Investigating the Depth of Penetration of Radionuclides in Concrete – 16292

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ABSTRACT

This paper focuses on some chemical and structural aspects for mature concrete structural substrate that functions as a barrier to radioactive material migration. Exposure to radioactive material may be a consequence of surface contact, such as resulting from exposure by spills or leaks. In properly-prepared waste storage areas, undamaged paint and sealant helps to protect the structural cement. However, damaged surfaces, cracks, and relatively porous slab seams can offer a preferred migration pathway for spilled contaminates, including radionuclides.

The cost of remediation of concrete structures is directly related to the amount of concrete that must be removed and subsequently disposed. A carefully implemented investigative plan can be utilized to determine how much concrete must be removed and the approximate level of volumetric radiological contamination can be used to estimate disposal costs.

Normal concrete pore solution is saturated with calcium hydroxide and also contains sodium and potassium hydroxide; the pH is typically 13 to 14. Contaminants (such as uranium) that hydrolyze in alkaline media that form precipitant phases and tend to deposit at the near-surface. However, more soluble contaminants, such as Cs-137 (as Cs^+) and Tc-99 (as the pertechnetate anion TcO_4^-) diffuse more rapidly (and deeply) into the porous substrate. Profiling the migration of the water-soluble radionuclides into a cure (hardened) cement surface is a challenge, since water-cooled saws, borers and similar implements are often used to excise and/or slice the core. Alternately, dry mechanical fracturing for excavation of cement may introduce the possibility of material cross-contamination and uncertainty for the average sampling depth for the sample collection event, potentially yielding non-representative samples [1], and may preclude determination of crack formation that may have been present in the native (nonfractured) substrate.

Structural concrete is comprised of cement and pozzolan paste, relatively impervious aggregate (typically stone and/or sand), and rebar (iron reinforcement). Near-surface aggregate may act as a hydrolytic barrier, causing contaminants leached into the porewater to by-pass the impervious grains, causing deeper-than expected penetration, especially if there are grain boundary cracks also present to facilitate migration.

INTRODUCTION

Cementitious stabilization/solidification (S/S) is one of the most widely used techniques for the treatment for ultimate disposal of hazardous, low-level radioctive and mixed wastes [2, 3, 4, 5]. From such waste treatment investigations, we learn that ions can slowly leach from the microporous cement host to differing degrees; many chemical species such as uranium and transition metals tend to hydrolyze and precipitate in the cement past pore water (typically pH > 12), often subsequently forming alteration phases (such as insoluble silicates) in the maturing grout that may have further diminished mobility or leaching potential. However, some species of concern, such as the high-yield nuclear fission products Tc-99 (which forms the pertechnetate anion, TcO_4^-) and Cs-137, do not hydrolyze and thus remain relatively mobile in the microporous cement host unless certain select reagents or sequestering agents (such as blast furnace slag for enhanced Tc-99 retention) are added to the cement paste blend formulation [6].

In addition to waste treatment applications, conventional high strength construction-grade concrete (formed from hydraulic cement blend, water, and aggregate) is used in facilities that handle radiological and/or hazardous materials to form structural elements (such as flooring and load support), construction of waste storage tanks and containment casks, and it may also be used as a containment barrier or backfill material to entomb/encase and thus isolate contaminated objects or contained waste packages form the environment. The cement host in all of these applications can become contaminated upon exposure to radionuclides from spills or surface contact with wet waste. Cementitious materials, as used for these latter applications, will be emphasized in this paper.

CONCRETE AS CONTAINMENT BARRIER

Investigators at the Pacific Northwest National Laboratory (PNNL) have conducted a long-term investigation on the migration rates of radionuclides from soil, sediments and sludge into a specified concrete composition designed for encasement of buried waste.[1] A laboratory-scale approximation of this concrete is prepared from sulfate-resistant Type I/II Portland cement, fly ash, aggregate (fine sand), and steel fiber shards (the latter used to assess the effects of groundwater and waste intrusion upon rebar reinforcement that would be deployed at full scale); see the recent summary for long-term performance assessment of migration potential for select radionuclides from contaminated sediment into small cement test cylinders; [7]. The test pieces were generally a so-called half-cell specimen, for which wet authentic or simulated waste was placed over pre-formed concrete cylinder, with contact exposures that were extended over long times (often years).

