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LEACHING INDUCED CONCENTRATION PROFILES IN THE SOLID PHASE OF CEMENT*

M. Fuhrmann and P. Colombo

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Nuclear Waste Research Group

Fuel Cycle Analysis Division

Brookhaven National Laboratory

Associated Universities, Inc.

Upton, NY 11973

MASTER

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ABSTRACT: Analysis of the solid phase of portland cement specimens by energy dispersive x-ray spectrometry before and after leaching provided elemental profiles within the cement. Releases of potassium were calculated from the solid phase profiles and were compared to releases determined from leachate analyses of potassium and cesium-137. The fraction of potassium released in the leachate was found to correlate closely to that of cesium-137 under varying time and temperature conditions, despite the different manner in which each was originally contained in the cement. Agreement was obtained among potassium releases as determined from the solid, potassium in the leachate and cesium-137 in the leachate. These correlations allowed the use of potassium as an analog for cesium-137 in cement.

Profiles of potassium in the solid showed varying degrees of depletion. A specimen, sectioned immediately after leaching for 471 days, showed complete removal of potassium to 9 mm depth from the specimens surface. From 9 mm to the center of the specimen, an apparently linear increase in concentration was observed. Specimens that had been air dried prior to sectioning had profiles that were produced by evaporative transport of dissolved species toward the surface. Carbonation of the surface appears to have retarded migration of the dissolved material. This prevented it from reaching the outer edge and resulted in increased potassium concentrations several mm inside the surface.

KEYWORDS: leaching, portland cement, solid phase analysis, potassium, cesium-137.

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INTRODUCTION

Portland cement is commonly used as a solidification agent for aqueous low-level radioactive wastes. Hydraulic cement-concrete will also be used extensively for engineered disposal structures for these wastes. Therefore, its response to exposure to water (leaching) is important when considering both short- and long-term releases of contaminants.

A full description of the leaching behavior of cement requires consideration of the effects of leaching on the solid phase. This includes analysis of solid specimens to determine internal concentration profiles. Ideally, such profiles may be described by mass transport equations, but concentration profiles in reactive, multi-phase materials are subject to many influences. For example, alteration of the solid may occur as incongruous dissolution, causing increases in porosity and changes in elemental composition. Alternatively, authigenic mineral formation may close off porosity. Conseqently, changes in both structure and chemistry must be investigated.

Unfortunately, sectioning and solid phase analysis of radioactive specimens is often prohibitively difficult. A non-radioactive tracer (that behaves similarly to the radioactive element of interest) is difficult to find for solid phase studies because most microprobes are not sufficiently sensitive to detect tracers at appropriate concentrations.

In order to use non-radioactive specimens for solid phase studies of cement waste forms, it was necessary to find an analog for cesium-137. Potassium is chemically similar to cesium and is present in detectable concentrations in cement. However, several potential problems could preclude the use of potassium for this purpose. First, the molar concentration of cesium-137

in radioactive waste is very small compared to concentrations of potassium in cement. Major differences in concentration may alter leaching behavior. There is a second related problem. At low concentrations sorbtion of tracers by the solid may be important, whereas at high concentration it may be negligible. This is a particular concern in cement where cesium may be incorporated into developing hydration products [1]. Third, cesium-137 is added to cement as an aqueous waste or tracer. In contrast potassium is contained in the cement powder and is subjected to high temperatures during firing of the clinker [2]. Depending on the compounds formed, releases of this element may be limited by dissolution kinetics, causing differences in potassium and cesium-137 leaching behavior.

This paper establishes the relationship of potassium and cesium releases from cement under a variety of leaching conditions. Solid phase analyses by scanning electron microscopy and energy dispersive x-ray spectroscopy were then used to observe changes in structure and potassium profiles within the cement. These profiles and the behavior of potassium in the solid during and after leaching can be taken as parallels to the leaching behavior of cesium-137.

PROCEDURE

All specimens used in this study were made with portland type I cement with a water-to-cement ratio of 0.43. They were cast in polyethylene containers and were right cylinders measuring 4.8 cm in diameter and 6.4 cm in length. Those specimens containing cesium-137 tracer were made with 10 μ Ci of the radionuclide included with the water used to hydrate the cement. Control samples, containing no radionuclides, were made under the same conditions.

Leach Test

The ANS 16.1 Leach Test [3] was modified for these experiments by the addition of several sampling intervals to better define the resulting curve shapes. This is a semi-dynamic test where the leachant is replaced periodically with fresh distilled water after intervals of static leaching. The volume of leachant was 1300 ml, 10 times the geometric surface area of the sample. For the 20°C, long-term leach test, specimens containing radionuclides were tested in triplicate for 483 days. A similar specimen, without radionuclides, was tested for 471 days and the leachate was used for elemental analysis. Other specimens were leached for 18 days at 30°C and 70°C.

Results were calculated according to Equation 1:

$$CFR = \frac{\sum A_n}{A_o} \qquad (1)$$

where CFR is the cumulative fraction released, A_n is the amount of a specie released at any one leaching interval and A_o was the original quantity of a specie in the specimen. Percent release is calculated by multiplying CFR by 100.

Leachate Analysis

Radionuclide gamma counting was performed with an automated NaI well-type detector and a multichannel analyzer. Analyses for calcium, silicon, aluminum, magnesium, sodium, potassium and strontium were done by atomic absorption spectrophotometry (AAS). Acid digests of the cement powder used to make the specimens were also analyzed by AAS to determine source term concentrations of acid soluble elements.

