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DESIGN OF A VARIABLE-FLOW-RATE, SINGLE-PASS LEACHING SYSTEM

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MASTER

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FOREWORD

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DESIGN OF A VARIABLE-FLOW-RATE, SINGLE-PASS LEACHING SYSTEM

ABSTRACT

We have designed leaching systems for experiments on several kinds of solids, including glassy debris from underground nuclear explosions at Nevada Test Site (puddle glass), refractory compositions for retention of radioactive nuclear reactor waste, and spent reactor fuel. The system used on puddle glass has a continuously variable flow rate from 13 to 460 cm³/d, a temperature range from 25 to 75°C, operating capacity for up to 20 simultaneous experiments, and one-pass operation with continuous exposure of samples to fresh solution. Results obtained on puddle glass are in qualitative agreement with those on silicate glasses designed for isolation of nuclear reactor waste.

INTRODUCTION

Programs at Lawrence Livermore Laboratory often require experimental studies of the interactions of solid materials with groundwater. For example, the environmental program at the Nevada Test Site (NTS) is concerned with the leaching of glassy debris (puddle glass) from underground nuclear explosions. The Waste Isolation Safety Assessment Program of the National Waste Terminal Storage Program is also concerned with the durability of refractory compositions for the retention of radioactive nuclear wastes. This report will describe a "one-pass" leaching system, originally developed for the NTS program, which has been used to determine dissolution rates for puddle glass in water.

Many different systems have been used for leaching tests, as shown in the review by Mendel.¹ The systems can be either static or dynamic. For purposes of this discussion, static systems are those without mechanical agitation of the liquid. The simplest static system is a sealed vessel at room temperature with the sample immersed in stagnant liquid.^{2,3,4} If the vessel is heated, the system becomes quasi-static because of convective mixing.^{5,6} Dynamic systems are those designed to move the liquid relative to the solid sample, either by mechanical agitation of a fixed volume of

liquid around it, or by flowing liquid past it in a sample chamber. Dynamic systems can be further classified as intermittent^{6,7} vs continuous,^{5,8,9} or single-pass^{5,7,9-12} vs multiple-pass.^{8,13} Multiple-pass systems are probably used more than single-pass systems in measuring low-leach rates. This is done principally to reduce the amount of water, which simplifies the experimental system. Multiple-pass systems such as Soxhlet extractors,⁷ reflux extractors,⁵ or recirculating ion-exchange columns⁸ expose the solid samples to distilled or deionized water; therefore, they are not used to investigate the effects of ionic solutions. Single-pass flow systems are less common than multiple-pass systems, but have the potential advantage of more closely simulating the leaching action of natural waters.

Static systems and some of the multiple-pass dynamic systems operate with constant volumes of liquid, which are completely changed at predetermined intervals. In such systems, leaching may be retarded by the increasing concentration of leached ions in solution. Dynamic systems in which the sample is always exposed to fresh leach solution control the concentration increase; some kinetic effects can be studied in them by adjusting the flow rate and hence the extent of resorption and other back reactions.

The single-pass system to be described was originally designed to simulate reported flow rates for NTS¹⁴ and to have the following desirable characteristics:

- maximum retention of solid particles,
- minimum sorption of activity by the filter or sample holder,
- low cost and ready availability of the filter,
- low resistance to solution flow,
- compact size of the activity-containing part of the assembly.

The present design allows the following experimental parameters to be explored:

- composition and particle size of the solid,
- aspect ratio of the sample assembly and sample,
- solution composition, such as distilled water, appropriate groundwater, or synthetic electrolyte,
- temperature,
- flow rate,
- frequency of sampling.

DESIGN DETAILS

OVERALL SYSTEM

A functional diagram is shown in Fig. 1, and the assembled 20-channel system in Figs. 2 and 3. The main supply tank, constant-level tank, supply manifold, and final filters constitute a gravity-fed supply system for the peristaltic-type metering pumps. The final filters have a pore size equal to that of the filters in the sample holders in order to prevent clogging of the sample holders by organic or inorganic particulates in the leaching solution. Valves are included between supply manifold and final filters to allow them to be replaced if necessary. The effluent from the sample holders flows through 0.69 mm (0.027 in.) I.D. tubing into plastic bottles through small holes in the lids.

