

Volatility and Extractability of Strontium-85, Cesium-134, Cobalt-57, and Uranium After Heating Hardened Portland Cement Paste

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Abstract

The objective of this preliminary investigation is to determine the effect of heating hardened Portland cement paste (the cementitious component of concrete) in aiding the removal of common radionuclide contaminants including ^{137}Cs , ^{90}Sr , ^{60}Co , and U. Direct volatilization of radionuclides during heating, as well as subsequent behaviors during extractions, were established over a range of temperatures up to the melting point of Portland cement paste. Techniques for spiking pulverized Portland cement paste with shorter-lived radioisotopes (^{134}Cs , ^{85}Sr , and ^{57}Co) and U were developed using gamma-ray spectroscopy to measure their activity nondestructively before and after heating. An extraction procedure (employing five sequential extractions each with water, followed by 0.1*N* CaCl_2 , followed by 0.2*N* HCl) for pulverized but fully-hydrated Portland cement paste was adapted to contrast behaviors after thermal treatments. Complete volatility of ^{134}Cs was observed at temperatures of 1200°C or greater. Thus, decontamination of ^{137}Cs from cement paste would be feasible by direct heating. However, no volatility of other radionuclides was observed and, thus, their potential for facilitated decontamination will likely depend on their extraction behavior following thermal perturbation.

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Both ^{134}Cs and ^{85}Sr were readily removed from cement paste during initial water-based extractions for final temperatures $<800^\circ\text{C}$. In contrast, both ^{57}Co and U exhibited negligible extractability into either water or 0.1 N CaCl_2 probably resulting from their precipitation as hydroxides in the highly alkaline Portland cement paste extracts where pHs were usually greater than 10. The release of both these radionuclides was delayed until sequential 0.2 N HCl extracts decreased the pH below 4. Significant patterns in the extraction behaviors of all radionuclides with temperature were observed in ranges where significant mineral alterations are known to occur.

Introduction

Contaminated concrete surfaces are a major impediment to the deactivation and decommissioning of DOE facilities because of the technical challenges for their decontamination. The total volume and surface area of concrete in DOE facilities is large and the technical needs for potential decontamination have been well defined (1). The total area of contaminated concrete within all DOE facilities is estimated at $7.9 \times 10^8 \text{ ft}^2$ or approximately 18,000 acres; this estimate has a high level of uncertainty because of the early stage of characterization at many DOE sites. Because most concrete surfaces become contaminated after full curing (i.e., after construction), the depth of contamination is usually found, but more often presumed, to be limited to a few centimeters depending on the duration of contact and amount of exposure to contaminating radionuclides. This limited depth of contaminant penetration into concrete is generally thought to result from diffusional transport into limited and discontinuous pore space with subsequent contaminant adsorption and precipitation within the concrete (2,3). However, because contaminant penetration into concrete is a diffusion controlled process, decontamination reactions suffer from similar restrictions at ambient temperatures because

potential leachants must both diffuse into and return from the same internal pore space of the concrete.

Dickerson et al. (1) summarized that the most frequently occurring radionuclide contaminants within the DOE complex were ^{137}Cs , ^{238}U (and its daughters), and ^{60}Co , followed closely by ^{90}Sr and tritium, which account for 30% of that total occurrence; 24% of the contaminants were listed as unknown indicative of a lack of characterization information.

Dickerson et al. (1) also provide an excellent review of decontamination technologies, both proven and potential, for application to such radioactive contamination. Almost all approaches to decontamination have focused on the physical removal of shallow contaminated material to a depth where only uncontaminated concrete would remain. A variety of technologies have been demonstrated to impart the required energy into concrete to attain the spallation, scabbling, or ablation of the concrete surfaces. These techniques include direct mechanical shock through the use of hammer-and-chisel, hydraulic shock, bombardment with shot, sand blasting, or carbon dioxide pellets, application of concrete dissolving or disintegrating chemicals, and thermal shock induced with high-temperature sources (flame or plasma arc torches), lasers, or microwaves. One technique (electrokinetics) attempted to remove contaminants without significant bulk concrete removal but had limited success with common radioactive contaminants (e.g., U, ^{90}Sr , and ^{60}Co) although ^{137}Cs was found to be readily removed (4). In addition to this electrokinetic technology demonstration, DOE has recently sponsored demonstrations of concrete decontamination using another electrokinetic technique (5), electro-hydraulic scabbling (6), laser-ablation (7), dry-ice pellet blasting (8), and microwave heating (9). These technologies all focus on physical removal of contaminated concrete layers. Waste volume reduction is addressed only in the sense of segregating scabbled contaminated material from uncontaminated

materials or by comparison with manual hammer-and-chisel methods and their associated secondary wastes.

Systematic thermal dehydration of Portland cement paste has been frequently studied to identify species and phases in the complex chemistry of cement paste curing and subsequent heating (10, 11); the various hydrated cement paste phases, including gypsum, lime, hydrated calcium silicates, and hydrated aluminates and ferrites, release their moisture at distinct and increasing temperatures with concomitant decreases in their adhesive and cohesive properties. Behavior of concrete physical properties, such as strength, has most often been studied from the concerns of the construction industry with fire-induced thermal stresses (12) and special needs during high-temperature applications such as nuclear reactor containment vessels (13, 14); these studies have focused on the significant decreases in strength and elasticity in thermally-stressed concrete with regard to load bearing capacities rather than changes in spalling or scabbling properties more germane to decontamination needs. Although the potential of thermal treatment to aid in the physical removal of layers on concrete is likely to prove beneficial, the behavior of radioactive contaminants, including ^{90}Sr , ^{60}Co , ^{137}Cs , and U, during and subsequent to the thermal treatment needs to be better defined and understood. Radionuclides like ^{137}Cs will likely volatilize significantly, if not completely, during thermal treatment resulting in direct decontamination of the heat affected zones of the concrete and as well as any scabbled solids. Thermal treatment, required to remove contaminated concrete layers, may render scabbled material more or less susceptible to subsequent leaching with decontamination agents. Alternately, if neither volatilization nor leaching potential of radionuclides can be increased, heating the concrete residue to its incipient melting or sintering temperature (1200-1300EC)

should produce an excellent vitreous waste form. An optimal decontamination approach for each of the four major radionuclides can be systematically identified through this approach.

Experimental

Material preparations - A 100 pound bag of ordinary Type I Portland cement (15) was obtained from a local construction supply merchant and provided the bulk source for all cement employed throughout this study. Several multi-kg batches of hydrated cement paste were prepared, at a water:cement ratio of 0.485 (16). After two weeks of curing at constant room temperature in water-tight containers to prevent dehydration, the resulting cement paste slabs were broken up into <1 in. diameter pieces using a hammer. The large cement paste pieces were then broken into smaller <0.1 in. diameter pieces using a Bico Chipmunk crusher (Braun Instrument Co.) fitted with steel plates. This crushed cement paste was subsequently ground between steel plates to <10 mesh (2 mm) using a Bico Pulverizer Type UA (Braun Instrument Co.). This <2 mm pulverized cement paste, was then sieved into three sizes [+100 mesh (150 μm), +200/-100 mesh, and -200 mesh (75 μm)] using 8-inch diameter brass wire cloth sieves and an electric vibratory shaker for 5 minutes in batches of 250-300 g. The +200/-100 mesh powder was selected for this study because it is a standard size for testing nuclear waste materials (17) with an average particle size (~110 μm) with an approximate surface area of 200 cm^2/g . Several kg of this +200/-100 mesh powder were prepared and stored in hermetic plastic containers for use throughout this investigation. Triplicate samples of the batch of +200/-100 mesh cement paste powder were analyzed for elemental composition via ICPMS after lithium borate fusion and nitric acid dissolution (18) along with reagent blanks and reagent blanks spiked with

standard multi-element solutions. The average elemental composition of this bulk pulverized cement paste material is presented in Table S1, Supporting Information.

Isotope spiking techniques - Standard solutions of carrier-free radioisotopes (^{85}Sr , ^{134}Cs , and ^{57}Co) were obtained commercially at nominal 1 mCi/mL in 0.1 M HCl. Aliquots of these radioisotopic solutions were diluted 2000-fold into 0.01 N CaCl_2 , as a neutral dilute salt carrier solution, for use in spiking cement paste powders. Only one isotope at a time was used to spike a given sample with a nominal 0.025 μCi of activity, usually dissolved in 100 μL . For uranium, a standard solution (Spex Certiprep Inc.) of 9,977 $\mu\text{g/g}$ in 2% HNO_3 was employed directly as 100 μL spikes for a nominal activity of 0.00071 μCi total uranium; for more dilute U spikes (i.e., 998 $\mu\text{g/g}$ of cement paste), a 10:1 dilution of this uranium standard solution was employed. The radionuclide tracer spike was added to a weighed amount of cement paste powder (0.999 ± 0.001 g) contained in a 2-mL-capacity 13-mm diam \times 25-mm high cylindrical refractory (99.8% alumina) gas-tight crucible (Coors Ceramics Co.). The liquid spike was placed in a central cavity within the cement paste powder such that wetted cement paste did not directly contact the walls of the crucible. After air-drying overnight, the cement paste powder was homogenized within the crucible by mixing thoroughly with a stainless steel spatula and the crucible reweighed. Spiked cement paste powders were generally aged for 20-40 days prior to imposing any thermal treatment by containing them in a 20-mL-capacity polypropylene scintillation vials after capping the crucible with a small piece of parafilm® and cork to prevent further drying or spilling during automatic sample changes during gamma spectroscopy. All crucible and extracts were assayed via gamma spectroscopy using NaI detector (19); details of the assay methods are given in the section on gamma activity assay techniques in the Supporting Information.

To contrast with radioisotopic behavior with pulverized cement paste, solid cement paste plugs of uniform size were also prepared and, after curing, spiked with either ^{134}Cs or ^{57}Co . Cement paste plugs were prepared by pipetting 1.74 ± 0.03 g of cement paste slurry (0.485 water:cement) using a tared 2-mL alumina crucible as a mold and container. After curing for 37 days in a sealed container, crucibles were weighed and spiked with 0.100 mL volume of either radioisotope in the top center of the plug. After air-drying for 24 hours, crucibles were stored in sealed scintillation vials for 2 days prior to initiating various heating treatments as described below. Twenty days after completing heat treatments, sequential extractions of the spiked plugs were initiated as described below.

Heating and volatility techniques - After completing gamma assays of the spiked pulverized cement paste samples, the crucibles and their contents were subjected to a variety of heating treatments. Within each group of samples subjected to different final temperatures, one suite of triplicate samples was subjected only to air-drying to constant weight (<48 hours) at room temperature (25°C). All other suites of triplicate cement paste samples were subjected to oven-drying at 100°C to constant weight (<24 hours) in a still-air oven. Additional heating was carried out in programmable high temperature furnaces (Thermolyne 1200°C muffle furnace or Lindberg 1700°C high-temperature furnace) with a regime to heat to the desired final temperature in 2.0 hours, holding at that temperature for 16 h, and subsequent cooling back to 30°C in 2 h or greater. Holding temperatures were generally selected at 100°C intervals between 200 and 1400°C with all groups of triplicate samples treated repeatedly to the lower temperature treatments through at least 200°C sequential increments. Weights were recorded for all crucibles when cooled after each heat treatment so that a thermogravimetric profile of the cement paste was attained with 100°C resolution up to the incipient melting point of the cement

paste; cement paste powders was fused into small cylinders above 1200°C and appeared to have been completely melted at or above 1350°C. At 1400°C, the melted cement paste began to corrode into the alumina crucibles within 4-8 hours at this temperature. Unspiked controls were carried along with each suite of isotopically-spiked samples through the highest temperature to verify that no cross-contamination of samples occurred within the furnace during heating; none was observed. After cooling and final weighing, thermally treated crucibles were capped as above, placed in scintillation vials, and assayed for residual radioisotopic activity as prior to treatment.