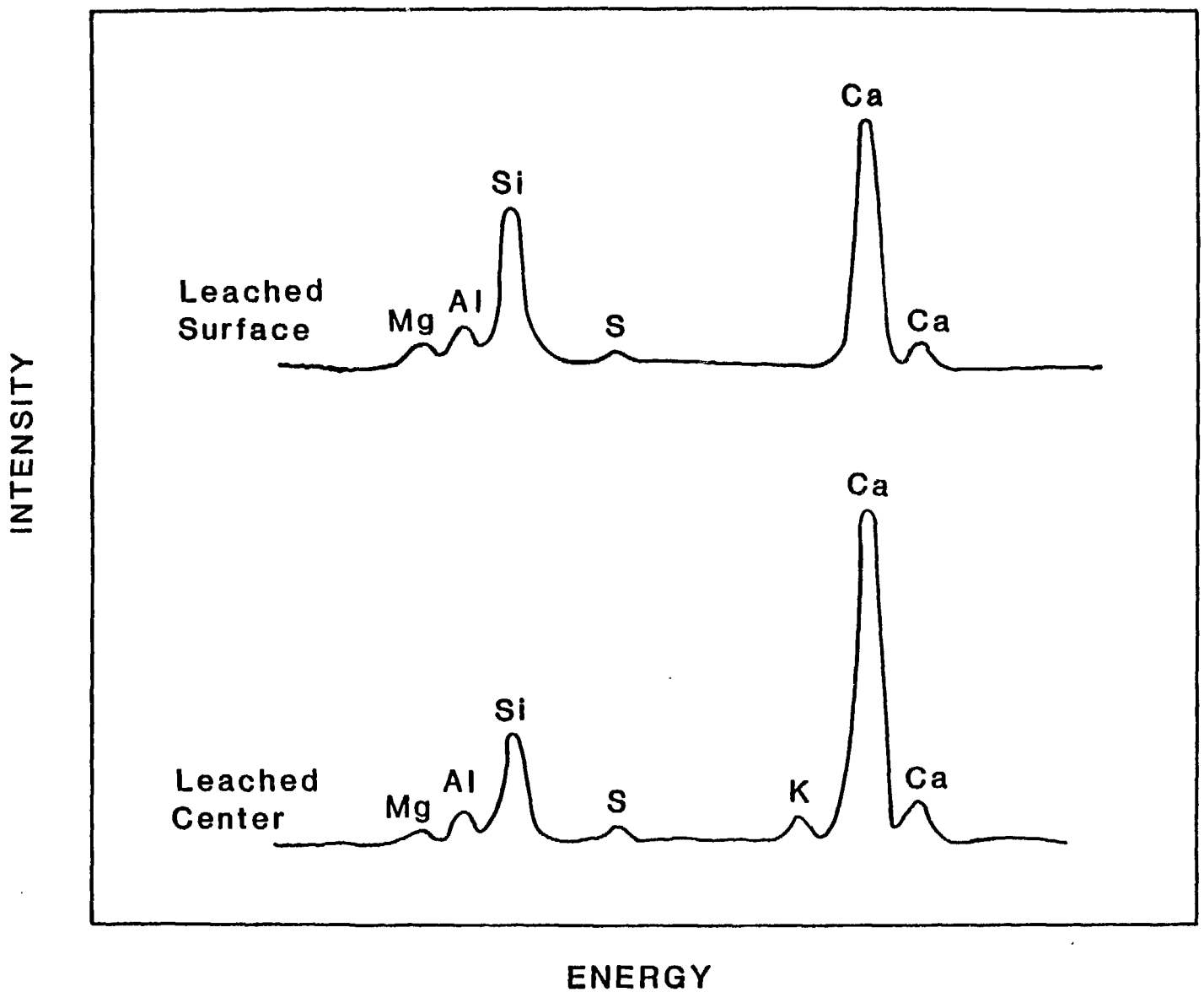
Solid Phase Analysis

Leached and unleached cement samples were analyzed with a scanning electron microscope (SEM) and an energy dispersive x-ray spectrometer (EDS). Samples were sectioned into 1 mm thick slices measuring approximately 5 mm on a side. They were analyzed for the elements Mg, Al, Si, S, K and Ca. Magnesium was not observed in the cement leachate and was assumed to be immobile in cement, therefore, it provided an internal reference to correct for any geometry and detector efficiency changes over time. Consequently, potassium data was presented as the K/Mg ratio. In addition, one of the cement samples was reanalyzed periodically to check for consistency and reproducibility of results.

RESULTS

Solid Phase Analysis

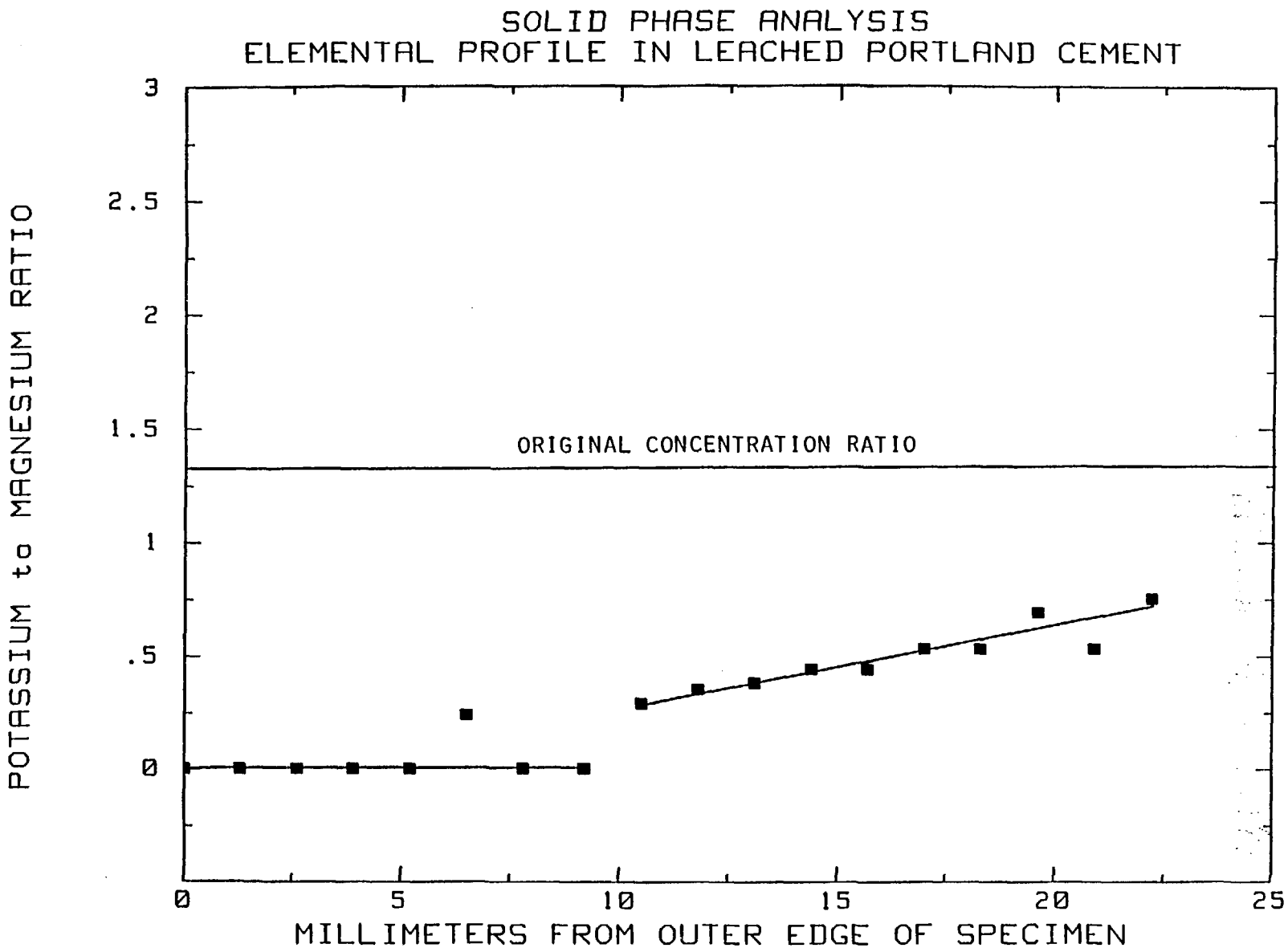
Solid phase analysis by SEM/EDS was initiated to observe physical and chemical changes in specimens that may have developed as leaching progressed. Elemental profiles within the solid specimen were of particular interest. In the original survey, to determine the feasibility of detecting significant changes in elemental profiles, an EDS spectrum was obtained from the center of a leached sample. This spectrum is shown in Figure 1. Magnesium, aluminum, silicon, sulfur, potassium and calcium were detected. Another spectrum was obtained for the surface of the same leached specimen. The greatest change between the two was the absence of potassium from the specimen surface. This observation prompted a more detailed study of potassium profiles in leached cement specimens.


