A Solution Density Model for Hanford Waste Treatment Plant Supernatants

J.G. Reynolds, J.K. Bernards
Washington Group International
1779 Terminal Drive, Richland, WA 99354, USA

R. Carter
Energy Solutions
2345 Stevens Drive, Suite 240, Richland, WA, 99354, USA

ABSTRACT

The density of nuclear waste solution is used as a process control parameter in the Hanford Waste Treatment Plant pretreatment process and is crucial to tank utilization evaluations. The supernatants, however, have many different dissolved sodium salts, including nitrate, nitrite, carbonate, sulfate, phosphate, hydroxide, and aluminate. The large concentrations and diversity of salts in the waste has made the predictions of solution densities difficult historically. The purpose of this study is to determine if a new model of multi-component electrolyte solution densities, recently published in the literature, is effective at predicting the density of nuclear waste supernatants. A statistically designed set of solution densities containing the most prevalent electrolytes in Hanford tank waste was used for model validation. The densities of the simulants were calculated by the model and compared to the experimentally determined densities. The average model error was just 0.1%. These results indicate that the model can be used to accurately predict the density of nuclear waste processed at the Hanford Waste Treatment Plant.

INTRODUCTION

Hanford nuclear waste supernatants have large concentrations of salt, generally two moles per liter or greater, and frequently much greater. Solutions with these large salt concentrations are much more dense than pure water [1]. Further more, the supernatants are multi-component solutions of many electrolytes ($NaCl$, Na_3PO_4, NaF, $NaOH$, $NaNO_2$, $NaNO_3$, Na_2SO_4, Na_2CO_3, $NaAl(OH)_4$), so the density is not well represented by the densities of solutions of the individual salts. Consequently, the relationship between solution density and solution composition has been challenging to define rigorously.

Solution density measurements are expected to be used to monitor the sodium concentration of supernatants in the Hanford Waste Treatment Plant. Density is also an important component of tank inventory and utilization evaluations because the total inventory of a tank is measured by volume rather than by mass. Consequently, it is important to be able to model the density of the supernatants as a function of composition. There are a number of correlations in the literature for density as a function of composition, but many of them are only useful for solutions of a single electrolyte [1], or require complex speciation of the ions in the solution [2]. One exception recently published is the model by Laliberte and Cooper [3], here denoted the Laliberte-Cooper model. This model predicts the density of aqueous mixtures of electrolytes using coefficients derived from the density of aqueous solutions containing a single electrolyte.

The model coefficients for most electrolytes relevant to nuclear waste are available and have already been published by Laliberte and Cooper [3]. These authors have been able to show that their model accurately predicts the density of simple mixtures of two electrolytes dissolved in water over a large concentration and density range. They have not, however, validated their model for more complicated solutions containing more than two electrolytes, such as nuclear waste supernatants. The purpose of this paper is to demonstrate that the Laliberte and Cooper [3] aqueous solution density model is accurate for nuclear waste supernatants treated at the Hanford Waste Treatment Plant.

LALIBERTE-COOPER MODEL

The Laliberte-Cooper model is given by Equation 1 [3].

$$\rho_m = \frac{1}{w_{H_2O}\bar{v}_{H_2O} + \sum_i w_i \bar{v}_{app,i}} \qquad \text{(Eq. 1)}$$

where ρ_m is the solution density in kg m^{-3}, w_i is the mass fraction of electrolyte i, and $\bar{v}_{app,i}$ is the electrolyte specific volume in m^3 kg^{-1}. The coefficient w_{H2O} is the water mass fraction and $\bar{v}_{H_2O}$ is the apparent specific volume of water, m^3 kg^{-1}. The apparent electrolyte specific volume ($\bar{v}_{app,i}$), for one electrolyte, is given by Equation 2,

$$\bar{v}_{app,i} = \frac{w_i + c_2 + c_3 t}{(c_0 w_i + c_1)e^{\left(0.000001(t+c_4)^2\right)}} \qquad \text{(Eq. 2)}$$

where c_0 to c_4 are empirical constants. The coefficients c_0 and c_1 are in kg m^{-3}, c_2 is dimensionless, c_3 is in ºC^{-1}, c_4 is in ºC, and t is in ºC. When the solution mixture contains more than one electrolyte, Laliberte and Cooper [3] suggested a modified form of Equation 2, where the total electrolyte concentration (1 – w_{H2O}) is used instead of just the electrolyte concentration in question, w_i. This modification gave much greater accuracy in density prediction and is given by Equation 3.