Sequential extraction techniques - Following completion of post heating gamma activity assays, uncapped crucibles were placed in 30-mL Oak Ridge polycarbonate centrifuge tubes. On the day prior to initiating an extraction sequence, radioisotopic assays were repeated with the cement paste-containing crucibles within the centrifuge tubes; immediately after completing an extraction sequence, radioisotopic assays were repeated on the residual crucibles with their disturbed cement paste contents within the same centrifuge tubes. Sequential extraction was repeated five times by delivering 20.0 mL of extracting solution to the centrifuge tube, capping and rotating it lengthwise at 8 rpm using a Thermolyne Labquake tube rotator for the extraction interval. The crucible slid back and forth within the centrifuge tube during rotation functioning as a continuous agitator for the powder or fused specimen within the tube. The initial 20-mL volume of each extracting solution (water, 0.1N CaCl₂, and 0.2 N HCl) was rotated for 16 hours; the subsequent four 20-mL volumes of each extractant were rotated for 1-hour intervals. Following each contact/rotation interval, the extraction tube was centrifuged at 35,000 relative centrifugal force for 5-7 min. The supernatant was then decanted into a 115-mL disposable filter unit (Nalgene No. 245-0045), with 0.45 μm cellulose nitrate membrane, and filtered under

vacuum; such filtration assured that occasional small cement paste fines were not included in the resulting extract. The filtrate was then poured from the unit's side spout into a scintillation vial. Quantitative transfer was not attempted during either centrifuge tube or filter unit decanting because all subsequent extract volumes were processed in the same centrifuge tube and disposable filter unit; thus, subsequent extractions functioned as a rinses for the previous extract volumes. Within one day, the five water extractions could be completed for a suite of 30 samples. On the following day, a group of five extractions with 0.1 N CaCl₂ was completed; on the third day, the five extractions with 0.2 N HCl were completed. Thus, each sample, through this sequential extraction procedure, resulted in 15 scintillation vials each containing 20-mL of extract. Each vial was assayed for its radioisotopic activity as described above and its activity expressed as a fraction of the total spike as measured with six replicate scintillation vials containing equal spikes into 20-mL of water. After completion of radioactivity assays, the pH of each extract was determined using a combination glass-reference electrode calibrated with certified standards at pH 4.00, 7.00, and 10.00; only the sequential cement paste extracts containing ⁵⁷Co spikes were assayed for pH to represent the chemical properties of the extracts which would not be affected by the nature of the radioisotope employed. The hardness of the five sequential water extracts from the suite of heated and ⁸⁵Sr-spiked samples was determined by titration with EDTA (20) using a Hach digital titrator with 5-mL aliquots.

Results and Discussion

Volatility of radionuclides - The retention of the four radioisotopes by pulverized cement paste after heating to various final temperatures is depicted in Figure 1. Uranium, ⁸⁵Sr, and ⁵⁷Co exhibited no evidence of volatility up through the vitrification temperature of the hardened

Portland cement paste (1400°C). Thus, heating of cement paste or concrete alone will not result in significant decontamination. However, ^{134}Cs exhibited measurable volatile losses from cement paste beginning at 800°C and was completely volatilized by heating to 1300°C. This volatile behavior is similar to that of ^{137}Cs during the heating and vitrification of soil (21). Thus, cement paste contaminated with ^{137}Cs should be amenable to decontamination techniques employing direct heating of surfaces or roasting of scabbled residues. Although the volatile species of ^{134}Cs was not identified here, previous work with the behavior of ^{137}Cs during soil vitrification (22) indicates that it will bind rapidly with any entrained cooled surface or particle in the process off-gas; both high efficiency particulate air (HEPA) filtration and/or gas-wet scrubbing techniques readily remove it from the off-gas. Although the volatilized ^{134}Cs was found at or near the cooled heating elements on the walls of the furnaces employed herein, no detectable cross-contamination of unspiked samples or samples spiked with other radioisotopes has been observed. The behavior of water (and, by inference, the behavior of cement paste contaminated with tritiated water, $^3\text{H}_2\text{O}$) during heating is depicted in the thermogravimetric response in Figure 1. The various mineral dehydration reactions, represented by this summary weight loss response, have been well studied previously in detail (23). When spiked cement paste plugs, in contrast to the spiked cement paste powders discussed above, were subjected to similar heat treatments, behavior of both ^{57}Co and ^{134}Cs were very similar (see Figure S1 in Supporting Information). More importantly, the conclusion seems warranted that spiked pulverized cement paste behaves similarly to cohesive cement paste specimens contaminated only on their surface.

Sequential extraction of ^{85}Sr The sequential extraction of heated cement pastes was designed to break down the behavior of their spiked radioisotopes into broad categories along a

gradient of increasing strength of contaminant adsorption from water-soluble through ion-exchangeable to acid-soluble. Although many common sequential extraction protocols encompass only a single extraction with each of a series of increasingly stronger reagents (24, 25), the present observations for cumulative fractions through five repeated extractions with each of the three sequential reagents provided good evidence that maximum plateaus were either attained or approached for each reagent (Figure 2). Although such evidence for an approach to equilibria or steady state is much more tedious to gather, it does provide some assurance that an implied form or chemical species of contaminant within or adsorbed to the solid material was being solubilized by the extractant. A very significant fraction of ^{85}Sr , contaminating the surface of the cement paste, was readily solubilized into water regardless of the antecedent temperature to which the contaminated cement paste was heated. With one notable exception (i.e., treatment to 500°C), heating generally decreased the water extractability of ^{85}Sr from cement paste up to 1400°C where the cement paste powder had sintered or vitrified and its subsequent extractability was minimal. Subsequent extraction with a neutral salt solution (0.1 N CaCl_2) produced another plateau of ^{85}Sr extraction in most samples. When the extractant aggressiveness was finally increased to 0.2 N HCl , most of the remaining ^{85}Sr was released from all heated samples except those treated at the highest temperatures. Many effects of heating cement paste to different final temperatures are difficult to interpret with all data on cumulative leaching (Figure 2). Using only the cumulative fractions leached after the fifth extract of each reagent (or the plateau in the cumulative fractions in Figure 2), provided a useful visual summary of temperature effects more amenable to interpretation (Figure 3). The decrease in water-soluble fractions and the concomitant increases in both acid-soluble and residual (non-extractable) forms of ^{85}Sr was much more apparent. The obvious anomaly in the overall decrease in water extractability with

treatment temperature was the increase to a maximum in ^{85}Sr extractability at 500°C . This is the temperature where the major $\text{Ca}(\text{OH})_2$ phase in hardened cement paste dehydrates and can be readily observed in both differential thermal analysis and thermogravimetric analysis of cured cement pastes (23). The carrier-free ^{85}Sr (spiked in 0.01 N CaCl_2) used in these studies likely partitioned into the relatively abundant and sparingly-soluble $\text{Ca}(\text{OH})_2$ phase of cement paste (rather than as a separate $\text{Sr}(\text{OH})_2$ phase) although additional partitioning into the less soluble calcium silicate hydrates may also have occurred. Dehydration of this $\text{Ca}(\text{OH})_2$ phase near this temperature also appeared to maximize the extractable Ca from cement paste (see Figure S2, Supporting Information) where extracts of cement paste powder treated at 600°C (no 500°C treated samples were analyzed for extract hardness) exhibited maximum hardness. Thus, these maxima in both calcium and ^{85}Sr extractability occurred near this known and characteristic dehydration temperature for $\text{Ca}(\text{OH})_2$ although both extractabilities decreased on heating to higher temperature.

Sequential Extraction pH- It would be incorrect to infer that water extraction of cement paste represented a low ionic strength or solvent-type extraction. The pH of all sequential extracts, regardless of the spiking radionuclide, through the entire extraction sequence are depicted in Figure S3 in the Supporting Information. Except for melted cement paste powder, all water extracts for all heated cement pastes were near $\text{pH} = 11$. This elevated pH continued into the 0.1 N CaCl_2 extraction sequence although the pH did decrease in some of the extracts of cement pastes heated above 1000°C . Hardened Portland cement paste typically contains up to 25% $\text{Ca}(\text{OH})_2$ identifiable as a separate chemical phase (11). For all but the melted samples, the hardness of the water extracts was approximately equivalent to 0.05 M Ca , which calculates to the equilibrium solubility maintained by excess $\text{Ca}(\text{OH})_2$ phase at the measured pHs. The five

successive water extractions removed an amount of CaO equivalent to approximately 10% of the sample weight (Figure S2, Supporting Information). Thus, the water extractions were, in effect, extractions with saturated calcium hydroxide. The spiked ^{85}Sr in these cement pastes likely equilibrated isomorphically with the calcium in this sparingly soluble $\text{Ca}(\text{OH})_2$ and likely represents the major form of ^{85}Sr in the contaminated cement paste as it does when radiostrontium is incorporated in cementitious waste forms prior to hardening (26).

All of residual $\text{Ca}(\text{OH})_2$ phase and other highly alkaline calcium silicate phases began to dissolve during the sequence of extractions with 0.2 N HCl. Cement paste can be viewed as a solid with a large acid neutralizing capacity (27) and, in essence, the pH profiles through five dilute acid extracts (Figure S2, Supporting Information) can be viewed as titration curves of the various heated cement pastes. In general, heating cement paste reduced its acid neutralizing capacity, thereby, decreasing the number of dilute acid extracts required to lower the extract's pH. Apparently, the dehydration of $\text{Ca}(\text{OH})_2$ and other hydrated silicates in cement paste becomes increasingly irreversible as more material is sintered or vitrified at temperatures above 1000°C.

Sequential Extraction of ^{134}Cs - Although the extractability of ^{85}Sr from cement paste exhibited major interactions with the abundant CaO-containing phases, the extractability of ^{134}Cs into water extracts was both greater in overall magnitude and much less dependent on antecedent heating of the powder (Figure 4). This figure depicts only the fractional extraction behavior of the non-volatilized ^{134}Cs remaining in the heated cement paste powders rather than their activities prior to heating. (Detailed extraction profiles for ^{134}Cs can be viewed in Figure S4,

Supporting Information.) On average, about 80% of the ^{134}Cs was extracted through five successive water extracts at all treatment temperatures less than 1200°C whereas ^{85}Sr extractability generally declined from 50 to 15% in this same temperature range. In addition, little of the remaining ^{134}Cs appeared in either the cation-exchangeable or acid-soluble phases as was commonly observed with ^{85}Sr . Although little ^{134}Cs remained unvolatilized in cement paste powder heated above 1200°C (Figure 1), what little did remain was converted into a non-extractable form in the sintered and/or melted cement paste (temperatures above 1300°C , Figure 4). Thus, most nonvolatile ^{137}Cs remaining in heated cement paste should remain readily water-extractable as has been observed in unheated cement pastes (4).

Sequential Extraction of ^{57}Co - In contrast to the behavior of both ^{85}Sr and ^{134}Cs , the extractability of ^{57}Co from cement paste powder after heating to any temperature was predominately in the acid-soluble fraction (Figure 5). (Detailed sequential extraction profiles at each temperature interval can be viewed in Figure S5, Supporting Information.) Only at temperatures $<400^\circ\text{C}$, was there any significant water-soluble or cation-exchangeable ^{57}Co extracted from spiked pulverized cement paste. The highly alkaline nature of cement paste apparently buffered both the water and calcium chloride extracts at such a high pH (Figure S3, Supporting Information), that any ^{57}Co would precipitate as $\text{Co}(\text{OH})_2$ phase and remain highly insoluble and, thus, unextractable with these reagents; when the extract was changed to dilute HCl, the ^{57}Co was rapidly removed once the extract's pH became less than 4 (Figure S5, Supporting Information). The acid-extractability of ^{57}Co decreased slightly as the powder was heated up to 900°C , then increased slightly between $1000\text{-}1200^\circ\text{C}$, followed by a decreasing extractability as the cement paste sintered and vitrified at higher temperature. All of the spiked

^{57}Co was retained in the cement paste heated to 1400°C (Figure 1) and these small 700-mg globules of vitrified cement paste still held more than 60% of their ^{57}Co against exhaustive leaching with dilute hydrochloric acid. Larger vitrified specimens (with smaller surface area:weight ratios) would exhibit much less fractional radioisotopic release (17, 22). Thus, because ^{57}Co neither volatilized nor increased in extractability following heating, decontamination strategies for ^{60}Co from concrete surfaces using thermal techniques ought to focus on melting thermally scabbled solids into a non-leachable vitrified waste form or finding more efficient and specific extractants for Co.

