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Development of an In-Line Grout Meter for Improved Quality Control: Final Report

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FOR THE UNITED STATES
DEPARTMENT OF ENERGY

ORNL/TM-11771

Chemical Technology Division

DEVELOPMENT OF AN IN-LINE GROUT METER FOR IMPROVED QUALITY CONTROL: FINAL REPORT

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Date of Issue: May 1991

Prepared for
Westinghouse Hanford Company

(Activity No. EW 10 10 03 0)

Prepared by the
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MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

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PREFACE

This report meets requirements for Milestone 3.4, "Report Results of Grout Meter Bench-Top Tests Pertinent to Purchase/Construction," as described in Statement-of-Work TMG-SOW-90, Revision No. 1, in support of the Westinghouse Hanford Grout Disposal Program.

EXECUTIVE SUMMARY

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

It has long been recognized that there was a need for a monitor for use with freshly prepared grouts that would facilitate improved quality control. In the past, efforts in this area have not proven successful because the freshly prepared grout tended to cake on the monitor probe, greatly reducing its effectiveness. This report documents efforts at Oak Ridge National Laboratory (ORNL) in support of the Westinghouse Hanford Company Grout Technology Program to develop an in-line monitor for mix-ratio verification and, hence, improved quality control in the Westinghouse Hanford Grout Treatment Facility (GTF).

Previously reported results demonstrate that the relationship between the electrical resistance of the grout and mix ratio is linear over a wide range.[1] Results presented in this report confirm that this linear relationship is maintained at temperatures between ambient and 60°C. Thus, the grout meter's applicability to operating temperatures expected in the GTF has been established. In addition, it has been shown that describing this relationship using an equation of the form: mix ratio = f (electrical resistance of the grout/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, a single algorithm may be used to interpret resistance measurements over the range of waste compositions and feed temperatures expected in the GTF. However, in order for this data reduction technique to be viable, a separate meter must be used to measure the electrical resistance of the waste.

The quantity of air entrained in the grout has been identified as a major variable affecting the electrical resistance measurements. Thus, calibration of the grout meter must be performed in the GTF in order to ensure representative air entrainment. It is also necessary that the quantity of entrained air present during calibration be representative of routine plant operation. It must be noted that if the quantity of entrained air in the grout during operations cannot be maintained at a consistent value, then the grout meter cannot be used for quantitative determinations of mix ratio.

Conversely, both the previously reported results[1] and the data presented in this report indicate that the electrical resistance is sensitive to inhomogeneous mixing and variable air entrainment. That is, changes in either the degree of homogeneity with respect to mixing or quantity of air entrainment are detected by the grout meter. Therefore, this meter can be used as a qualitative indicator of grout homogeneity during operation of the GTF.

DEVELOPMENT OF AN IN-LINE GROUT METER FOR IMPROVED QUALITY CONTROL: FINAL REPORT

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ABSTRACT

This report documents progress to date on the development of an in-line grout meter and demonstration of its applicability at operating temperature of 50°C. The grout meter, which is based on measurement of grout electrical resistance/capacitance, is intended to provide real-time measurements of grout mix ratio (ratio of dry-solids-blend materials to waste).

1. INTRODUCTION

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

It has long been recognized that there was a need for a monitor to use with freshly prepared grouts that would facilitate improved quality control. In the past, efforts in this area have not proven successful because the freshly prepared grout tended to cake on the monitor probe, greatly reducing its effectiveness. This report documents efforts at Oak Ridge National Laboratory (ORNL) in support of the Westinghouse Hanford Company (WHC) Grout Technology Program to develop an in-line monitor for mix ratio verification and hence improved quality control in the Westinghouse Hanford Grout Treatment Facility (GTF). Specifically, this report addresses the monitor's applicability at operating temperatures between ambient and 50°C. Proof-of-principal studies performed at ambient temperature have been reported previously.[1]

2. BACKGROUND

This section describes the expected behavior of a freshly prepared grout, hereafter simply referred to as grout, when subjected to an alternating electrical current. As such, it provides the basis for the grout meter development.

2.1 THEORY

When a dry-solids blend containing cement materials is mixed with an aqueous waste to form a grout, a series of chemical reactions begins to take place. The reactions of the various cementitious phases proceed at different rates and involves both hydrolysis and hydration processes. All of the physicochemical properties are going to change while the system evolves from the initial plastic state to the hardened state.

When an electrical current is applied to a grout, some ions are free to drift producing a conduction effect. In addition, other charges that are bound to the solid particles (and, hence, not free to drift) can oscillate under the action of an alternating electric current. The electrical behavior of this system can be modeled as a circuit with a resistive (R) and a capacitive (C) element in parallel. The impedance (Z) of such a circuit is given by:[2]

$$Z = \frac{R}{\sqrt{(2 \cdot f \cdot C \cdot R)^2 + 1}} , \qquad (1)$$

where f is the frequency of the applied electrical current. At a relatively high frequency (on the order of 1 kHz), the electrical measurement on the grout is relatively insensitive to the movement of the grout as a whole (e.g., flow through a pipe). In addition, the fast alternating current inhibits the electrolysis of the solution because any reaction induced during the first half of a cycle will be reversed by the second half of the cycle.

2.2 APPLICATION TO GROUT METER DEVELOPMENT

When the dry-solids-blend materials are mixed with the aqueous waste, there is an initial fast adsorption of the liquid on the surface of the solid particles. Associated with this adsorption are the creation of an electrical double layer along the surface of the solid particles as well as dissolution of soluble components and some hydrolysis. This initial stage, which is virtually instantaneous, is followed by an interval of nearly constant behavior that is often referred to as the dormant period. During this dormant period, the grout should be characterized by a stable electrical response from an applied electrical field.

For a given meter geometry, the resistance of the system will increase with increases in mix ratio (i.e., the ratio of dry-solids blend to waste) because of the growing fraction of volume occupied by poorly conducting solids (as compared with the liquid waste). In addition, the solid particles can effect the movement of some of the free ions in solution. The movement of some of these ions in a direction other than parallel to the applied electrical current due to the solid particles dispersed in the liquid phase will further increase the resistance of the grout.

The capacitance of the system is due to polarization processes following the alternation of the electrical current (i.e., a separation between centers of positive and negative charges). The nature of the different polarization processes will strongly depend on the frequency of the alternating current. At a frequency of 1 kHz, the two main processes are (1) the orientation of both permanent and induced dipoles in the liquid phase in sympathy with the alternating electrical field and (2) polarization of the double layer adjacent to the surface of the solid particles. As the mix ratio is increased, the amount of liquid phase present will decrease and the capacitance due to process one will diminish. On the other hand, the total solid particle surface area will grow as mix ratio increases, and the capacitance due to process two will increase.

