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Thermal Properties of Simulated and High-Level Waste Solutions Used for the Solvent Extraction Demonstration

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Abstract

Researchers measured the heat capacity and thermal conductivity of supernate from a blend of Tank 37H and 44F, of a simulant of this blend, and of a simulant[1] specifically designed for solvent extraction experiments. The measured heat capacity of the blend from the Tanks 37H and 44F equaled 0.871 cal/(g°C). The simulant of this blend produced an identical result. The heat capacity of the simulant designed for solvent extraction testing equaled 0.859 cal/(g°C). All three solutions have thermal conductivities in the range of 0.54 to 0.6 Watts/(m°C). The slight variation in the thermophysical properties of these solutions successfully explains the different flowmeter readings observed during the real waste demonstration of the solvent extraction technology.

Keywords: Thermal Conductivity, Heat Capacity

Introduction

During the Fiscal year 2001, the Waste Processing Technology Section conducted a radioactive waste demonstration of the Caustic Side Solvent Extraction (CSSX) technology in the Shielded Cells Facility. During that demonstration, personnel measured flow rates by two methods. Balances measured changes in mass of the waste feed tank, and combined with the density of the solution and elapsed time, yielded one measure of the flow rate. The second measure used a RheothermÒ flowmeter which measured the flow rate from the rate of the heat transfer from a heated resistor in flowing solution. The rate of heat transfer is a function of the convective (free or forced) heat transfer coefficient of the fluid. During the testing personnel observed unexplained flowmeter readings when switching solutions. The flow rate

discrepancies proved large between Tanks 37H/44F waste and the CSSX simulant. Researchers postulated that the thermophysical properties of the solutions accounted for the discrepancies as measured by the balances when the RheothermÒ flowmeter showed no change in the flow. To verify this hypothesis, we measured the thermal properties of a blend from Tanks 37H and 44F, a simulant of this blend, and the CSSX simulant. We used the data to estimate the impact on the RheothermÒ flowmeter.

Experimental Technique

Three samples were submitted for thermal analysis. About 69 mg of each sample were taken and placed in stainless steel cups. The cups were sealed with VitonÔ O-rings and placed in an Instrument Specialist Incorporated (ISI) model 550 Differential Scanning Calorimeter (DSC) unit. The samples were heated from 15°C to 80°C at 10°C per minute. The amount of energy required to heat the sample at 10°C per minute was recorded. At a given temperature, the heat taken in by the sample was compared to the heat absorbed by a sapphire (standard) at that temperature. The ratio of these values equals the ratio of the heat capacity of the sample to that of sapphire.

$$C_p = \left(\frac{\text{Sample Signal} - \text{Reference Signal}}{\text{Sapphire Signal - Reference Signal}}\right) x \left(\frac{\text{Saphire mass}}{\text{Sample mass}}\right) \times \text{Sapphire Heat Capacity}$$

The heat capacity of sapphire published in the literature allows the estimation of the sample heat capacity.[2]

The thermal conductivity of each sample was determined from the sample temperature response curve following a step increase in the DSC temperature. The samples were kept at 30°C for 3 minutes and then the temperature of the DSC was raised to 80°C at a rate of 20°C per minute. The sample temperature was monitored as function of time. After a short period (about 10 seconds) the sample temperature increased linearly with time. Extrapolating the linear portion of the temperature-time curve back to early times and recording the intercept with the line extension from the initial temperature gave the time due to heat transport in the sample. That time is related to the thermal conductivity of the sample as shown in the expression below for thermal diffusivity.[3]

$$t = \frac{\rho \times C_p \times (\textit{sample thickness})^2}{4\,k}$$

In this expression, r is the density (g/m^3), C_p is the heat capacity (J/(g°C)) and k is the thermal conductivity (Watts/(m°C)). No standard sample was run to check the accuracy of this technique. However, a run with water yielded a thermal conductivity of 0.616 W/(m°C). The literature value for water at 20°C is 0.598 W/(m°C).[4] This approach assumes no convective heat transfer mechanism operated 100 seconds after introducing a sudden temperature increase to the sample. In fact, calculation of the Rayleigh number (Grashof x Prandlt) for this experiment yields 7.61. A Rayleigh number of 1000 marks the beginning of convective heat transfer in enclosed spaces.[3] Below this number, heat transfer is conductivity controlled.