Sequential Extraction of Uranium - In many aspects, the extractability of U from spiked cement paste powders (Figure 6) was quite similar in behavior to that of ^{57}Co . The probable $\text{U(VI)O}_2(\text{OH})_2$ phase, formed on contact of the spiked $\text{U(VI)O}_2(\text{NO}_3)_2$ with the alkaline cement paste surfaces, would remain highly insoluble at the elevated pH of the cement paste-buffered water or calcium chloride extracts. When extract pH decreased below about 4, U was removed from cement paste powders heated to all temperatures below vitrification. (Detailed sequential extraction profiles for all thermal treatments are depicted in Figure S6, Supporting Information.) As with ^{57}Co , very little U was extractable into water or calcium chloride after heating the cement paste to any temperature. The fraction of U extractable into dilute hydrochloric acid decreased slightly as the powder was heated to increasing temperatures; more than 85% of the U retained in the small globules of vitrified cement paste could not be extracted with the hydrochloric acid. Thus, thermal treatment of concrete or scabbled concrete solids will neither volatilize nor increase the extractability of uranium and decontamination approaches probably should focus on vitrification of the cement paste into a much more stable waste form. Unlike the

other radioisotopes (^{90}Sr , ^{137}Cs , and ^{60}Co), uranium, when present at readily detectable activity, will result in a significant mass loading of potential concrete surfaces. The concentration of uranium in the cement pastes depicted in Figure 6 amounted to approximately 10,000 $\mu\text{g-U/g-cement paste}$. Notably, an equivalent suite of thermal treatments and subsequent extractions, carried out at a concentration of approximately 1,000 $\mu\text{g-U/g-cement paste}$, exhibited an identical extraction profile (See Figure S7, Supporting Information). Thus, these generalizations about uranium (VI) extraction behavior likely hold for most cement paste contamination levels <1% U.

Radioisotope-cement paste contact time - It is very likely that the time of contact between radioisotopic contaminants (like those employed in this study) and the cement paste surface can lead to changes in the forms and distribution of the phases responsible for contaminant adsorption. Indeed, cement paste itself has been described as a continuously reacting solid whose component phases change, albeit only slowly after the initial few weeks of hardening, over hundreds of years (10, 11). All of the pulverized cement paste employed in this study had been cured for at least 14 days prior to pulverizing and the resulting pulverized material was stored for several months before any radionuclide-spiking studies were initiated. However, the time of contact between this pulverized cement paste and the radioisotopic spike was examined in some detail. The minimum contaminant contact time, which could reasonably be attained with unheated cement paste with our counting and extraction techniques, was approximately 2 days. Routinely, contaminant contact times for the suites of heated samples described above were between 20 and 50 days. An additional suite of unheated cement paste powder samples were spiked with ^{85}Sr , ^{134}Cs , and ^{57}Co and allowed to age for 175 days prior to sequential

extraction; an otherwise identical suite was spiked and aged for the minimum 2 days prior to extraction. After only two days of contact with the cement paste powder, ^{85}Sr was much more extractable into water and calcium chloride solution, than it was after 25, 42, or 175 days of contact; the later three contact intervals exhibited only minor and nonsystematic differences in their extraction profiles (Figure S8, in Supporting Information); this likely arises from a relatively rapid reaction between ^{85}Sr and the most soluble phase of cement paste, $\text{Ca}(\text{OH})_2$, which approached an apparent equilibrium after a minimum of 25 days of contact. In contrast, ^{134}Cs was only slightly more extractable with water after 2 days of contact than it was after 49 or 175 days (Figure S9, in Supporting Information) while ^{57}Co exhibited no significant difference in sequential extraction profiles after aging 2, 24, or 175 days (Figure S10, in Supporting Information). Thus, effects on radioisotopic contaminant extraction characteristics did not seem to be changing significantly over the 20-175 day contact period although decreases in extractability of both ^{85}Sr and ^{134}Cs did occur between 2 and 20 days.

Cement paste as waste form - Portland cement paste has been investigated extensively for many years as a potential waste form for disposal of radioactive waste. Most of this work has involved mixing radioactive liquids, sludges, and/or solids with cement paste prior to curing or setting. However, much of the excellent work on radionuclide behavior in Portland cement paste focuses on radionuclides which have become constituents of hardened cement pastes rather than, as is the case here, adsorbed to or reacted with cement paste surfaces long after the cement paste hardening and curing processes have peaked. Thus, a large fraction of the leaching studies of radionuclides from cement paste waste forms focuses on cohesive or monolithic blocks of cement paste (2, 17, 26) rather than cement paste surfaces. Physical processes like diffusion,

mass transport, and porosity characteristics can dominate the radionuclide release processes rather than rapid surface chemical reactions as is likely the case in the present studies.

Other radionuclide-concrete interactions - Before the volatile and extractive behavior of the four radioactive contaminants of cement paste examined here can be integrated into an optimal or effective thermal treatment technique for concrete surfaces, several additional aspects merit further exploration. First, the effect of common aggregate materials, which compose the remaining 80% of the weight of concrete, should be examined for radionuclide adsorption properties and how these might change with thermal treatment. Notably, some aggregates composed of magnetite and gneiss, or other rock types which contain illite minerals, can exhibit preferential and specific adsorptive properties for ^{137}Cs (28). Second, contaminated aged cement paste could behave significantly different during thermal treatment and subsequent extraction from the relatively fresh hardened cement paste employed in this preliminary study. Although the composition of fresh cement paste is dominated by calcium hydroxide and calcium silicate hydrates (10,13), cement paste continues to evolve with age into more complicated or polymeric calcium silicate hydrates into which polymeric framework contaminants like cobalt and uranium may diffuse and react. The behavior of these contaminants in the present fresh cement pastes will be compared with their behavior in actual contaminated cement paste from walls of 50-year-old radioactive waste storage tanks at ORNL which have been obtained through this project but not yet analyzed via the present techniques. Third, hardened cement paste readily undergoes carbonation during aging (29) which, in addition to significant decreases in concrete permeability and contaminant diffusion rates (30), can result in a significant change in extraction behavior of contaminants like ^{90}Sr as it will likely change speciation from a coprecipitate with

sparingly-soluble $\text{Ca}(\text{OH})_2$ to an insoluble CaCO_3 . Again, samples of well-aged concrete from actual contaminated facilities should provide the opportunity to assess the importance of aging processes like carbonation and polymeric hydration in the retention and behavior of radioactive contaminants.

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Supporting Information Available

Detailed description of the gamma spectroscopic assay techniques is included along with the elemental analyses of the bulk cement paste (Table S1) used throughout this investigation.

Volatilization of ^{134}Cs and ^{57}Co from cohesive cement paste plugs is depicted in Figure S1.

Detailed sequential extraction graphs of the removal of CaO and extract pH are presented in Figures S2 and S3. Sequential extraction profiles for ^{134}Cs , ^{57}Co , and U (at both 1,000 and 10,000 ppm) are presented (Figures S4 - S7) along with sequential extraction results for ^{85}Sr , ^{134}Cs , and ^{57}Co after various contact intervals with hardened cement paste (Figures S8-S10).

Sequential extraction graphs for the removal of ^{134}Cs and ^{57}Co from cement paste plugs are also presented (Figures S11 and S12).

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List of Figures

Figure 1. The retention of radioisotopes and moisture by pulverized cement paste when heated sequentially to different maximum temperatures.

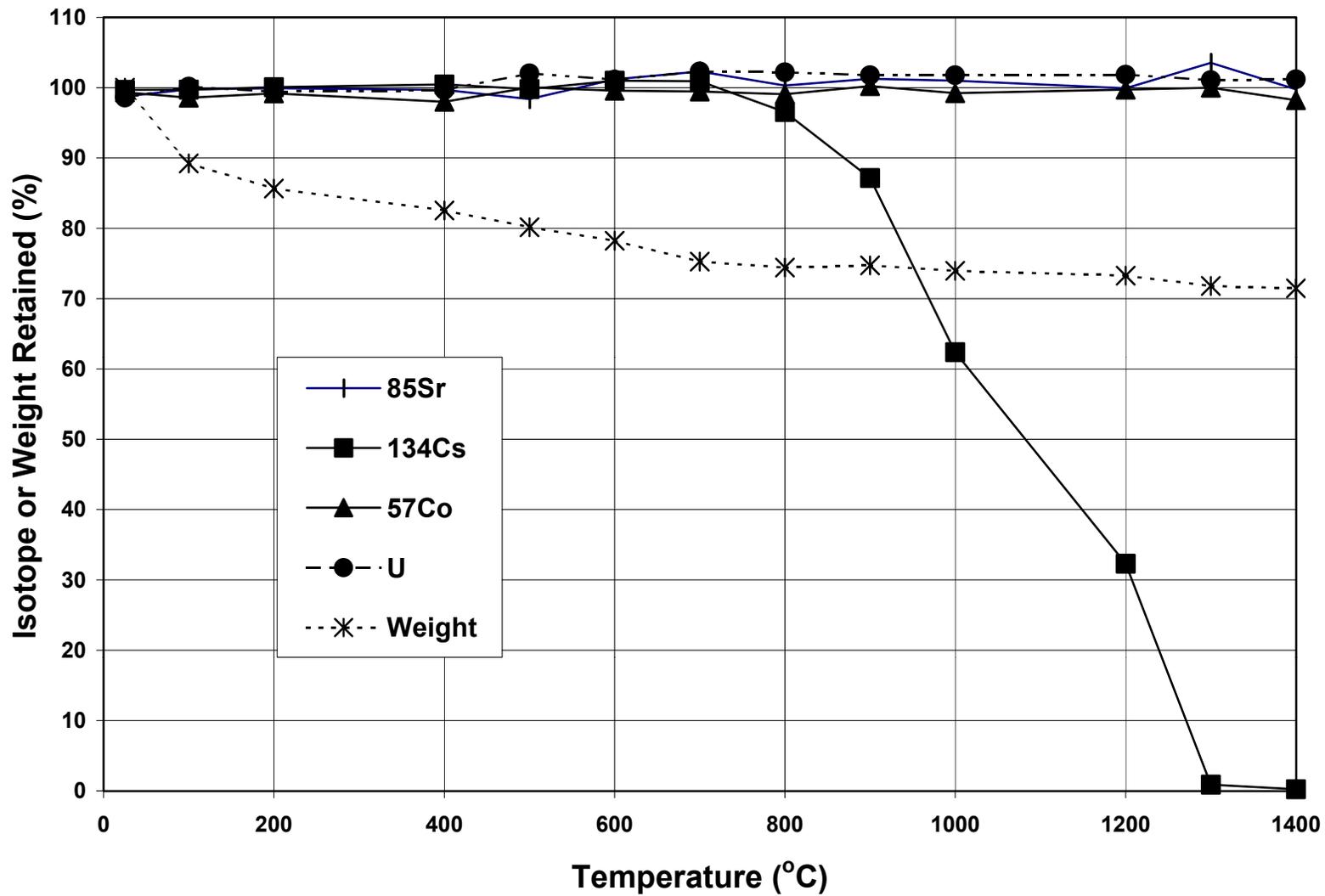
Figure 2. Sequential extraction with water, 0.1 *N* CaCl₂, and 0.2 *N* HCl from ⁸⁵Sr-spiked pulverized Portland cement paste after heating to various final temperatures.