Ca
Si
Leached
Surface
Mg
Al
S
Ca
INTENSITY
Ca
Si
Leached
Center
Mg
Al
S
K
Ca
ENERGY

EDS analysis of sectioned, unleached portland cement samples provided a baseline against which any changes that occurred during leaching could be compared. The average value for the K/Mg ratio was 1.3. There was no observed change in this baseline value with distance into the cylinder for the unleached sample.

Results of the solid phase analysis for a specimen leached for 471 days are shown in Figure 2. The original K/Mg concentration ratio of unleached cement is shown as a line at 1.3. After leaching for 471 days the sample was completely depleted in potassium to a depth of 9 mm. From 9 mm to the center of the specimen the K/Mg ratio increased to a value that was approximately one half of the original concentration ratio. This increase appeared to be linear with distance. Comparing the area under the original concentration ratio line and the area under the sample profile indicates that 18% of the potassium that was originally present in the cylinder remained while 82% had leached out.

Examination of the leached surface by SEM showed that it was significantly altered when compared to the surface of an unleached specimen. Figure 3 is a micrograph of the surface after leaching for 471 days. When compared to Figure 4, which is a micrograph of the surface of an unleached specimen, the altered surface is much less porous than the original surface. Visual inspection of the sectioned specimen showed that this altered layer extended approximately 1 mm into the specimen. A sample of the new surficial material was analyzed by x-ray diffraction to determine its mineralogical composition. The resulting diffractogram is shown in Figure 5. The leached surface consisted of calcite ($CaCO_3$) and vaterite (μ-$CaCO_3$). Also shown in Figure 5, to facilitate comparison, is a diffractogram of cement taken from the center of the


SOLID PHASE ANALYSIS
ELEMENTAL PROFILE IN LEACHED PORTLAND CEMENT
POTASSIUM to MAGNESIUM RATIO
3
2.5
2
1.5
1
.5
0
ORIGINAL CONCENTRATION RATIO
0
5
10
15
20
25
MILLIMETERS FROM OUTER EDGE OF SPECIMEN

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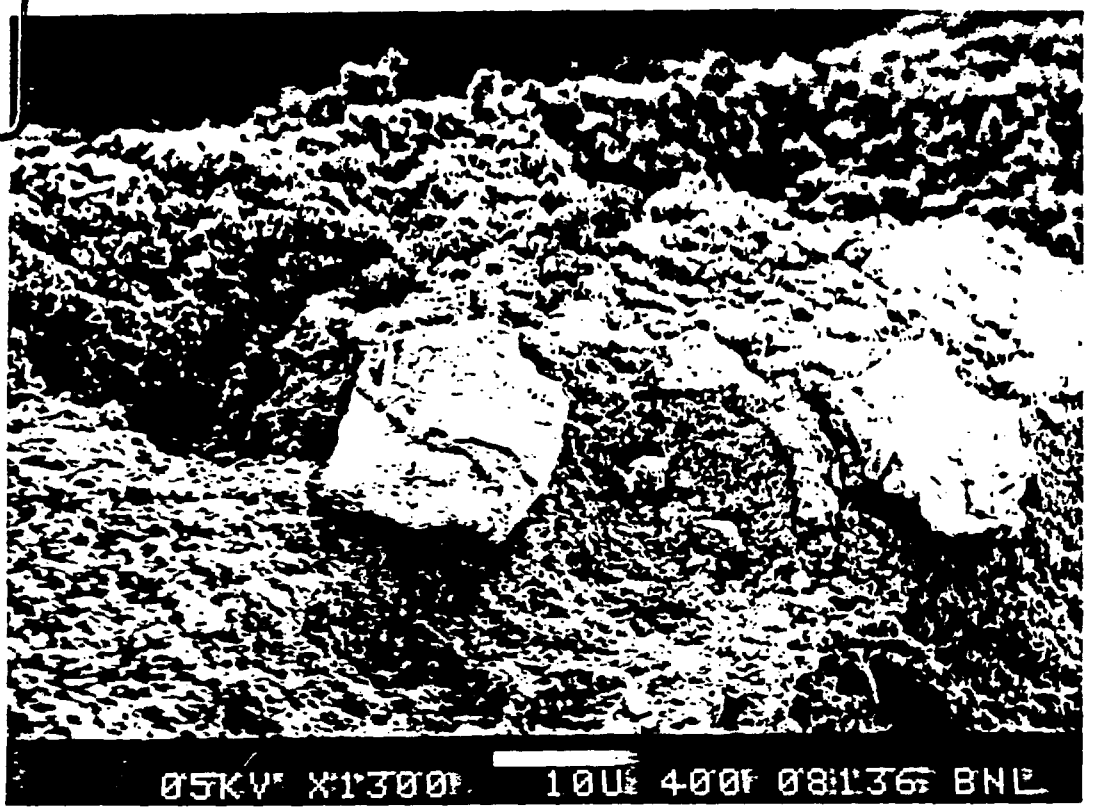
AVAILABLE COPY