3. EQUIPMENT CONFIGURATION

The configuration of the grout meter was designed based on two principal criteria: (1) the meter, which would be considered a prototype, be compatible with the GTF (i.e., connectible to a pipeline) and (2) the electrodes be as unobtrusive as possible to minimize and hopefully avoid caking by the grout during operation. The first criterion was met quite easily by requiring the monitor to be flanged for installation to an existing pipeline. In order to meet the second criterion, several geometries were considered. The one chosen was the use of electrically isolated stainless steel (SS) rings (i.e., electrodes) made with the same materials as the pipeline and configured such that when flanged into the pipeline, the rings would be flush with the pipe. Thus, the electrodes would be completely unobtrusive.

As discussed previously, upon application of an electrical current to the grout, some ions are free to drift through the material producing a conduction effect. The electrical resistivity (the reciprocal of the conductivity) is equal to the electrical resistance offered by the material to the flow of current times the cross-sectional area of current flow and per unit length of current path. Thus, the resistivity will be a function of the monitor configuration dimensions such as length between electrodes. In order to address this issue, the monitor design also needed to allow for variable electrode spacing, which became the third criterion.

The design chosen to meet all three criteria is shown in Fig. 1. The monitor body was made of PVC in the shape of a right circular cylinder with a hole drilled through the center. In the center of the hole is a 1-in.-wide lip with a nominal 2-in. I.D. Either SS or PVC 0.33-in. wide

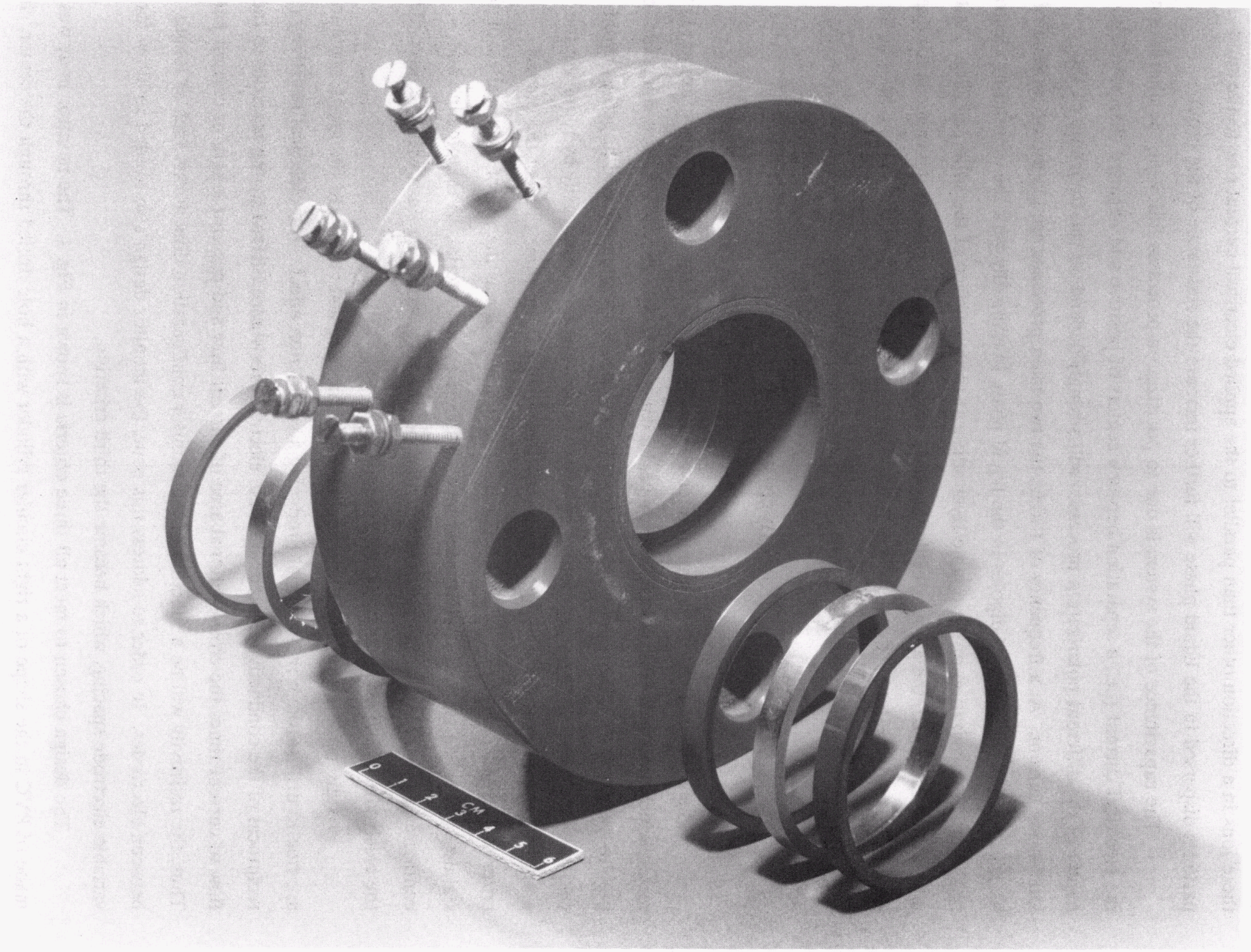

Fig. 1. Disassembled grout monitor.

rings of nominal 2-in. diam were placed on either side of the lip to form a nominal 2-in.-diam "pipe" through which the fluid of interest will flow. The metal rings serve as the electrodes, while the PVC rings serve as spacers. Changing the dispositions of the metal rings and spacers readily allows the spacing to vary between 1 and 2.33 in. between electrodes. 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 either the resistance or capacitance between the 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 2-in.-diam bench-top pumping loop as shown in Figs. 2 and 3. The loop consists of a plastic 10-gal stirred holding tank, a Warren Rupp Model SB11/2-A Type 4 air-powered diaphragm pump, and sufficient nominal 2-in.-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 variable of interest (resistance or capacitance).

3.1 EQUIPMENT MODIFICATION

As discussed in the previous progress report, several experiments were performed with the monitor being dismantled and cleaned following each run.[1] Reproducibility was poor, and duplicate runs were inconsistent. It was observed that the rubber gasket did not make a proper seal on the outermost electrode. The electrode configuration used in the initial efforts had one electrode in the outermost position of the monitor and the other surrounded by two PVC rings. That is, the configuration of the electrodes were ring-spacer-spacer-lip-spacer-ring-spacer. Lack of a proper seal on the outermost ring by the rubber gasket would allow the electrode area to vary slightly during each run, which would effect the electrical response measurements by altering the electrical field. Consequently, the monitor was modified to improve the seal on the outermost electrode. This modification consisted of reducing the width of one of the PVC spacers between the outermost electrode and lip by 0.0625 in. and fabrication of a 0.0625-in. PVC spacer to be placed between the outermost electrode and the rubber gasket (i.e., the new monitor configuration is 0.0625-in. spacer-ring-spacer with width reduced 0.0625-in.-spacer-lip-spacer-ring-spacer). This modification would ensure that the only area of the electrode rings exposed to the grout would be the internal face in contact with the grout. This modification was used throughout the experiments presented in this report.