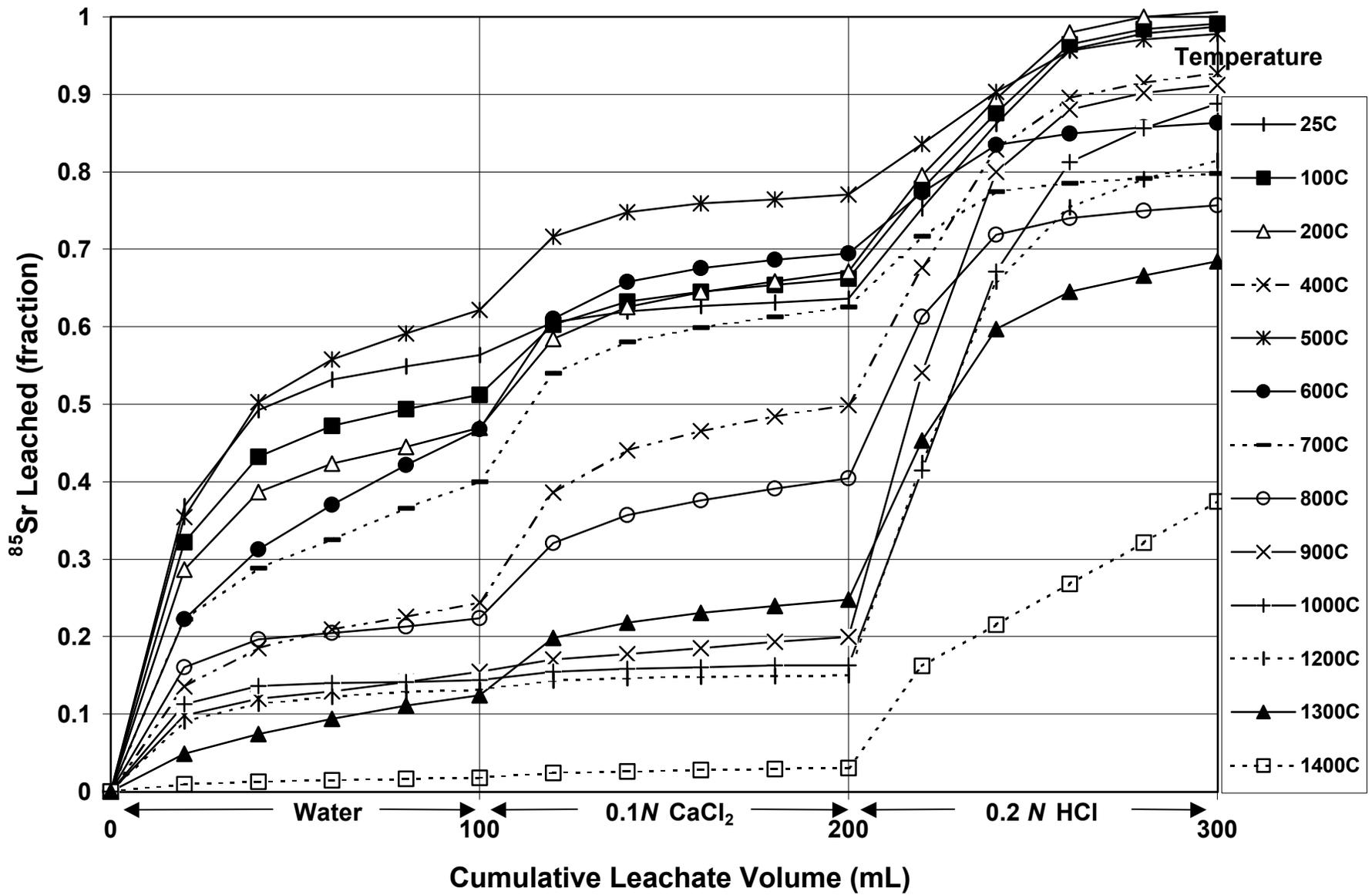
Figure 3. Extractability of ⁸⁵Sr from pulverized Portland cement paste into water-soluble, ion exchangeable, acid-soluble, and residual forms after heating to various final temperatures.

Figure 4. Sequential extraction of ¹³⁴Cs from pulverized Portland cement pastes after heating to different temperatures.

Figure 5. Sequential extraction of ⁵⁷Co from pulverized Portland cement pastes after heating to various temperatures.

Figure 6. The sequential extraction of uranium (spiked at 9,977 μg-U/g) from pulverized Portland cement pastes after heating to various temperatures.





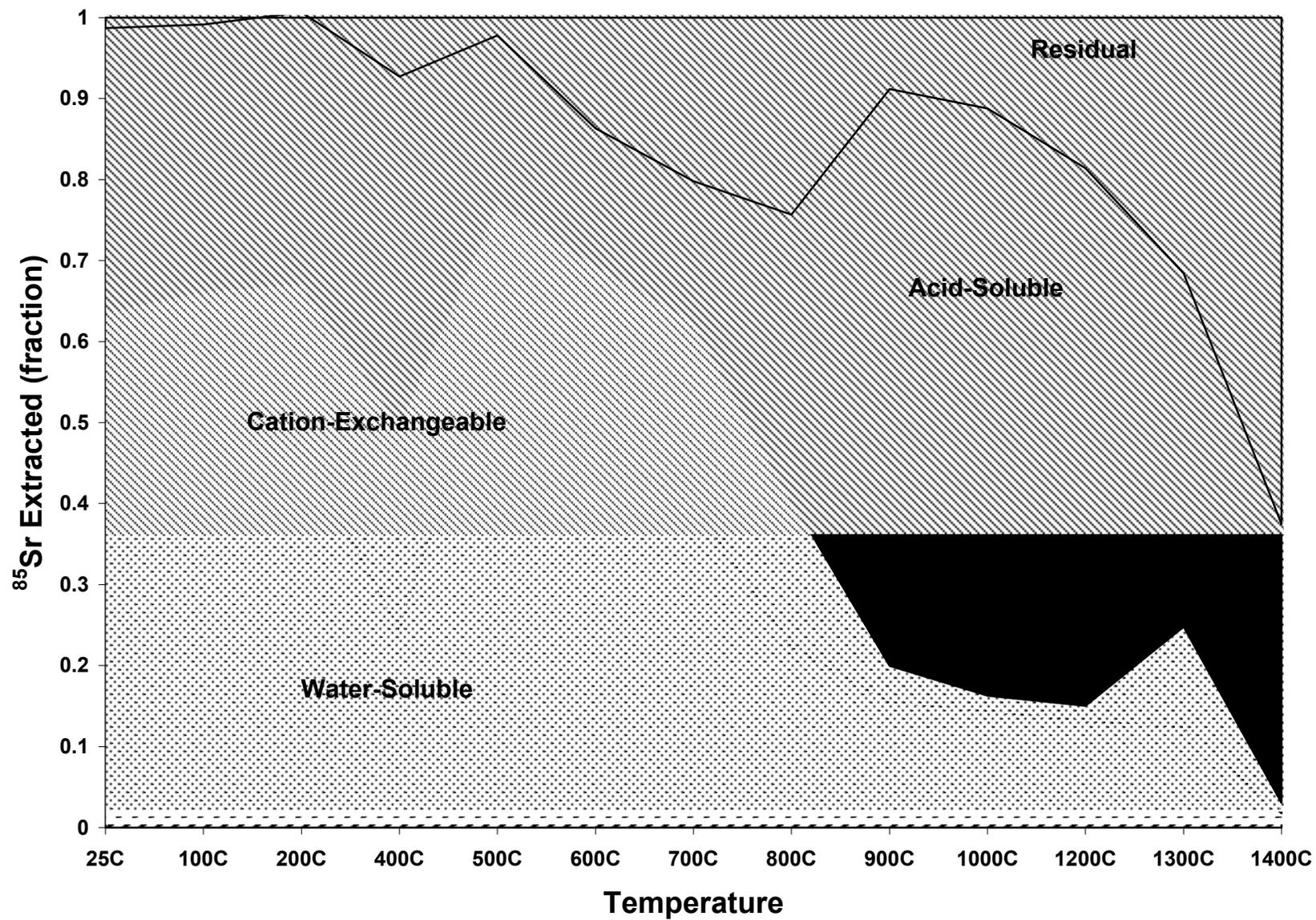
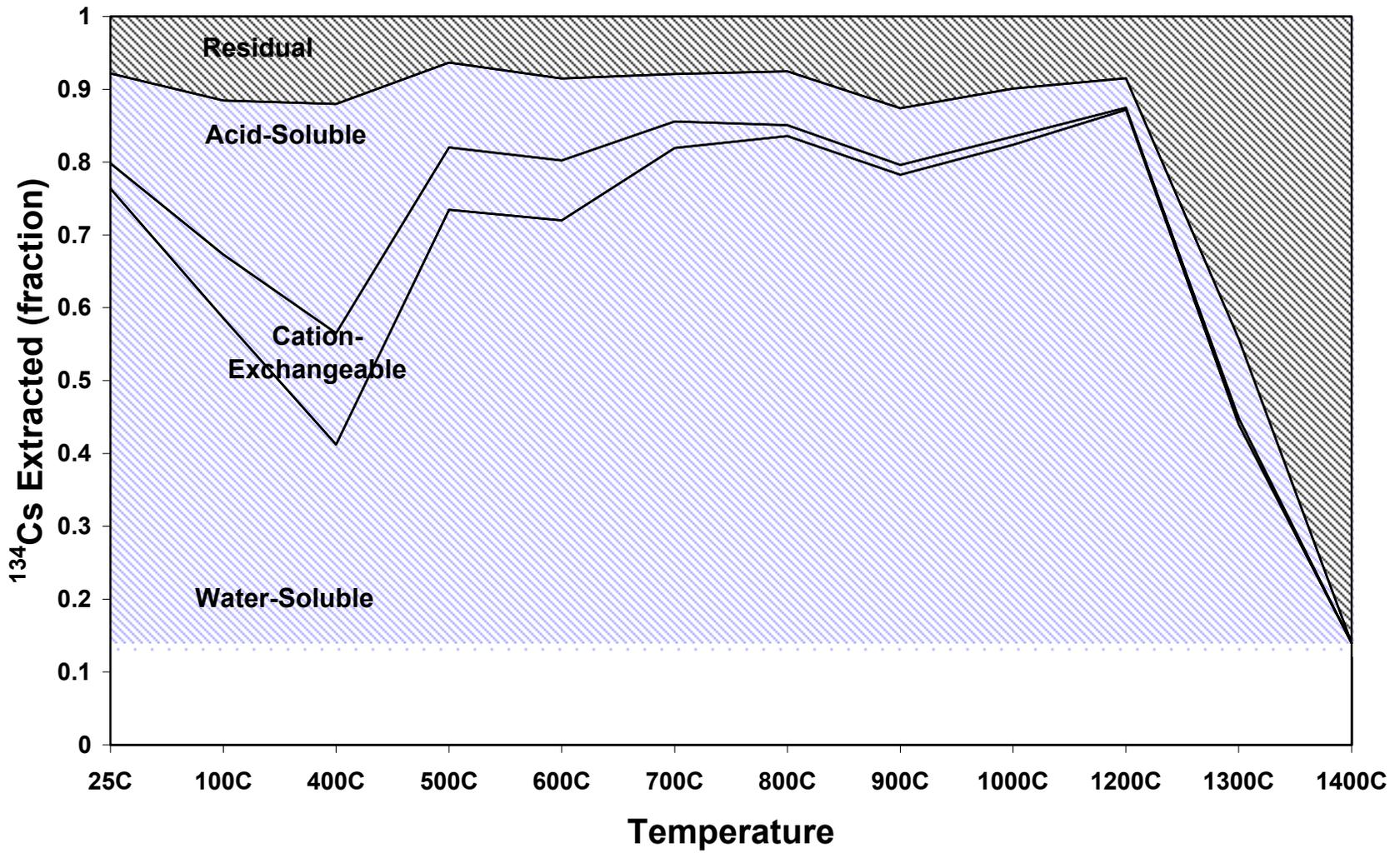


