# Permeable Environmental Leaching Capsules (PELCAPs) for Nondestructive *In Situ* Quantification of Contaminant Immobilization

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## Abstract

Remediation strategies for in situ immobilization of contaminants in soil and sediments need to demonstrate both (1) an increased contaminant immobilization in some insoluble phase such as a stable mineral and (2) evidence for the permanence of that immobilized contaminant phase under the prevailing geochemical conditions after intentional manipulation (i.e., site management) can no longer be maintained. Relatively little attention has been paid to the latter criterion owing, in part, to the technical difficulty and expense of collecting the large number of soil samples needed, both spatially and temporally, to decipher statistically significant effects in a heterogeneous soil/sediment environment. A nondestructive assay technique is being developed, using permeable environmental leaching capsules (PELCAPs) containing soil with short-lived radioactive tracers for priority contaminants (e.g., Cs, Sr, U, Tc, Pb, As, Cr, and Cd). The PELCAPs will be repeatedly retrieved and replaced for time-series evaluation of each contaminant's long-term behavior under field situations. Such gel-contained soils represent a unique opportunity to nondestructively assay the same soil or sediment samples, containing an immobilized contaminant phase, over and over again while allowing them to weather in situ under ambient physiochemical conditions. Thus, the heterogeneity of soil sampling in the field can be largely overcome and accurate measurements of small changes in a large amount of immobilized contaminant can be observed which otherwise would be completely obscured by sample variation. Many promising techniques for the *in situ* immobilization of priority pollutants in soils and sediments have been and continue to be developed. Nevertheless, the comparative evaluation of immobilization strategies at several sites or over a range of conditions remains extremely costly and difficult to demonstrate in the field. The primary reason for these costs is the requirement for repeated soil and groundwater sampling and the associated destructive analysis of those samples. PELCAPs can help to reduce these costs.

## Background

One of the most challenging problems for the advocates of contaminant immobilization in soil is to assess and evaluate the long-term availability of the target contaminant. A number of remedial strategies have shown great promise in the laboratory and/or in pilot-scale field tests. Nevertheless, in the case of contaminant immobilization, it is neither conclusive nor sufficient to simply measure decreases in soluble (mobile) contaminant in groundwater monitoring wells. One must also measure the concomitant increases in the immobilized contaminant phases as well as their long-term stability. Major factors that contribute to the difficulty of the assessment of contaminant immobilization in the field include: (i) virtually none of the usual soil and aquifer sampling approaches are truly nondestructive, (ii) expensive and statistically complicated sampling designs are required to distinguish treatment effects from normal background spatial and temporal variability, and (iii) repeated sampling at the same or nearby locations will likely introduce artifacts (e.g., changes to groundwater flow patterns) that are difficult and expensive to

evaluate in the field. The scientific and technical challenges for understanding and measuring contaminant availability in soils have been identified as a compelling national need for all environmental remediation. Laboratory measurements, such as sequential extraction and isotopic dilution discussed below, can provide good evidence for the amount of immobilized contaminant in a soil sample. However, the only unambiguous and straightforward method to assess the permanence or long-term effectiveness of contaminant immobilization is to obtain actual field performance information. Field information is usually gained through intensive sampling at some "pilot-scale" demonstration at a representative field site. Field performance information typically consists of a large data set of contaminant(s) and groundwater characteristics based on analyses of many samples from groundwater monitoring wells over many years. The process is time-consuming, expensive, and difficult to assess, particularly if it is desired to compare several promising remedial alternatives before deciding which to implement as a preferred alternative. The field-scale performance information (dissolved groundwater contaminant concentrations as a function of time within the three-dimensional geologic setting) must be condensed into a more manageable time- and expense-frame from which the regulatory and stakeholder community can make extrapolations into future time and space with some assurance and/or acceptance.

Measurements of changes in the amount of "immobile" contaminant within soil, resulting from a chemical or microbial treatment, will be of more value for assessing long-term performance than measurement of either soluble or total contaminant concentrations because continued contaminant recharge may mask any changes either in total contaminant in the soil or in concentrations of dissolved contaminant in the groundwater. Selective sequential extraction of soils and isotopic dilution methods have become much more widely practiced and appreciated; sequential extraction can be quite informative by separating total contaminant into operationally defined "labile" and "immobile" species. Distinguishing between labile and immobile species has great value in assessing the quality and persistence of immobilized contaminant phases. As excellent as both selective extraction and isotopic dilution methods are in assessing immobilized contaminant phases, they are inherently neither nondestructive nor *in situ*. Field sampling of soil to measure its immobilized contaminant levels by either method is difficult to evaluate because of the inherent destructive nature of soil sampling and costly because of the large number of samples required to observe statistically significant differences between sampling times and/or treatment locations.