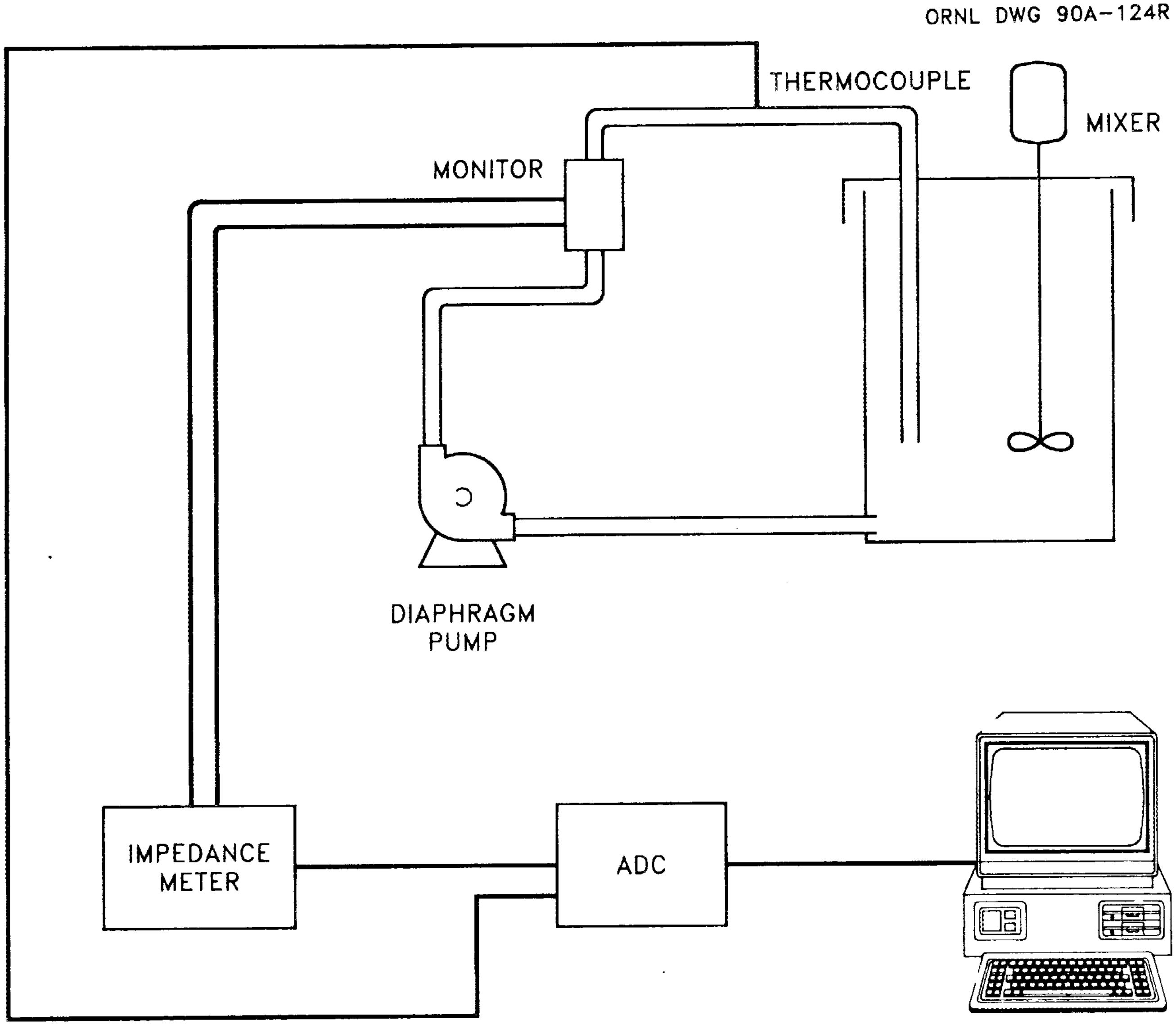

Fig. 2. Schematic of pumping loop.