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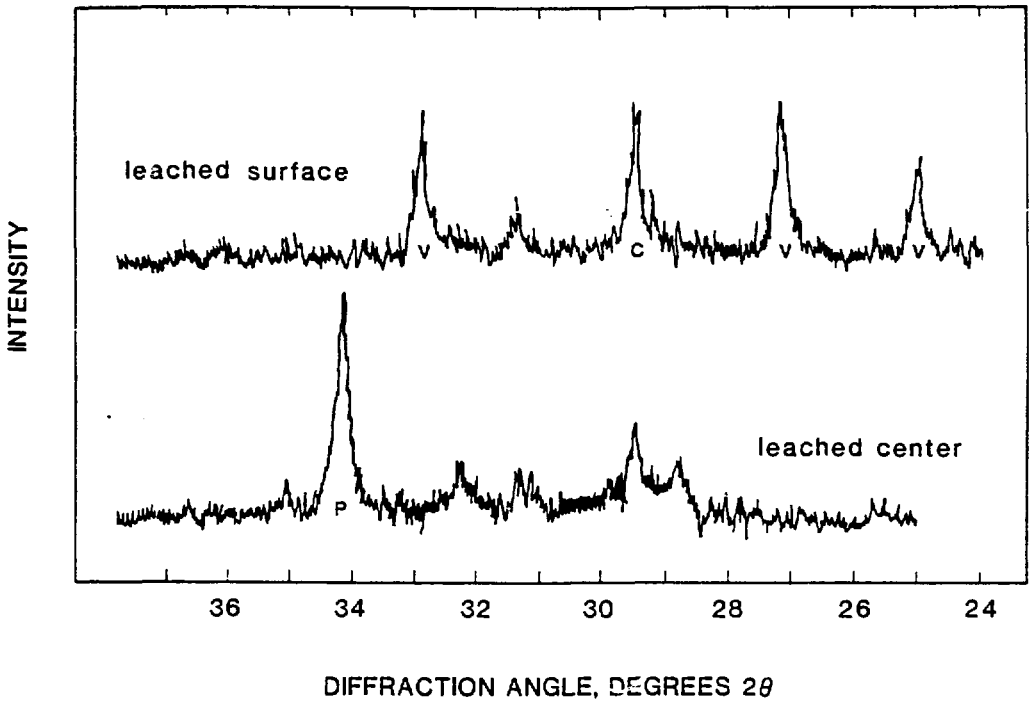
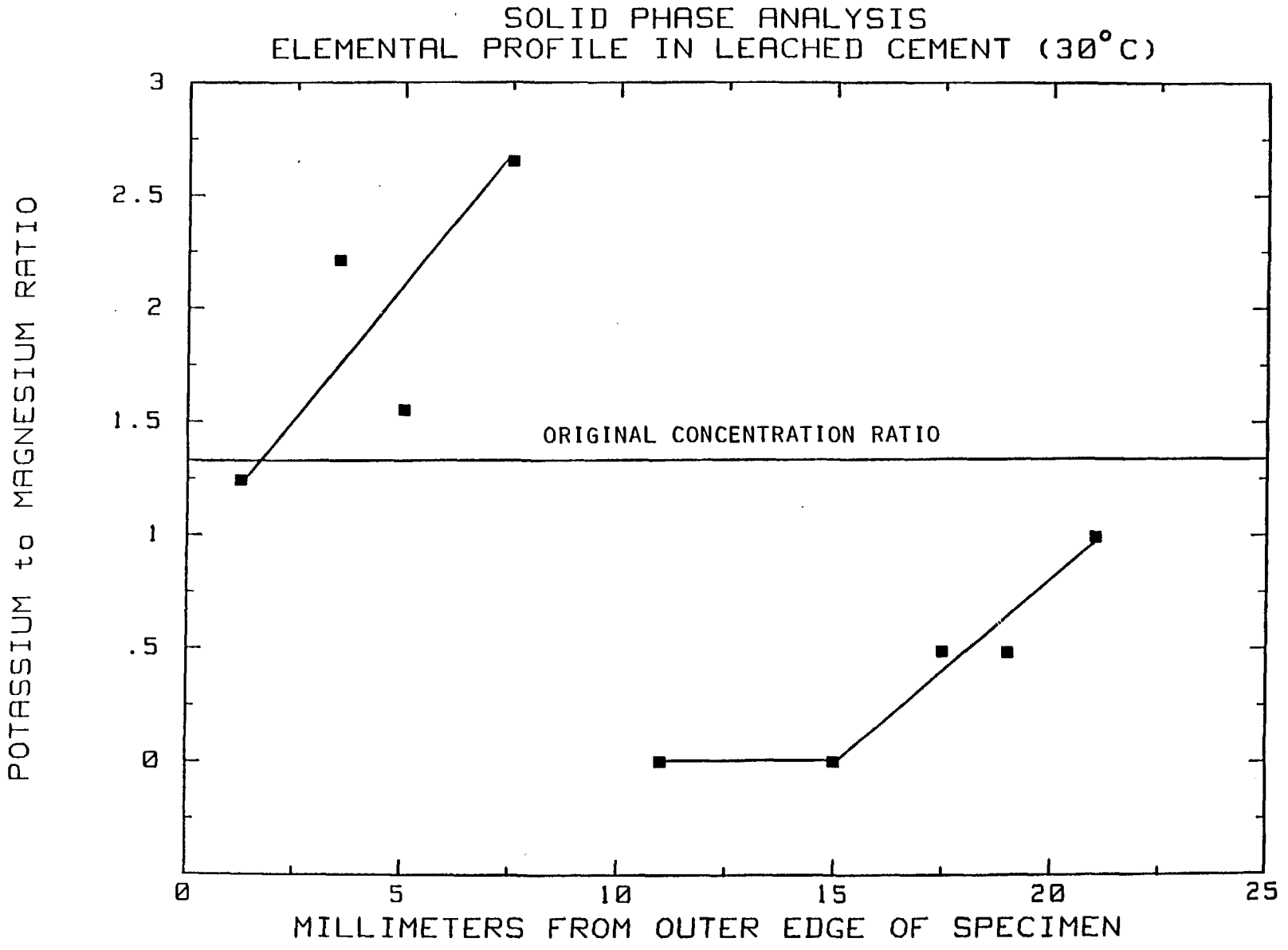

leached surface
v
c
v
v
leached center
p
INTENSITY
36
34
32
30
28
26
24
DIFFRACTION ANGLE, DEGREES 2θ

