DEVELOPMENT OF AN IN-LINE GROUT METER FOR MIX-RATIO VERIFICATION

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ABSTRACT

Stabilization/solidification technology is the most widely used technique for the treatment and ultimate disposal of both radioactive and chemical hazardous waste. Cement-based products, commonly referred to as grouts, are the predominant materials of choice because of their associated low processing costs, compatibility with a wide variety of disposal scenarios, and ability to meet stringent processing and performance requirements.

In order to support the continuing improvement and utilization of this technology, a proof-of-principle study has been conducted at the Oak Ridge National Laboratory (ORNL) for the development of an in-line meter for real-time measurement of grout-mix ratio. The development of the meter is based on the premise that the electrical resistance of the freshly prepared grout is linear with respect to mix ratio. Laboratory-scale results indicate that the relationship is, in fact, linear at temperatures between ambient and 55°C.

INTRODUCTION

It has long been recognized that there is a need for a monitor to use with freshly prepared grouts that would facilitate improved quality control. This paper summarizes efforts at ORNL in support of the Westinghouse Hanford Company (WHC) Grout Technology Program to develop an in-line monitor for real-time mix-ratio verification and, hence, improved quality control. Specifically, this paper addresses the monitor's applicability at operating temperatures between ambient and 55°C. Proof-of-principle studies, performed at ambient temperatures, have been reported previously (1,2).

EQUIPMENT CONFIGURATION

The monitor design is shown in Fig. 1. The monitor body was made of polyvinyl chloride (PVC) in the shape of a right circular cylinder with a hole drilled through the center. In the center of the hole is a 2.54-cm-wide (1-in.) lip with a nominal inside diam of 5.08 cm (2 in.). 0.85-cm (0.33-in.) rings, either stainless steel (SS) or PVC, of nominal 5.08-cm diam, were placed on either side of the lip to form a nominal 5.08-cm-diam "pipe" through which the fluid of interest (i.e., freshly prepared grout) would flow. The metal rings serve as the electrodes, while the PVC rings serve as spacers. Data presented in this paper were obtained using a spacing of 5.08 cm between the two metal rings. Metal screws contacting the metal rings through the side of the monitor make the connection with the impedance meter. A model IET IMF-600 impedance meter, with a frequency of 1 kHz, was used to measure the resistance between electrodes. The monitor, in combination with the impedance meter, is hereafter referred to as the grout meter.

The monitor was connected with flanges (with rubber gaskets between the monitor and flanges) to a nominal 5.08-cm-diam bench-top pumping loop as shown in Fig. 2. The loop consists of a plastic 10-gal- (37.85-L-) stirred holding tank, a Warren Rupp Model SB11/2-A Type 4 air-powered diaphragm pump, and sufficient nominal 5.08-cm-diam SS pipe to close the loop. A type K thermocouple was inserted upstream of the monitor to record grout temperature. A data acquisition board Metrabyte model DAS-8 and IBM-AT personal computer were used to continuously record temperature and electrical resistance.

For experiments performed at temperatures above ambient, the pump loop was enclosed in a plexiglass box with the interior lined with aluminum foil. Placed inside the box was a three-element heater with an Omega Model 6000 temperature controller. The temperature sensor connected to the controller was an Omega platinum resistance temperature detector (RTD) air-probe model PRP-AP-100-E12. In order to achieve temperature uniformity, three fans were placed inside of the box to maintain air circulation. The equipment configuration used for elevated temperature experiments is shown in Fig. 3, with the aluminum foil partially removed.

EXPERIMENTAL PROCEDURE

All experiments discussed in this paper used variations of simulated 106-AN waste. This particular waste is representative of a major fraction of LLW contained in double-shell storage tanks located on the Hanford Reservation. A companion study being conducted by WHC personnel is assessing the effects of expected waste composition variations on resulting grout properties. In that study, 36 waste composition variations (i.e., solutions with varying compositions of the following components: $NaNO_3$, $NaAlO_2$,