Fig3Spalding



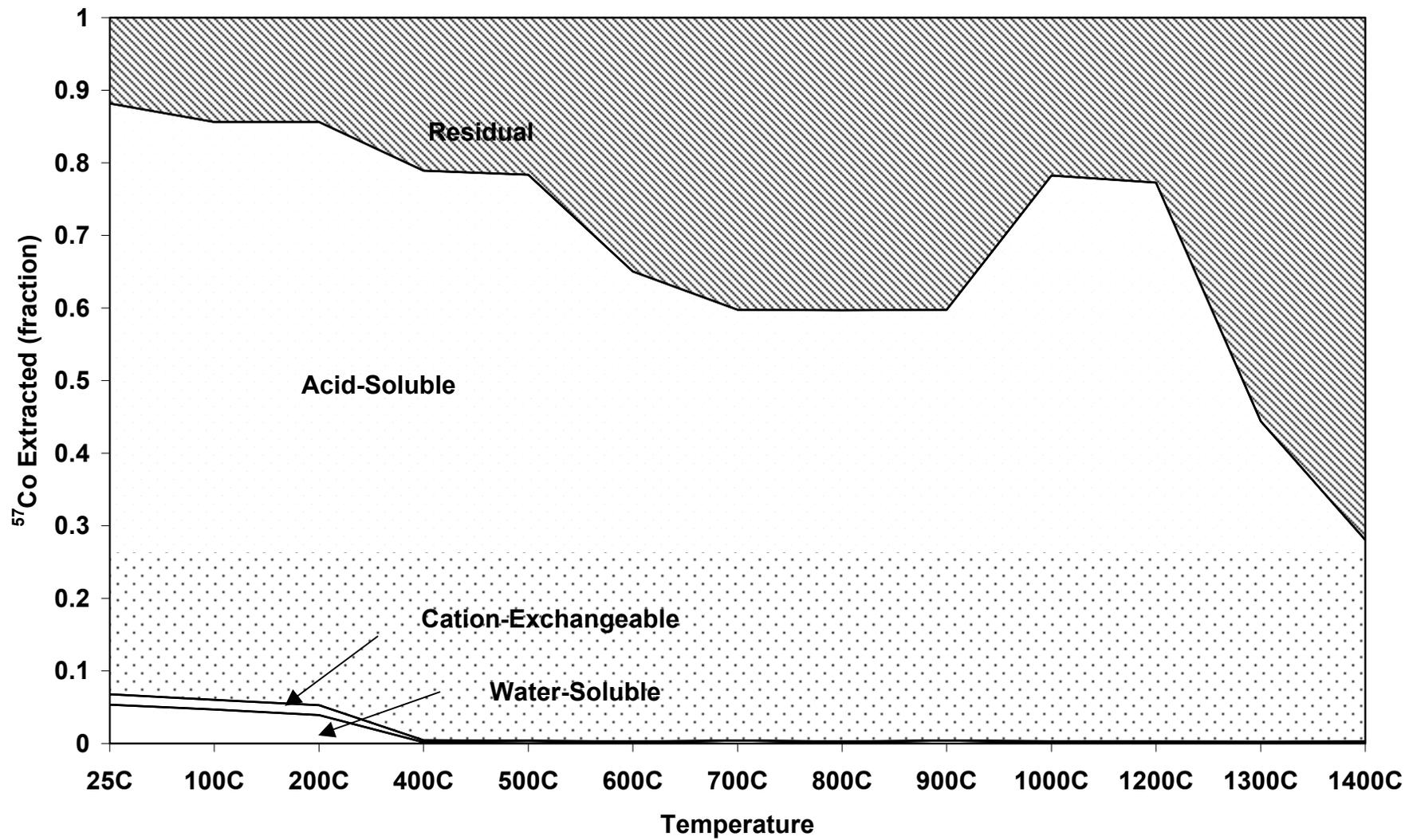


Fig5Spalding

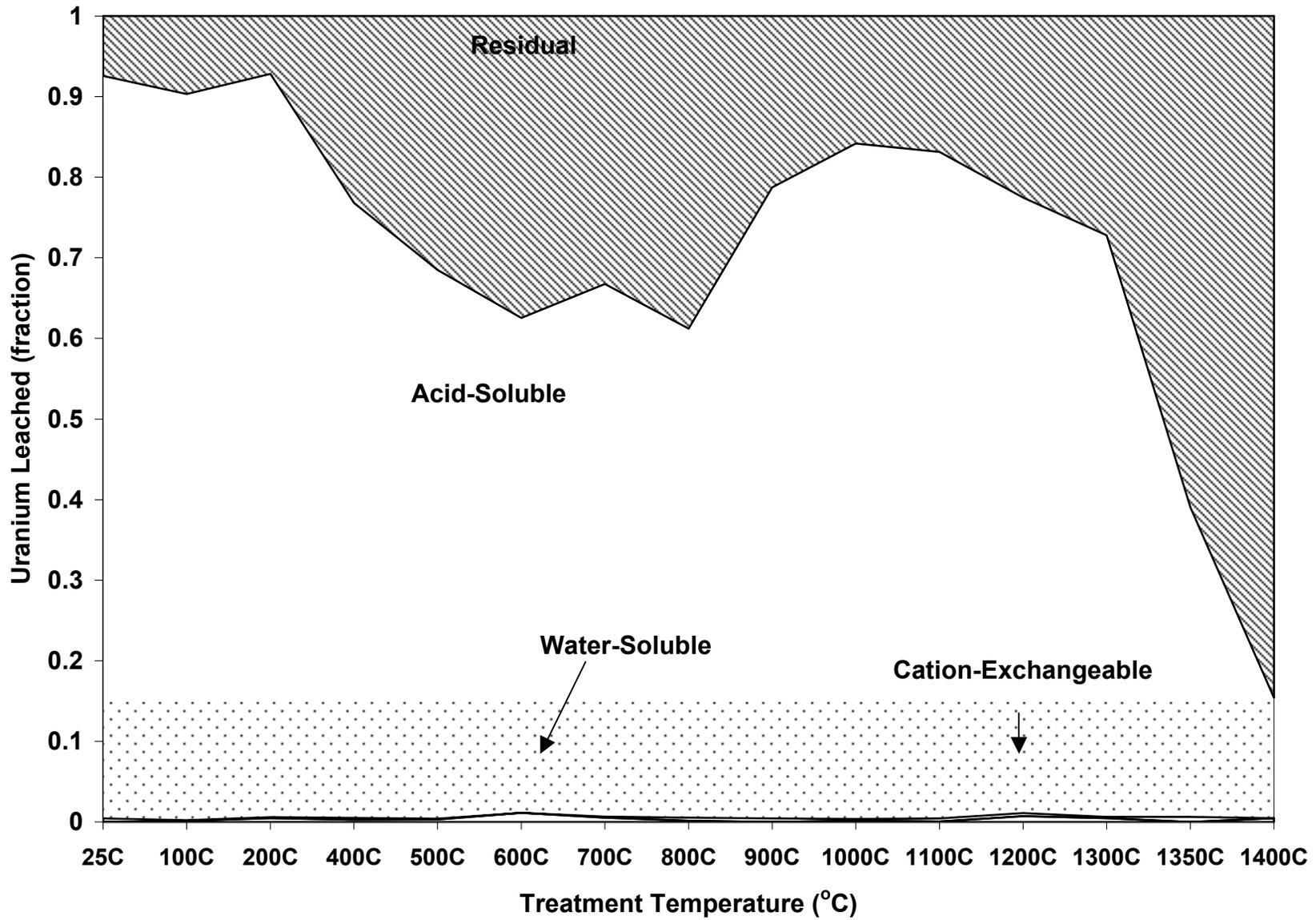


Fig6Spalding

Supporting Information for:

Volatility and Extractability of Strontium-85, Cesium-134, Cobalt-57, and Uranium After Heating Hardened Portland Cement Paste

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Gamma activity assay techniques - All radioisotopes were assayed using a well-type 3-in. diameter NaI (Tl-activated) gamma scintillation detector coupled with a multichannel analyzer (APHA 1995) controlling a Nuclear Data Model 5400 automatic changer for standard 25-mL scintillation vials. Although resolution of compound gamma-ray spectra, arising from multiple gamma-emitting isotopes within a single sample, is experimentally feasible using the available multichannel analyzer software employed (Accuspec©Canberra Nuclear Products Inc., Version 03), this technique would introduce inherent variability in detection limits and counting rate uncertainties among samples depending on the relative activities of the various isotopes. Thus, in the present study, the various spiked cement pastes and their resulting extracts contained only one isotope per sample. Three regions-of-interest (channel intervals) were established within the 2048 channels of the 0.05 to 2000 MeV gamma-ray energy range and were regularly collected covering various gamma-ray emission energies of each isotope including 0.05-0.39 MeV (region 1, channel numbers 47-350 for ⁵⁷Co and U), 0.42-0.65 MeV (region 2, channel numbers 384-594 for ⁸⁵Sr), and 0.43-1.62 MeV (region 3, channel numbers 384-1477 for ¹³⁴Cs). For ⁸⁵Sr, ⁵⁷Co, and ¹³⁴Cs, counting intervals were typically 10 minutes, which, in most cases, were adequate to

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attain an uncertainty in the gross count rate of $<0.1\%$ ($\pm 1\sigma$). Because of uranium's lower specific activity, counting intervals of 1-4 h were generally used to attain uncertainty in the counting rate of $<1\%$. The channel numbers of each isotope's characteristic gamma ray(s) were checked daily for possible drift in their position but none was observed during the study interval (12 months). For ^{85}Sr (region 2), ^{57}Co (region 1), ^{134}Cs (region 3), and U (also region 1), initial gross counting rates of 20,000, 80,000, 100,000, and 2,300 counts per minute (cpm) were typical. Background counting rates in the same regions-of-interest were collected from unspiked but otherwise identical cement paste powders in crucibles and were subtracted from the gross counting rates in spiked samples; for the regions of interest for ^{85}Sr , ^{57}Co , ^{134}Cs , and U, background counting rates were typically 194, 1640, 450, and 1640 cpm, respectively, varying only slightly daily due to activities of other proximate samples within the sample changer queue. Background counting rates in all three regions-of-interest for samples containing either crucibles-plus-cement pastes, 20-mL of water, or empty scintillation vials were indistinguishable indicating that no experimental materials or containers introduced detectable gamma emissions. For extracts of cement powders, 20-mL volumes of solution in scintillation vials were employed for the same gamma spectrum regions-of-interest and the same counting intervals; typically, for all four isotopes, counting rates in 20-mL of aqueous solution in a scintillation vial were approximately 94% of the same activity contained in 1-g of cement paste within an alumina crucible in an identical scintillation vial. For both pulverized cement paste in crucibles and 20-mL liquid volumes, standard untreated spiked samples were prepared in triplicate for each radioisotope; these functioned as relative controls (containing maximal starting activity spiked material) to which subsequently heated or extracted samples could be compared (as fractions of

this starting spiked activity) using the ratio of total net counts in the region-of-interest. Under the identical detection geometries employed (either 1-g of cement paste within a crucible in a scintillation vial or 20-mL of aqueous liquid within a scintillation vial) and the daily use of sealed single-isotope standards, containing identical starting activities, to compute ratios, decay corrections within a given daily group of samples were unnecessary. Computer files of complete gamma-ray spectra were saved in ASCII format for every sample and standard counted, as backup in case inconsistencies, ambiguities were observed in regions-of-interest summary data output; routinely, only regions-of-interest gross count totals were processed along with sample identification and date and time of counting.

APHA (American Public Health Association). 1995. 7120 B. Gamma Spectroscopic Method. pp. 7-18-7-20, In, Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, D.C.

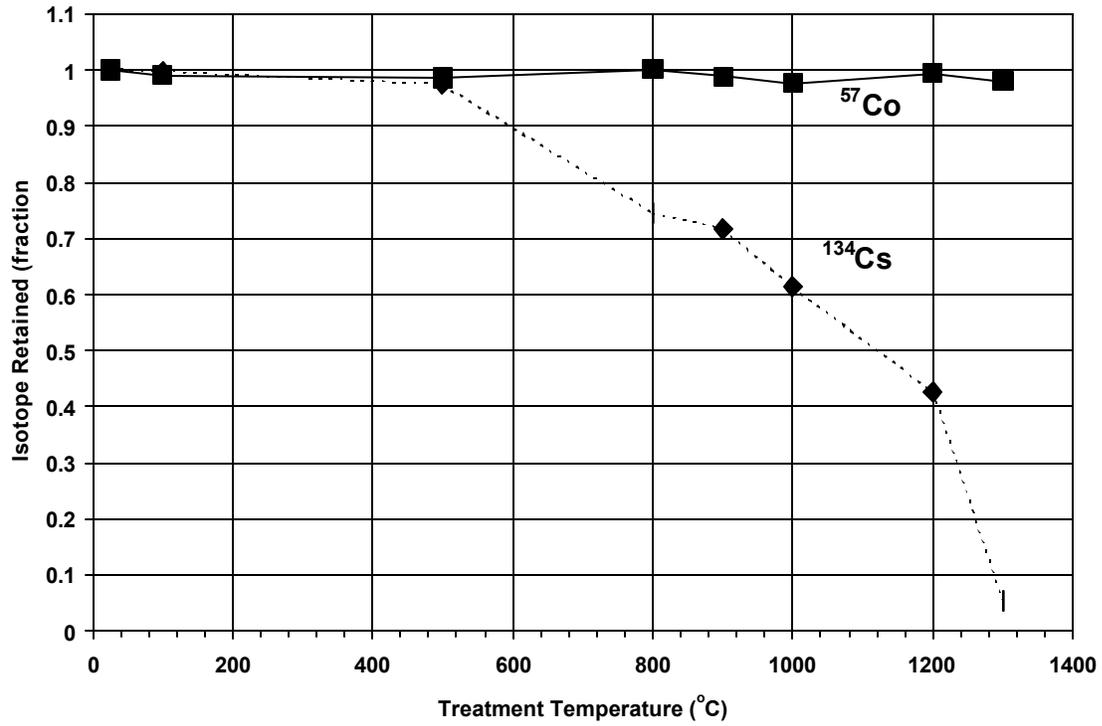


Figure S1. Retention of radioisotopes by cohesive cement paste plugs when heated sequentially to various final temperatures.

