

STABILITY OF LOW-LEVEL CEMENT-BASED WASTE SYSTEMS

R.I.A. Malek and D.M. Roy
Materials Research Laboratory
The Pennsylvania State University
University Park, PA 16802

ABSTRACT

A low temperature hydrated ceramic waste form has been designed for solidification and stabilization of low-level radioactive waste. The suggested waste forms were based mainly on cementitious materials. A solution composed of 2.5M NaNO₃, 0.8M NaNO₂ and 1.2M NaOH was used as a waste solution. This represents both the high alkalinity and high nitrate/nitrite contents of many LLW solutions. The high alkalinity of the waste solution made it possible to blend some by-product materials (e.g., ground granulated blast-furnace slag and fly ashes) with minimum amounts of cement to obtain a lightweight, low density waste form of economic value and excellent processibility. The chemical environment created by mixing this LLW solution with cementitious materials will affect the stability and long-term performance of the waste form. In addition, the information gained from studying such an environment will certainly help attaining best performance. For such purposes, the Eh and pH of the pore fluids expressed from hydrating waste forms were measured. The measured values were located on various Eh-pH diagrams to find the stability/instability regions for compounds of major concern. Furthermore, the dimensional and thermal stabilities of the hardened waste forms were determined by measuring expansive stresses, and length changes as a function of time and heat cycle. The effects produced by such findings on long-term durability of the waste forms are discussed.

INTRODUCTION

Cement-based systems are widely used hosts for radioactive low-level waste streams solidification and stabilization. This is mainly due to economic and technical concerns including the high waste loading level. Regardless of how it is applied [e.g., ORNL-hydrofracture injection (1), Hanford transportable grout (2), or Savannah River Plant nitrate saltstone (3)] fresh cementitious waste forms should be pumpable for a considerable distance to the emplacement sites. A Reynold's Number of >2100 has been set up to ensure that the grout would be pumped under turbulent flow conditions to minimize the potential for plugging. Various formulae are designed to meet such specifications but all are based on cement + fly ash blends. We found (4) that slag addition improves the engineering properties of the hardened matrix and allows minimizing cement content, thus enhancing technical and economic values of the process.

Cementitious mixture qualifications for low-level radioactive waste solidification is based on: a) the hydraulic reactivity and availability, b) the slurry properties, and c) the adiabatic temperature rise. The qualified mixtures should then be tested for the radioactive and toxic ion release rate and those with maximum ion fixation/stabilization are selected for waste disposal. Although the radioactive species in many low-level wastes are very low, factors which retard their release are also discussed. Finally, the engineering properties will determine the long-term structural performance. In addition, chemical and dimensional stabilities are important factors that assure a long-term durability and better performance of the solidified waste form.

TEST PROGRAM

Materials Selection and Formulation

The chemical nature of cementitious solid ingredients defines their course of reaction when brought in contact with waste solution. Figure 1 shows a diagrammatic representation of the relative chemical composition of the potential cementitious material. It could

be seen that as the chemical composition of the solid approaches one of the pure components at the apices, the resulting hydration products are of inferior engineering properties both regarding processing and potential long term stability of the waste form. Ordinary portland cement hydration can generate a considerable amount of heat. Depending upon the way the waste form is applied, this heat generation can significantly affect the processing and stability of the waste form, especially in large pours.