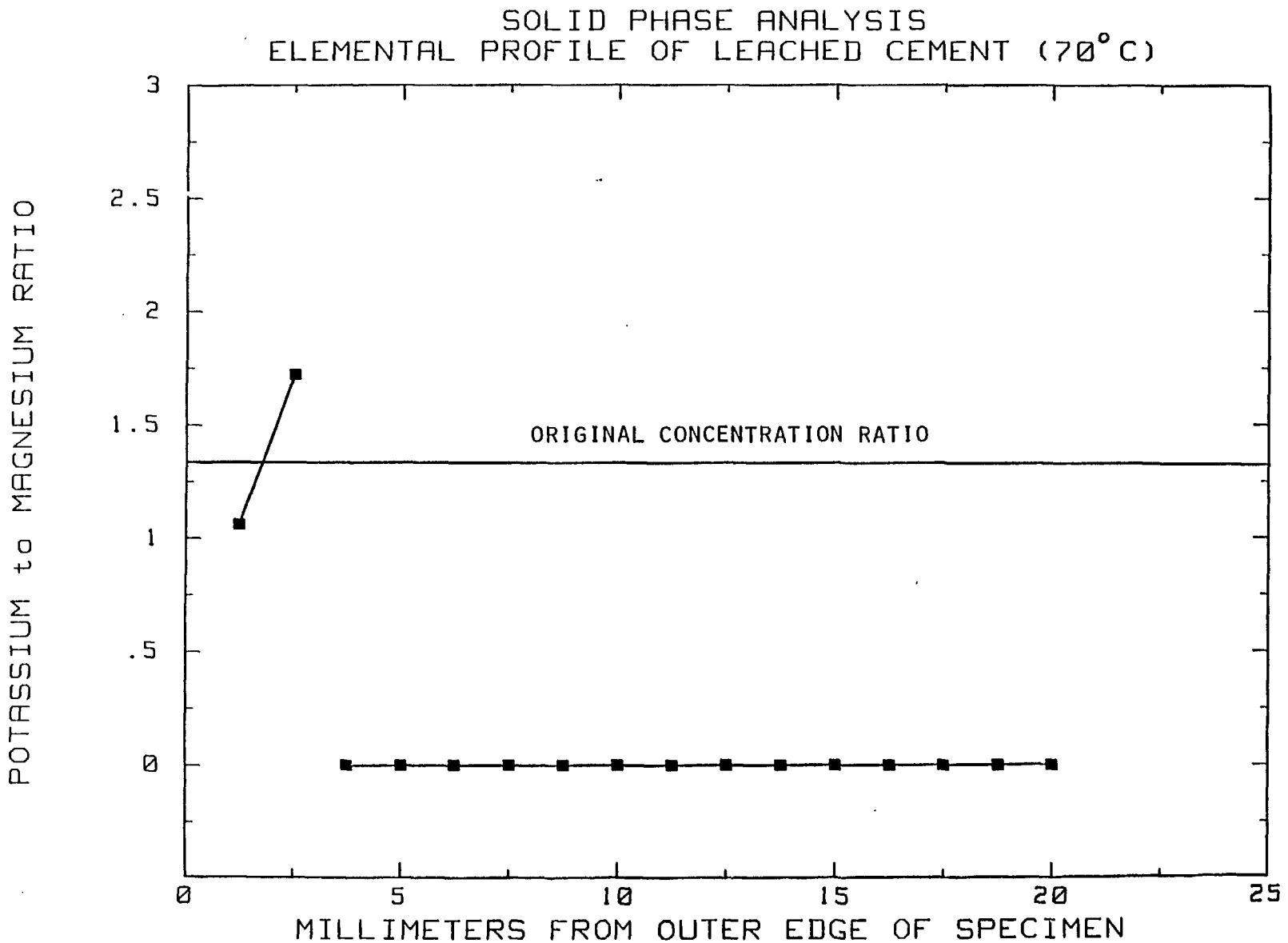
same specimen. Distinct peaks for portlandite ($Ca(OH)_2$), and the broader peaks of the cement hydration products were present. No peaks for calcite or vaterite were observed in the center of the sample.

Other cement cylinders were leached at 30°, 40°, 50° and 70°C for 18 days to determine effects of temperature on leaching. Results of these experiments relative to accelerated leaching are discussed elsewhere [4,5], but for this study the 30°C and 70°C cylinders were sectioned for solid phase analysis. Unlike the long-term test specimen leached at 20°C, these samples were allowed to air dry prior to sectioning.

Figure 6 shows the interior potassium profile for the specimen leached at 30°C. The K/Mg ratio increased dramatically (to double the original concentration ratio) to a depth of 7 mm from the surface of the specimen. Total potassium depletion was observed between 7 and 15 mm. From 15 mm to the center of the specimen the K/Mg ratio increased to a value slightly below the original concentration ratio. The percentage of potassium remaining in this specimen, as calculated from areas under the profile in Figure 6, was 69%; the remainder, 31%, had leached out.

Figure 7 shows the K/Mg ratio profile from the solid phase analysis for a sample leached at 70°C. Most of the potassium has been leached and no potassium was detected at the center of the specimen. However, near the surface potassium was observed to a depth of 3 mm at K/Mg ratios that were similar to the original concentration ratio. The potassium remaining in the solid was calculated from the solid phase analysis to be approximately 15% of the original value, 85% having leached out.


SOLID PHASE ANALYSIS
ELEMENTAL PROFILE IN LEACHED CEMENT (30°C)
POTASSIUM to MAGNESIUM RATIO
3
2.5
2
1.5
1
.5
0
ORIGINAL CONCENTRATION RATIO
0
5
10
15
20
25
MILLIMETERS FROM OUTER EDGE OF SPECIMEN


SOLID PHASE ANALYSIS
ELEMENTAL PROFILE OF LEACHED CEMENT (70°C)
POTASSIUM to MAGNESIUM RATIO
3
2.5
2
1.5
1
.5
0
ORIGINAL CONCENTRATION RATIO
0
5
10
15
20
25
MILLIMETERS FROM OUTER EDGE OF SPECIMEN

All specimens leached at elevated temperatures were observed to have carbonate coatings on their surfaces. These formed much faster than the coatings on specimens leached at 20°C and carbonation was particularly rapid on first exposure to air after removal from the leachate.

Leach Tests

Leachates from all tests were analyzed for calcium, aluminum, silicon, strontium, sodium, potassium, alkalinity and cesium-137. Results are tabulated in References 4 and 5.