$$\bar{v}_{app,i} = \frac{(1 - w_{H_2O}) + c_2 + c_3 t}{(c_0(1 - w_{H_2O}) + c_1)e^{\left(0.000001(t+c_4)^2\right)}} \qquad \text{(Eq. 3)}$$

This equation reduces to Equation 2 for a solution of just one electrolyte. This equation assumes that the apparent specific volume of electrolyte “i” depends on the total concentration of electrolytes in solution rather than the concentration of just electrolyte “i”. The specific volume of water was calculated from the inverse of the following correlation given in Laliberte and Cooper [3]:

$$\rho_{H_2O} = \frac{(((((-2.8054253\times10^{-10}t + 1.0556302\times10^{-7})t - 4.6170461\times10^{-5})t - 0.0079870401)t + 16.945176)t + 999.83952)}{1 + 0.01687985t} \qquad \text{(Eq. 4)}$$

where *t* is the temperature in ºC and ρ is the density of water in kg/m^3.

Laliberte and Cooper [3] report c_0 to c_4 coefficients for 59 common electrolytes, including the sodium salts: NaCl, Na_2CO_3, NaF, $NaNO_2$, $NaNO_3$, NaOH, Na_3PO_4, and Na_2SO_4. The coefficients c_0 through c_4 for Equations 2 and 3 for each salt relevant to nuclear waste is shown in Table I, and most of these data come from Laliberte and Cooper [3]. All of the coefficients presented by Laliberte and Cooper [3] came from fitting Equation 2 to data from individual salt solutions. Two major electrolytes present in nuclear waste are absent from Laliberte and Cooper [3]: sodium oxalate ($Na_2C_2O_4$) and sodium aluminate ($NaAl(OH)_4$). $NaAl(OH)_4$ is only stable in water in the presence of large quantities of NaOH. Consequently, $NaAl(OH)_4$ cannot exist as an individual salt, so Equation 2 cannot be used to determine coefficients for it. In a companion paper to the current one [4], the coefficients for $NaAl(OH)_4$ are determined by regression using Equation 3 rather than Equation 2, while subtracting out the contribution of dissolved NaOH using the coefficients for NaOH published by Laliberte and Cooper [3]. These coefficients for $NaAl(OH)_4$ are also reported in Table I.

Table I. Electrolyte Coefficients used in Equations 1-3

Electrolyte	c_0	c_1	c_2	c_3	c_4
$NaAl(OH)_4$	-258.681	851.308	48.50073	-0.15934	-2266.55
$Na_2C_2O_4$	12.694	218.218	0.304984	0.004552	1508.402
NaCl	-0.00433	0.06471	1.0166	0.014624	3315.6
Na_2CO_3	0.012755	0.014217	-0.091456	0.002134	3342.4
NaF	2.82E-06	2.18E-07	-0.041483	0.000218	4586.9
$NaNO_2$	78.365	298	0.96246	0.0022	1500
$NaNO_3$	49.209	94.737	0.77927	0.007545	1819.2
NaOH	385.55	753.47	-0.10938	0.000695	542.88
Na_3PO_4	1015.6	1533.7	-0.1518	0.000137	173.71
Na_2SO_4	-1.21E-07	4.35E-07	0.15364	0.007251	4731.5

Oxalate is one of the most prevalent organic anions in nuclear waste [5]. Measured densities reported by Sohnel and Novotny [6] were used to develop model coefficients c_0 to c_4 for sodium oxalate. Their data covers the composition range 1 to 4 wt% $Na_2C_2O_4$ and temperatures ranging from 0 to 60 ºC. To determine the c_0 to c_4 parameters for sodium oxalate, a nonlinear least squares method for minimizing the square of the absolute errors between the experimental density and the predicted density (from eqs. 1, 2, and 4) was used. Laliberte and Cooper [3] recommend initial values for c_0 to c_4 (1, 1, 1, 0.0025, 1500) to use at the start of the iterative process. The values of c_0 to c_4 were varied using Solver in Microsoft Excel to obtain the minimum sum of absolute errors squared. Table I gives the values of the c_0 to c_4 parameters obtained for sodium oxalate using this procedure. This procedure is the same procedure of model parameterization used by Laliberte and Cooper [3].