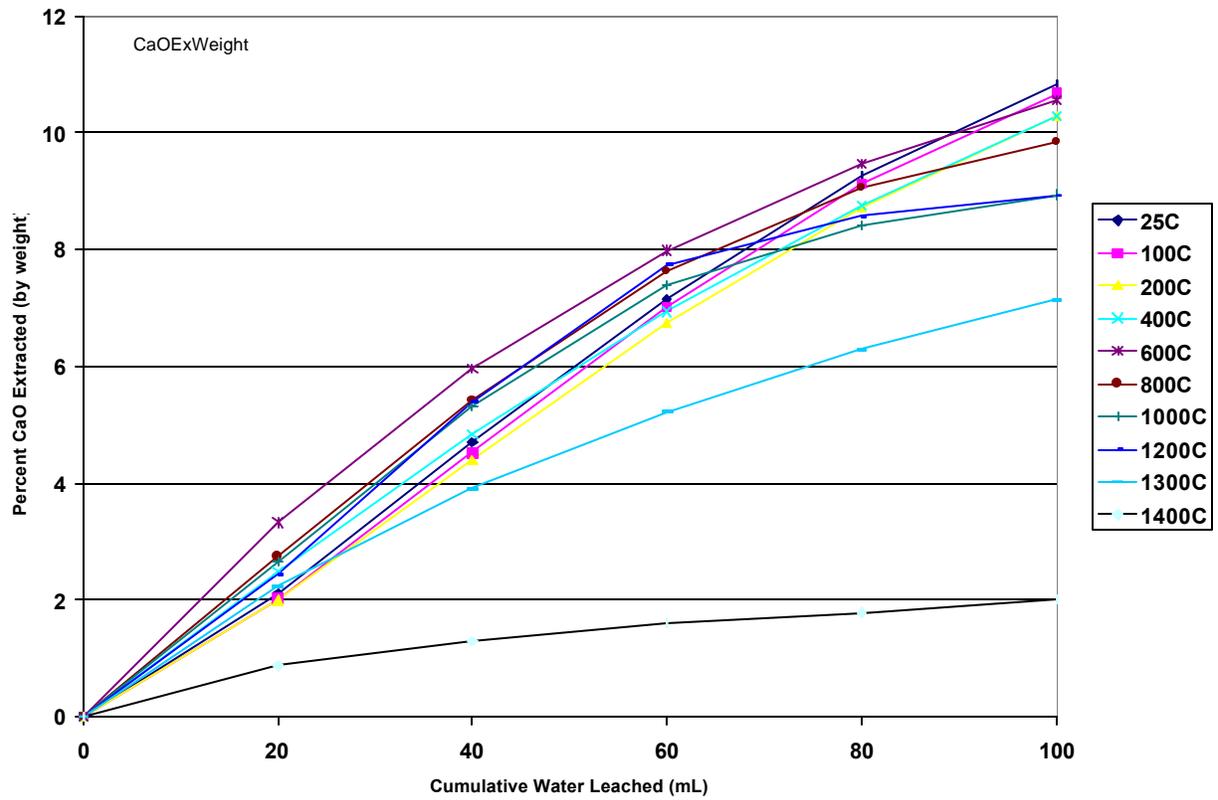


Figure S2. Extraction of CaO weight equivalent by water from pulverized Portland cement paste after heating to various temperatures.

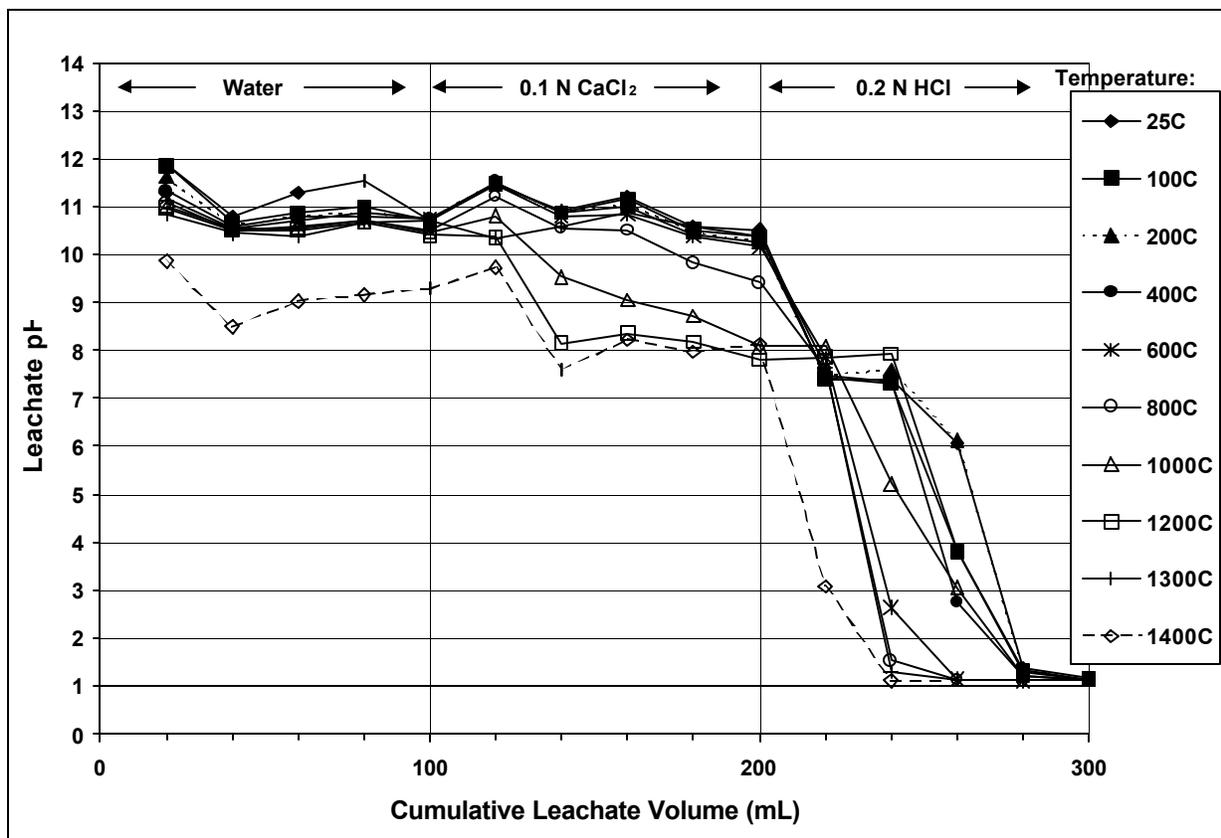


Figure S3. The average pH of sequential extracts of pulverized Portland cement pastes after heating to various temperatures.

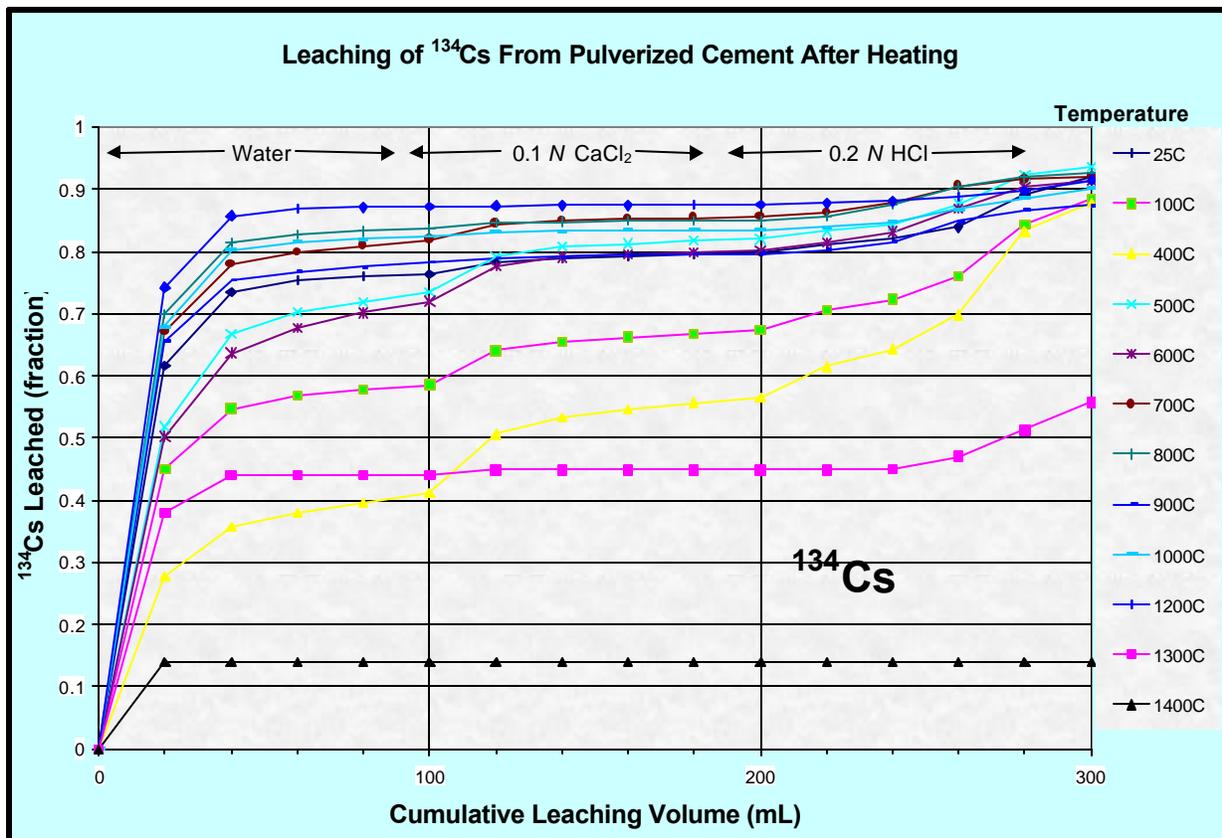


Figure S4. Sequential extraction profiles of ^{134}Cs from pulverized Portland cement paste following heating to various temperatures.

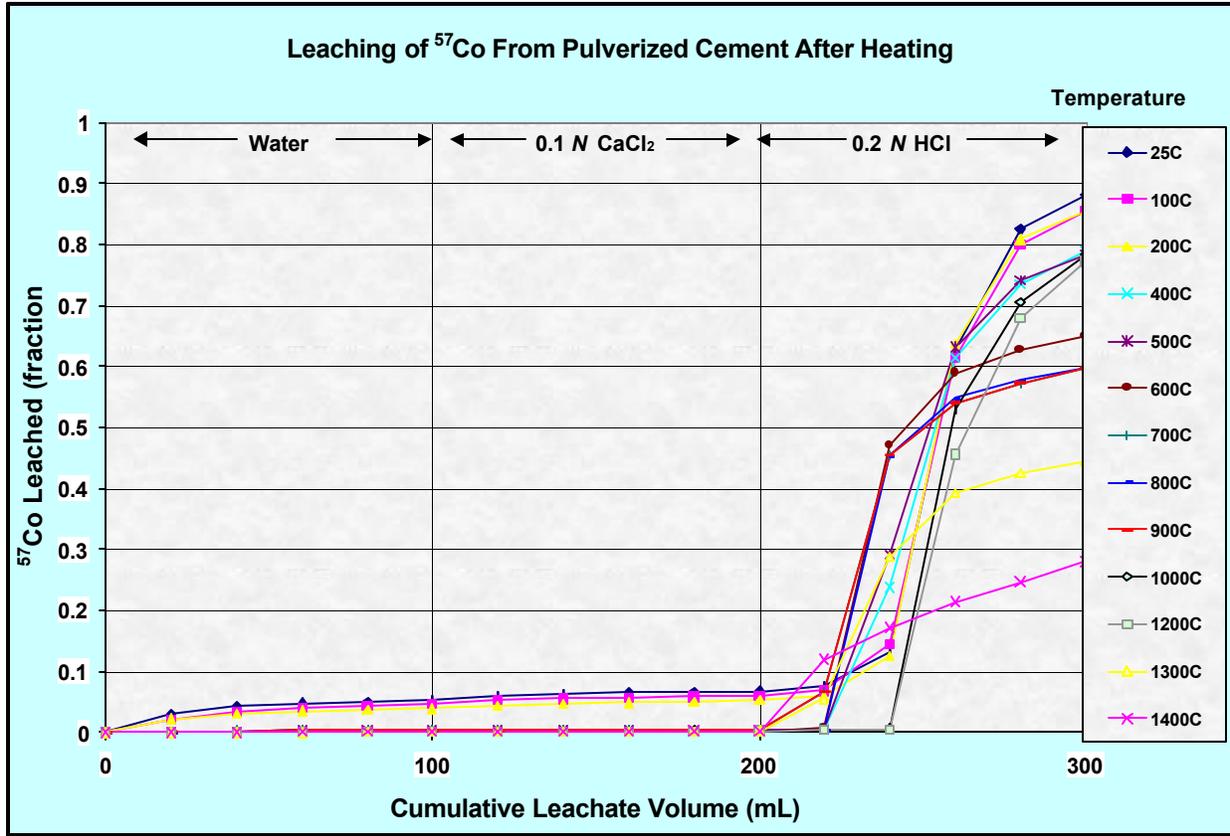


Figure S5. Sequential extraction profiles for ^{57}Co from pulverized Portland cement paste following heating to various temperatures.