DISCUSSION

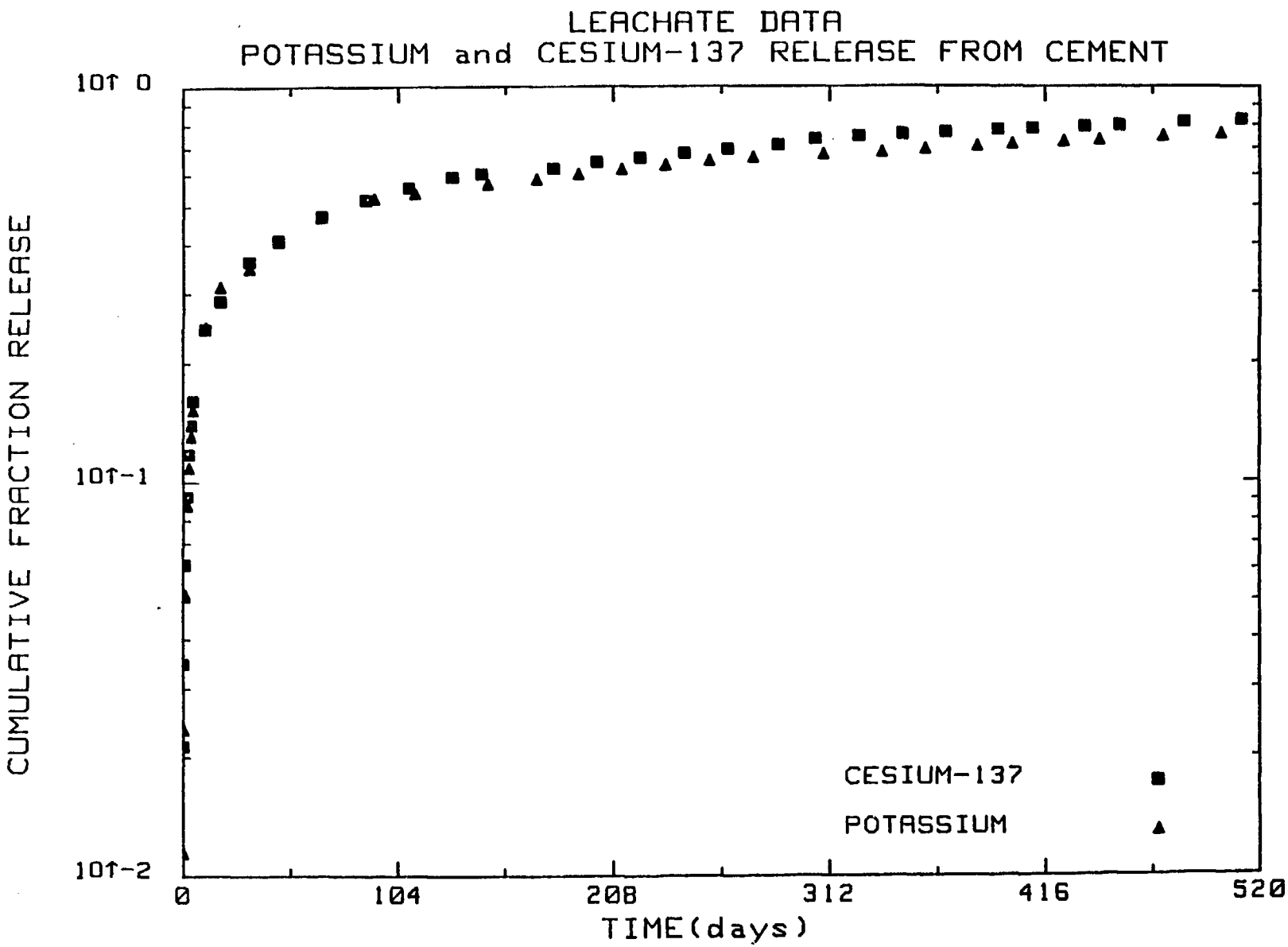
Potassium/Cesium Comparison

Comparisons of releases of the various elements were accomplished using correlation matrices such as the one shown in Table 1 for specimens leached at 70°C. This table gives the correlation coefficient (R) that approaches 1 as the correlation between any two species improves. The correlation coefficient of 0.99 for cesium-137/potassium was particularly high. A similar result was obtained for samples leached at 30°.

This approach was not useful for the long-term leach tests because of differences in sampling intervals between the radioactive and non-radioactive specimens. However, cumulative fraction release data for potassium from the long-term, 20°C leach test are shown on Figure 8. The final cumulative release was 76% of the potassium originally present. Figure 8 also shows a CFR curve for cesium-137 from a replicate specimen leached under identical conditions. Although, for clarity, only one set of cesium-137 data is

TABLE 1--Correlation matrix for portland cement leached at 70°C.

	Aluminum	Silicon	Strontium	Sodium	Potassium	Cs-137	Alkalinity
Calcium	0.77	-	0.94	0.89	0.80	0.81	0.52
Aluminum		-	0.60	0.76	0.77	0.77	0.49
Silicon			-	-	-	-	-
Strontium				0.91	0.80	0.78	0.58
Sodium					0.98	0.97	0.61
Potassium						0.99	0.60
Cs-137							0.59
Sr-85							0.64


LEACHATE DATA
POTASSIUM and CESIUM-137 RELEASE FROM CEMENT
CUMULATIVE FRACTION RELEASE
10↑0
10↑-1
10↑-2
0
104
208
312
416
520
TIME(days)
CESIUM-137
POTASSIUM

plotted, this specimen was one of a set of triplicates leached during this test. The final cesium-137 CFRs were 79.3%, 81.4% and 81.6% (mean = 80.8 ± 2.1 at the 95% confidence interval) after 483 days.

Potassium and cesium-137 releases from the 30°C and 70°C leaching experiments are compared on Figure 9. In the 30°C test, 31% of the potassium was released while a replicate specimen released 32% of its cesium-137. At 70°C, the final cumulative release for potassium was 92% while 86% of the cesium-137 was leached from a replicate.

As shown in Figures 8 and 9 the leaching behavior of potassium and cesium-137 from cement are similar for both long-term, room temperature experiments and for short-term tests at elevated temperatures. Plotting the potassium CFR against that of the cesium-137, as in Figure 10, for the two elevated temperature experiments, illustrates the close correlation. Based on these data, releases of potassium from cement can be used as an analog for cesium-137 leaching releases under a variety of conditions. By extension, the behavior of potassium in the solid phase is also useful as a model for the transport behavior of cesium-137 in the solid.