Figure 1 shows that the prediction of the density of aqueous sodium oxalate using the Laliberte-Cooper model are in excellent agreement with the experimental data of Sohnel and Novotny [6]. The mean error and standard deviation of the fit is 4.3×10^{-5} (g/mL) and 0.000295 respectively.

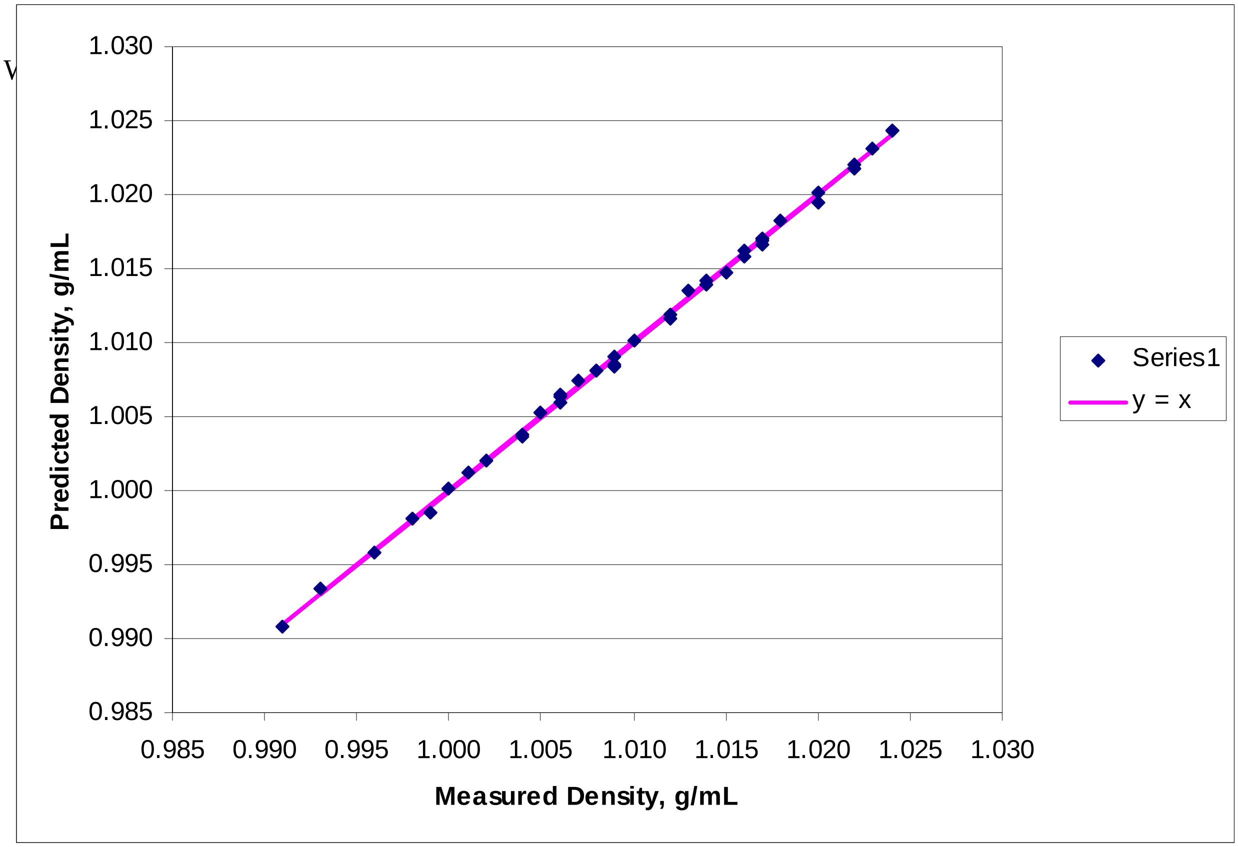

Fig. 1. Predicted versus Measured Density for Aqueous Sodium Oxalate between 0 and 60 ºC

There are no model coefficients available for NaH_3SiO_4, which is a trace component of nuclear waste supernatants. Given the small quantities of silica in waste, NaH_3SiO_4 was neglected in the present study.