It appears that the most successful cementitious formula is a blend with a total chemical composition being in the middle region of the CaO-Al₂O₃-SiO₂ triangular diagram. Hoyle (1986) has also shown the effectiveness of cements in the middle region for solidifying non-salt compositions. This shows that the use of fly ash is significant from the chemical point of view, as well as providing filler for diluting thermal effects, i.e., reducing heat of hydration. In addition, the particles tend to reduce viscosity of the mixtures, making processing easier. The low reactivity of the Class F ash in particular helps moderate the temperature rise in massive pours. We found (4) that ground granulated blast furnace slag (by-product from the steel industry) improves the engineering properties of the waste form. Portland cement plus Class-C fly ash blends have the potential for reacting more rapidly than desired, and forming dimensionally unstable matrices, especially in the presence of alkalis. On the other hand, the hydration of mixtures with small amounts of Portland cement plus Class-F fly ash blends tends to result in highly porous and weak matrices. Slag addition was found to give a dimensionally stable hydration product (cement-Class C fly ash systems) and a fine pore structure (cement-Class F fly ash systems). A simulated waste solution (2.5M NaNO₃, 0.8M NaNO₂ and 1.2M NaOH) was used as a waste solution, representing the high alkalinity and high nitrate/nitrite contents of many LLW solutions (2-4). The solution was mixed with a blend containing ~20% cement plus ~80% class C fly ash (40% solution and 60% solid blend). In some cases, the effects produced by Class F fly ash replacement for Class C fly ash and by slag substitution for 50-100% of the cement in both classes of fly ash mixtures were investigated.

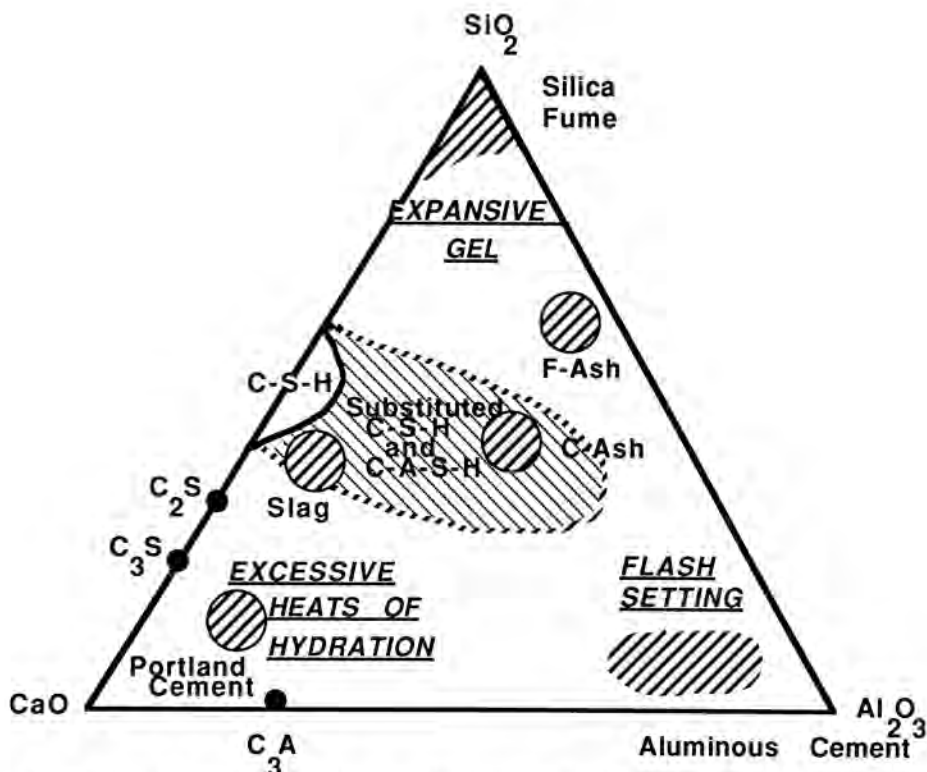


Fig. 1. The $\text{CaO-Al}_2\text{O}_3\text{-SiO}_2$ System Showing the Average Bulk Composition of Potential Solid Cementitious Material for Low-Level Radioactive Waste Disposal. Indicated also are the main hydration products as well as the physical property (underlined) resulting from the interaction between a solid (rich in one of the components at apices) with the waste solution.

