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**Characterization Of The Physical
Parameters And Sampling
Procedure Of A Modified Rocking
Autoclave Apparatus**

Barry E. Scheetz

Prepared for the United States
Department of Energy
Under Contract DE-AC06-77RL01030

Rockwell International

Rockwell Hanford Operations
Energy Systems Group
Richland, WA 99352

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RHO-BWI-C-65

**CHARACTERIZATION OF THE PHYSICAL PARAMETERS
AND SAMPLING PROCEDURE OF A MODIFIED ROCKING AUTOCLAVE APPARATUS**

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April 1980

Prepared for Rockwell Hanford Operations
A Prime Contractor to the U.S. Department of Energy
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CHARACTERIZATION OF THE PHYSICAL PARAMETERS AND SAMPLING
PROCEDURE OF A MODIFIED ROCKING AUTOCLAVE APPARATUS

INTRODUCTION

Contract research programs (fiscal years 1978 and 1979) designated to investigate the stability of several candidate nuclear waste forms under thermal and pressure regimes relevant to deep geological disposal have established that significant partitioning of cations between new solid phases and the liquid phase in contact with the simulated waste does occur. These experimental studies have in the past relied upon hydrothermal experimentation to achieve the relevant temperature and pressure conditions. The experimental design involved static, closed system experiments from which the liquids were sampled after a thermal and pressure quench. The initial experiments were designed to provide data relevant to the formation of new solid phases and the compositions of the liquids in contact with these assemblages. It was appreciated⁽¹⁾ that a limitation of the experimental design employed in these studies involved the precipitation of phases (with subsequent solution concentration changes) during the thermal cooling period. The solution data⁽²⁾ thus obtained therefore represented, under the best circumstances, minimal values for endothermic heat of solution reactions and maximal values for exothermic heat of solution reactions. These experiments were not designed for use with theoretical models.

To obtain solution concentration data that are applicable to transport modeling, the solutions need to be sampled at temperature and pressure for complete elemental analysis of both the liquid and of solids that may form. This total elemental analysis thus should represent the solution composition that was present at temperature. This approach does not, however, include gaseous phases.

EXPERIMENTAL PROCEDURES

HARDWARE

The rocking autoclave (Figure 1) that was modified for these new experiments was an American Instrument Company^A (AMICO) Microreactor Series apparatus. This consisted of a 300 ml vessel of unknown composition that was heated with a conventional resistance heating element. During operations the furnace and vessel are continually pivoted normal to a point midway along the cylindrical axis of the furnace at a rate of 36 cycles per minute and through an angle of plus and minus 15°.

FIGURE 1. The Rocking Autoclave Apparatus.

The vessel was plated to provide an inert inner surface. The plating was accomplished by a speciality company by honing the interior of the vessel followed by sand blasting in preparation for the electrolytic deposition of a chromium metal layer 2 mils (5 μ m) thick. The plating company (Jersey Chrome Plating Company)^B experienced difficulty in achieving an acceptable coating because of the unknown nature of the alloy. To achieve an acceptable coating required some experimentation on their part and this experimentation has not been completely documented.

The sampling system of the AMICO apparatus was abandoned and replaced with a SNO-TRIK air-operated, normally closed valve equipped with high temperature packings. In series with the pneumatically operated valve are a Teflon-coated block valve, an inline NUPRO^C (2 μ m) stainless steel filter, and a SWAGELOK^C full-flow female quick-connect. The sample container consists of a HIGH PRESSURE EQUIPMENT COMPANY^D 6 cc micro series reactor that was lined with a Teflon sleeve. The sampling container is equipped with Teflon-lined block valves at either end and at the male quick-connect.

Through the access connector in the bottom of the vessel, a Pneu-Hydro^E resetting, backpressure-regulator valve that is adjustable and a rupture disc were added for overpressure safety. The backpressure regulator was adjusted to 30 MPa by comparison against a dead-weight testing apparatus. This feature allows for the vessel to self-pressurize as the temperature of the vessel is raised. For added protection a rupture disc designed to fail at 56.7 MPa was connected in parallel.

Additionally through this access connection, an interior thermocouple and/or a solution replenishment system can be added.

