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Adiabatic Heat of Hydration Calorimetric Measurements for Reference Saltstone Waste

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INTRODUCTION

The production of nuclear materials for weapons, medical, and space applications from the mid-1950's through the late-1980's at the Savannah River Site (SRS) generated approximately 35 million gallons of liquid high-level radioactive waste, which is currently being processed into vitrified glass for long-term storage. Upstream of the vitrification process, the waste is separated into three components: high activity insoluble sludge, high activity insoluble salt, and very low activity soluble salts. The soluble salt represents 90% of the 35 million gallons of overall waste and is processed at the SRS Saltstone Facility, where it mixed with cement, blast furnace slag, and flyash, creating a grout-like mixture.

The resulting grout is pumped into aboveground storage vaults, where it hydrates into concrete monoliths, called saltstone, thus immobilizing the low-level radioactive salt waste. As the saltstone hydrates, it generates heat that slowly diffuses out of the poured material. To ensure acceptable grout properties for disposal and immobilization of the salt waste, the grout temperature must not exceed 95°C during hydration. Adiabatic calorimetric measurements of the heat generated for a representative sample of saltstone were made to determine the time-dependent heat source term. These measurements subsequently were utilized as input to a numerical conjugate heat transfer model to determine the expected peak temperatures for the saltstone vaults.

DESCRIPTION

An adiabatic "bath" calorimeter was designed for measuring the reference saltstone hydration temperature rise and heat of hydration (see Figure 1). The calorimeter is contained in a large cylindrical Dewar filled with ethylene glycol for operation beyond the boiling point of water. The saltstone sample was contained in a smaller test vessel Dewar and sealed with a machined rubber stopper. A slightly larger Dewar was placed over the test vessel to minimize heat transfer. Steel flanges were placed on top of the two Dewars to keep the assembly from floating in the bath. A mechanical stirrer was placed in the ethylene glycol to reduce temperature gradients in the bath and was adjusted during shakedown testing to minimize bath temperature gradients while not generating more that about 15 Watts of dissipated heat in the liquid.

Two type-T thermocouples were placed inside the test vessel Dewar and embedded in the saltstone sample to measure the saltstone temperature and to provide control for the bath temperature to maintain adiabatic conditions. Additional T-type thermocouples were used to measure the bath temperature and ambient air temperature adjacent to the overall experimental setup. The thermocouples from the bath and saltstone were configured to measure the differential temperature between the bath and saltstone and were used as input to a data acquisition system (DAS) to provide a control signal to a 1 kW immersion heater to maintain the bath and saltstone at the same temperature throughout the test to assure adiabatic conditions. The differential thermocouple arrangement was utilized to significantly reduce the overall error to the DAS controller. Two-point thermocouple calibrations consisting of saturated steam and ice-points were conducted to further minimize error and resulted in an uncertainty in measuring temperature of ±0.3°C.

Shakedown tests were conducted to adjust the deadband and proportional control constants on the immersion heater control system. These tests involved placing 450 ml of ethylene glycol at an initial temperature of 90°C in the test vessel Dewar and monitoring the temperature of the ethylene glycol over several days. 90°C was selected as the initial temperature since this was estimated to be the temperature at which the most critical saltstone adiabatic heat generation