Techniques

a) Eh-pH of the Pore Fluids: The pore fluids of hydrated waste form (18 month age) were expressed from samples using a special high pressure cell designed in this laboratory for such purpose. Special precautions were taken to avoid contact with the atmosphere. Eh was measured using a combination of platinum electrode and reference electrode in one body. For matching the potential characteristics of a conventional Ag/AgCl reference electrode, the filling electrolyte chamber (containing the reference element) was filled with 4M KCl saturated with silver chloride. The Ag/AgCl reference electrode was selected because it works successfully in high ionic strength solutions (a Calomel electrode is more successful in solutions having total ionic strength $<0.2\text{M}$). The potential developed by the reference electrode portion relative to the normal hydrogen scale at 25°C is -0.199 volts. The electrode combination was connected to an ORION model 611 pH/millivoltmeter. According to the experimental setup, the following cell is established:



Therefore,

$$E_{\text{measured}} = E_{\text{solution/Pt}} + E_{\text{Ag/AgCl, KCl}_{\text{sat}}} \quad (2)$$

$$E_{\text{h}}(\text{Solution}) = E_{\text{measured}} - E_{\text{Ag/AgCl, KCl}_{\text{sat}}} \quad (3)$$

The liquid junction potential effects were avoided by keeping a proper flow of the concentrated filling electrolyte into the sample. This is assured with an open electrolyte filling hole and a constant height of the filling electrolyte above the level of the solution in which the electrode is immersed during calibration and/or measurements.

The electrode combination was checked by measuring the potential of Zobell's solution (solution consisting of $3.33 \times 10^{-3}\text{M K}_4\text{Fe}(\text{CN})_6$, $3.33 \times 10^{-3}\text{M K}_3\text{Fe}(\text{CN})_6$ and 0.10M KCl) (6) then used to measure the Eh values of different solutions. All measurements were made at 25°C , and all the potential values are based on the standard hydrogen scale at 25°C and one atmosphere. In addition, the pH values were measured at 25°C using a glass electrode.

b) Dimensional Changes: The dimensional changes of the hydrating cement based waste forms were monitored by measuring the expansive stresses imposed on a surrounding confinement as well as the length change. The expansive stresses were determined using a special device, designed in this laboratory for such purpose (7). It consists of a strain gage instrumented steel cylinder and its associated signal condition/amplifier (Fig. 2). A thermocouple is attached to the outer surface of the cylinder, in close proximity to the strain gage, to record temperature variation and supply the necessary corrective factors for the temperature-induced strains. Details of the system specification, calibration and operation are described elsewhere (7). After loading the cylinder with the fresh test mixture, the entire system is placed in a chamber programmed to the desired heat cycle.

The equipment used for length-change determination is illustrated in Fig. 3. It consists of a 1-inch square x 7.25-inch sample cell which offers restraint in the radial direction. The cell assemblage is maintained within a vessel adjusted to the desired curing conditions (humidity, temperature, and if desired, pressure). An outer furnace assembly permits controlled temperatures from ambient to 100°C . Length-change is determined by use of a linear variable-displacement transducer (LVDT) and its accessory signal conditioner/amplifier. This LVDT has an accuracy of ± 0.002 inches.