VALIDATION DATA

The model was validated by comparing the density predicted by the model against the measured density of nuclear waste simulants. Simulants were used because a statistically designed density data set is available for simulants [7] and are shown in Table II. The simulants were made from the sodium salts of carbonate, aluminate, nitrite, nitrate, hydroxide, sulfate, phosphate, silicate, oxalate, chloride, and fluoride. These are the most prevalent electrolytes in nuclear waste. The researchers analytically determined the concentration of aluminum, sulfur, phosphate, silica and total sodium, and these measured values were used for the concentrations of aluminate, sulfate, and phosphate. For the rest of the anions, the concentrations targeted by the experimenters, but not analytically verified, were used. In some cases, the sum of the charge from anions did not equal the total measured concentration of sodium in the simulants (Table II), a discrepancy attributed to small analytical or batching errors. The concentration of sodium, the lone cation in the mixture, was adjusted to obtain charge balance.

Table II. WTP Waste Simulant Compositions and Supernatant Densities [7]

Experimental ID	Na (M)	Al (M)	Target CO3 (M)	Target NO2 (M)	Target NO3 (M)	Target OH- (M)	S (M)	P (M)	Si (M)	Oxalate (M)	Target Cl (M)	Target F (M)	Density (g/mL)
SM-01-INIT-A	2.1	0.343	0.274	0.292	0.40	0.41	0.002	0.003	0.002	0.002	0.041	0.004	1.10572
SM-02-INIT-A	1.97	0.0967	0.277	0.296	0.49	0.40	0.022	0.003	0.002	0.008	0.041	0.095	1.09616
SM-03-INIT-A	2.02	0.0970	0.173	0.642	0.40	0.40	0.022	0.022	0.002	0.002	0.041	0.004	1.09594
SM-04-INIT-A	1.97	0.0996	0.0133	0.298	0.40	1.02	0.002	0.005	0.002	0.008	0.042	0.096	1.088725
SM-05-INIT-A	2.09	0.0998	0.0134	0.295	0.40	1.11	0.022	0.003	0.003	0.002	0.041	0.004	1.09146
SM-06-INIT-A	2.01	0.0961	0.146	0.294	0.84	0.40	0.002	0.018	0.002	0.002	0.041	0.004	1.09903
SM-07-INIT-A	2.14	0.6514	0.0129	0.290	0.39	0.67	0.022	0.012	0.002	0.008	0.040	0.004	1.109595
SM-08-INIT-A	2.02	0.0970	0.0133	0.648	0.80	0.40	0.002	0.003	0.002	0.008	0.042	0.004	1.095955
SM-09-INIT-A	2.03	0.315	0.0130	0.292	0.83	0.39	0.022	0.003	0.002	0.002	0.041	0.094	1.10368
SM-10-INIT-A	2.07	0.385	0.0130	0.636	0.40	0.46	0.002	0.003	0.001	0.002	0.041	0.094	1.101535
SM-11-INIT-A	2.1	0.262	0.0900	0.402	0.54	0.50	0.010	0.006	0.002	0.005	0.041	0.045	1.10047
SM-12-INIT-A	2.07	0.264	0.0902	0.403	0.54	0.50	0.010	0.006	0.002	0.005	0.041	0.045	1.10038
SM-01-06-A	6.01	0.981	0.784	0.835	1.13	1.17	0.007	0.008	0.007	0.004	0.117	0.011	1.28641
SM-02-06-A	5.8	0.285	0.817	0.871	1.43	1.17	0.065	0.008	0.005	0.024	0.121	0.281	1.262255
SM-03-06-A	5.83	0.280	0.5000	1.85	1.16	1.15	0.063	0.064	0.005	0.005	0.119	0.011	1.26162
SM-04-06-A	5.62	0.284	0.0380	0.851	1.15	2.91	0.007	0.014	0.006	0.023	0.119	0.275	1.237665
SM-05-06-A	6.02	0.287	0.0380	0.851	1.15	3.20	0.063	0.008	0.007	0.005	0.119	0.011	1.24526
SM-06-06-A	5.83	0.279	0.422	0.852	2.43	1.15	0.007	0.052	0.005	0.005	0.119	0.011	1.272245
SM-07-06-A	6.25	1.90	0.0378	0.847	1.15	1.96	0.063	0.036	0.005	0.023	0.118	0.011	1.291195
SM-08-06-A	5.79	0.278	0.0381	1.86	2.29	1.15	0.007	0.008	0.005	0.023	0.119	0.011	1.26509
SM-09-06-A	5.95	0.923	0.0381	0.855	2.43	1.15	0.064	0.008	0.006	0.005	0.119	0.276	1.287595
SM-10-06-A	6.04	1.12	0.0381	1.86	1.16	1.35	0.007	0.008	0.004	0.005	0.119	0.276	1.27726
SM-11-06-A	6.14	0.766	0.263	1.18	1.58	1.46	0.029	0.016	0.007	0.014	0.119	0.133	1.276225
SM-01-08-A	7.29	0.350	0.0480	2.34	2.88	1.45	0.009	0.010	0.006	0.029	0.150	0.014	1.334765
SM-02-08-A	7.4	0.355	0.0487	2.37	2.93	1.47	0.009	0.010	0.006	0.030	0.152	0.014	1.32778
SM-03-08-A	7.63	0.3663	0.050	2.45	3.02	1.51	0.009	0.011	0.006	0.031	0.157	0.014	1.33379
SM-04-08-A	7.34	0.3524	0.0483	2.35	2.90	1.46	0.009	0.010	0.006	0.030	0.151	0.014	1.30125
SM-05-08-A	7.87	0.378	0.0518	2.52	3.11	1.56	0.009	0.011	0.006	0.032	0.162	0.015	1.311605
SM-06-08-A	7.62	0.366	0.0501	2.44	3.01	1.51	0.009	0.011	0.006	0.031	0.157	0.014	1.346015
SM-07-08-A	8.17	0.392	0.0537	2.62	3.23	1.62	0.010	0.012	0.006	0.033	0.168	0.015	1.368305
SM-08-08-A	7.56	0.363	0.0497	2.42	2.99	1.50	0.009	0.011	0.006	0.031	0.156	0.014	1.33908