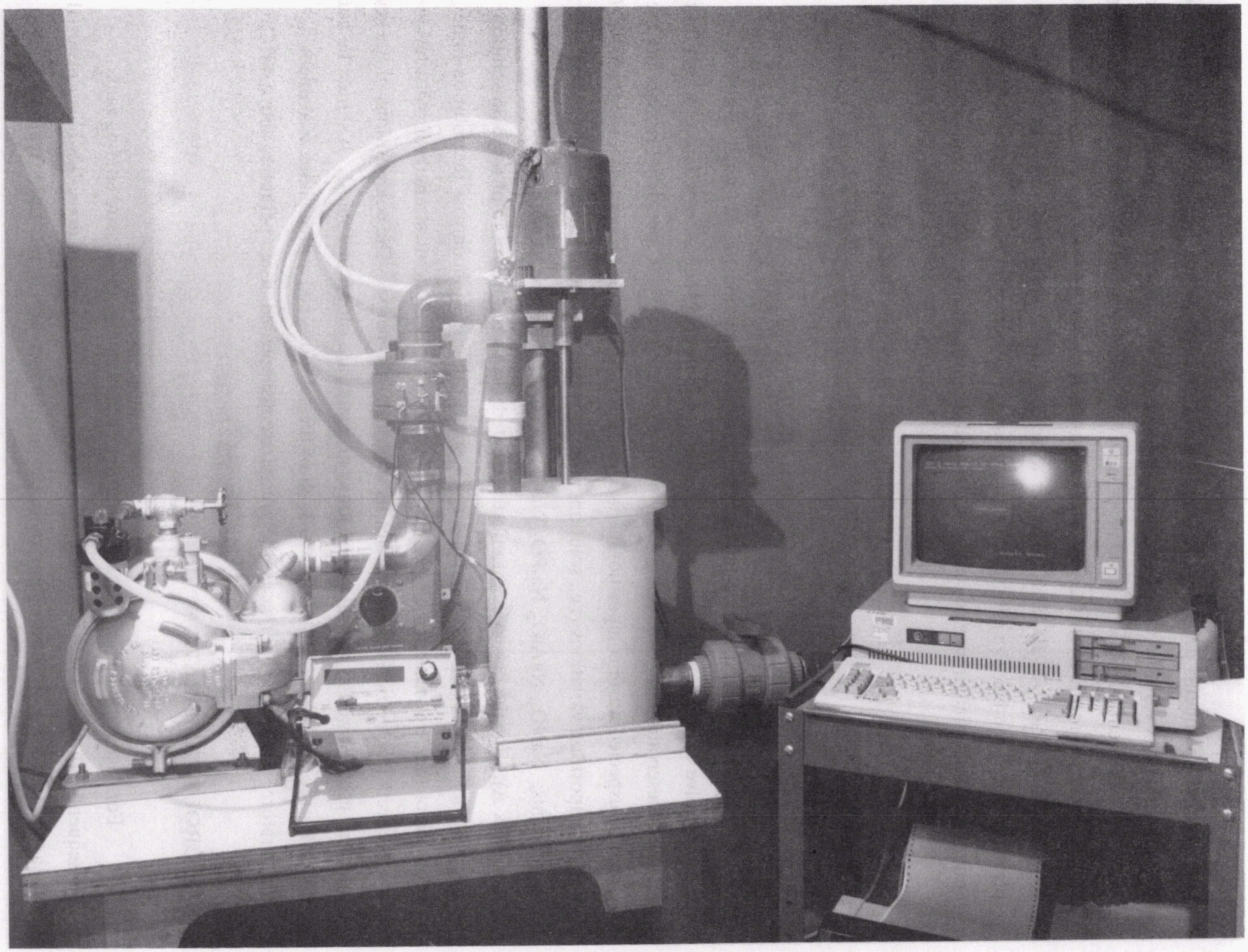

Fig. 3. Pumping loop.

3.2 ELEVATED TEMPERATURE EXPERIMENTS

For experiments performed at temperatures above ambient, the pump loop was enclosed in a plexiglass box with the interior of the box 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, with the aluminum foil partially removed, used for elevated temperature experiments is shown in Fig. 4.

4. METER DEVELOPMENT: EFFECTS OF ENTRAINED AIR

4.1 WASTE COMPOSITION

All experiments discussed in this report utilized simulated 106-AN waste, which is representative of a major fraction of waste 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 from the following components: $NaNO_3$, $NaAlO_2$, Na_3PO_4, NaOH, Na_2CO_3, and $NaNO_2$) were used (see Appendix A). For the development effort presented in this report, seven of these 36 solution compositions were used. These seven 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 effects its electrical resistance, not its concentration, per se. The compositions of the seven solutions used, as well as the calculated ionic strengths, are shown in Table 1. It should be noted that, with the exception of solution No. 2, all of the solutions had a precipitate at ambient temperature. However, in all cases, the precipitate disappeared at temperatures above 40°C.

4.2 GROUT PREPARATION

For each experiment, 2.5 gal of solution were placed in the plastic holding tank. Subsequently, the pump was turned on, and the appropriate weight of dry-solids-blend material was added to achieve the desired mix ratio. Sequential increases in mix ratio (typically 2,

Fig. 4. Equipment configuration (with aluminum foil partially removed) used for elevated temperature experiments.

Table 1. Waste compositions (mol/L) used in grout meter development

Ion	Hanford designated solution Nos.						
	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
I[a]	2.88	3.80	3.07	4.36	4.37	4.83	5.44

[a]Ionic strength I was calculated using[3] $I=0.5\Sigma C_i Z_i^2$, where I = ionic strength, C_i = molar concentration of species i, and Z_i = valence of species i.

4, 6, 7, 8, 9, 10, 11, and 12 lb/gal) 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, that is, 40 wt % limestone, 28 wt % granulated blast furnace slag, 28 wt % American Society for Testing and Materials (ASTM) Class F fly ash, and 4 wt % Type I-II-LA Portland cement. Prior to the addition of the dry-solids-blend materials to the solution, they were blended in a 3 ft^3 V-blender for 23 h.

4.3 EXPERIMENTAL RESULTS

During the first series of experiments conducted at ambient temperature, an unusual behavior was noticed. After each sequential addition of dry-solids blend, and particularly during the first three additions (e.g., 2, 4, and 6 lb/gal), there was a gradual increase over time of the electrical resistance of the grout (Fig. 5). Initially, this increase was thought to be due to rapid progression of the hydration reactions. However, at a mix ratio of 12 lb/gal, the diaphragm pump rate was increased to full capacity, resulting in a significant drop (equivalent to 1 lb/gal in mix ratio, as determined by the electrical resistance) in the electrical resistance of the grout (Fig. 5). In some cases, decreasing the pump rate to a lower speed resulted in increasing the electrical resistance of the grout to its original "high" value, while in others it did not. It was then hypothesized that the speed of the stirrer in the plastic holding tank was affecting the electrical resistance measurements of the grout.

In order to test this hypothesis, a run was performed with solution No. 2 and dry-solids blend added sequentially to achieve mix ratios ranging from 2 to 12. At each mix ratio, the stirrer in the holding tank was turned on and off intermittently, while the pump rate was increased from the lowest to the highest setting. Observations made during this experiment are as follows:

1. At a given pump rate, the electrical resistance of the grout increased as the speed of the stirrer in the holding tank increased.

2. At a given stirrer speed, the electrical resistance of the grout decreased with increases in pump rate.

3. The observations noted in 1 and 2 were, in most cases, completely reversible by lowering the stirrer speed or pump rate, respectively.