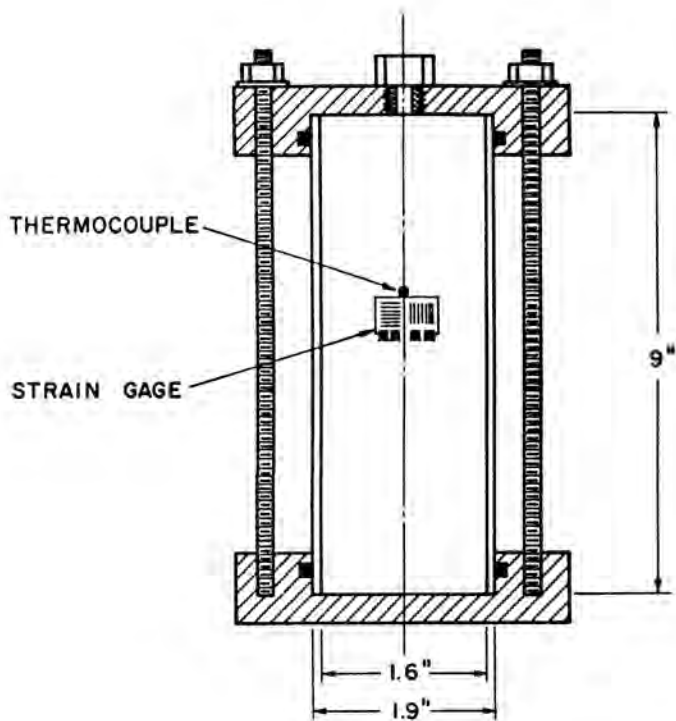


Fig. 2. Test Cell for Determination of Expansive Stress.

An initial cell constant was determined for the system to compensate for heat/dimensional changes of the mold and curing vessel. This was accomplished by using a 303 stainless steel bar of known thermal properties.

c) **Thermal Expansion:** That same equipment used for length-change determination was used to monitor the thermal expansion by measuring the length change of the specimen (removed from its cell) using a programmed temperature cycle applied to the vessel.

DISCUSSION OF RESULTS

Chemical Stability

The chemical stability of cement-based waste forms is multifold; the most important is the chemical fixation of the immobilized waste (transformation of waste elements into chemically stable insoluble species). In addition, the compliance with Federal, State and other pertinent regulatory requirements for the amounts of nitrate, nitrites and sulfate released through leaching is of major concern. The chemical environment created in the cementitious material-waste blends will determine the chemical stability of the waste species.

The Eh-values were found to range between +156 in cement + fly ash system to +8 in cement + fly ash + slag systems, with pH values of about 12 in both cases. These values reflect some important points:

a) Of significance is the drop in the pH values from 14 for the original waste solution to 12 in the pore fluids of the waste form reflecting the consumption in OH^- ions in reacting with glassy components, and formation of a silicate binder.

b) The positive Eh indicates an oxidizing environment. Ordinary Portland cement and slag cements (50% slag) as well as cement/fly ash blends (30% fly ash) gave an Eh value in the range +30 mv to +85 mv under

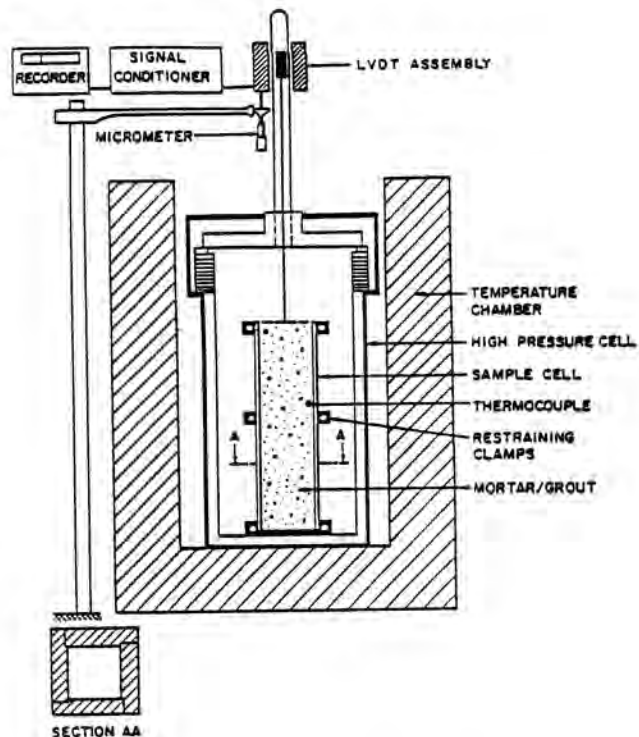


Fig. 3. Apparatus for Length Change Determination.