Recently, MCLinc was asked to perform limited concrete petrology and to use the analytical technique of Scanning Electron Microscopy (SEM) with ancillary Energy-Dispersive X-ray Spectroscopy (EDS) to help assess the migration of uranium (from a simulated caustic sludge) into cast cylinders of cured laboratory-scale grout. In addition to achieving a high magnification (up to 200,000-X and greater) with great depth of field, SEM imaging techniques include the ability to measure the intensities of back-scattered electrons (BE), which are much greater for materials containing heavy metals (such as uranium) than for lighter elements (such as the oxygen, silicon, and calcium that are predominant in the cement host composition). Impinging the surface of a material with electrons also stimulates atoms in the selected field of view to emit characteristic X-ray fluorescence, which identifies the specific elements that are

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[1] "Specification for Concrete Encasement for Contact-Handled Category 3 Waste." 1998. *Proceedings of Waste Management*.

present at trace to major concentration levels. Ancillary computer software can also present the characteristic X-ray emission intensity distribution for selected elements in a two-dimensional array.

Figure 1 illustrates SEM-EDS results for a specimen that had been exposed to simulated caustic sludge, containing uranium and technetium-99 (Tc-99). The mass quantities of traced Tc-99 (specific activity 0.017 Ci/g) were too low to detect by the SEM-EDS. Figure 1A is a low-magnification (100-X) BE image of a polished cross-section of exposed cement (the exposed surface appears on the right hand side of the image as presented here). The bright contrast area (indicative of heavier average atomic composition) extends to a maximum depth of only about 150-µm (0.06-in.) into the exposed surface. Figure 1B is an X-ray fluorescence map, selectively indicating the distribution of uranium; the BE image and the intensity distribution for uranium closely correspond for this specimen. Similar X-ray maps for silicon and oxygen confirm that the uranium contamination migrates around the impervious silica (SiO_2) aggregate grains (which appear as brick-like structures in Figure 1A. The apparent reduced migration rate for uranium when exposed to a concrete surface is consistent with the relatively low leachability observed for uranium purposely admixed with cemetitious material for the purpose of waste treatment.

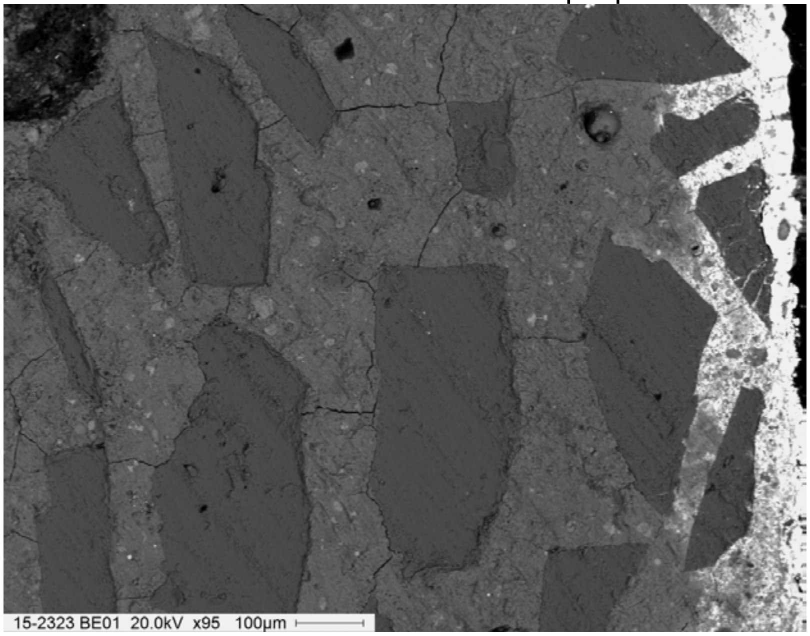

Figure 1 A. Back-scattered Electron Image of a Concrete Test Specimen Exposed to Uranium-traced Sludge Surrogate.