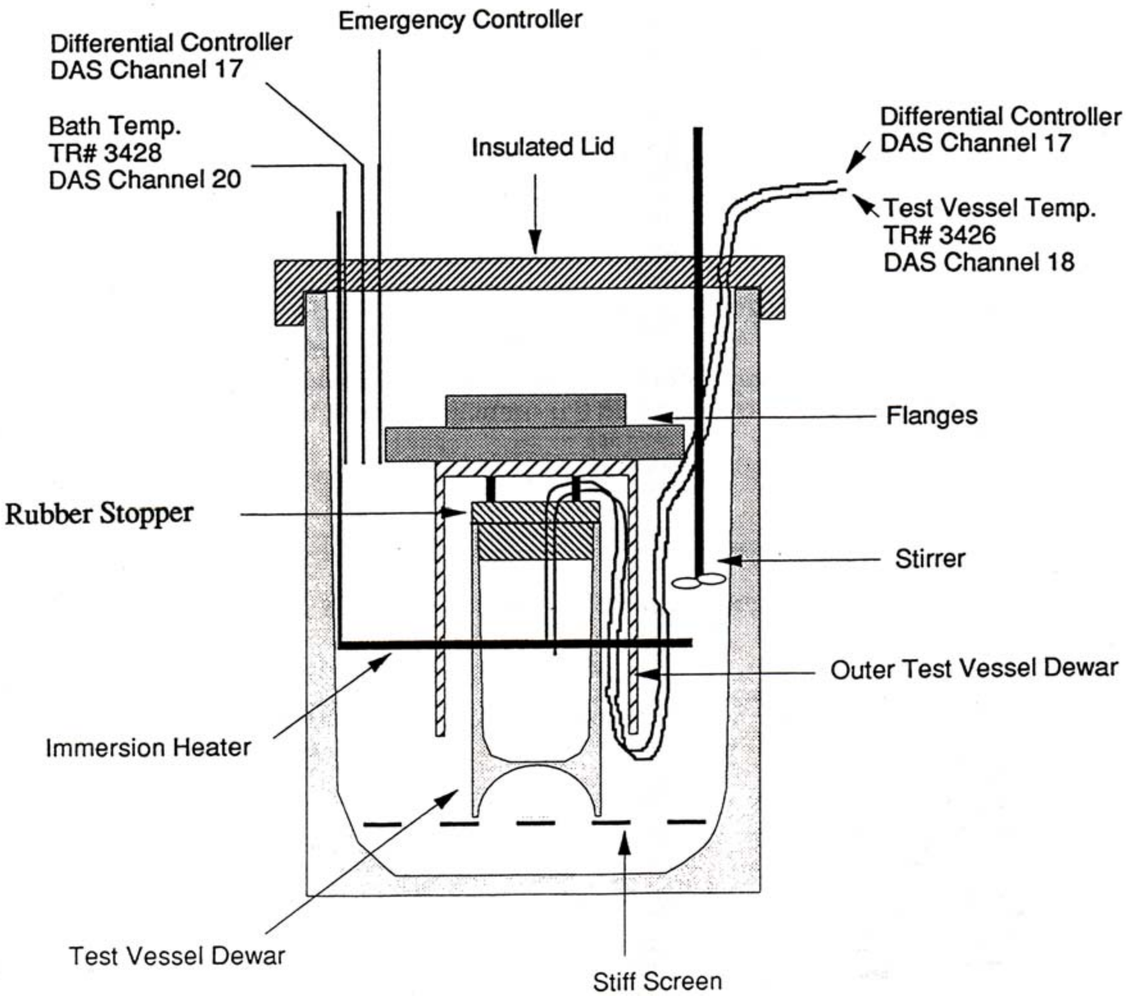

Figure 1. Adiabatic calorimeter setup.

measurements were required. Drift in the initial ethylene glycol temperature was compensated for by adjusting the control parameters mentioned above so that the final drift was reduced to less than 0.3°C per day.

RESULTS

Testing with reference saltstone was conducted with the saltstone reactants at 40°C as this is approximately the operational temperature of the saltstone mixture to be placed in the long-term storage vaults. After carefully weighing and mixing the saltstone reactants, the resulting mixture was placed in the test vessel Dewar and the calorimeter was assembled as illustrated in Figure 1. Testing was conducted for approximately 260 hours and the resulting saltstone temperature and heat generation results are provided in Figures 2 and 3. The heat generation rate per unit mass illustrated on Figure 3 was determined from the following relationship for an adiabatic process

$$Q = c_p \frac{dT}{dt}$$

where Q is the heat generation rate, c_p is the constant pressure specific heat capacity, and dT/dt is the time derivative of the saltstone temperature. An uncertainty analysis was conducted indicating that the overall uncertainty in measured heat generation rate to be approximately 30% primarily due to the 0.3°C per day temperature drift. The heat generation measurements provided in Figure 3 were used to numerically model the saltstone heat transfer to determine that the 95°C limit would not be exceeded during operation of the long-term storage vaults.