similar circumstances. Some investigators (8) found that in slag-cement-water systems and up to 75% slag content the Eh remains comparatively high (oxidizing), and the S^{2-} rises. The authors did not offer any explanation for the sharp break in Eh but it seems related to the $\text{SO}_4^{4-} \rightleftharpoons \text{S}^{2-}$ transformation. In highly alkaline solutions, however, S^{2-} tends to react giving rise to higher Eh values (i.e., less reducing). The existence of a high NO_3^- concentration will help maintain high (more oxidizing) Eh values.

c) The stability-instability regions of several important radioactive species are shown in Fig. 4 (adapted from ref. 9). The diagrams indicate that these species are less soluble, or insoluble, in a reducing environment. This signifies the role of slag addition to the stability of the radioactive species in the cement-based waste form as shown in Fig. 4. Moderate reducing conditions also favor preservation of U ions, in the insoluble UO_2 form.

d) When Class C fly ash was replaced by Class F fly ash the Eh values showed considerable increase. This result indicates clearly that the Eh value of pore fluids is controlled by nitrate concentrate. The availability of calcium ions (to precipitate a complex calcium aluminate nitrate) will cause removal of nitrate ions from pore fluids giving rise to a less oxidizing (lower Eh) environment in systems with high calcium fly ash compared to those with low calcium fly ash. The deliberate addition of Ca^{++} might be beneficial to the stability of the latter case.

Dimensional Stability

Hydration reactions of cementitious materials are exothermic. The heat generation has significant effects on both the integrity of the waste form as well as the design of the disposal system. Class F fly ash and slag addition were found to reduce the total heat evolution