Our concept to monitor contaminant behavior using replaceable radioisotope-spiked soil contained in PELCAPs at field sites (Fig 1) offers potential advantages for assessment of contaminant immobilization strategies including:

- Nondestructive measurement of the amount of immobilized contaminant in a soil thereby avoiding the necessity for repeated, costly, and destructive soil sampling.
- Direct comparison of several immobilization treatments, including a no-treatment control, under identical field conditions within the same well.
- Internal PELCAP leaching calibration relative to specific reference tracers ($^{85}Sr$ and $^{134}Cs$) that have predictable known environmental leaching behaviors.
- Accelerated treatment evaluations by deploying PELCAPs in uncontaminated regions of a site to avoid masking by continued contaminant releases.

- The immobilized contaminant is monitored directly in the soil via a gamma-emitting radioisotope tracer.
- Correlation of PELCAP behavior with accepted selective extraction and isotopic dilution protocols can be established under a variety of groundwater conditions.
- Demonstration of immobilized contaminant behavior in soil, supporting priority contaminants, in laboratory and field environments.

## Progress to Date

For this proof-of-principle work, we have focused on some of the basic characteristics of the PELCAPs using $^{85}Sr$ and $^{134}Cs$ as short-lived surrogates ($t_{1/2}$ $^{85}Sr$ = 64 d; $t_{1/2}$ $^{134}Cs$ = 2.05 y) for the environmentally-important $^{90}Sr$ and $^{137}Cs$ ($t_{1/2}$ $^{90}Sr$ = 28.1 y; $t_{1/2}$ $^{137}Cs$ = 30.23 y). Our first PELCAPs (Fig. 2) were prepared with polyacrylamide gel; although we have refined the technique since these were made, the picture gives an idea of the size and shape of the capsules. These two radioisotopes will be used to represent end members in a broad spectrum of radionuclide retention behaviors. PELCAPs will be spiked with $^{134}Cs$, which would be fixed in the interlayer of clay minerals and unavailable for exchange. Retention of this radionuclide will be interpreted as evidence for the physical integrity of the gels because any loss of Cs could only result from the removal of soil particles. Other non-destructive techniques for assessing soil particle retention (e.g., mass balance by weighing) do not have the necessary sensitivity. To represent a relatively "available" end-member contaminant type, PELCAPs will also be spiked with $^{85}Sr$. Adsorbed or available $^{85}Sr$ is readily exchanged with other dissolved cations in groundwater (e.g., stable Sr, Ca, Mg); its leaching rate from the soil is relatively rapid; its chemical behavior in soil is well understood; and Sr migration in soil has been quantitatively modeled (JACKSON and INCH, 1983; SPALDING and SPALDING, 2001). The kinetics of the disappearance of $^{85}Sr$ from PELCAPs will serve both to verify and to quantify the effective degree of groundwater leaching the PELCAP has experienced.

Evaluation of polyacrylamide-contaminant chemical interactions/ free diffusion of solute. The PELCAP gel formation process (free-radical polymerization) must be demonstrated to exert little reactivity with or other effects on the solubility of the radionuclides ($^{85}Sr$ and $^{134}Cs$). To date, we have demonstrated that the gel formation process does not affect the solubility or speciation of Sr or Cs. PELCAPs were formed in the presence of $^{85}Sr$ and $^{134}Cs$ but without soil. They were subsequently leached using a $CaCl_2$ solution as a simple groundwater simulant. Both radioisotopes were readily removed from the gels demonstrating that (i) the gels allow free diffusion of these solutes and (ii) that the gel formation reaction does not retard their movement (Fig 3). In addition, a diffusion based leaching model described the data well with apparent diffusion coefficients within the expected range of values.

Evaluation of physical stability and resistance to microbial/chemical degradation. The optimal PELCAP polyacrylamide material will also need to be non-biodegradable, at least over a several month period, an anticipated interval for their deployment in field groundwater or soil. Criteria for this evaluation will include the maintenance of (a) the physical integrity of PELCAPs, (b) soil particle retention within the gel, and (c) continued inertness to contaminant adsorptive interaction. Soil particles have been labeled with $^{134}Cs$, a strongly and specifically adsorbing radionuclide which is fixed in the interlayer sites of clay minerals in a non-

exchangeable form (ABSALOM et al., 1999; COMANS et al., 1991; COMANS and HOCKLEY, 1992). The $^{134}$Cs-spiked soil, encapsulated in PELCAPs, is being continuously leached with simulated groundwater. Control treatments include $^{134}$Cs spiked soils without encapsulation in the PELCAP material. The loss of any $^{134}$Cs from the spiked soil PELCAPs can be interpreted as physical transport of soil particles from the gels. However, retention of radiolabeled soil particles during continuous leaching would be interpreted as evidence of stable gel pore structure and, thus, maintenance of physical integrity of the encapsulating gel.