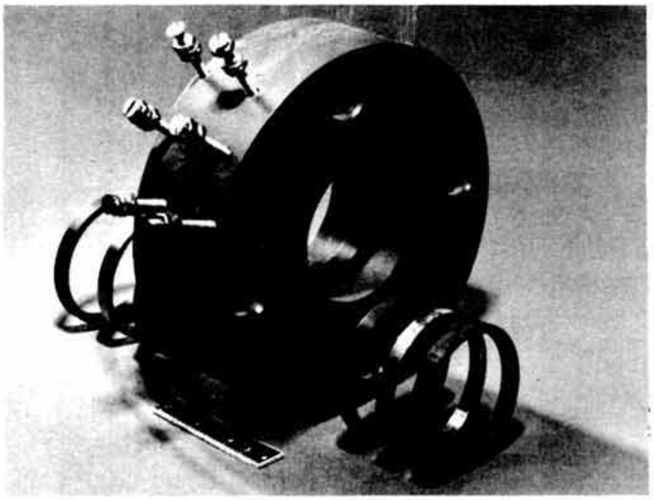

Fig. 1. Disassembled grout monitor.

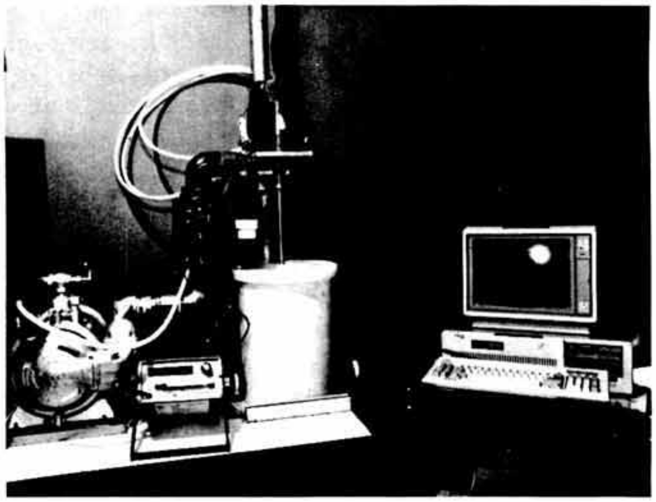

Fig. 2. Bench -top pumping loop.

Na_3PO_4, NaOH, Na_2CO_3, and $NaNO_2$) were used (3). For the development effort summarized in this paper, 7 of these 36 solution compositions were used. These 7 were chosen because they encompass the solution ionic strengths of the 36 variations being evaluated by WHC. It is the ionic strength of the solution which affects its electrical resistance, not its composition, *per se*. The compositions of these seven simulated waste solutions are shown in Table I.

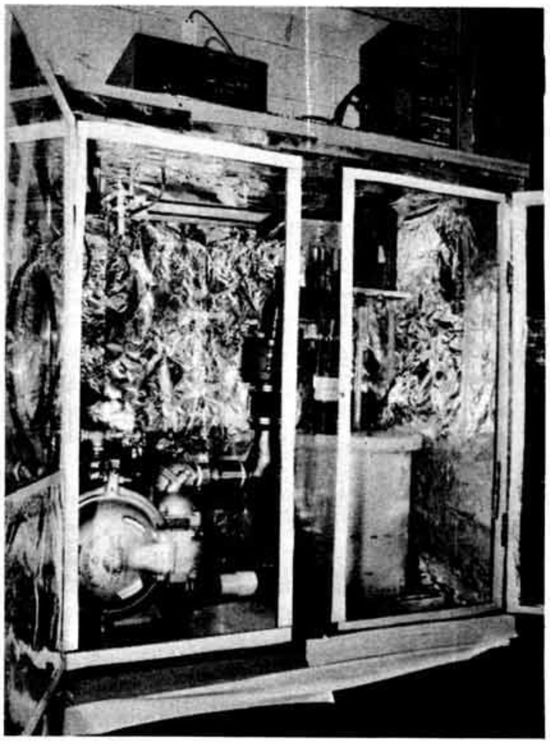

Fig. 3. Equipment configuration (with aluminum foil partially removed) used for elevated temperature experiments.