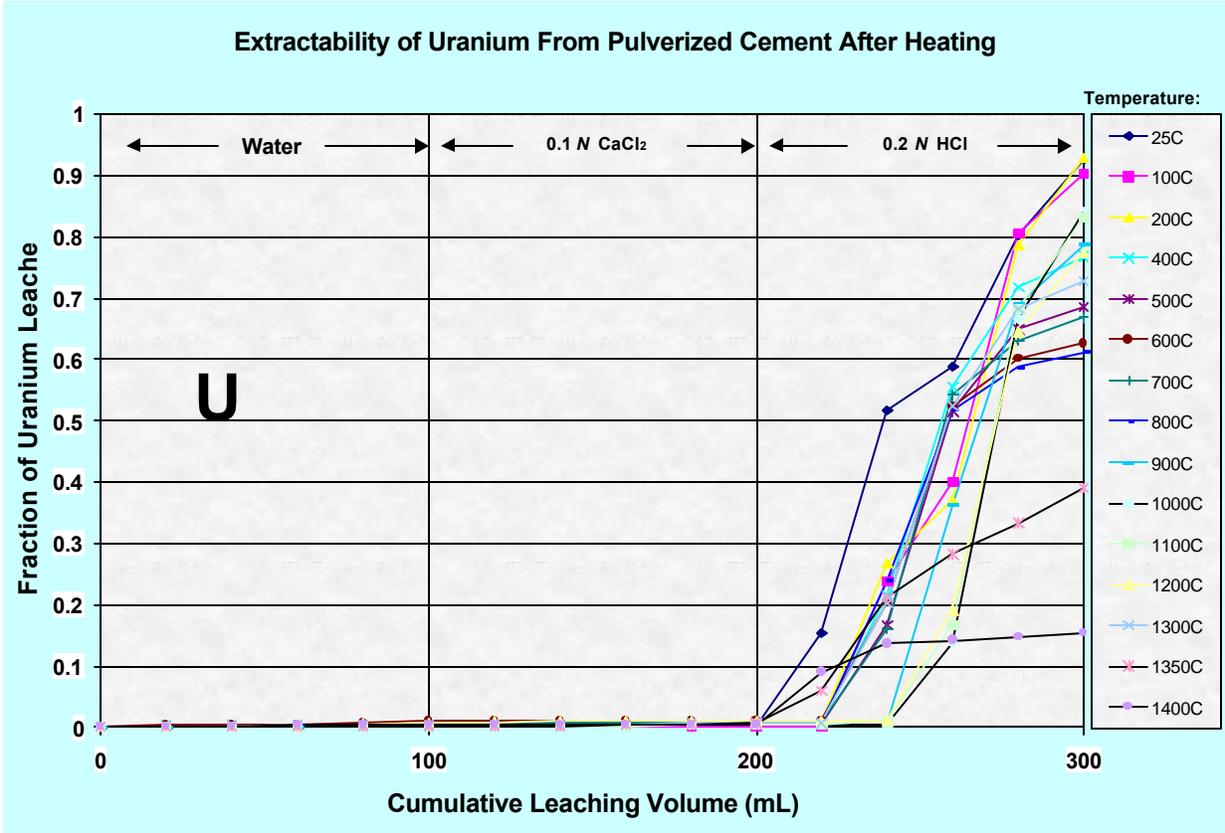


Figure S6. Sequential extraction profiles for uranium (total concentration = 9,977 $\mu\text{g/g}$) from pulverized Portland cement paste following heating to various temperatures.

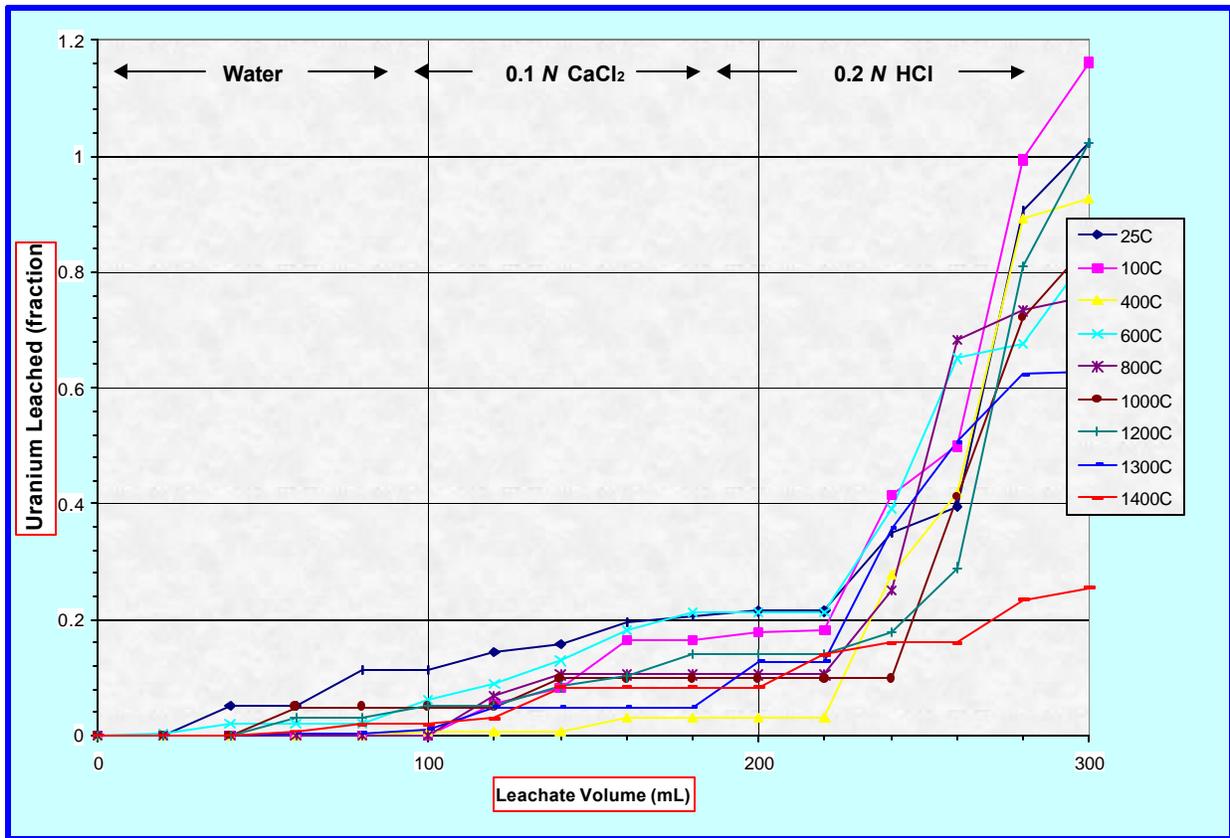


Figure S7. Sequential extraction profiles for uranium (total concentration = 997 μg/g) from pulverized Portland cement paste following heating to various temperatures.

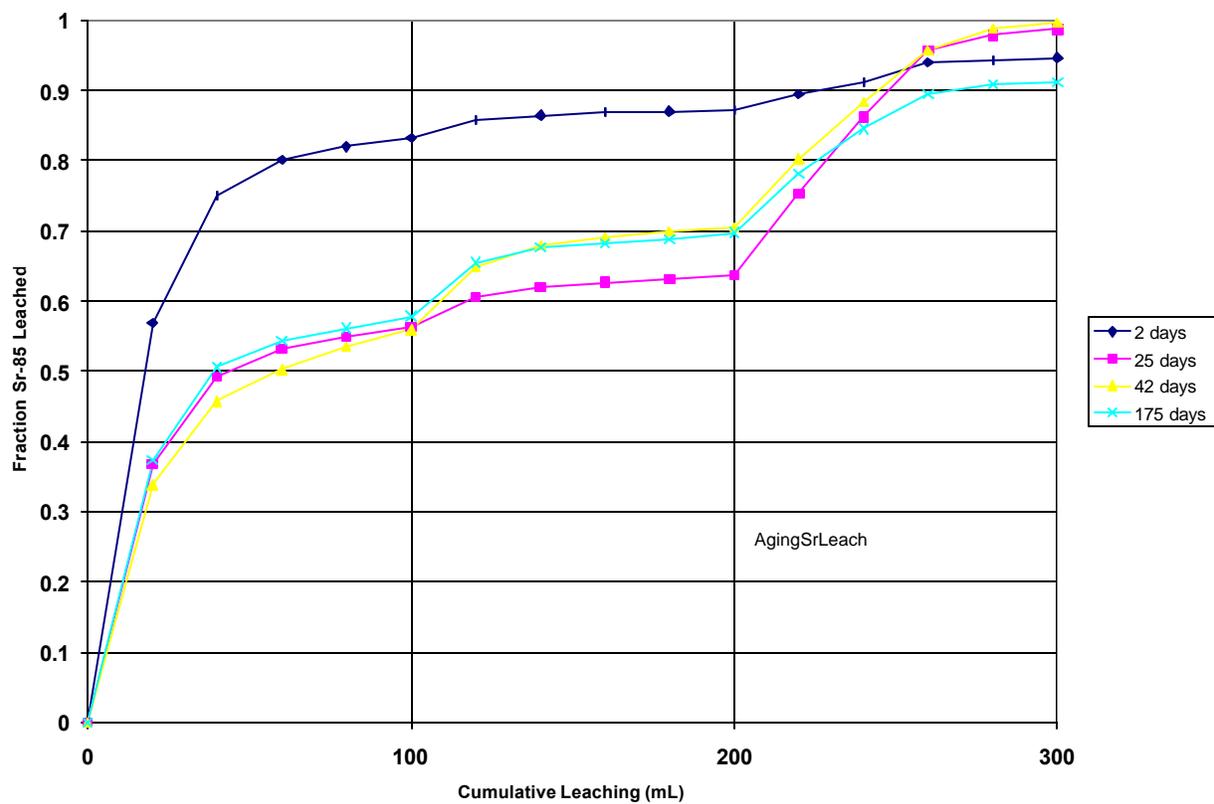


Figure S8. Sequential extraction profiles for ^{85}Sr from cured but unheated Portland cement paste after contact periods of 2, 25, 42, and 175 days.

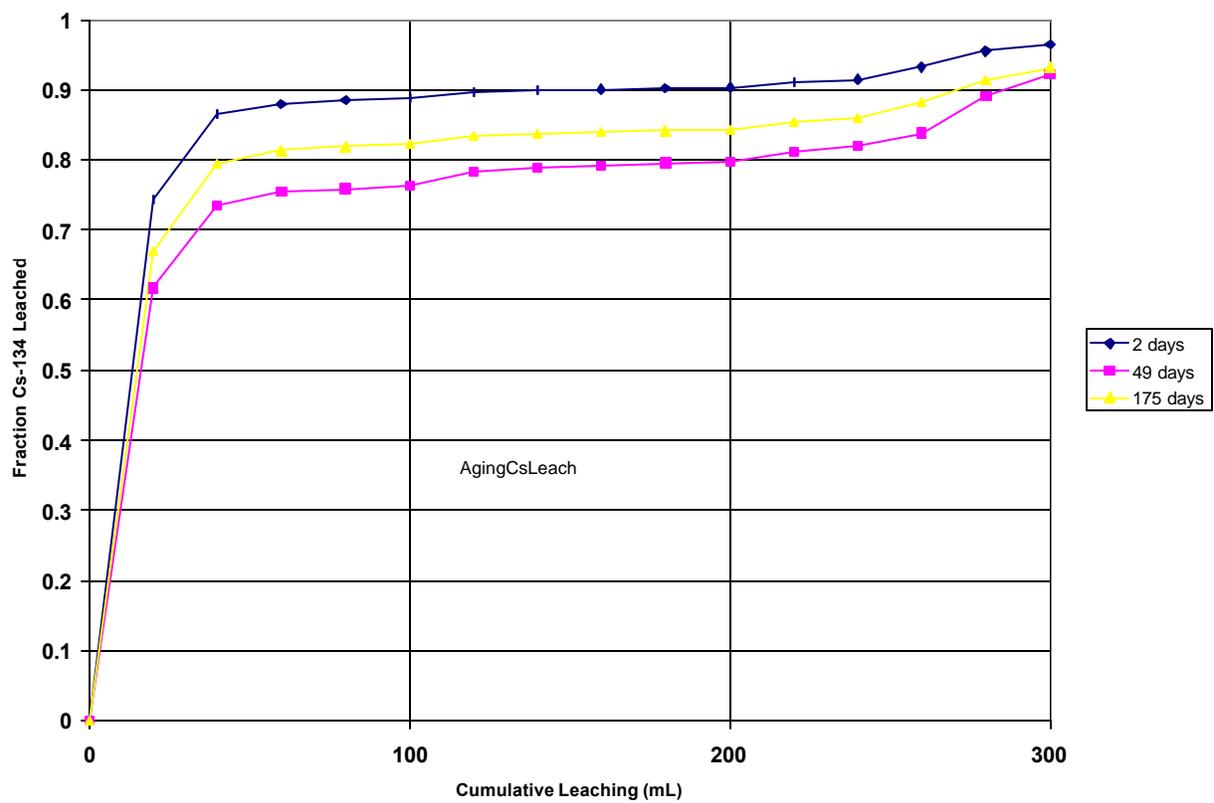


Figure S9. Sequential extraction profiles for ^{134}Cs from cured but unheated pulverized Portland cement paste after contact periods of 2, 49, and 175 days.