Correlation of PELCAP behavior with selective extraction protocol. PELCAPs spiked with radioisotopes, both with and without soil are being subjected to a sequential extraction protocol. Isotope release from these is being compared to their release from the same soils that are not encapsulated in polyacrylamide. Initial results are very promising, and provide good evidence of the physical and chemical robustness of the cylinders.

Field-deployed PELCAPs! We have begun testing the PELCAPs with actual field deployment in a stream and, after much negotiation by Brian Spalding, in the Core Hole 8 sump on the Oak Ridge reservation. In keeping with the conceptual scheme, the cylinders (in a freely permeable protective case) (Fig 4, Fig 5) are periodically retrieved, assayed, and re-deployed giving us time-series information on radioisotope behavior under representative field conditions. Initial results have been extremely encouraging.

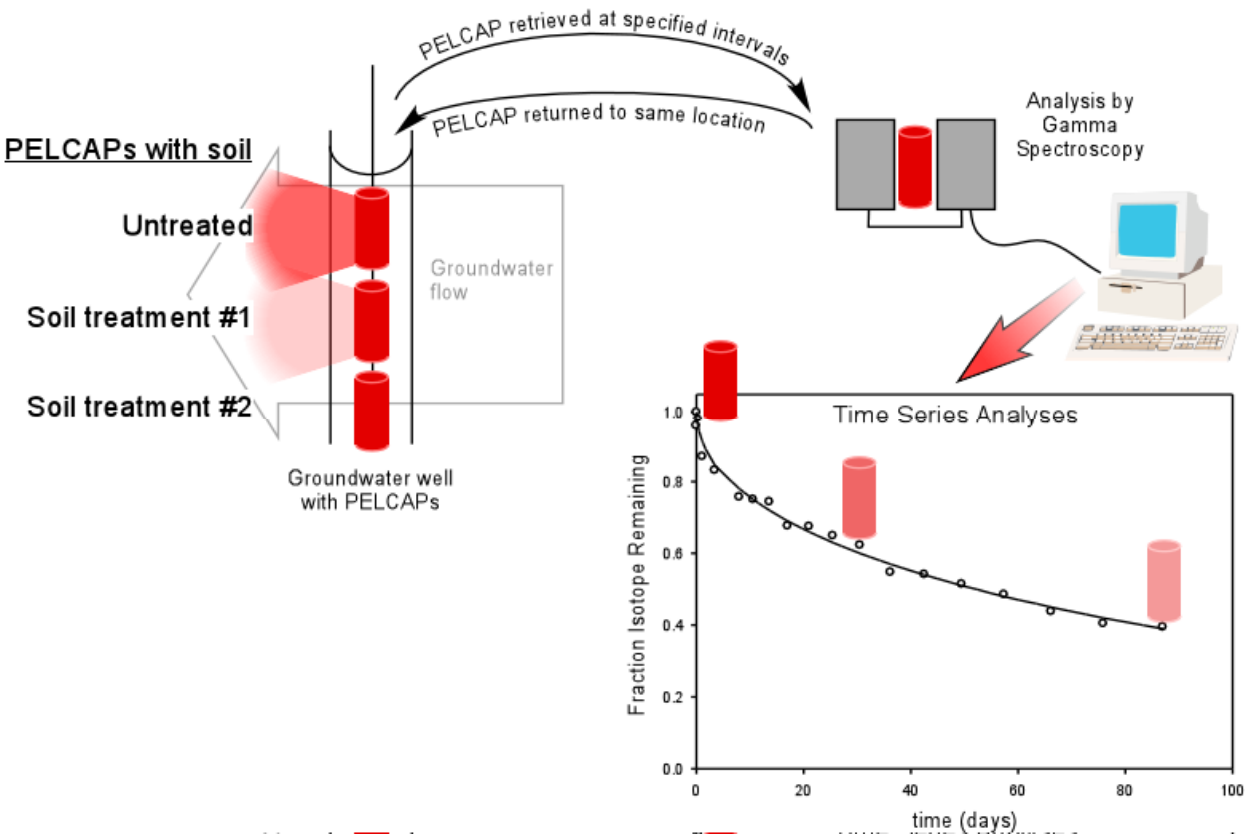


**Figure 1** Conceptual scheme for assessment of contaminant immobilization *in situ* using spiked soil within permeable environmental leaching capsules (PELCAPs).