For each experiment, 9.46 L (2.5 gal) of the selected simulated waste solution was placed in the plastic holding tank. Appropriate weights of dry-solids-blend material, preblended for 23 h in a 0.085 m^3 (3 ft^3) V-blender, were placed in plastic buckets inside the plexiglass box. Upon activation of the heater and fans, the temperature of the waste and the surrounding air was continuously monitored until a constant (±0.5°C) temperature was reached. In addition to the RTD probe used in conjunction with the temperature controller, two other thermocouples were used to determine process temperature. One thermocouple was located in the liquid waste contained in the holding tank, and the other was located near the plastic buckets containing the dry-solids blend. Steady state was assumed with respect to temperature, after all three of the thermocouples indicated that the desired constant temperature had been reached. Upon achieving steady state, the pump was turned on, and the appropriate weight of dry-solids-blend material was added to the solution in the plastic holding tank to achieve the desired mix ratio. Sequential increases in mix ratio (240, 359, 719, 839, 959, 1198, 1318, and 1438 kg/m^3) were achieved by the addition of dry-solids-blend material over a 2-min. interval. In all cases, the dry-solids blend was at the WHC reference composition,

TABLE I

Waste Compositions (mol/L) Used in Grout-meter Development

	Hanford designated solution number						
Ion	2	8	1	36	12	28	30
NO_3^-	0.736	1.400	0.736	1.068	1.400	1.068	1.068
OH^-	0.605	0.605	0.323	0.464	0.605	0.464	0.464
AL^{+3}	0.204	0.204	0.204	0.344	0.424	0.515	0.565
PO_4^{-3}	0.143	0.237	0.143	0.190	0.143	0.190	0.276
NO_2-	0.368	0.700	0.368	0.534	0.700	0.534	0.534
CO_3^{-2}	0.231	0.231	0.395	0.463	0.231	0.313	0.313

that is, 40 wt % limestone, 28 wt % granulated blast furnace slag, 28 wt % ASTM Class F fly ash, and 4 wt % Type I-II-LA Portland cement. Also, all experiments were performed at a constant stirrer speed and pump rate in an attempt to approximate constant operating conditions.

NORMALIZATION WITH RESPECT TO TEMPERATURE

The actual relationship between temperature and grout conductivity is complex but may be approximated by the Nerst-Einstein equation (4):

$$\sigma = \frac{F^2}{RT}(\Sigma C_i Z_i^2 D_i)\varepsilon \qquad \text{(Eq. 1)}$$

where

σ = Ionic conductivity, $\Omega^{-1}m^{-1}$;

F = Farraday constant, 96485 C/mole;

R = Molar gas constant, 8314 J/mole °K;

T = Absolute temperature, °K;

C_i = Ionic concentration of species, mole/m^3;

Z_i = Species valence,

D_i = Diffusion coefficient of species, m^2/s; and

ε = Volume fraction occupied by liquid.

It must be recognized that the Nerst-Einstein equation is not being used here to model the electrical behavior of the grout. Rather, it is being used to provide guidance on the identification of variables which may affect the electrical resistance of the grout, since electrical resistance is a function of the reciprocal of ionic conductivity.

As shown by the Nerst-Einstein equation, the ionic conductivity of the grout is a function of temperature. The equation suggest that the effects of temperature dependency can be minimized by relating ionic conductivity to a reference value, such as, the ionic conductivity of the waste solution. Thus, for experiments presented in this paper, data were normalized with respect to temperature by fitting the data to an equation of the form:

$$M = S(R/R0 - 1) \qquad \text{(Eq. 2)}$$

where

M = mix ratio, kg/m^3;

S = slope of line, kg/m^3;

R = electrical resistance of grout, Ω; and

R0 = electrical resistance of waste solution at mix ratio of zero, Ω.

It must be noted that, although presenting the data in the form of Eq. 2 should minimize the temperature dependency of electrical resistance, it may not eliminate it. This is because both the diffusion coefficient of the species and volume fraction occupied by the liquid (see Eq. 1) are also temperature dependent. Also, note that presenting the data in this form (Eq. 2) allows use of the slopes (S) for comparison of different experimental runs.