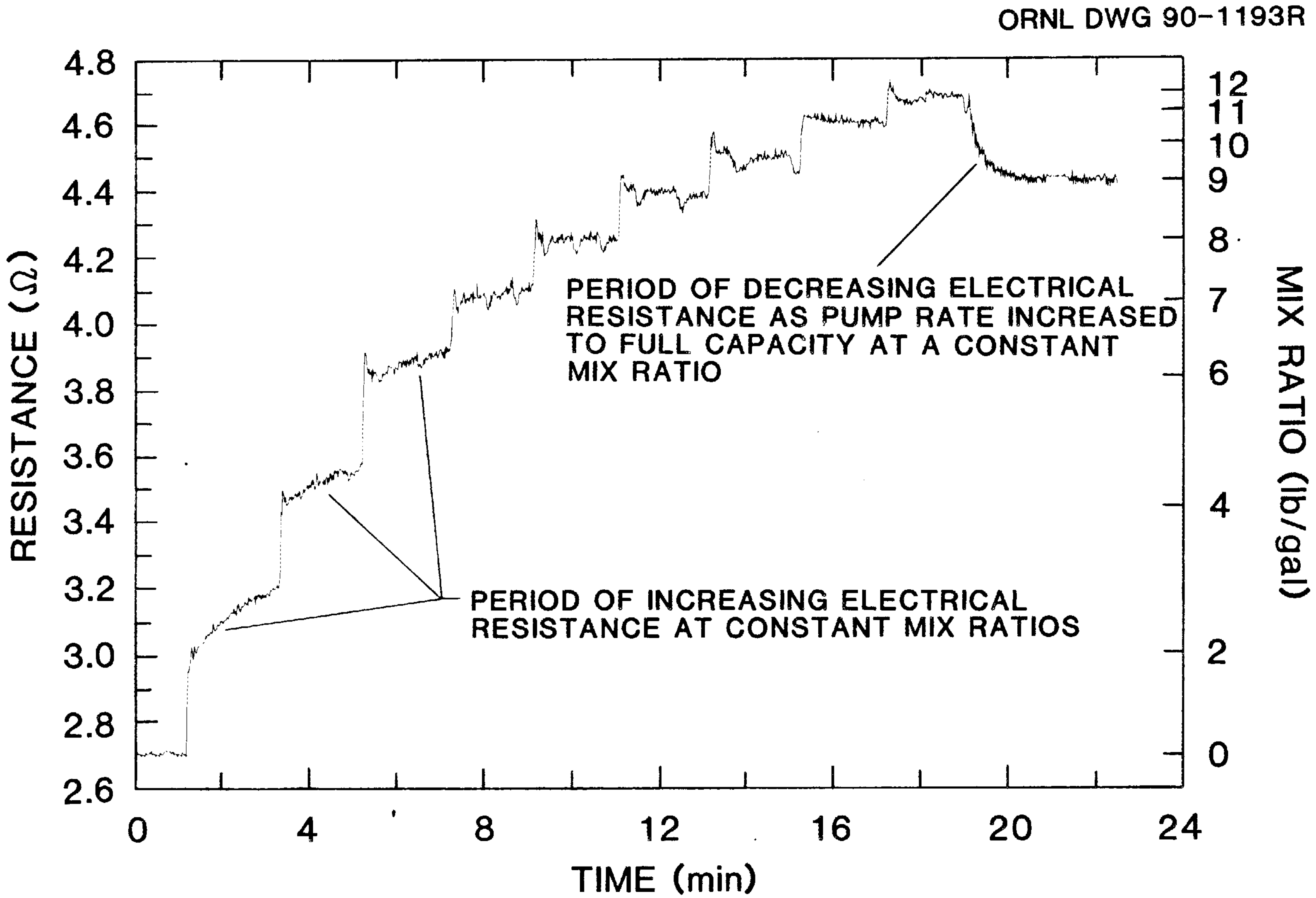

Fig. 5. Example showing effects of changes in stirrer speed and pump rate on electrical resistance.

4. In each and every case where the electrical resistance of the grout decreased over time, there was an observed formation of a supernate of foam on the surface of the grout contained in the plastic holding tank.

These observations, as illustrated in Fig. 6, led to the conclusion that changes in the electrical resistance of the grout over time were due to variations in the quantity of air entrained in the grout. That is, these variations were not due to the configuration (e.g., stirrer speed and pump rate) of the pump loop, per se, rather, they were due to the effects of the configuration on the quantity of entrained air. The presence of significant quantities of entrained air, which is relatively nonconducting compared with the liquid waste, would increase the electrical resistance of the grout. This increase, in turn, would result in the grout meter predicting an "apparent" mix ratio that is higher than the actual mix ratio. It should be noted that for monitors/meters that are density related the reverse would be expected. That is, such monitors/meters would predict an "apparent" mix ratio that is lower than the actual mix ratio.

In order to test the grout meter's performance under "controlled" air entrainment conditions, two experiments were performed that were designed to minimize air entrainment. In these experiments, the stirrer was turned on only for a short period of time after each sequential addition of dry-solids blend, while the pump was on at all times. Electrical resistance measurements were taken only after the stirrer was turned off. The design of the pump loop is such that the intake of the pump is located at the bottom of the plastic holding tank, and the pump loop return line is located on the other side of the holding tank approximately 5 in. from the bottom of the tank. The fluid grout contained in the holding tank covers both the intake and return lines of the loop. As such, with the stirrer turned off, the grout should entrain a minimal quantity of air, while the pump should maintain grout homogeneity. Under these conditions, the electrical resistance of the grout did not change, while the pump rate was increased from the lowest to the highest setting.

Mix ratios, as a function of electrical resistance for these two experiments utilizing solutions Nos. 2 and 12, are shown in Tables 2 and 3, respectively. As shown in these tables, the relationship is linear over a wide range of mix ratios, and the slopes of the resulting curve fits are consistent. It should be noted that the form of the curve fit was chosen in an attempt to normalize the equation with respect to composition variations of the waste solution and has the following form:

$$M = S(R-R0), \tag{2}$$

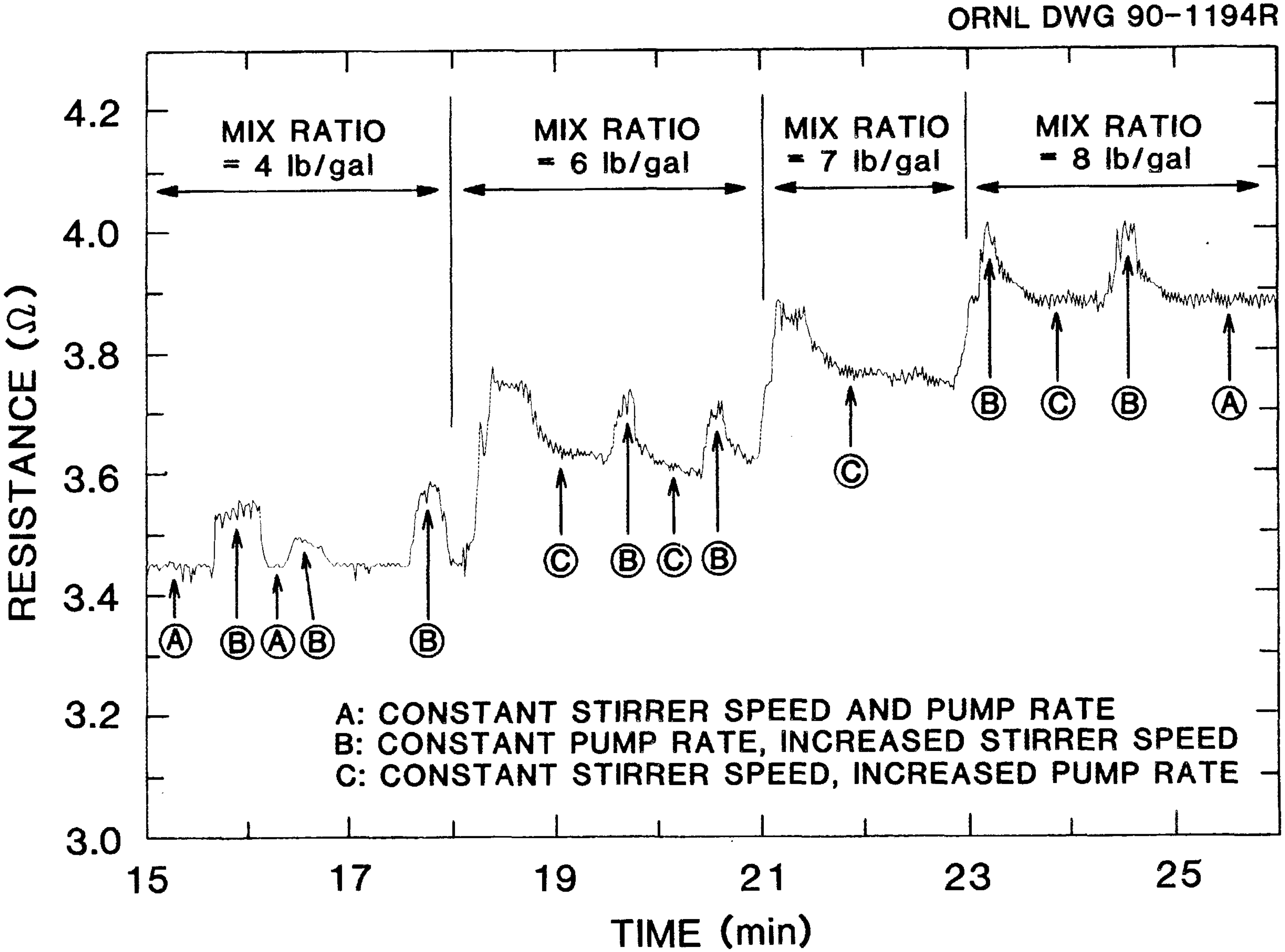

Fig. 6. Examples of instability of resistance measurements due to experimental configuration using grouts prepared with solution No. 12.

Table 2. Mix ratio as a function of electrical resistance for grouts prepared with solution No. 2 at minimum air entrainment conditions

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)	
			Actual	Calculated[a]
2.544	2.544	0.000	0.0	0.0
2.825	2.544	0.281	2.0	2.0
3.114	2.544	0.570	4.0	4.0
3.415	2.544	0.871	6.0	6.1
3.545	2.544	1.001	7.0	7.0
3.684	2.544	1.140	8.0	8.0
3.814	2.544	1.270	9.0	8.9
3.950	2.544	1.406	10.0	9.9
4.121	2.544	1.577	11.0	11.1

[a]Calculated from the equation: MIX RATIO = 7.04(R-R0).

Table 3. Mix ratio as a function of electrical resistance for grouts prepared with solution No. 12 at minimum air entrainment conditions

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)	
			Actual	Calculated[a]
2.760	2.760	0.000	0.0	0.0
3.013	2.760	0.253	2.0	1.9
3.303	2.760	0.543	4.0	3.9
3.603	2.769	0.843	6.0	6.0
3.722	2.760	0.962	7.0	6.9
3.883	2.760	1.123	8.0	8.0
4.007	2.760	1.247	9.0	8.9
4.157	2.760	1.397	10.0	10.0
4.319	2.760	1.559	11.0	11.1
4.469	2.760	1.709	12.0	12.2

[a]Calculated from the equation: MIX RATIO = 7.12(R-R0).

where

M = mix ratio, lb/gal;

S = slope of line, lb/gal-Ω;

R = electrical resistance of grout, Ω; and

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

The slopes obtained from these two experiments are on the order of 7, which is lower than slopes obtained from experiments reported in ref. 1 (i.e., slopes from data reported in ref. 1 were on the order of 9). Data reported in ref. 1 were obtained on a formulation which used a dry-solids blend, consisting of 47 wt % ASTM Class F fly ash, 47 wt % granulated blast furnace slag, and 6 wt % Type I-II-LA Portland cement. The data presented here were obtained on a formulation containing a significant quantity of limestone. The limestone, with its associated lower density, will occupy a greater volume of space on a per pound basis. The resistance of the grout, as measured by the grout meter, is dominated by the fraction of the grout occupied by the liquid waste. Consequently, the increased volume of the solids will correspond to a decrease in volume occupied by the liquid waste for a given meter geometry. This, in turn, will result in a higher resistance value and, hence, a lower slope, for a given mix ratio.

4.4 IMPACT ON FIELD OPERATION

These data establish that the variations observed in earlier experiments were due to variations in entrained air. Clearly, this has implications on operation of the grout meter in the GTF. That is, the grout meter must be calibrated under conditions identical to the operations of the GTF with respect to air entrainment. In reality, this probably means that meter calibration can only be performed after installation in the GTF.

5. METER DEVELOPMENT: EFFECTS OF TEMPERATURE

5.1 GROUT PREPARATION

Waste solutions used for these studies were identical to those described in Sect. 4.1. First, 2.5 gal of solution were placed in the plastic holding tank. Appropriate weights of dry-solids-blend material in plastic buckets were placed 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 these thermocouples indicated that the desired constant temperature had been reached. The time required to reach steady state was approximately 7 h. After achieving steady state, grouts were prepared as described in Sect. 4.2.

5.2 NORMALIZATION WITH RESPECT TO TEMPERATURE

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

$$\sigma = \frac{F^2}{RT}(\Sigma C_i Z_i^2 D_i)\epsilon \ , \tag{3}$$

where

σ = ionic conductivity, $\Omega^{-1}m^{-1}$;
F = Faraday constant, 96485 C/mol °K;
R = molar gas constant, 8314 J/mol °K;
T = absolute temperature, °K;
C_i= ionic concentration of species, mol/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, this equation is 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 the ionic conductivity. As shown by the Nerst-Einstein equation, the ionic conductivity of the grout is a function of temperature. The equation suggests that the effects of temperature dependency can be minimized by relating ionic conductivity to a reference value (i.e., σ/σ_o). Thus, for experiments presented in this section, data were normalized, with respect to temperature, by fitting the data to an equation of the following form:

$$M = S(R/R0 - 1), \tag{4}$$

where

M = mix ratio, lb/gal;

S = slope of line, lb/gal;

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. 4 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. 3) are temperature dependent. Also, note that presenting the data in these forms allow use of the slopes (S) for comparison of different experimental runs.

5.3 EXPERIMENTAL RESULTS

Based on visual observation, it appears that, at elevated temperatures, the grouts show a significantly increased propensity toward air entrainment, probably due to the low viscosity of the grout. However, for these experiments, no attempt was made to minimize air entrainment as described in Sect. 4.3. Rather, the experiments were performed at a constant stirrer speed and pump rate in an attempt to approximate constant operating conditions. It should be noted that the ability to control air entrainment in this system is limited due to the plastic holding tank being vented to the atmosphere.

Resulting data, showing the relationship between mix ratio and electrical resistance at various temperatures, are shown in Appendix B. Significantly, the relationship between mix ratio and electrical resistance remains linear at these elevated temperatures. The slopes of the resulting equations are summarized in Table 4.

As discussed in Sect. 4.4, the impact of variable air entrainment is significant and is believed to account for the minor differences in the slopes obtained for data at 42 to 55°C. Slopes of equations from data derived at 58 and 60°C (see Table 4) are significantly less than those obtained at temperatures of 42 to 55°C. It is believed that this reduction in slope is due to a significant loss in entrained air caused by these higher temperatures (i.e., >55°C). This belief is based on the fact that the slopes obtained at 58 and 60°C are (1) consistent with each other, (2) approach the slope of the equation obtained for the experiment performed to minimize air entrainment with solution No. 2 at ambient temperature (see Sect. 4.3), and (3) correspond to an observed increase of foam supernate above the grout in the holding tank.