Experimental Results and Discussion

Researchers measured the heat capacity of the combined Tanks 37H and 44F waste, combined Tank 37H and 44F simulant, and CSSX simulant using a DSC instrument in the Shielded Cells. The Tank 37H and 44F waste and its simulant have identical heat capacities. The CSSX simulant had a smaller heat capacity. This instrument determined the heat capacities as: Tanks 37H and 44F waste, 0.53 cal/(g°C); Tanks 37H 44F simulated waste, 0.54 cal/(g°C); and the CSSX simulant, 0.49 cal/(g°C). Comparing the CSSX simulant result to previous measurements at ORNL[5] suggested an error in the measurements. The poor performance of the instrument was confirmed by measuring the melting point of indium. The measured enthalpy for melting indium was 19.6 J/g, compared to the literature value of 28.4 J/g.[2]

The researchers proceeded to measure the heat capacity of CSSX and Tanks 37H and 44F simulant in a non-radioactive DSC unit to identify any instrument bias in the data. The measurement in the second unit gave a heat capacity of 0.859 cal/(g°C) for the CSSX simulant and 0.871 cal/(g°C) for the Tanks 37H and 44F simulant in good agreement with the value obtained at ORNL with average SRS simulant (0.868).[5] Although, the measurements from the Shielded Cells DSC unit were inaccurate, we assume the relative magnitude of the different solutions is correct. The calculated heat capacity of the CSSX simulant is 0.80 cal/(g°C).[6] This calculation neglects SiO_3^{2-} and $C_2O_4^{2-}$ contributions to the heat capacity (since we could not find heat capacity data on these components). Our measured value is similar to, but slightly larger than the calculated value. The calculated heat capacity for the Tanks 37H and 44F waste (based on measured composition of this solution) is 0.848 cal/(g°C). Again the measured value is slightly larger than the prediction. The calculations have a ± 10% error.[6]

Researchers measured the thermal conductivity of the Tanks 37H and 44F waste, its simulant, and the CSSX simulant using the DSC unit in the Shielded Cell facility. The Tanks 37H and 44F waste and its simulant had the same measured thermal conductivity (0.572 W/(m°C)). The CSSX simulant measured a slightly higher value at 0.605 W/(m°C). The researcher measured the thermal conductivity of the Tanks 37H and 44F and the CSSX simulants with a second DSC unit. The measured value for the Tanks 37H and 44F simulant was 0.675 W/(m°C) while the CSSX simulant measured 0.617 W/(m°C). Again, this indicates the data obtained with the DSC unit at the Shielded Cells is inaccurate and it contains the wrong relative position of the thermal conductivity from the simulant.

The Researchers felt that the measured thermal conductivity data from the second DSC unit was still inaccurate (since, the DSC indirectly estimates the thermal conductivity) and proceeded to calculate the thermal conductivity of the simulant. The predicted thermal conductivity[7] of the Tanks 37H and 44F simulant is 0.713 W/(m°C) (see Table 1) while the prediction for the CSSX simulant is 0.649 W/(m°C). In this calculation, the thermal conductivity of water at 20°C used was 0.6 W/(m°C).[4] Due to the high sodium hydroxide concentration in these solutions, an offset was added to the sum of product in Table 1 of 0.0232 for CSSX simulant and 0.0349 to Tank 37H/44H waste.[7] Researchers at ONRL measured a value of 0.68 W/(m°C) for a similar CSSX simulant.[5]

Table 1. Thermal conductivity calculation for CSSX simulant

Charge	Component	Ion Coefficient	Concentration (molar)	Product
-1	OH	0.02094	2.064	0.043216
-1	F	0.00209	0.028	5.86E-05
-1	Cl	-0.00547	0.024	-0.00013
-1	NO2	-0.00465	0.5	-0.00233
-1	NO3	-0.00698	2.034	-0.0142
-2	CO3	-0.00757	0.15	-0.00113
-2	SiO3	-0.00930	0.03	-0.00028
-2	SO4	0.00116	0.14	0.000163
-3	PO4	0.02094	0.007	0.000147
-3	C2O4	-0.00349	0.008	-2.8E-05
1	Na	0	5.6	0
1	K	-0.00756	0.015	-0.00011
-1	AlO2	0.00116	0.28	0.000326

Implications for Flow Measurements

The importance of these thermal measurements is revealed when estimating the cooling effect of the supernate as it flows in a pipe past a heated wire, as it does in the RheothermÒ flowmeter. Consider the supernate flowing past a constantly heated wire as in a rheotherm. As the supernate past flows the wire, the temperature of the wire decreases.

To maintain the wire isothermal, additional current is past through the wire to raise its temperature to its original value. The amount of heat generated by the extra current is given in the next expression.

$$q = h \times Area \times \left(T_{wire} - T_{fluid}\right)$$

In this expression, the symbol q stands for the heat transfer rate (Watts per seconds), h is the convective heat transfer coefficient, A is the surface of the wire and T is the temperature of either the wire or the solution. If different solutions flow past the RheothermÒ at the same speed, different responses from the RheothermÒ are expected. To estimate the convective heat transfer rate coefficient the relationship between the Nusselt, Reynolds and Prandlt numbers is used.[8]

$$Nu = 0.86 \times Reynolds^{0.488} \times Prandlt^{0.333}$$

The Reynolds number is determined for the solution flowing through the pipe connected to the RheometerÒ . For example in the case of CSSX simulant flowing past a 0.159 cm diameter wire at a flow rate of 0.716 mL/s (cross sectional area of flowing pipe is 0.049 cm^2) and using the physical properties in Table 2, the Reynolds number is 115 (see the calculation below).

$$Re = \frac{\rho \times v \times d}{\mu} = \frac{1.236 \times 10^{-3} \times 0.716 \times 0.159}{2.5 \times 10^{-5} \times 0.049} = 115$$

Table 2. The physical properties of Tanks 37H and 44F waste, its simulant, and the CSSX simulant.