Since it was anticipated that the experiments might last as long as 30 months, the leach solution stored in the supply tanks is protected from evaporation by air inlets. These are small containers (A and B) of leach solution, as shown in Fig. 4. Containers A and B are connected near the bottom so that as air flows in either direction, it bubbles through the solution in the tube. This saturates the air with respect to the water in the solution. Assuming that $P_1 < P_2 \leq P_3$ because Raoult's Law holds to a better and better approximation for the water in the vapor phase in containers A and B, P_3 (the resulting partial pressure of water in container B) is approximately the same as in the supply tank, so that water does not evaporate from the supply tank. Thus, only air is transported between the tank and laboratory atmosphere with changes in barometric pressure or water level in the tank.

METERING PUMPS

Each pump assembly consists of a chassis and from 1 to 10 cassettes. The chassis contains the electric motor with a continuously variable speed control, and the drive train, which terminates in two cassette gears. The low-speed gear drives the cassettes when they are clamped in the chassis in

FIG. 1. One-pass continuous leaching system--functional diagram.

FIG. 2. One-pass teaching system—general view.

FIG. 3. One-pass leaching system--details of pumps, sample holders, and receivers.

FIG. 4. Air inlet to reservoir.

one orientation, and the high-speed gear drives them when they are in the other orientation. Each cassette controls a single channel; the peristaltic action of the cassette is produced by rollers squeezing a silicone polymer tube against a curved backing plate. Pumping rate is determined by the cassette orientation in the chassis, the continuously variable speed setting for the electric motor, and the inside diameter of the tube. Flow rates vary from 13 to 460 cm^3/d as shown in Table 1. The corresponding linear flow speeds are 9 to 331 m/yr for a 25-mm diameter sample cell. These rates were chosen early in the design of the system to correspond as nearly as possible to groundwater flow rates for the Nevada Test Site of 1.8 to 180 m/yr at Yucca Flat and 2 to 76 m/yr at Pahute Mesa.¹⁴

TABLE 1. Characteristics of the one-pass leaching system for the radionuclide migration program at LLL.

Flow rates:		High range	Low range
	Volume, cm ³ /d	26-460	13-158
	Linear, m/yr	18-331	9-114
Sample holder filter:	Diameter:	25.4 mm	
	Pore size:	0.1 μ m	
Operating temperature:	25-75°C		
Volume of powder sample:	2.1 cm ³ maximum		
Number of types of solutions, for each pump:		up to 10	

SAMPLE HOLDER

A cross-sectional view of an assembled holder is shown in Fig. 5, and its components in Fig. 6. The sample-holder material is polymethyl methacrylate (PMMA). Other materials such as Teflon could be used, but PMMA has the advantage of transparency, so that one can observe the sample during experiments. The end plugs and associated grids and O-ring seals hold the filters in place at the ends of the sample chamber. The filters are 25-mm diameter Nuclepore polycarbonate membranes with pore size selected to be about 10% of the minimum sample-particle-diameter in order to ensure complete retention of the solid particles and to minimize clogging of the pores. The side opening is used to introduce powdered samples, or to remove air bubbles, which sometimes collect in the sample chamber during operation. The assembly is axially aligned by the sleeve and bolted together through the end plates. The sleeve has enough clearance at each end so that end load is supported by the end plugs and sample chamber. The load is adjusted by tightening the tension bolts to a torque reading of 0.64 N·m (5 in·lb). The length of the sample chamber can be increased up to about 1 m and is probably limited only by the length for which the axial-alignment sleeve can be made with sufficient accuracy. Luer fittings are used to connect the sample chamber to the

small-bore Teflon entry and exit tubes in order to simplify the design of the end plugs. Although the system is made of plastic, we do not anticipate any problem from radiation damage due to "hot" samples or effluent solutions.

SAMPLE COLLECTION AND PREPARATION FOR COUNTING

In order to sample the effluent, the appropriate collection bottle is removed and weighed, and the effluent is transferred to a plastic bag held in another bottle. The water is evaporated leaving the water-soluble residue in the bottom of the bag. The bag and residue are then folded up, inserted into a 31.75 mm (1.25 in.) die, and compacted into a right-circular cylinder by heating in a press to 100°C under a ram pressure of 30.3 MPa (4400 psi). The heating time required is 10 min. The resulting cylinder containing the leached activity is gamma-counted to determine the activity level.

FIG. 5. Sample-holder assembly, one-pass leaching system.