Table 4. Slopes of equations obtained from data at elevated temperature

Solution No.	Temperature (e)	Slope of equation
28	42	24.1
1	47	23.8
30	50	24.9
36	55	24.4
12	58	21.9
8	60	22.2

5.4 IMPACT ON FIELD OPERATION

Based on the data presented in Sect 5.3, it appears that relatively constant operating conditions, with respect to entrained air, are obtained in the pump loop at temperatures between 42 and 55°C. Consequently, an experiment was performed at 50°C with an "unknown" waste composition. The "unknown" waste composition was produced by combining the quantities of solutions remaining from previous experiments, numbered 1, 2, 8, 12, 28, 30, and 36. Thus, although the resulting composition was unknown, it was bracketed by waste compositions discussed in Sect. 5.3. Resulting data are shown in Table 5. The slope of the equation obtained from the data was 23.5. Clearly, this indicates that if the issue of variable entrained air can be dealt with, then calibration in the field using waste compositions that bracket expected waste compositions can be interpolated to other compositions within those bracketed.

This is an important point in regard to field implementation because it suggests that there is no need for the generation of numerous algorithms for interpretation of electrical resistance measurements. That is, a single algorithm can be used to interpret resistance measurements over the range of waste compositions and feed temperatures expected in the GTF. To illustrate this point, all data obtained from the four experiments performed at temperatures between 42 and 55°C, with known waste compositions, were fit to a single equation (or algorithm), resulting in the following equation:

$$M = 24.3(R/R0 - 1) \tag{5}$$

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 5. The accuracy of the predicted values can be improved by a larger calibration data base and improved control over quantity of entrained air.

6. SUMMARY

Previously reported results demonstrate that the relationship between the electrical resistance of the grout and mix ratio is linear over a wide range of mix ratios.[1] Results presented in this report confirm that this linear relationship is maintained at temperatures between ambient and 60°C. Thus, proof-of-principal, the grout meter's applicability to operating temperatures expected in the GTF, has been established. In addition, it has been shown that describing this relationship, using an equation of the form: mix ratio = f (electrical resistance of the

Table 5. Mix ratio as a function of electrical resistance for grouts prepared with "unknown" solution at 50° C

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)		
			Actual	Calculated[a]	Calculated[a]
1.87	1.87	0.00	0.0	0.0	0.0
2.03	1.87	0.09	2.0	2.1	2.2
2.19	1.87	0.17	4.0	4.0	4.1
2.35	1.87	0.26	6.0	6.0	6.3
2.43	1.87	0.30	7.0	7.0	7.3
2.51	1.87	0.34	8.0	8.0	8.3
2.58	1.87	0.38	9.0	8.9	9.2
2.66	1.87	0.42	10.0	9.9	10.2
2.75	1.87	0.47	11.0	11.1	11.4
2.82	1.87	0.51	12.0	11.9	12.4

[a]Calculated from the equation: MIX RATIO = 23.5(R/R0-1).
[b]Calculated from the equation: MIX RATIO = 24.3(R/R0-1).

grout/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, a single algorithm may be used to interpret resistance measurements over the range of waste compositions and feed temperatures expected in the GTF. However, in order 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 assess the meter's sensitivity in a statistically sound manner.

The quantity of air entrained in the grout has been identified as a major variable affecting the electrical resistance measurements. Thus, calibration of the grout meter must be performed in the GTF in order to ensure representative air entrainment. It is also necessary that the quantity of entrained air present during calibration also be representative of routine plant operation. It must be noted that if the quantity of entrained air in the grout during operations cannot be maintained at a consistent value, then the grout meter cannot be used for quantitative determinations of mix ratio. It should also be noted that the quantity of entrained air will most probably affect other types of mix-ratio detectors such as densitometers and neutron-attenuation based meters. However, in these cases, the predicted mix ratio, based on monitor measurements, would be expected to be less than the actual mix ratio. Due to this sensitivity, it is recommended that operational procedures of the GTF be reviewed to assess the potential for minimization of air entrainment.

Conversely, both the previously reported results[1] and data presented in this report indicate that the electrical resistance is sensitive to inhomogeneous mixing and variable air entrainment. That is, changes in either the degree of homogeneity with respect to mixing or quantity of air entrainment are detected by the grout meter. Therefore, this meter can be used as a qualitative indicator of grout homogeneity during operation of the GTF.

The monitor used during this development effort was constructed of PVC and SS. For implementation in the GTF, it is only necessary that the electrodes be an electrically conductive material (e.g., SS) and that the body of the monitor be an electrically nonconductive material (e.g., PVC). Beyond these requirements, the materials of choice will be dictated by safety and performance constraints consistent with design and operation of the GTF. These same plant specific constraints will also dictate the materials and installation requirements related to the electrical connections. In addition, it has been established that the electrodes cannot be in direct contact with the gasket used in the flange connection. That is, the electrodes must be electrically isolated by a nonconducting material, such as that used for the body of the monitor.

Three electrode spacings (1.67, 2.00 and 2.33 in.) were evaluated during this project.[1] Of the three, a spacing of 2.33 in. between the electrodes proved to be the most sensitive and would be the recommended spacing in construction of the monitor for use in the GTF based on the existing development effort data base. However, it has been demonstrated that the measured value for the electrical resistance of the grout is proportional to the electrode spacing.[1] Consequently, increasing the electrode spacing beyond 2.33 in. would result in higher resistance values and should increase the meters sensitivity. Thus, an increased spacing between electrodes should be considered.

The impedance meter used in this study was the IET model IMF-600 with a four-terminal Kelvin connector operating at 1 kHz with an analog output connected to a data acquisition board. For actual use in the GTF, the instrument should have similar electrical characteristics. That is, four-terminal configuration, operating frequency greater than 500 Hz, similar or better accuracy for AC resistance and/or conductance measurements, and a suitable output to be interfaced to a computer. The main difference would be that the instrument selected for field use should have a more sturdy enclosure and be compatible with an industrial type environment.

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8. ACKNOWLEDGEMENTS

The authors gratefully acknowledge technical review comments provided by C. H. Byers and E. S. Harrington, Martin Marietta Energy Systems, Inc.