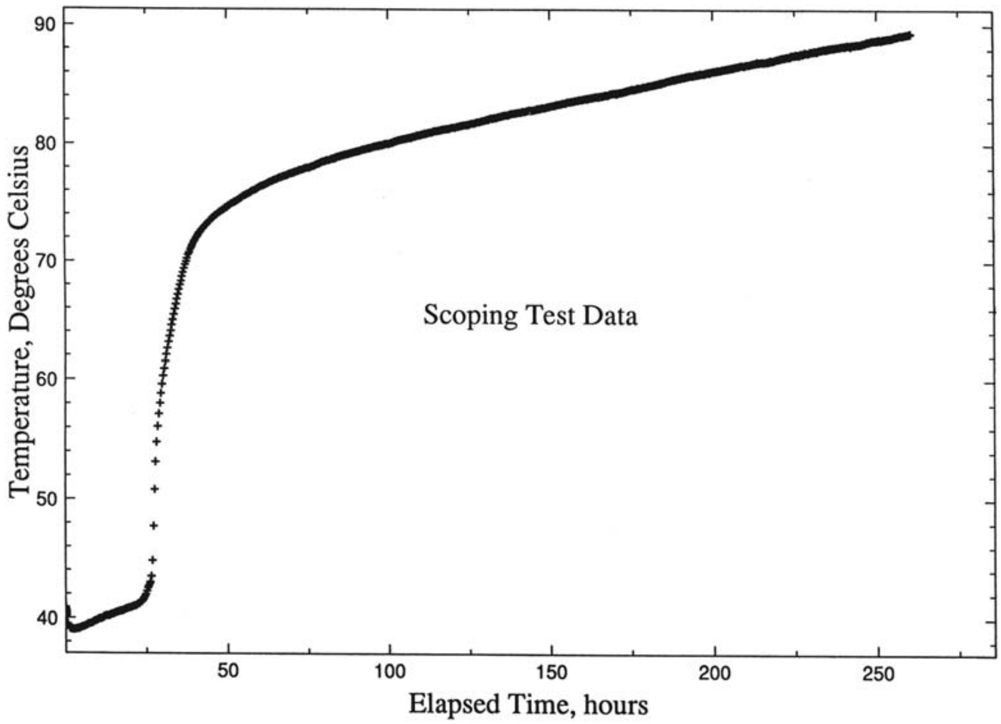

Figure 2. Reference saltstone temperature vs. time.

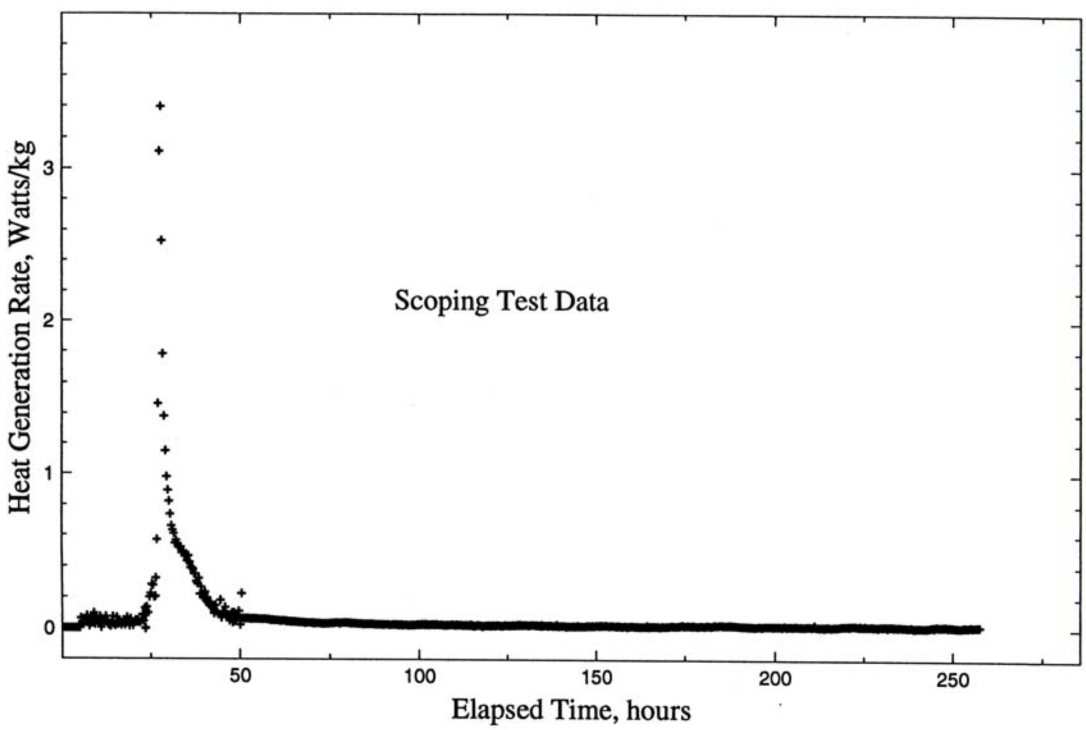

Figure 3. Reference saltstone heat generation rate versus time.