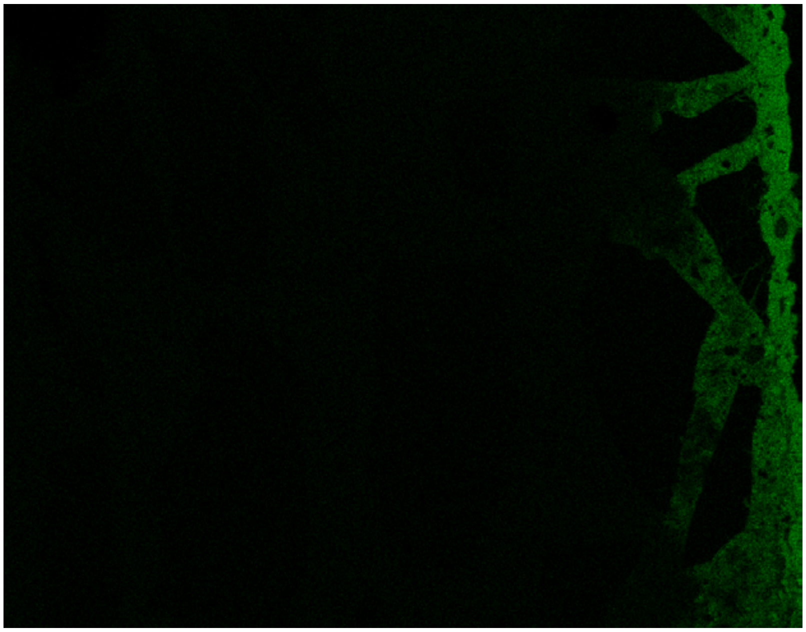

Figure 1B. Characteristic X-ray map for the distribution of uranium (same field of view as in Figure 1A). (Uranium characteristic X-ray fluorescence intensity (count rate) is represented in faux-green color).

We attempted to determine the specific uranium phase(s) by the technique of X-ray diffraction, which aids in the identification of crystalline phases. Because the uranium "stain" was very superficial, we took limited amounts of material from the exposed surface and also from the bottom portion of the test specimen (i.e., an area not affected by the uranium). Persistent crystalline and semi-crystalline phases that typically appear in mature cement grout include silica (from cement and aggregate, and calcite ($CaCO_3$)); poorly-crystalline phases, such as metastable calcium silicate hydrogel (C-S-H) contribute to an amorphous "hump" in the diffraction pattern [8]. The exposed material was analyzed as a control to help identify unique phases that were produced by the uranium exposure (Figure 2). There were two strong reflections that were unique to the upper surface of the specimen; these peaks occurred at 48.7 and 74.9 degrees 2Θ**.** A comparison of these peaks to International Centre for Diffraction Data (ICDD) reference database suggests a match to two of the peaks for the compound soddyite ($(UO_2)_2SiO_4 \cdot 2H_2O$). The unique diffraction peaks in the uranium-impacted specimen (Figure 2) are tentatively assigned to the mineral soddyite, an uranium silicate phase. This is a tentative identification, since several of the confirming peaks were not identified, possibly because they were obscured by the relatively intense features of the amorphous quartz and calcite phases. Soddyite is a plausible alteration phase for poorly-soluble uranate (from alkaline waste) seeping into silica-rich cement porewater [9, 10]).