FIG. 6. Sample-holder assembly.

An alternative sampling procedure has been considered, in which the effluent from the sample containers is not weighed, but instead is passed through ion-exchange resin columns. These would then be eluted at suitable intervals, and the eluate counted. If ion-exchange columns were being used as collectors, the effluent from them would be low-conductivity water. The conductivity of the effluent could be monitored so that if break-through and consequent increase in conductivity occurred, the effluent in the waste receiver could be reprocessed.

COST

The current costs of the components of the system for the 20-channel installation shown in Figs. 1 to 5 are shown in Table 2. They do not include costs for the radiochemical enclosure or for fabrication and assembly of the system.

TABLE 2. Approximate equipment costs, one-pass leaching system for the radionuclide migration program at LLL.

2	Pump drive chassis @\$500	\$1,000
20	Pump cassettes @\$60	1,200
20	Sample holders @\$90	1,800
2	Reservoirs @\$40	80
1	Constant temperature water bath @\$720	720
1	Prefilter Unit @\$110	110
21	Plastic tubing assemblies @\$25	525
1	Manifold @\$100	100
1	Constant level assembly @\$120	120
TOTAL		\$5,655

OPERATION

START-UP

Before introduction of a sample, each sample holder is tested for leaks by pressurizing it with N_2 to 136 kPa (5 psig) and submerging it in a one-liter beaker of water. The sample holder is dried and a funnel is inserted in the filler entrance. Room air is drawn into the sample chamber through the funnel and out of it through one of the 0.1- μ m filters and the supporting end plug by connection to a vacuum line. Weighed amounts of sample are poured into the chamber through the funnel; the air current prevents dust from spreading on the outside of the assembly. The funnel is removed, the filler plug inserted, and the vacuum line then removed. Enough water to fill the sample chamber almost completely is introduced a drop at a time through the filler entrance using a blunt 22-gauge needle and 10-cc hypodermic syringe. The inlet end chamber is also filled with the syringe, and the inlet line from the metering pump is plugged into it. The filling time is noted. The effluent line is then connected to the sample holder and effluent receiver, and the sample assembly placed in the constant temperature bath. This starts the leaching experiment for the sample. In most of the sample chambers the flow direction is upward, but as partial check on the effect of flow direction, two sample chambers are installed with flow direction downward.

ROUTINE OPERATION

The main tasks during routine operation are collection, weighing, and evaporation of effluent samples. However, a considerable amount of maintenance is also necessary. This includes replacement of worn silicone pump tubing, replacement of final filters as they become clogged by particulates or bacterial growth, and removal of air from the sample chambers to keep the bubbles from blocking fluid flow through the chambers.

On each of the sampling days, a cumulative sample is taken, which includes all the effluent collected since the previous sample. Aliquots of the cumulative sample are then taken for analysis. For instance, cumulative samples on days 1, 2, 3, and 6 have intervals of 1, 1, 1, and 3 days, respectively. For this reason, the results are averages over the sampling intervals.

EXPERIMENTAL RESULTS

The experimental data consist of the initial sample weight, radionuclide-activity level, and surface area; and temperature readings, effluent weights, and radionuclide-activity levels as functions of time. Mean times, flow rates and leach rates are calculated from these data as follows:

$$t_{mi} = t_{i+1} - \Delta t_i / 2 \quad (1)$$

$$\Delta t_i = t_{i+1} - t_i \quad (2)$$

$$f_i = m_i / (\rho \cdot \Delta t_i) \quad (3)$$

$$R_i = A_i / (A_o \cdot S \cdot \Delta t_i) \quad (4)$$

where f_i is the flow rate in (cm^3/d) , m_i is the mass (g) of effluent collected in time Δt_i (d), ρ is the density of the effluent in (g/cm^3) , S is the surface area of the sample in m^2 , R_i is the leach rate in $(\text{g}/\text{m}^2 \cdot \text{d})$, A_o is the specific activity in the original sample (dpm/g), and A_i is the activity (dpm) leached during time Δt_i . An example of the experimental results is shown in Fig. 7 and Table 3, for a sample of silicate puddle glass from a nuclear event at the Nevada Test Site.¹⁵ Here, the leach rate R decreases with time in agreement with a relation discussed by Diebold¹⁶:

$$R = at^{-0.5} + b \quad (5)$$

where the first term corresponds to diffusion through surface film and the second term corresponds to dissolution of the silicate high-polymer network, as rate-determining steps. The nearly identical leach rates of the Co isotopes are in agreement with their production early in the course of the nuclear event, and highly similar chemical behavior during melting and solidification of the puddle glass. Leach rates increase with flow rates, but this is probably not significant except for the first two days. The flow rates are constant within $\pm 11\%$ for the high rate, and within $\pm 4\%$ for the low rate.