In the experimental design of Josephs et al. [7], the simulants are 12 separate mixtures of sodium salts; each one concentrated to roughly 2, 6 and 8 moles of sodium per liter. The difference between the simulants at 2, 6 and 8 molar sodium concentration is simply the water content. Density values were unavailable for one simulant at six molar sodium and 4 simulants at 8 molar sodium concentrations because salts precipitated at those sodium concentrations. The densities of the simulants were measured at 25 ºC [7].

When evaluating a model, it is important that individual component concentrations in the samples are uncorrelated, or the effects of one component will be masked by the change of another component [8]. The correlation coefficients for the anions (all sodium salts) are shown in Table III for the 12 simulants (using the two molar sodium data). The small correlation coefficients in Table III indicate that the concentrations of most of the salts are uncorrelated, as desired. Hence, this dataset is an appropriate data set for model validation.

Table III. Component Correlation Coefficient for the 12 Simulants

	Na^+	$Al(OH)_4^-$	CO_3^{2-}	NO_2^-	NO_3^-	OH^-	SO_4^{-2}	PO_4^{3-}	$H_3SiO_4^-$	$C_2O_4^-$	Cl^-	F^-
Na^+	1.00											
$Al(OH)_4^-$	0.74	1.00										
CO_3^{2-}	-0.20	-0.23	1.00									
NO_2^-	-0.07	-0.14	-0.17	1.00								
NO_3^-	-0.32	-0.25	-0.15	0.00	1.00							
OH^-	0.09	-0.10	-0.47	-0.36	-0.45	1.00						
SO_4^{-2}	0.11	0.11	0.04	-0.22	-0.17	0.11	1.00					
PO_4^{3-}	-0.07	-0.07	0.18	0.17	0.03	-0.20	0.17	1.00				
$H_3SiO_4^-$	0.40	-0.03	0.04	-0.46	-0.14	0.37	0.06	-0.28	1.00			
$C_2O_4^-$	-0.23	0.03	-0.12	-0.07	-0.05	0.17	-0.02	-0.21	-0.21	1.00		
Cl^-	-0.75	-0.82	-0.04	0.25	0.06	0.32	-0.19	-0.05	-0.21	0.37	1.00	
F^-	-0.45	-0.02	-0.12	-0.09	-0.02	0.01	-0.01	-0.48	-0.21	0.18	0.09	1.00

MODEL VALIDATION

The data in Table II were used to validate the density model of Equations 1 and 3 using the coefficients in Table I and the water densities calculated from Equation 4. Table IV contains the densities predicted by the model next to the measured densities and the relative error of the model. The R^2 statistic of the model prediction was calculated to be 0.9949. The largest relative error was 0.03 (3 %). The average error (Table IV) is just 0.001 (0.1%)! By comparing the experimental and predicted densities in Table IV, it can be seen that the model is accurate to within 0.04 grams per mL for the entire composition range, and within 0.01 g/mL when the sodium molarity was less than eight. What should be emphasized is that this high level of accuracy came without using any of the data in Table II to develop the model coefficients in Table 1. Hence, this model is predictive and can be used without resorting to scaling the results to individual wastes.