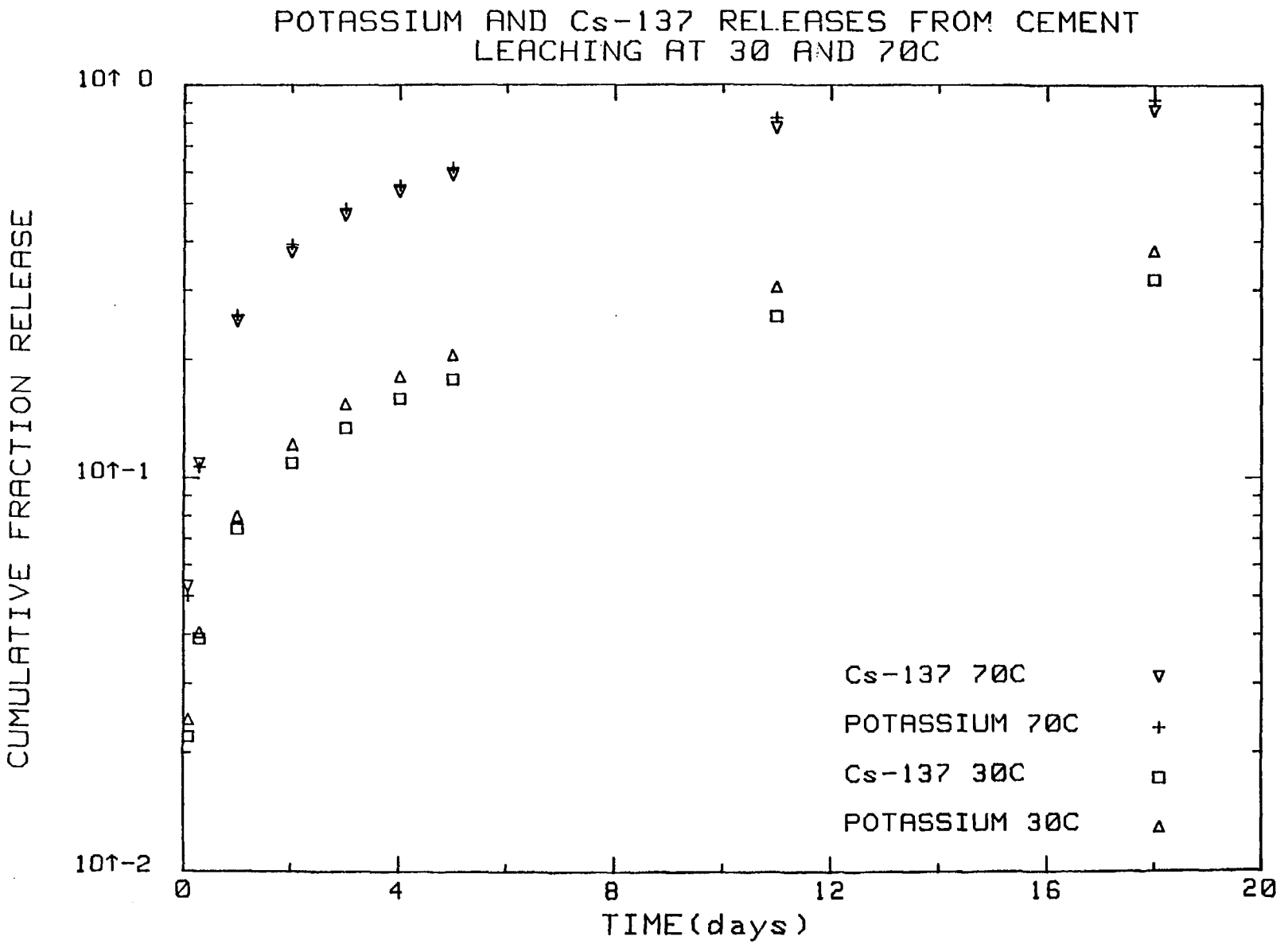
Table 2 summarizes the releases of potassium and cesium-137 during the leach tests as well as potassium releases calculated from the solid phase profiles. Agreement among these data is good, especially considering the different techniques used to obtain the data.

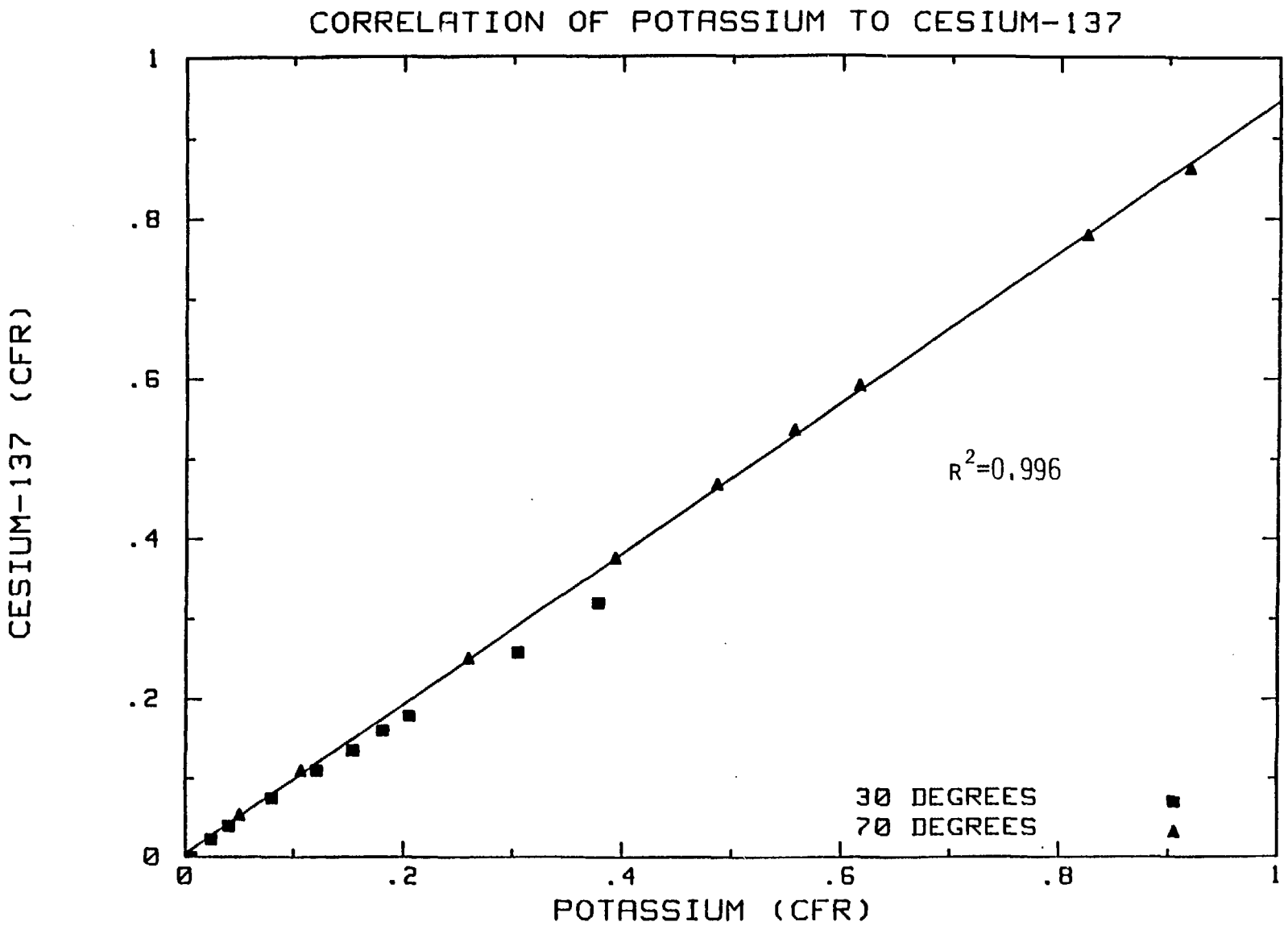
Solid Phase Analysis

Each of the figures showing a profile of the K/Mg ratio represents a snapshot of the potassium concentration gradient within the specimen at the

TABLE 2--Final releases of Cs-137 and potassium as determined by leachate and solid phase analysis.