**Figure 2** Our first PELCAPs prepared from polyacrylamide. The PELCAP on the left contains soil, the one pictured on the left is plain polyacrylamide gel. Although we have refined the preparation technique, the picture provides a representative scale and geometry of the field-deployed PELCAPs.

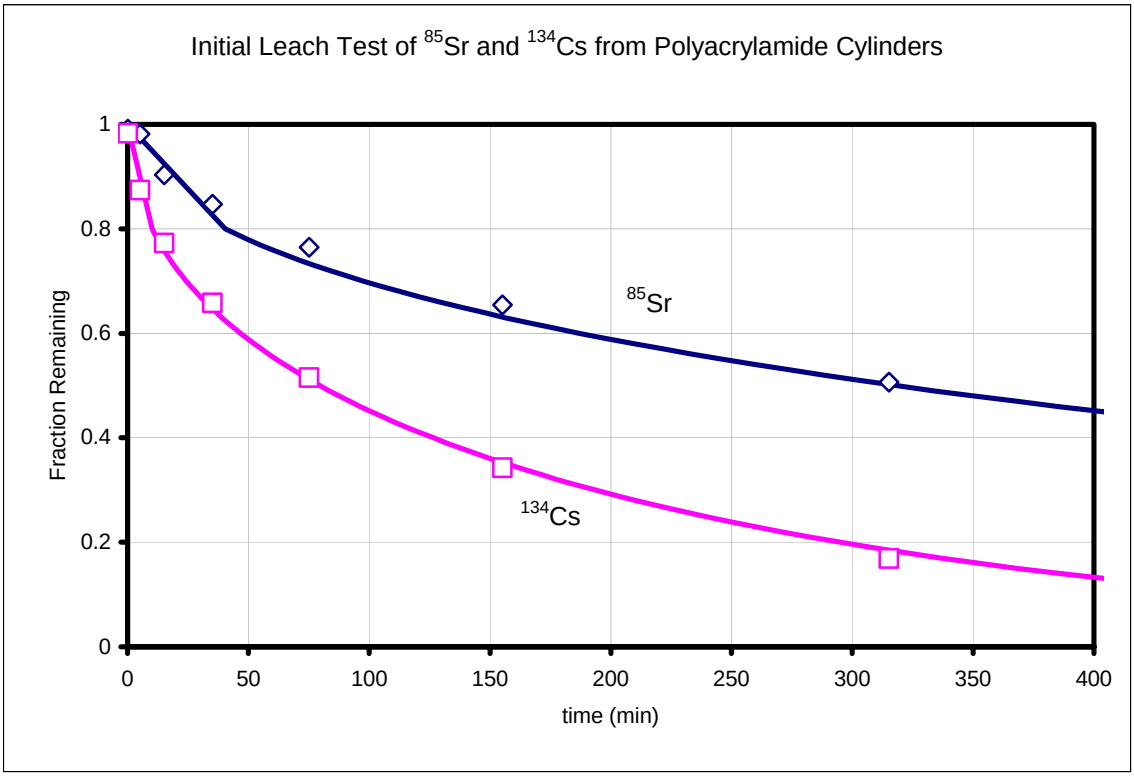


**Figure 3** Initial leach test (first ~5 h data shown) of $^{85}Sr$ (∀) and $^{134}Cs$ (9) from polyacrylamide cylinders. Complete recovery of these isotopes was achieved within ~ 1day. Data are well described by a diffusion model with apparent diffusion coeffients for Sr = $3.6 \times 10^{-6}$ $cm^2/s$ and for Cs = $1 \times 10^{-5}$ $cm^2/s$. Tracer diffusion coefficients for these ions at infinite dilution in water: Sr = $8 \times 10^{-6}$ $cm^2/s$; Cs = $2 \times 10^{-5}$ $cm^2/s$;. Considering path tortuosity within the gels, the apparent diffusion coefficients are in excellent agreement with the expected range of values demonstrating that (i) the gels allow free diffusion of these solutes, and (ii) that the gel formation reaction does not retard their movement.

**Figure 4** PELCAPs being readied for deployment into the Core Hole 8 sump. The perforated plastic vials allow free movement of water around the PELCAPs contained within.

**Figure 5** PELCAPs deployed in Core Hole 8 sump. This cistern collects contaminated water and directs it to an on-site treatment plant. In conjunction with periodic PELCAP retrieval we are collecting groundwater chemical characterization data.