FIG. 7. Leach rate of Co isotopes vs time for glass no. 3.

TABLE 3. Leaching rates for Co isotopes in glass no. 3.

Day	Cassette position	f		tm mean time (days)	R × 10 ⁴ (g glass/(m ² .d))		
		Vol. Flow			⁵⁷ Co	⁵⁸ Co	⁶⁰ Co
		Rate	Δt (days)				
		ml/day					
Hi/Low	($\bar{x} \pm \sigma$)						
01	High	134 ± 3%	0.936	0.468	7.0 ± 2.0	5.0 ± 1.0	6.0 ± 1.0
02		193 ± 4	0.930	1.40	4.0 ± 0.2	3.6 ± 0.4	3.4 ± 0.2
03		191 ± 7	0.984	2.36	2.5 ± 0.1	2.2 ± 0.2	2.0 ± 0.1
06		194 ± 4	2.68	4.19	1.4 ± 0.1	1.2 ± 0.1	1.1 ± 0.1
11		197 ± 3	5.27	8.17	0.74 ± 0.09	0.6 ± 0.1	0.63 ± 0.06
32		189 ± 6	21.3	21.4	0.47 ± 0.01	0.40 ± 0.01	0.39 ± 0.02
38		217 ± 8	5.65	34.9	0.46 ± 0.07	0.44 ± 0.09	0.40 ± 0.07
70		190 ± 4	32.1	53.8	0.36 ± 0.06	0.34 ± 0.06	0.33 ± 0.05
120		163 ± 15	49.7	94.7	0.32 ± 0.11	0.24 ± 0.05	0.22 ± 0.05
230		161 ± 14	110.1	174.6	0.13 ± 0.03	0.12 ± 0.02	0.12 ± 0.03
420		161 ± 3	190.0	324.6	0.07 ± 0.02	-	0.07 ± 0.02
	Mean	186 ± 11%					
01	Low	32.1 ± 6%	0.938	0.419	1.5 ± 0.7	1.0 ± 0.4	1.4 ± 0.6
02		35.2 ± 3	0.930	1.30	1.2 ± 0.1	1.2 ± 0.2	1.0 ± 0.04
03		35.0 ± 4	0.984	2.26	1.2 ± 0.2	1.1 ± 0.3	1.1 ± 0.1
06		35.1 ± 4	2.68	4.09	1.0 ± 0.2	0.9 ± 0.2	0.8 ± 0.2
11		35.1 ± 4	5.27	8.07	0.5 ± 0.1	0.4 ± 0.1	0.4 ± 0.1
32		35.1 ± 5	21.3	21.3	0.28 ± 0.04	0.23 ± 0.04	0.22 ± 0.04
38		37.5 ± 5	5.65	34.8	0.24 ± 0.01	0.22 ± 0.03	0.19 ± 0.01
70		36.0 ± 5	32.1	53.7	0.19 ± 0.01	0.17 ± 0.01	0.16 ± 0.01
120		36.6 ± 6	49.7	94.6	0.17 ± 0.02	0.16 ± 0.02	0.14 ± 0.01
230		36.0 ± 6	110.1	174.5	0.11 ± 0.03	0.12 ± 0.02	0.095 ± 0.02
420		38.5 ± 14	190.0	324.5	0.05 ± 0.02	0.07 ± 0.04	0.04 ± 0.02
	Mean	35.7 ± 4%					

CONCLUSIONS

We have designed and operated a leaching system with the following features:

- continuously-variable flow rate, from 13 to 460 cm³/d,
- operating temperature from 25 to 75°C,
- performance of up to 20 simultaneous experiments,
- continuous exposure of samples to fresh solution,
- retention in the sample cell of particles down to 0.1 μm in diameter,
- collection and gamma-counting of transported radionuclides in a solid polyethylene cylinder.

Results obtained on silicate puddle glass from a nuclear event are in qualitative agreement with those on silicate glasses designed for isolation of nuclear reactor waste.

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