Table IV. Supernatant Density Predictions for WTP Waste Simulants

Experimental ID	Measured Density (g/mL)	Predicted Density (g/mL)	Relative Error[1]
SM-01-INIT-A	1.10572	1.101914	-0.00344
SM-02-INIT-A	1.09616	1.093707	-0.00224
SM-03-INIT-A	1.09594	1.094378	-0.00143
SM-04-INIT-A	1.088725	1.086765	-0.0018
SM-05-INIT-A	1.09146	1.089426	-0.00186
SM-06-INIT-A	1.09903	1.097005	-0.00184
SM-07-INIT-A	1.109595	1.111988	0.002157
SM-08-INIT-A	1.095955	1.095424	-0.00048
SM-09-INIT-A	1.10368	1.102018	-0.00151
SM-10-INIT-A	1.101535	1.09985	-0.00153
SM-11-INIT-A	1.10047	1.097519	-0.00268
SM-12-INIT-A	1.10038	1.097925	-0.00223
SM-01-06-A	1.28641	1.271854	-0.01132

Experimental ID	Measured Density (g/mL)	Predicted Density (g/mL)	Relative Error[1]
SM-02-06-A	1.262255	1.258428	-0.00303
SM-03-06-A	1.26162	1.254601	-0.00556
SM-04-06-A	1.237665	1.231147	-0.00527
SM-05-06-A	1.24526	1.238448	-0.00547
SM-06-06-A	1.272245	1.264121	-0.00639
SM-07-06-A	1.291195	1.313268	0.017095
SM-08-06-A	1.26509	1.259054	-0.00477
SM-09-06-A	1.287595	1.284808	-0.00216
SM-10-06-A	1.27726	1.276922	-0.00026
SM-11-06-A	1.276225	1.26813	-0.00634
SM-01-08-A	1.334765	1.317314	-0.01307
SM-02-08-A	1.32778	1.324864	-0.0022
SM-03-08-A	1.33379	1.334906	0.000837
SM-04-08-A	1.30125	1.329456	0.021676
SM-05-08-A	1.311605	1.354204	0.032478
SM-06-08-A	1.346015	1.330848	-0.01127
SM-07-08-A	1.368305	1.352162	-0.0118
SM-08-08-A	1.33908	1.329792	-0.00694
		Minimum	-0.01307
		Maximum	0.032478
		Mean	-0.00138
		Standard Deviation	0.00937

[1] Relative Error = (predicted density – measured density)/measured density.

Figure 2 visually demonstrates the model accuracy by plotting the predicted densities against the measured densities. As can be seen with the slope of 0.9988 reported in the figure, the measured and predicted values are highly correlated.