Appendix A. WASTE COMPOSITIONS

Table A.1. Waste compositions (mol/L) used in a Westinghouse Hanford Company comparison waste variability study

Hanford designated solution No.	Ion					
	NO_3^-	OH^-	Al^{+3}	PO_4^{-3}	NO_2^-	CO_3^{-2}
1	0.736	0.323	0.204	0.143	0.368	0.395
2	0.736	0.605	0.204	0.143	0.368	0.231
3	1.400	0.323	0.204	0.143	0.700	0.231
4	1.400	0.605	0.204	0.143	0.700	0.395
5	0.736	0.323	0.204	0.237	0.368	0.231
6	0.736	0.605	0.204	0.237	0.368	0.395
7	1.400	0.323	0.204	0.237	0.700	0.395
8	1.400	0.605	0.204	0.237	0.700	0.231
9	0.736	0.323	0.424	0.143	0.368	0.231
10	0.736	0.605	0.424	0.143	0.368	0.395
11	1.400	0.323	0.424	0.143	0.700	0.395
12	1.400	0.605	0.424	0.143	0.700	0.231
13	0.736	0.323	0.424	0.237	0.368	0.395
14	0.736	0.605	0.424	0.237	0.368	0.231
15	1.400	0.323	0.424	0.237	0.700	0.231
16	1.400	0.605	0.424	0.237	0.700	0.395
17	1.068	0.464	0.314	0.190	0.534	0.313
18	1.068	0.464	0.314	0.190	0.534	0.313
19	1.068	0.464	0.314	0.190	0.534	0.313
20	1.068	0.464	0.314	0.190	0.534	0.313
21	1.068	0.464	0.314	0.190	0.534	0.313
22	1.068	0.464	0.344	0.190	0.534	0.313
23	0.763	0.323	0.204	0.143	0.368	0.395
24	0.763	0.323	0.424	0.237	0.368	0.395

Table A.1 - continued

Hanford designated solution No.	Ion					
	NO_3^-	OH^-	Al^{+3}	PO_4^{-3}	NO_2^-	CO_3^{-2}
25	0.763	0.605	0.424	0.237	0.368	0.231
26	1.400	0.605	0.424	0.237	0.700	0.395
27	1.068	0.464	0.113	0.190	0.534	0.313
28	1.068	0.464	0.515	0.190	0.534	0.313
29	1.068	0.464	0.314	0.104	0.534	0.313
30	1.068	0.464	0.565	0.276	0.534	0.313
31	0.463	0.464	0.344	0.190	0.232	0.313
32	1.673	0.464	0.344	0.190	0.836	0.313
33	1.068	0.208	0.344	0.190	0.534	0.313
34	1.068	0.720	0.344	0.190	0.534	0.313
35	1.068	0.464	0.344	0.190	0.534	0.163
36	1.068	0.464	0.344	0.190	0.534	0.463

Appendix B. MIX RATIOS AS A FUNCTION OF ELECTRICAL RESISTANCE

Table B.1. Mix ratio as a function of electrical resistance for grouts prepared with solution No. 28 at 42°C

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)	
			Actual	Calculated[a]
1.95	1.95	0.00	0.0	0.0
2.13	1.95	0.09	2.0	2.2
2.28	1.95	0.17	4.0	4.1
2.43	1.95	0.25	6.0	5.9
2.50	1.95	0.28	7.0	6.8
2.59	1.95	0.33	8.0	7.9
2.68	1.95	0.37	9.0	9.0
2.76	1.95	0.42	10.0	10.0
2.85	1.95	0.46	11.0	11.1
2.92	1.95	0.50	12.0	12.0

[a]Calculated from the equation: MIX RATIO = 24.1 (R/R0-1).

Table B.2. Mix ratio as a function of electrical resistance for grouts prepared with solution No. 1 at 47°C

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal) Actual	Mix ratio (lb/gal) Calculated[a]
2.00	2.00	0.00	0.0	0.0
2.16	2.00	0.08	2.0	1.9
2.34	2.00	0.17	4.0	4.0
2.51	2.00	0.25	6.0	6.1
2.58	2.00	0.29	7.0	6.9
2.67	2.00	0.33	8.0	8.0
2.75	2.00	0.38	9.0	8.9
2.84	2.00	0.42	10.0	10.0
2.92	2.00	0.46	11.0	10.9
3.02	2.00	0.51	12.0	12.1

[a]Calculated from the equation: MIX RATIO = 23.8 (R/R0-1).

Table B.3. Mix ratio as a function of electrical resistance for grouts prepared with solution No. 30 at 50° C

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)	
			Actual	Calculated[a]
1.63	1.63	0.00	0.0	0.0
1.77	1.63	0.09	2.0	2.1
1.89	1.63	0.16	4.0	4.0
2.02	1.63	0.24	6.0	6.0
2.08	1.63	0.28	7.0	6.9
2.15	1.63	0.32	8.0	7.9
2.22	1.63	0.36	9.0	9.0
2.28	1.63	0.40	10.0	9.9
2.35	1.63	0.44	11.0	11.0
3.42	1.63	0.48	12.0	12.1

[a]Calculated from the equation: MIX RATIO = 24.9 (R/R0-1).

Table B.4. Mix ratio as a function of electrictal resistance for grouts prepared with solution No. 36 at 55°C

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)	
			Actual	Calculated[a]
1.62	1.62	0.00	0.0	0.0
1.75	1.62	0.08	2.0	2.0
1.89	1.62	0.17	4.0	4.1
2.03	1.62	0.25	6.0	6.2
2.09	1.62	0.29	7.0	7.1
2.15	1.62	0.33	8.0	8.0
2.21	1.62	0.36	9.0	8.9
2.28	1.62	0.41	10.0	9.9
2.35	1.62	0.45	11.0	11.0
3.42	1.62	0.49	12.0	12.0

[a]Calculated from the equation: MIX RATIO = 24.4 (R/R0-1).

Table B.5. Mix ratio as a function of electrical resistance for grouts prepared with solution No. 12 at 58°C

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)	
			Actual	Calculated[a]
1.54	1.54	0.00	0.0	0.0
1.68	1.54	0.09	2.0	2.0
1.81	1.54	0.18	4.0	3.8
1.96	1.54	0.27	6.0	6.0
2.02	1.54	0.31	7.0	6.8
2.10	1.54	0.36	8.0	8.0
2.18	1.54	0.42	9.0	9.1
2.25	1.54	0.46	10.0	10.1
2.32	1.54	0.51	11.0	11.1
3.38	1.54	0.55	12.0	11.9

[a]Calculated from the equation: MIX RATIO = 21.9 (R/R0-1).

Table B.6. Mix ratio as a function of electrical resistance for grouts prepared with solution No. 8 at 60°C

Electrical resistance of grout, R (Ω)	Electrical resistance of solution, R0 (Ω)	R/R0-1 (Ω)	Mix ratio (lb/gal)	
			Actual	Calculated[a]
1.49	1.49	0.00	0.0	0.0
1.62	1.49	0.09	2.0	1.9
1.75	1.49	0.17	4.0	3.9
1.89	1.49	0.27	6.0	6.0
1.96	1.49	0.32	7.0	7.0
2.03	1.49	0.36	8.0	8.0
2.09	1.49	0.40	9.0	8.9
2.16	1.49	0.45	10.0	10.0
2.23	1.49	0.50	11.0	11.0
2.30	1.49	0.54	12.0	12.1

[a]Calculated from the equation: MIX RATIO = 22.2 (R/R0-1).

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