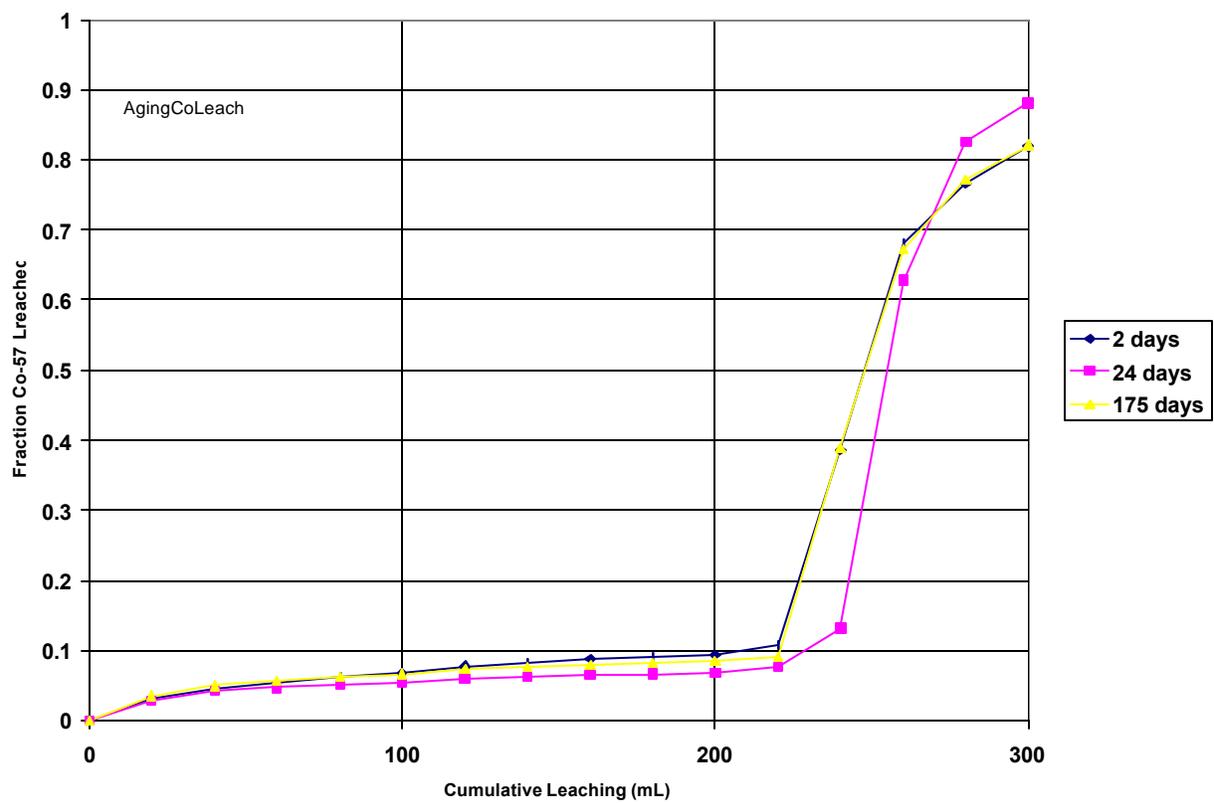


Figure S10. Sequential extraction profiles of ^{57}Co from cured but unheated pulverized Portland cement paste after contact periods of 2, 24, and 175 days.

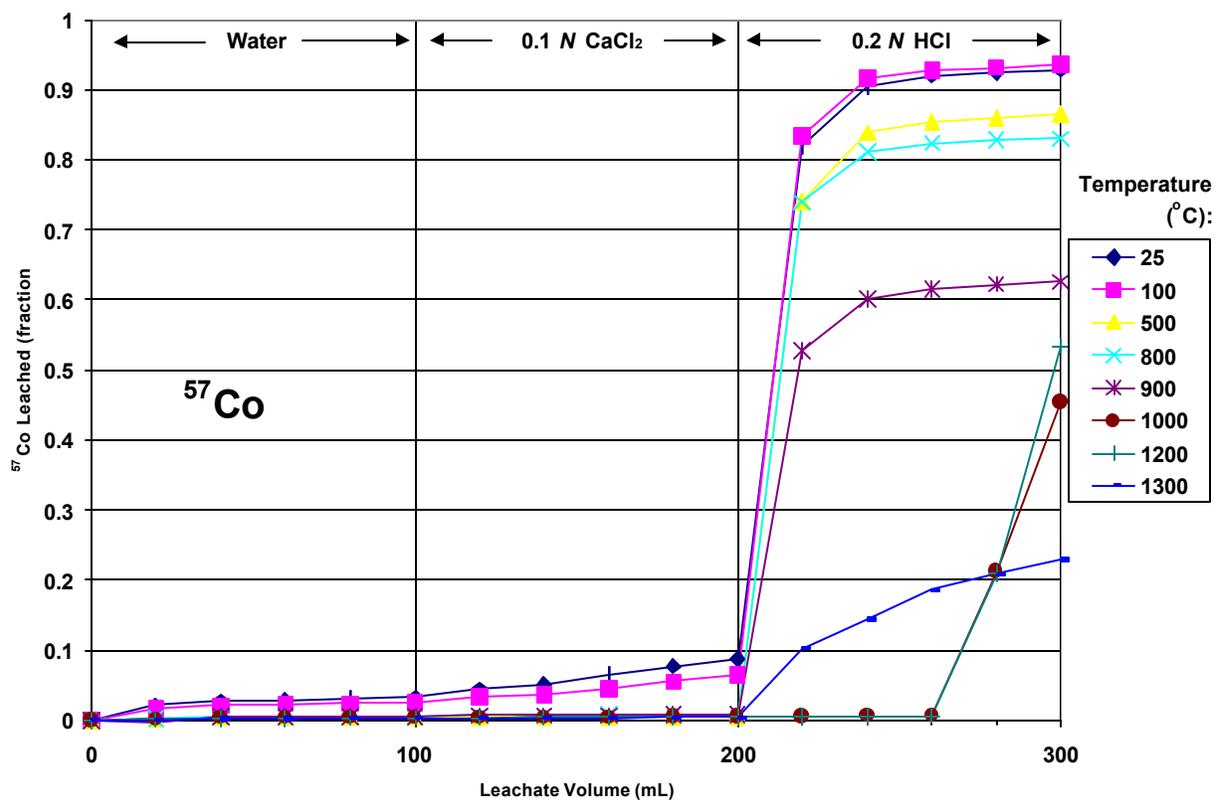


Figure S11. Sequential extraction profiles of ^{57}Co from the surface of cured Portland cement paste plugs following heating to various temperatures.

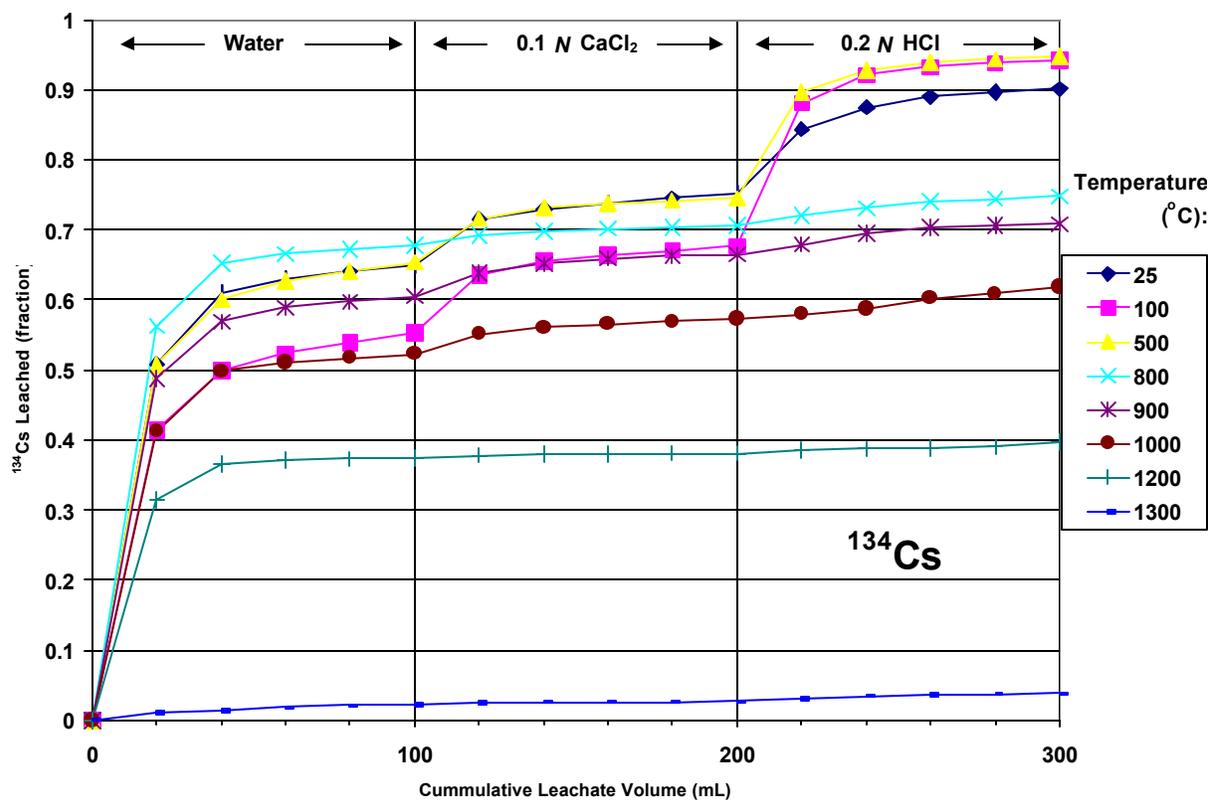


Figure S12. Sequential extraction profiles of ^{134}Cs from surface of cured Portland cement paste plugs following heating to various temperatures.

Table S 1. Average Elemental Analyses of Bulk Pulverized Hydrated Portland Cement Paste via Inductively Coupled Plasma Mass and Atomic Adsorption (for Na and K) Spectroscopy.

<u>Elemental Oxide</u>	<u>(Percent)</u>
Al ₂ O ₃	3.35
CaO	44.79
Fe ₂ O ₃	2.66
K ₂ O	0.49
MgO	2.01
MnO ₂	0.06
Na ₂ O	0.14
SiO ₂	16.65
SrO	0.04
TiO ₂	0.21
Loss-on-ignition (1400°C)	28.53
Sum of Oxides	98.95
Minor Elements:	
Ag	<0.04
As	<0.38
Ba	0.01
Be	<0.002
Cd	<0.02
Co	<0.04
Cr	<0.04
Cu	<0.04
Mo	<0.01
Ni	<0.09
P	<0.91
Pb	<0.19
Sb	<0.38
Se	<0.38
V	<0.004
Zn	<0.09
Zr	<0.38