	Leachate Analysis		Solid Phase Analysis
Sample	Cs-137 Release (%)	Potassium Release (%)	Potassium Release (%)
20°C (471 days)	79, 81, 82	76	82
30°C (18 days)	32	38	31
70°C (18 days)	86	92	85


POTASSIUM AND Cs-137 RELEASES FROM CEMENT
LEACHING AT 30 AND 70C
CUMULATIVE FRACTION RELEASE
10↑ 0
10↑-1
10↑-2
0
4
8
12
16
20
TIME(days)
Cs-137 70C
POTASSIUM 70C
Cs-137 30C
POTASSIUM 30C


CORRELATION OF POTASSIUM TO CESIUM-137
CESIUM-137 (CFR)
POTASSIUM (CFR)
0
.2
.4
.6
.8
1
R²=0.996
30 DEGREES
70 DEGREES

time it was sectioned. The profile shown in Figure 2 represented a time immediately after leaching was stopped. showing the K/Mg ratio after leaching for 471 days at 20°C. Two distinct regions were present. The outer region was characterized by complete depletion of potassium. The inner zone was still undergoing leaching in a way that resulted in a linear increase in potassium to the center of the specimen. If the specimen had not been so depleted, a third region would presumably have been present near the center of the cylinder with a constant ratio characteristic of the original unleached specimen. However, in the specimen analysed, leaching had proceeded to such an extent that the unleached region was no longer present.

The outer edge of this sample was significantly altered by both calcium depletion and carbonation. X-ray diffraction analysis of surficial material showed only peaks for vaterite (μ-$CaCO_3$) and calcite ($CaCO_3$). Another sample taken from the center of the same specimen showed no vaterite or calcite peaks, but did show strong portlandite ($Ca(OH)_2$) peaks as well as broad peaks attributed to cement hydration products. The change observed in the specimen surface is due to loss of $Ca(OH)_2$ and reaction of Ca from the cement with CO_2 from the atmosphere to form $CaCO_3$. This surface carbonation effect is common in cement and has been reported to cause a decrease in permeability [6,7]. The micrographs showing the surfaces of leached and unleached samples confirm that the surface porosity appears to be significantly reduced.

Potassium profiles for specimens leached at 30°C and 70°C, shown in Figures 6 and 7, represent potassium gradients for specimens that had been air dried prior to sectioning. The elevated K/Mg ratios observed several millimeters in from the surface of the specimens was an artifact of drying. As

water evaporated from the surface of the specimen the pore water, carrying dissolved elements with it, was drawn outward. This evaporative transport has been postulated as having significant effects on leaching during wet/dry cycles in disposal environments [8]. Where this efflorescence process became inhibited by the surficial carbonation, which plugged the porosity of the cement, there was a buildup of dissolved species. It is unclear in what form the transported species were contained at this point. However, it has been shown that potassium will coprecipitate with calcite, particularly in the presence of magnesium ions [9]. The observed profiles of potassium in the air dried specimens may therefore be caused by the interaction of calcite precipitation with the outward transport of alkali metals.

CONCLUSIONS AND APPLICATIONS

Potassium has been confirmed as an analog for cesium-137 in leaching studies of cement. Their behavior is similar in both long-term leach tests and short-term tests at elevated temperatures. Elemental concentration profiles of potassium can be observed by EDS in the solid phase of leached cement and these profiles appear to reflect a variety of mass transport phenomena (leaching via diffusion and evaporative transport). There is a quantitative similarity between potassium releases calculated from the solid phase analysis and releases of potassium and cesium-137 observed in the leachates.

Additional work can now be done to determine effects of surficial alteration and longterm aging of cementitious materials on cesium-137 releases. Application of these techniques to other radionuclides will clarify the more complex leaching behavior of other species of concern, including strontium-90 and soluble complexes of cobalt-60.

The approach taken in this paper may have important implications for efforts to determine the long-term durability of concrete barriers for radioactive waste disposal. Potassium has been shown to be an analog for cesium-137 and its behavior in the solid phase readily reflects various transport phenomenon that operate in cement. Therefore, it will be useful to look for solid phase profiles of potassium in old concrete structures. The degree of potassium depletion will be a direct indicator of the mobility of cesium through these materials. By observing this effect in a variety of cementitious materials and in a variety of environments it will be possible to determine what factors influence concrete durability with regard to radionuclide mobility. With this information improved barriers for radioactive waste can be constructed.

ACKNOWLEDGEMENTS

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FIG. 1--Energy dispersive x-ray spectra of samples from the center of a leached cement specimen and from the surface of the same leached specimen. Note the absence of the potassium (K) peak from the surface sample.

FIG. 2--Internal profile of K/Mg in a cement sample leached for 471 days at 20°C in distilled water. From this figure it is estimated that 82% of the potassium had leached out.

FIG. 3--Surface of unleached portland cement at a magnification of 1900 times.

FIG. 4--Outer surface of a cement sample leached for 471 days. Compare this to Figure 3. The texture is smoother and porosity appears much lower.

FIG. 5--X-ray diffractogram for the surface and center of a cement sample leached for 471 days at 20°C in distilled water. Peaks labeled with V are vaterite, C are calcite and P are portlandite. Most other peaks in the diffractrogram from the center of the specimen are cement hydration products.

FIG. 6--Internal K/Mg profile in a cement sample leached for 18 days at 30°C. As calculated from this figure 31% of the potassium had leached out.

FIG. 7--Internal K/Mg profile in a cement sample leached for 18 days at 70°C. As calculated from this figure 85% of the potassium had leached out.

FIG. 8--Potassium and cesium-137 cumulative fraction releases for the long-term leach test.

FIG. 9--Cumulative fraction releases of potassium and cesium-137 from specimens leached at 30°C and 70°C.

FIG. 10--Cumulative fraction release of potassium plotted against CFR of cesium-137 for samples leached at 30°C and 70°C.