Property	CSSX Simulant	Tanks 37H and 44F Waste	Tanks 37H and 44F Simulant
Density (g/mL)	1.236#	1.217#	1.212
Dynamic Viscosity (cP)	2.5#	3.2 (estimated)	3.2#
Thermal Conductivity W/(m°C)	0.649&	0.713&	0.713
Heat Capacity cal/(g°C)	0.859&	0.871 (estimate)	0.871

*This measured value was obtained with uncalibrated equipment.
D. D. Walker, Laboratory Notebook, WSRC-NB-2001-00070, p. 107.
D. D. Walker et al. "Demonstration of Caustic-Side Solvent Extraction with SRS High-Level Waste," WSRC-TR-2001-00223, May 2001.
& Calculated, this work.

After substituting for the Nusselt, Reynolds and Prandlt number, and taking the ratio between the convective heat transfer coefficient for two different solutions, the following expression estimates the effect of the solution on the heat transfer.

$$\frac{h_1}{h_2} = \frac{k_1}{k_2} \times \left(\frac{\rho_1}{\rho_2} \times \frac{\mu_2}{\mu_1}\right)^{0.466} \times \left(\frac{\mu_1}{\mu_2} \times \frac{C_{p1}}{C_{p2}} \times \frac{k_2}{k_1}\right)^{0.333}$$

In this expression, k_1 and k_2 are the thermal conductivities of one of the supernate, r is the density, m is the viscosity and C_p is the heat capacity.

Substituting the physical constants for the CSSX simulant (h_2) and the Tanks 37H and 44F simulant (h_1) provides the expected change in the RheothermÒ response. Table 2 lists the values used.

$$\frac{h_1}{h_2} = (1.100)^{0.666} \times (0.9805)^{0.466} \times (1.28)^{-0.133} \times (1.0139)^{0.333} = 1.026$$

The heat transfer rate of Tank 37H/44F is predicted as 2.6% higher than the corresponding value of the CSSX simulant. The higher the heat transfer rate, the lower the implied flow rate. Therefore, the blend from Tanks 37H and 44F should register a lower velocity (by at least 2.7%) than the CSSX simulant. The researcher also estimated the heat transfer rate from free convection. This is another heat loss mechanism that may be significant and may differ from the Tanks 37H and 44F simulant to the CSSX simulant. The expression governing free convection of fluids is given next.[8]

$$Nu = a \times \left(\frac{d^3 \times \rho^2 \times g \times \beta \times \Delta T}{\mu^2} \times Pran\,dtl\right)^m$$

In this expression, a is constant that depends on the Prandtl number, b is the thermal expansion coefficient, D T is the temperature difference between the fluid and the heated wire of the RheothermÒ, and m is constant that also depends on the Prandtl number. The collection of terms preceding the Prandtl number is also known as the Grashof number. For the CSSX simulant, assuming a temperature difference between the heated wire and the liquid to be 7.5°C, the product of the two terms inside the bracket (Grashof x Prandtl) in the previous equation is 6 x 10^{-9}.

$$\frac{d^3 \times \rho^2 \times g \times \beta \times \Delta T}{\mu^2} \times Prandtl = \frac{(0.159)^3 (.001236)^2 (980)(2.0710^{-4})(7.5)(0.0036)(2.5 \times 10^{-5})}{(0.025)^2 \times (0.00649)} = 6 \times 10^{-9}$$

The corresponding values for "a" is 1.36 and for "m" is 0.2.[8] Substituting these values into the previous, the predicted heat transfer rate due to free convection is 0.001 W/($cm^{2\circ}$C). This value is eight times smaller than the heat transfer rate due to forced convection. Therefore, the free convection is negligible. In fact the Graetz number (= Reynolds number x Prandlt number x diameter of wire/length of wire) for this process is 0.0001 which is less than 10.[8] This number marks the boundary of combined free and forced convection heat transfer.

Conclusion

The authors determined the thermal properties of a blend from Tank 37H and 44F, a simulant of this blend, and a CSSX simulated waste. The slight difference in thermal and rheological properties between the solutions can explain the discrepancy of the observed flow readings.

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