EXPERIMENTAL RESULTS

Data obtained indicate that the relationship between mix ratio and electrical resistance at various temperatures is linear over a wide range of mix ratios. Furthermore, fitting the data, using Eq. 2, allows the prediction of mix ratios to within 12 kg/m^3 of the actual mix ratios (3). The slopes of several of the resulting equations are shown in Table II.

The consistency of the slopes shown in Table II indicate that the normalization discussed in the previous section does appear to minimize temperature dependency. It also appears that this normalization minimizes the effects of waste-composition variations as well. In an effort to address these implications, an experiment was performed at 50°C with an "unknown" waste composition. The "unknown"

TABLE II

Slopes of Equations Obtained From Data at Elevated Temperatures

Solution No.	Temperature (°C)	Slope of equation
28	42	2887
1	47	2851
30	50	2983
36	55	2923

waste composition was produced by combining the quantities of waste solutions remaining from previous experiments. Thus, although the resulting composition was unknown, it was bracketed by waste compositions shown in Table I. The slope of the equation obtained from these data was 2815. The consistency of this slope with those in Table II, clearly implies that calibration of the meter with waste compositions that bracket those expected in the field allows interpolation to other compositions within those bracketed. It is recognized that a significantly larger data base will be required in order to assess the sensitivity of the measurements to operational variables in a statistically sound manner.

These implications are important in regard to field implementation because they suggest that there may not be a need for the generation of numerous algorithms for interpretation of electrical resistance measurements. That is, a single algorithm may allow interpretation of resistance measurements over the range of waste composition and feed temperatures expected during operation of a controlled process. To illustrate this point, all data obtained from the four experiments summarized in Table II were fit to a single equation (or algorithm), resulting in an equation with slope of 2929. This equation was then used to interpret electrical resistance data obtained from the grouts prepared with the "unknown" waste composition at 50°C. Results are shown in Table III. Again, the data illustrate the merits of the approach, but clearly indicate that a larger data base is needed to establish precision and accuracy.

SUMMARY

Previously reported results demonstrate that the relationship between the electrical resistance of freshly prepared grout and mix ratio is linear over a wide range of mix ratios (1,2,3). Results summarized in this paper confirm that this linear relationship is maintained at temperatures between ambient and 55°C. Collectively, these data provide proof-of-principle as to the applicability of a grout meter for real-time mix-ratio determinations at operating temperatures expected during routine cement-based grouting processes. It has also been shown that relating the electrical resistance of the grout to some reference value (such as the

TABLE III

Mix ratio as a Function of Electrical Resistance for Grouts Prepared With "Unknown" Solution at 50°C

Electrical resistance of grout, R	Electrical resistance of solution, RO	R/RO-1	Mix ratio (kg/m^3)	
(Ω)	(Ω)	(Ω)	actual	calculated[a]
1.87	1.87	0.00	0.0	0.0
2.03	1.87	0.09	239.7	263.6
2.19	1.87	0.17	479.3	491.3
2.35	1.87	0.26	719.0	754.9
2.43	1.87	0.30	838.8	874.7
2.51	1.87	0.34	958.6	994.6
2.58	1.87	0.38	1078.4	1102.4
2.66	1.87	0.42	1198.3	1222.2
2.75	1.87	0.47	1318.1	1366.0
2.82	1.87	0.51	1437.9	1485.8

[a] Calculated from the equation: MIX RATIO = 2929(R/R0-1).

electrical resistance of the waste) minimizes the effects of variations in temperature and waste composition. This may eliminate the need for the generation of numerous algorithms for interpretation of electrical resistance measurements; that is, it may be possible for a single algorithm to interpret resistance measurements over the range of waste compositions and feed temperatures expected during a controlled process (i.e., one with well-defined waste compositions and operating limits). However, it must be noted that for this data-reduction technique to be viable, a separate meter must be used to measure the electrical resistance of the waste. It is also noted that a larger data base will be required prior to field implementation, in order to determine the meter's sensitivity in a statistically sound manner.

ACKNOWLEDGEMENT

This research was performed at ORNL, in support of the Westinghouse Hanford Company Grout Technology Program. ORNL is managed by Martin Marietta Energy Systems, Inc., for the U.S. Department of Energy under contract DE-AC05-84OR21400.

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