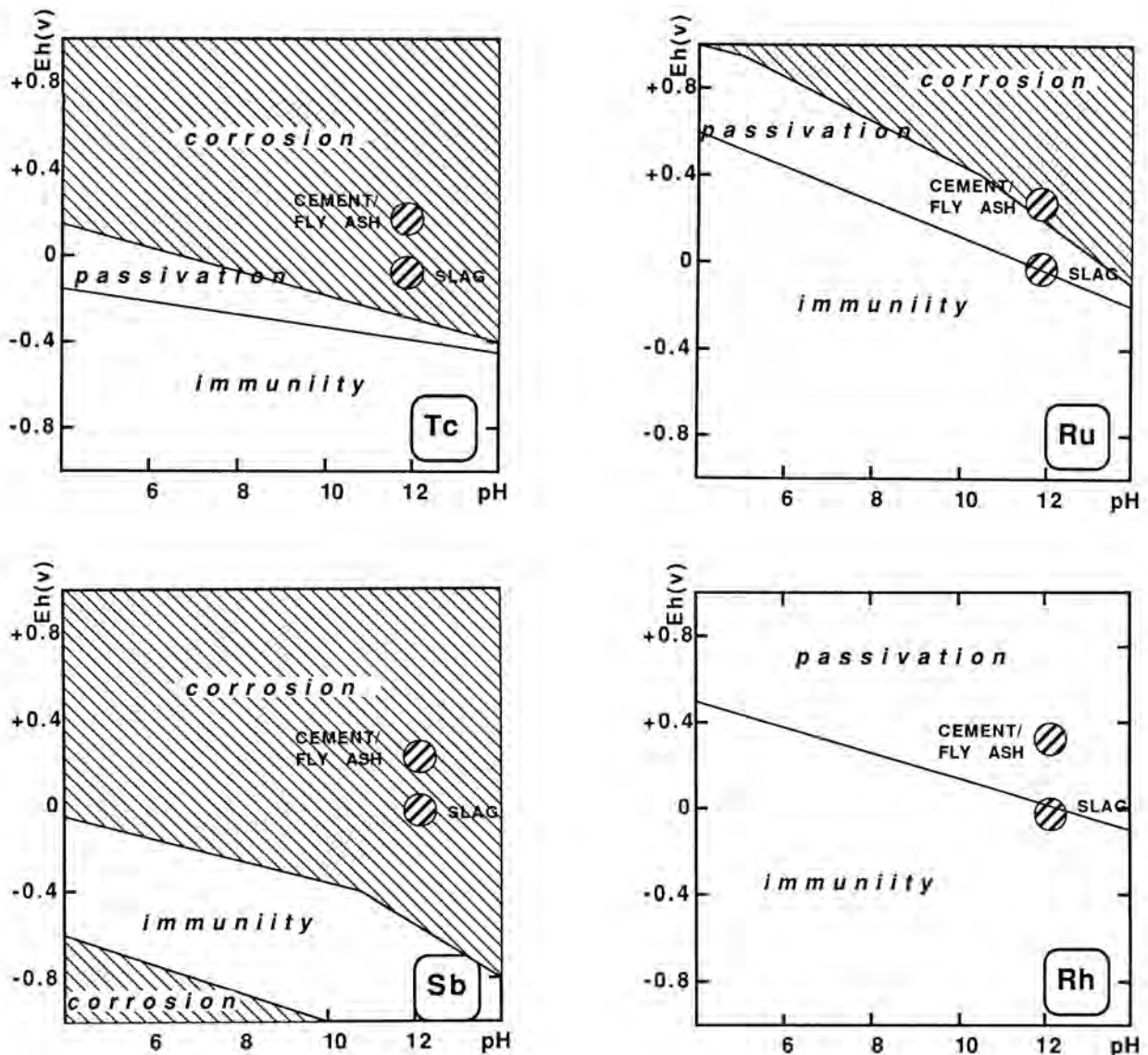


Fig. 4. Stability-Instability Regions of the Potential Radioactive Elements in the Waste Forms. Corrosion=dissolution; passivation = formation of insoluble oxide or hydroxide; immunity = precipitation of the metallic element.

and decrease the rate of temperature rise, which reduce the risk of cracking and thereby loss of matrix integrity. Both thermal and dimensional changes need to be monitored to establish suitable guidelines for practice.

The adiabatic temperature rise as a function of time is shown in Fig. 5. The thermally controlled chambers for both expansive stresses and length change devices were programmed to approximate adiabatic curing conditions shown in Fig. 5. The radial expansive stress is given in Fig. 6. After making corrections for the temperature induced stresses of both the strain gage and cell, the waste form shows no expansive stress, as indicated by the black squares. The length change of the adiabatically cured sample is given in Fig. 7 which indicates neither expansion nor contraction in the testing period. This is typical for a good performance of a waste form.

In spite of the good performance in the early ages of hydration, some risk may still exist at longer times. This arises from the high osmotic pressure arising from

the concentrated pore fluid (saturated with salts) which may imbibe water (liquid or vapor) into the waste form causing internal pressure. This could be minimized by controlling/reducing the humidity of the surrounding atmosphere by placing a clay cap over the waste form that is capable of deflecting rainfall and reducing the humidity.

Thermal Stability

Depending on the design of the disposal site, and of the solidified waste form, the exposure to heat is likely to occur and then the thermal stability of the solidified waste form should be known. Increase in temperature from the maximum adiabatic temperature, 85°C, to 115°C, could result from the reaction of the concentrated, highly alkaline waste solution with pore water. Alternately the heating/cooling cycles with ambient heating could occur, following cooling from the maximum temperature.

To predict such effects, samples that were tested for longitudinal dimensional change during the adiabatic

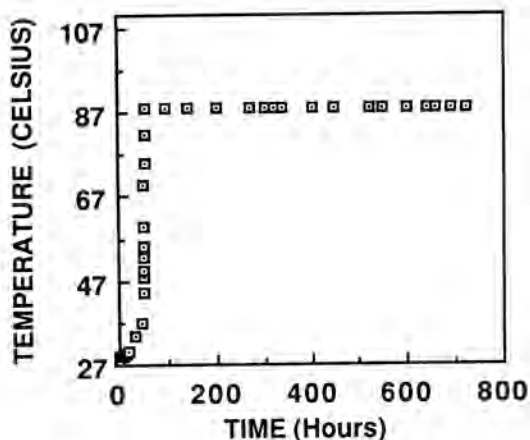


Fig. 5. Adiabatic Temperature Rise in the Sample Tested.