EVALUATION PROCEDURES

THERMAL

The initial design modifications of this apparatus did not accommodate an internal thermocouple for use during the experiment. This feature required that carefully determined temperature measurements between the interior and exterior of the vessel be made. Figure 2 contains partial data for four experimental determinations of internal vs. external temperature. Through the temperature interval from about 150° to 300°C a rigorous straight line can be fitted to the data; however,

FIGURE 2. A Typical Data Set Obtained from the Comparison Between an Internally and Externally Placed Thermocouple on the Rocking Autoclave Apparatus.

at 300°C a break in slope occurs with subsequent deviation from the former straight line curve fit. These data were fitted to a power curve of the form:

$$T_{\text{INT}} = 0.35T_{\text{EXT}}^{1.16}$$

$$R^2 = 0.992.$$

In the intermediate temperature range (up to 300°C) the error in the measurements is estimated to be $\pm 3^\circ\text{C}$ and in the range from 300° to 400°C is estimated to be $\pm 5^\circ\text{C}$.

During subsequent pressure testing at temperature, this type K thermocouple failed and was replaced. It was observed that the replacement type K thermocouple possessed an entirely different set of thermal characteristics than were previously measured. For this reason, and to maintain consistency, it was deemed necessary to maintain an internal thermocouple through all experimental runs.

PRESSURIZED SAMPLING

The goal of the pressurized testing of the modified apparatus was to evaluate the effectiveness of the sampling method. The operation of the newly designed and constructed sampling system was tested by charging the autoclave with deionized water and pressurizing it at room temperature. It performed according to expectations. The second step in the procedure was to raise the temperature to the operating range and repeat the sampling. This too was accomplished according to expectations. The volume of the liquid sampled amounted to 3.3 ± 0.06 ml for six samples.

The final step in the procedure was to conduct an experiment with an aqueous sample for chemical analysis. The liquid chosen for this experiment was a 15 $\mu\text{g/ml}$ solution of $\text{Sr}(\text{NO}_3)_2$ adjusted from pH 1 to an unbuffered pH of 4.0 with 1 molar NH_3 . $\text{Sr}(\text{NO}_3)_2$ was used as an internal monitor of the solution. It was also chosen because of the ease and precision of detection with atomic emission spectroscopic techniques.

The autoclave was rocked for 145 hours at 350°C and sampled. The solution data presented in Table 1 are somewhat surprising. The top line data represent the solution analysis for the sampled fluid while the bottom line represents the chemical analysis for the cumulative amount of solution expelled from the vessel as it pressurized.

The chemical analysis of the sampled solution indicates appreciable amounts of the constituents of the exposed stainless steel, a significant reduction in the concentration of the spiked Sr, and an unusually high concentration of Si. The loss of Sr in the sample compared with the initial solution can be accounted for by sorption onto the interior surface of the vessel, an unexpected result or by subsequent precipitation of Sr phase. The varying amounts of the components of stainless steel (including Cr) are accountable from the approximate 10% of exposed stainless steel pressure tubing (the tubing bore was not plated). The high concentration of silica, however, is quite unexpected. At this point, the only possible explanation for the presence of Si is the possibility that residual sand grains from the sand-blasting step remained inbedded in the steel vessel and were leached by the hydrothermal fluids which penetrated a porous Cr plating. If a grain of sand used in the sand blasting procedure was assumed to have a mass of 5 mg, then this observed concentration of Si could be accounted for by less than 7 such grains. It is remarkable that this much Si was still detectable even after the initial pressurized sampling tests with deionized water.

Continued efforts will be directed to identifying the source of the Si detected in solution and toward the identification of the sorptive capability of the vessel toward Sr.

TABLE 1. Solution Analysis ($\mu\text{g/ml}$).

	Fe	Cr	Ni	Si	Sr	pH
Sample	7.42 $\pm$ 0.05	2.33 $\pm$ 0.02	0.15 $\pm$ 0.02	125 $\pm$ 5	1.88 $\pm$ 0.01	7
Overflow	0.03 $\pm$ 0.01	0.41 $\pm$ 0.02	0.24 $\pm$ 0.02	10.3 $\pm$ 0.1	0.44 $\pm$ 0.01	4.5

- A. American Instrument Company
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- B. Jersey Chrome Plating Company
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- C. Distributed by
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- D. High Pressure Equipment Company, Inc.
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- E. Pneu-Hydro Products
Hibernia Ave.
Rockaway, New Jersey 07866

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