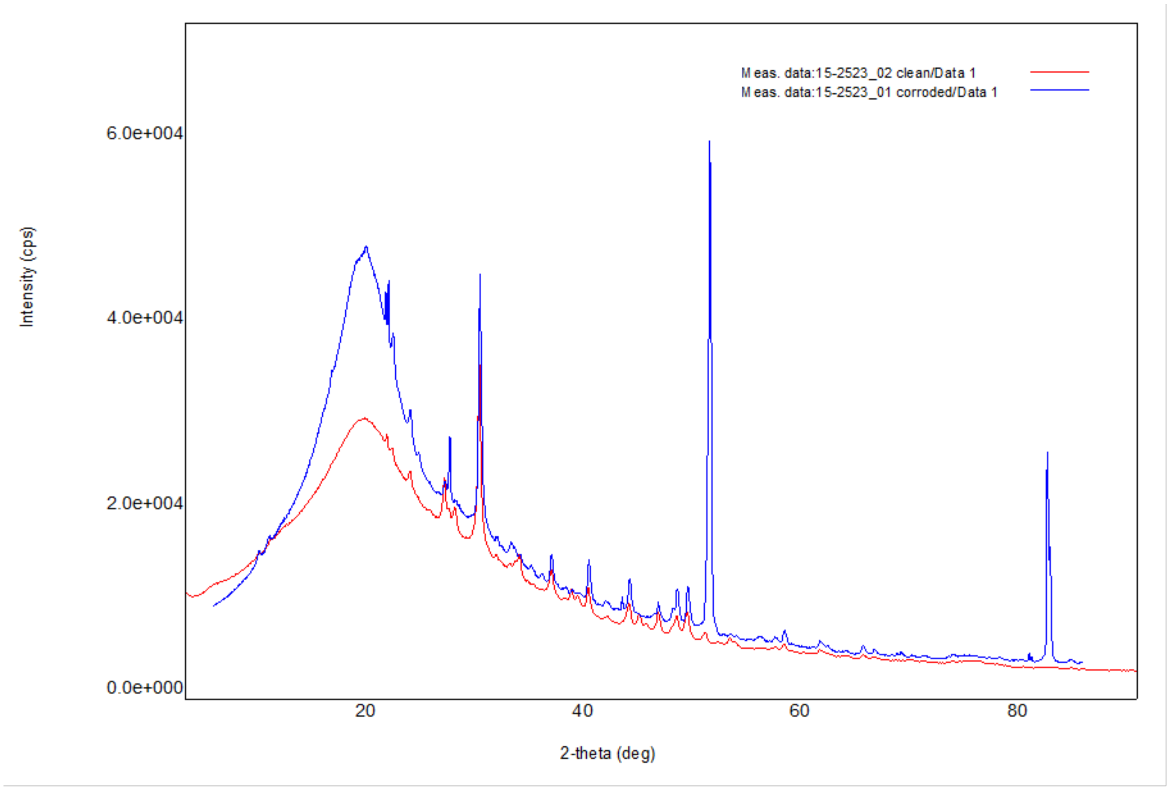

Figure 2. Raw X-ray diffractograms for grout Specimen 15-2323. The tracing in red is for a portion of material that was taken from the bottom portion of the specimen, whereas the tracing in blue was taken at the top of the specimen, which was rich in uranium. The unique peaks in the uranium-impacted specimen are tentatively assigned to the mineral soddyite, a uranium silicate phase.

CONTAMINATED STRUCTURAL CONCRETE

Dickerson et al. (1995)[11] present a good summary of the data from both DOE and NRC-licensed sites that was available at the publication time (1994). Contaminants that hydrolyze at the alkaline conditions (pH typically > 12) in cement pore water (including uranium and transuranics) tend to precipitate out within the near-surface of the slab (e.g., top ¼-in., such as the surface usually scabbled, scarified or shaved away during D&D activities).

Deeper penetration of contaminants can occur at cracks, surface flaws and seams. Strontium 90 has an intermediate solubility under alkaline conditions, and can often migrate farther. Radionuclides that are generally soluble in the cement pore water, such as Cs-137 and Tc-99 (as the pertechnetate anion) can diffuse more freely into the surface.

As noted by Dickerson et al. (1995)[11], the penetration of contaminants into a concrete host, and also the effectiveness of a decontamination method, is often related to the presence of sealant coatings and paint. If the concrete had a previous coating, and that coating has remained intact, decontamination was generally more successful than if the coatings were damaged or the concrete was bare. This is attributed to the fact that most contaminants will not penetrate sealants as compared to the more porous surface of concrete.

Concrete shielding derived from use at nuclear reactors has additional issues in that components within the cement host can become activated (the major activation nuclides formed are Ba-133 in the concrete, Co-60 in steel rebars); such neutron activation products may be found deep into the cement host (i.e., meters). Also, tritium (H-3, as HTO) can diffuse widely in the pore water. An excellent review of decontamination and decommissioning (D&D) characterization and decontamination and demolition technologies for concrete at nuclear power plants (NPP) has been prepared by the Nuclear Energy Agency [12]. The depth and total amount of concrete that must be removed (and subsequently disposed) to meet regulatory compliance is a major cost factor.

Obtaining representative samples from contaminated reinforced structural concrete (with, e.g., compressive strength 3000 to 6000 pounds per square inch [psi]) in order to determine the depth of radiological penetration is not an easy task. Fracture excavation samples are subject to cross-contamination and uncertainty in the average depth from which the material has been removed. Figure 3 illustrates laboratory subsampling at MCLinc for highly-radioactive NPP excavation samples, as was required to obtain a defensible representative sample for radiological measurements. The presence of large impervious aggregate within a small concrete sample may confound the interpretation of the depth penetration for radionuclides, since the preferred contaminant migration pathway will bypass the aggregate (as illustrated in Figure 1) and will be most favored where there are large pores or fractures (for relatively unimpeded migration routes).

