble metals in the melter if collected in a layer on the floor. If the melter holds 5000 kg of glass and the noble metals are 0.2 wt%, then the mass of noble metals is 10 kg. The top area of a 45 kg/h melter is around 2.5 m². The bottom area is assumed to be 1.5 times the top area or 3.8 m². The layer thickness is thus:

\[ T = \frac{10 \text{ kg}}{5100 \text{ kg/m}^3 \times 3.8 \text{ m}^2} = 5 \times 10^{-4} \text{ m} \]

Substituting these parameters into Equation (1) results in the following velocities as a function of bottom slope:

<table>
<thead>
<tr>
<th>θ</th>
<th>( &lt;V&gt; ), cm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.0000</td>
</tr>
<tr>
<td>15</td>
<td>0.0005</td>
</tr>
<tr>
<td>45</td>
<td>0.0013</td>
</tr>
<tr>
<td>90</td>
<td>0.0019</td>
</tr>
</tbody>
</table>

It should be noted that the velocities in the above table are steady-state. The time to reach this condition is unknown and to make a determination would require a much more complicated analyses involving tenuous assumptions. Also, the effective viscosity could be much higher than 200 poise if the sludge is pseudo-plastic and shear rates are low (see Figure 1). Nevertheless, this simple analysis provides an upper bound on the effectiveness of a sloped bottom to move sludge to the bottom drain. To move sludge 100 cm using the 45° slope would take about 20 hours, which is a reasonable time.

**Sludge Flow Due to Bulk Fluid Velocity**

The motion of the glass in the cavity will exert shear force on the sludge layer. A straight-forward calculation can be done to determine an upper bound on the effect of this motion on moving the sludge. The sludge is assumed to be collected on a horizontal surface to eliminate gravity effects and isolate the shear force. The sludge moves in a direction parallel to the
surface which is also parallel to glass flow direction. The layer has thickness \( T \) with variable velocity in the direction normal to the surface as shown in the following sketch:

![Diagram showing bulk glass and sludge layers with velocity profile]

If the fluid is Newtonian, then the following governing equation applies:

\[
d\frac{2V}{dy^2} = 0 \tag{3}
\]

At \( y = T \), \( V = V_\infty \) and at \( y = 0 \), \( V = 0 \). The velocity profile is thus:

\[
V = V_\infty y / T \tag{4}
\]

The average velocity over \( T \) is obtained by integration to give:

\[
<V> = V_\infty / 2 \tag{5}
\]

As mentioned above, physical modeling suggests velocities of up to 0.4 cm/s. If this fluid motion can be transferred to the sludge layer as equation (5) suggests, then there is a chance for mobilization and removal of accumulations by this method alone. However the analysis is for steady state, and as in the development for Equation (2), it is unknown how long this will take.

The effect of shear rate on sludge rheology is shown in Figure 1. An estimate of shear rates encountered in the LFCM can be obtained from physical model velocity data. Bulk liquid velocities of up to 0.2 cm/s are measured along the 45°-sloping bottom of the physical model being studied for HWVP this fiscal year. This corresponds to about 0.4 cm/s in an LFCM. From examining photographs of the cavity, it is estimated that such velocities are present at about 0.5 cm away from the sloped floor. The linear scaling factor is 1/4 so this corresponds to 2 cm in an LFCM. The velocity decreases
to zero as the wall is approached so the velocity gradient or shear rate is estimated to be:

\[
\frac{\Delta V}{\Delta y} = \frac{0.4 \text{ cm/s}}{2 \text{ cm}} = 0.2/\text{s} = 12/\text{min}
\]

Looking at Figure 1, the apparent viscosity under these conditions is about 100 poise at 1150°C. The viscosity climbs rapidly with decreases in shear rate so it is much more difficult to mobilize sludge at lower velocities.

**Critical Velocity to Suspend Sludge**

Much literature has been devoted to sludge mobilization as it is important in coal-slurry technology and numerous civil engineering problems involving silt movement in channels or stream beds. The critical bulk fluid velocity to re-suspend settled solids has been calculated using a correlation found in the literature for flow in pipes. As a rough approximation, the relationship is applied to the open tank geometry of the melter cavity because a specific correlation is not available for this situation. The correlation taken from Oroskar and Turian (1980) is:

\[
V_C = [gd(s - 1)]^{0.5}1.85C^{0.156}(1 - C)^{0.3564}(d/D)^{-0.378}Re^{0.80}X^{0.83}
\]

where

- \( d \) = particle diameter = 50 micron
- \( D \) = glass pool depth = 122 cm
- \( s \) = density of particle/density of molten glass = 5.7
- \( C \) = concentration of particles in sludge (volume fraction) = 0.4
- \( Re \) = Reynolds number = \( Dp[gd(s - 1)]^{0.5}/\mu \)
- \( X \) = fraction of eddies exceeding terminal velocity \( \approx 1 \)

The calculated resuspension velocity is 400 cm/s. Convection currents encountered in waste glass melters are on the order of 0.2 - 0.4 cm/s which are about 1000 times too low to re-suspend noble metals sludge. This analysis thus indicates that it will be very difficult to resuspend settled sludge via natural glass convection currents. It appears that keeping noble
metals in suspension by maximizing liquid velocity in the bottom of the cavity is important.

References