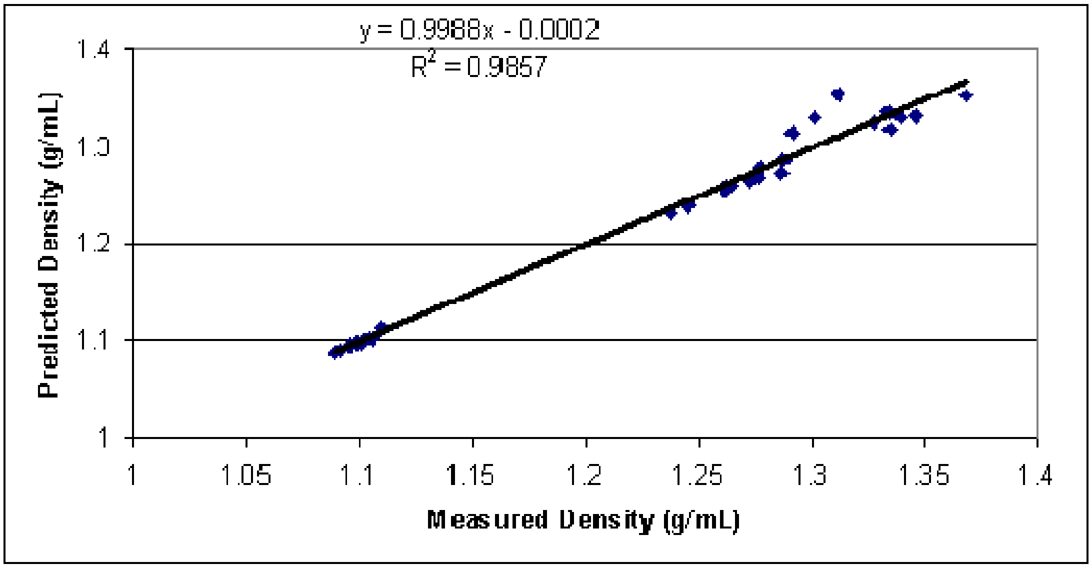

Fig. 2. Predicted versus Measured Densities

While the model has been shown to be highly accurate, it still needs to be shown that there is no small systematic error associated with one of the waste constituents. In order to determine if one of the constituents is the cause of a disproportionate amount of the model error, the relative error in Table IV was correlated to the constituent concentrations in Table II, and is shown in Table V. A correlation coefficient near one or negative one indicates that the relative error in the sample is highly positively or negatively correlated to the model error. In contrast, a correlation coefficient near zero indicates that the error is not systematically correlated to the model component concentration. As can be seen in Table V, the correlation coefficient for most components except carbonate, oxalate and aluminate were between 0.1 and -0.1, indicating that the components were not systematically responsible for the model error. The correlation coefficient for carbonate, oxalate and aluminate were greater than the remaining components but still small, between -0.25 and 0.25. Even though NaH_3SiO_4 was neglected in the density calculation, silicon was included in this correlation in order to determine if leaving it out of the density correlation had any noticeable effect. As is evident by the low correlation between silicon concentration and model predicted error (correlation coefficient =-0.03), neglecting NaH_3SiO_4 in the model did not affect the model error appreciably.

Table V. Correlation Coefficient for Each Component

Component	Correlation Coefficient to Relative Error
Na	0.08
Al	0.23
CO_3	-0.24
NO_2	0.11
NO_3	0.09
OH	0.04
S	0.07
P	0.02
Si	-0.03
Oxalate	0.20
Cl	0.07
F	-0.08

CONCLUSION

An empirical model has been validated for the prediction of the density of Waste Treatment Plant supernatants. The accuracy of the model was tested against a statistically designed set of WTP waste simulant densities. The average relative error in density was –0.00138 with a standard deviation of 0.00919 over the range of total sodium concentration of 2 to 8 molar. The R^2 of the fit was 0.9949. These results indicate that the model is acceptable for the prediction of supernatant densities.

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REFERENCES

1. F. J. Millero. The Molal Volumes of Electrolytes. Chem. Reviews 71: 147-176. (1971).
2. B. S. Krumgalz, R. Pogorelsky, and K. S. Pitzer. Ion-Interaction Approach to Calculations of Volumetric Properties of Aqueous Multiple-Solute Electrolyte Solutions. J. Solution Chem., 24: 1025-1038 (1995).
3. M. Laliberte, and W. E. Cooper. . Model for Calculating the Density of Aqueous Electrolyte Solutions, J. Chem. Eng. Data, 49: 1141-1151 (2004).
4. R. Carter and J. G. Reynolds. The Density of Aqueous Sodium Hydroxide Sodium Aluminate Solutions, Submitted to Hydrometallurgy (2007).
5. A. K. Sharma, S. A. Clauss, G. M. Mong, K. L. Wahl, and J. A. Campbell. Analysis and Quantification of Organic Acids in Simulated Hanford Tank Waste and Hanford Tank Waste. J. Chromatography A805: 101-107 (1998).
6. O. Sohnel, and P. Novotny. *Densities of Aqueous Solutions of Inorganic Substances*, Elsevier, New York, NY. (1985).
7. J. E. Josephs, M. E. Stone, T. B. Calloway, R. E. Eibling, C. D. Barnes, and E. K. Hansen. Treated LAW Feed Evaporation: Physical Properties and Solubility Determination. WSRC-TR-2003-00119, Rev. 0. Savannah River National Laboratory, Aiken, SC (2003.).
8. J. G. Reynolds, and J. K. Bernards. The Density of Sodium Hydroxide-Sodium Aluminate Solutions: Data Review and Model Development. Waste Management '06 Proceedings. Feb. 26-Mar. 02. 2006. Tucson, AZ. (2006).