Figure 3. Sub-sampling Contaminated Concrete Cores
to Obtain a Defensible Sample for Analysis.

Core samples are good alternatives for contamination assessment, but use of water-cooled drills or tools can affect the apparent distribution of water-soluble radionuclides (such as H-3, Tc-99, Cs-137). A core sample may be subsequently segmented for analysis by a variety of analytical techniques, such as SEM-EDS (as previously described) and various radiometric or chemical methods. The latter approaches are especially useful for difficult-to-detect radionuclides, such as Tc-99 or H-3 (which are weak beta particle emitters with relatively high specific activities). Another technique that can be applicable to cross sections from core samples is autoradiography (*vide infra*), which can provide two-dimensional radionuclide distributions. MCLinc is investigating the potential adaptation of digital autoradiography, now used extensively in medical technology, for such applications. Shielded radiological monitors that have been successfully applied to survey of contaminated soil cores, such as the FIDDLER device described by McDaniel, et al. (2005)[13], could potentially be adapted to the survey of concrete cores.

CASE STUDY – LEGACY CHARACTERIZATION OF CONCRETE CONTAMINATION AT THE HISTORIC K-25 GASEOUS DIFFUSION PLANT

The gaseous diffusion uranium enrichment process buildings at the former K-25 Plant (now the East Tennessee Technology Park, ETTP) had enormous “footprints.” At the time of its construction during the Manhattan Project era (1943), the iconic K-25 building was the world’s largest building under one roof, with a footprint of about 44 acres [14]. Before its demolition, essentially completed in late 2014 (Figure 4), MCLinc staff had an opportunity to examine some heavily contaminated areas on concrete in the K-25 operations level, in preparation for a then-proposed innovative D&D technology demonstration [15]. Some candidate localized “hot spots” of contaminated concrete flooring were identified with use of conventional hand-held radiation detectors (Figure 5). The most highly contaminated areas had been impacted by spillage of materials containing both enriched uranium and Tc-99. As noted previously, the high-yield fission product Tc-99 is a weak-beta particle emitter that is relatively mobile in wet systems (including concrete pore water). Figure 6 (from Bostick et al., 1993 [15]) illustrates a cross-section of construction concrete and a photographic film autoradiogram indicating the spread of activity along a surface flaw (large crack). The contamination illustrated in Figure 6A was believed to be primarily due to uranium, but laboratory testing of grout specimens with applied Tc-99 also indicated that Tc-99 activity (if present) could also be imaged by autoradiography. In summary, accepted metallographic and radiographic technique have been successfully adapted to the determination of both uranium and technetium depth distribution in cement and construction-grade concrete. Subsurface uranium was generally only seen on the near-surfaces with the exceptions of greater penetration in the vicinity of clearly defined cracks and pores and other discontinuities (damage and seams) in cascade floor surfaces. Technetium, on the other hand, was observed to penetrate the basic cement structure.

In general, the concrete flooring at gaseous diffusion plants undergoing D&D were not extensively characterized prior to removal of equipment and demolition, other than to identify cautionary “hot spots” (e.g., as illustrated in Figure 5). Where physical access permitted, some slabs were pre-scanned for surface contamination “hot spots,” often with use of cart-mounted gas-proportional counters or similar “drive-over” instruments. But limited access around equipment and piping, and the possibility of recontamination during equipment dismantlement, generally precluded extensive pre-demolition surveying. Once demolition debris was removed, pneumatic scabblers (needle guns, with ancillary dust collection systems) were often used to remove the near-surface (where uranium deposition may have occurred). At some other associated buildings, there was a technical specification for the contractor to perform surface removal to 3/8” depth before considering covering or fixative as an option.[2] This was generally adequate to remove uranium contamination. However, in some instances, there was deeper contamination that required “surgical” excavation of portions of the concrete.

Figure 4A. The K-25 Building, Before D&D

Figure 4B. The K-25 Building Pad, after Demolition
(2014, with concrete slab still largely intact).

Figure 4. The Historic K-25 Building at Oak Ridge, Tennessee

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[2] Josh Pope, UCOR Health Physics Specialist, personal communication to W.D. Bostick (MCLinc), October, 2015.