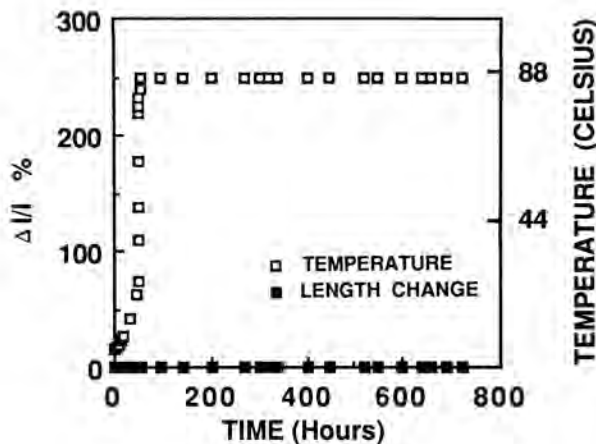


Fig. 7. Length Change During Adiabatic Curing.

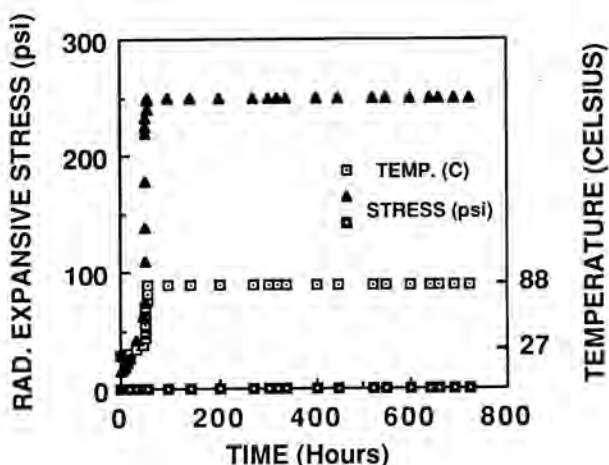


Fig. 6. Radial Expansive Stress During an Adiabatic Curing Condition. Filled squares represent stresses after correcting for temperature-induced stresses in both the cell and strain gage.

heat cycle were cooled to room temperature (27°C), demolded and placed in the apparatus shown in Fig. 3 in an unrestrained mode, i.e., restraining sides of the sample cell were removed. The test samples were then placed in a saturated water vapor environment at atmospheric pressure. The temperature was programmed from room temperature (27°C) to 98°C at a rate of 2.5°C per hour. Change in length was determined by the LVDT assembly and recorded. $\Delta L/L$ was determined and the resulting best fit line (correlation coefficient = 0.99) was plotted in Fig. 8. A temperature coefficient of expansion was found to be $4.6 \times 10^{-6}/^\circ\text{C}$ for the waste form tested. This is lower than the coefficient of thermal expansion of normal cement paste under similar test conditions ($\sim 10 \times 10^{-6}/^\circ\text{C}$) (10-12).

Figure 8 shows also the length change resulting from cooling the sample at a rate of 1.5°C/hour. Hysteresis was observed, and the sample did not return to its original length. However, the low coefficient of thermal expansion indicates a matrix of good integrity and overall performance.

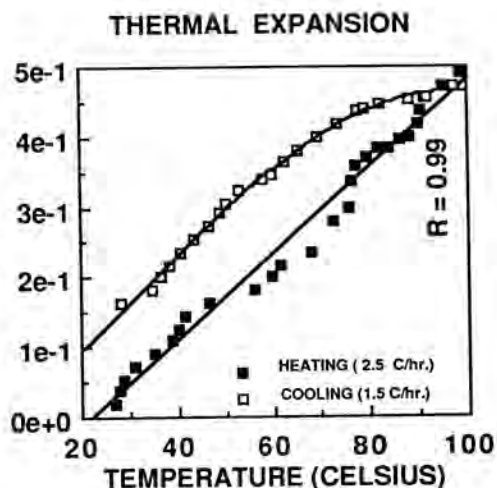


Fig. 8. Thermal Expansion of the Test Sample.