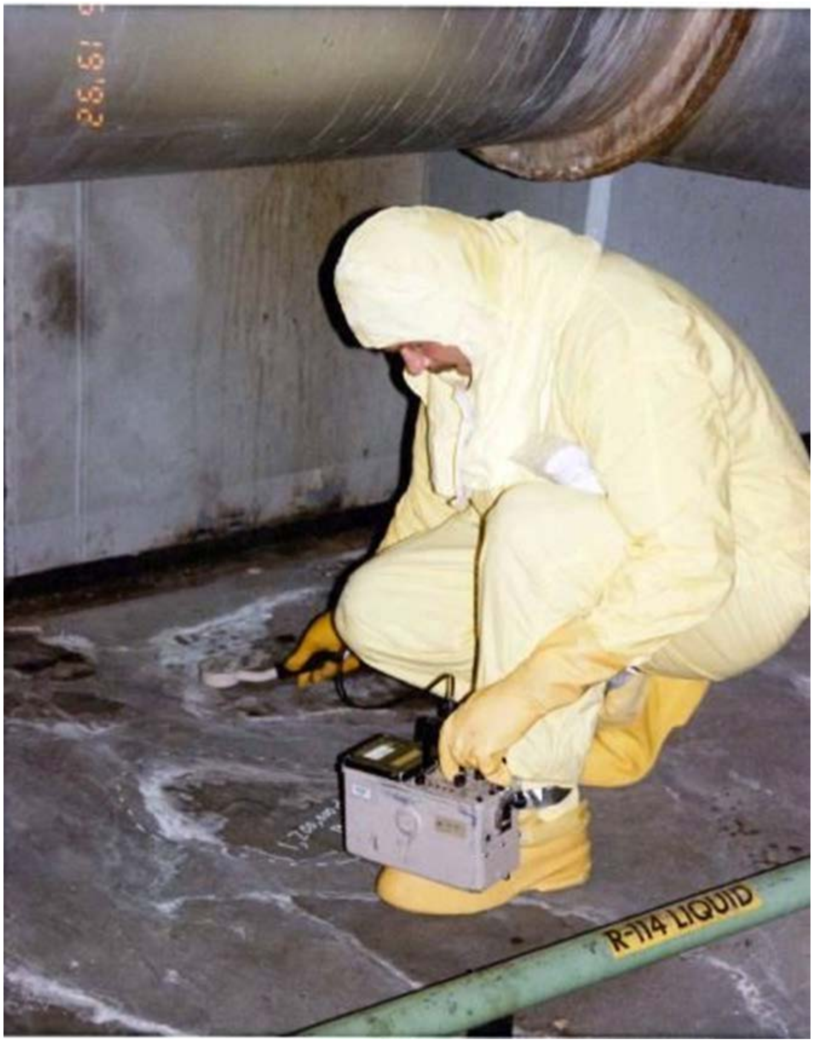

Figure 5. Use of hand-held radiation detector to identify a localized “hot spot” (activity approximately 1.2 million disintegrations per minute) on spill-impacted concrete flooring at the K-25 Building.

Because of the historic significance of the K-25 Building, preservationists had hoped to have some tangible vestige remain as part of the proposed Manhattan Project National Park [14]. With the structural building now demolished (Figure 4), attention has shifted to determining whether the “footprint,” or slab, of the original K-25 Building can be preserved and sampling and analysis will be conducted to determine the contamination levels on and beneath the slab. Officials are evaluating alternatives and the costs associated with leaving, covering, or removing the slab. The fate of the K-25 slab has not been resolved (as of 2015), since some areas of the slab remain significantly contaminated by Tc-99 activity.[3]

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[3] http://knoxblogs.com/atomiccity/2015/02/13/will-k-25-preservation-project-live-promise/

Figure 6A. Polished Cross-section of Construction-grade Concrete From a Section of K-25 Flooring

Figure 6B. A Photographic Film Autoradiogram Illustrating the Spread of Contamination (Principally Uranium) Along a Near-surface Crack Fault Adjacent to a Large Aggregate Grain Boundary. The Contamination has Diffused into the Cement Host for Several Millimeters.

Figure 6. Construction Concrete from K-25 Flooring and a Photographic Film Autoradiogram of a Radiological-contaminated Area.

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