CONCLUSIONS

Stability of the cement-based waste systems is based on many factors. It starts by careful selection of cementitious material that have been proven to give sufficiently stable products. The compatibility and specific reactivity towards the waste solution is an important factor. Several forms of stability (chemical, dimensional and thermal) have been studied on selected waste forms, and the results obtained led to the following conclusions:

a) A reducing or low oxidizing environment may be produced in the pore fluids which will help stabilize certain radioactive waste species, markedly decreasing their solubilities. Diminishment of NO_3^- concentration and addition of slag are significant in this respect.

b) Depending on the design of the disposal system (disposal site and waste form) the dimensional stability is of high importance to the long term integrity of the form. This is more significant for large dimensional waste forms. The example of waste form studied in a specially designed measuring system showed good performance up to a month of age. Long term expansion should

also be avoided by controlling the composition of the material and/or the external humidity.

c) Depending also on the design of a disposal site and waste form, thermal stability of the form is important. The length change of a test waste form was monitored during a heating-cooling cycle and the coefficient of thermal expansion was found to be lower than that of normal cement paste; a smaller redissual increase in length was observed on cooling.

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REFERENCES

1. H.O. Weeren, E.W. McDaniel, and L.C. Lasher, Proceedings of the Symposium on Waste Management in Tucson, AZ, R.G. Post (Ed.), Vol. II, pp. 465-471 (1985).
2. R.L. Treat, R.O. Lokken, S.L. Stein, and C.A. Geffen, *ibid.*, Vol. II, pp. 497-501 (1985).
3. C.A. Langton and M.B. Dukes, *ibid.*, Vol. I, pp. 297-301 (1984).
4. R.I.A. Malek, D.M. Roy, P.H. Licastro, and C.A. Langton, 'Slag Cement Low-Level Radioactive Waste Forms at Savannah River Plant,' *Cer. Bull.*, Vol. 65, No. 12, pp. 1578-1583 (1986).
5. S. Hoyle, M.S. Thesis, The Pennsylvania State University (1986).
6. D.K. Norstrom, 'Thermodynamical Redox Equilibria of Zobel's Solution,' *Geochim. Cosmochim. Acta.* 41, 1835-1841 (1977).
7. a. R.I.A. Malek, P.H. Licastro, and D.M. Roy, 'The Compatibility Between an Expansive Grout and its Restraining Environment,' *Intl. Congress on Chem. Cement*, Vol. V, pp. 263-267, Brazil (1986).
b. P.H. Licastro, R.I.A. Malek, and D.M. Roy, 'Expansive Stresses of a Grout Plug on the Walls of a Borehole,' *Proceedings of the Symposium on Waste Management in Tucson, AZ*, R.G. Post (Ed.), Vol. III, pp. 475-478 (1985).
8. M.G. Angus and F.P. Glasser, 'The Chemical Environment in Cement Matrices,' *Proceedings of the Symposium on Waste Management*, MRS Proceedings Volume 50, L.O. Werme (Ed.), pp. 547-556, Materials Research Society, Pittsburgh, PA (1985).
9. M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford (1966).
10. S.L. Meyers, 'Thermal Expansion Characteristics of Hardened Cement Paste and of Concrete,' *Proc. Highw. Res. Bd.*, 30, pp. 193-203 (1950).
11. A. Helmuth, 'Dimensional Changes of Hardened Cement Pastes Caused by Temperature Changes,' *ibid.* 40, pp. 963-977 (1961).
12. F.H. Wittmann and J. Lukas, 'Experimental Study of Thermal Expansion of Hardened Cement Paste,' *Mater. Struct.*, 7, No. 4, pp. 247-252 (1974).