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Assessment of Radioactive Elements in Coal Combustion Products

2014 TECHNICAL REPORT

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3002003774
Final Report, August 2014

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Acknowledgments

The following organization, under contract to the Electric Power Research Institute (EPRI), prepared this report:

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This report describes research sponsored by EPRI.

EPRI would like to acknowledge the support of Robert Zielinski of the U.S. Geological Survey in Denver, Colorado, for his input and valuable reviews of earlier versions of this document.

This publication is a corporate document that should be cited in the literature in the following manner:

Assessment of Radioactive Elements in Coal Combustion Products.
EPRI, Palo Alto, CA: 2014.
3002003774.

Abstract

Coal combustion products (CCPs) such as fly ash and bottom ash contain naturally occurring radioactive elements such as uranium, thorium, and their decay products that were initially present in the feed coal. There have been concerns that the presence of radionuclides in CCPs could pose radiological hazards during the management, disposal, or utilization of CCPs. The purpose of this critical review is to summarize the current state-of-knowledge of radionuclides in CCPs, and their potential radiological impacts. The concentrations of radionuclides in many Pennsylvanian-age coal seams are on the same order of magnitude as those found in other geologic materials. Uraniferous coals (those high in uranium) are relatively rare worldwide, and none are currently being used in the United States for electricity production. Laboratory studies have suggested that CCPs are not a significant source of leachable radionuclides at environmental pH levels, and exposure studies have determined that use of CCPs in concrete, wallboard, and structural fills is not a significant source of exposure to the public. The United States Geological Survey concluded that coal fly ash does not represent a significant radiological risk. This critical review did not locate any published studies that suggested typical CCPs posed any significant radiological risks above background in the disposal scenarios considered, or when used in concrete products.

Keywords
Coal combustion products
Fly ash
Radionuclides
Radioactivity
Uranium
Radium

Unit Conversions

Commonly Used Units

Activity, or radioactivity: curie (Ci) or becquerel (Bq); 1 pCi (picocurie) = 1 trillionth of a curie

Dose equivalent (or effective dose): roentgen equivalent in man (rem) or sievert (Sv)

Absorbed dose: radiation absorbed dose (rad) or gray (Gy)

Activity Conversion

1.0 pCi = 0.037 Bq (1 Bq = 1 disintegration/sec)

Concentration Conversions

1.0 pCi/g = 37.037 Bq/kg

1.0 pCi/L = 37 Bq/m^3

Mass to Activity Conversions

^{238}U: 1.0 mg/kg = 0.33 pCi/g

^{236}U: 1.0 mg/kg = 65.0 pCi/g

^{235}U: 1.0 mg/kg = 2.2 pCi/g

^{234}U: 1.0 mg/kg = 6,250 pCi/g

^{nat}U: 1.0 mg/kg = 0.69 pCi/g [^{nat}U = ^{238}U (99.27%) + ^{235}U (0.72%) + ^{234}U (0.0054%)]

^{226}Ra: 1.0 mg/kg = 1 x 10^6 pCi/g

^{228}Ra: 1.0 mg/kg = 2.8 x 10^8 pCi/g

^{230}Th: 1.0 mg/kg = 1.9 x 10^4 pCi/g

^{232}Th: 1.0 mg/kg = 0.11 pCi/g

^{210}Pb: 1.0 mg/kg = 7.7 x 10^7 pCi/g

^{40}K: 1.0 mg/kg = 7.1 pCi/g

Dose Conversions

1.0 mrem = 10 μSv

1.0 Gy = 100 rad

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Section 1: Summary

Coal contains naturally occurring radioactive elements—most importantly uranium, thorium, radium, and potassium-40 (^{40}K)—and these radionuclides become concentrated in coal combustion products (CCPs) relative to the source coal. As the ash content of coal increases, the degree of enrichment tends to decrease. Assuming the mean concentrations in coal and mean ash content of U.S. coals of about 10%, typical coal ash would contain about 7 pCi/g uranium, 4 pCi/g thorium, and 15 pCi/g ^{40}K per gram of ash (Table 1-1). Low-ash coals would yield greater enrichment of radionuclides, and high-ash coals would yield less enrichment. Because of the likelihood of attaining secular equilibrium between uranium and some of its decay products in both coal and fly ash, it is possible to predict the concentrations of the decay products. Typical coal ash would also contain 7 pCi/g radium because radium is a decay product of uranium. Comparisons of these calculated concentrations with analytical results suggest that the calculated values are reasonable order-of-magnitude estimates for some types of coal ash, while they are overestimates for others (Table 1-1). The concentrations of ^{238}U, ^{232}Th, and their decay products in CCPs tend to be slightly enriched when compared to U.S. soils.

The concentrations of radionuclides in Pennsylvanian-age coal seams commonly used for generation of electricity in the United States are comparable to those in the earth's crust (USGS, 2006; Earnshaw and Greenwood, 1997). Mesozoic and Cenozoic lignite and subbituminous coals used in other countries tend to contain larger amounts of uranium and its decay products (Seredin and Finkelman, 2008). When these high-uranium coals are combusted, the resulting CCPs also contain anomalously large amounts of radionuclides. There are some fly ash sources in China that are currently being evaluated as an economic source of uranium. However, no high-uranium coals are used for electricity production in the United States.

Table 1-1
Summary of radionuclide concentrations in coal ash compared with U.S. soils.

Radio-nuclide	Calculated for all coal ash	Zielinski and Budahn (1998)	Roper et al. (2013)	EPRI (CP-info) as total uranium	UNSCEAR (2000) in U.S. soil	Smith et al. (2013) in 0 to 5 cm U.S. soils
^{238}U	21 mg/kg (7 pCi/g)	Fly ash: 14.3 mg/kg[a] (4.71 pCi/g) Bottom ash: 11.4 mg/kg[a] (3.77 pCi/g)	Fly ash: 9.72 mg/kg[a] (3.21 pCi/g) 9.42 mg/kg[b] (3.11 pCi/g)	Fly ash: 11.2 mg/kg[a] 5.63 mg/kg[b] 4.14 mg/kg[c] Bottom ash: 7.89 mg/kg[a] 6.49 mg/kg[b] 3.88 mg/kg[c]	2.87 mg/kg (0.95 pCi/g)	2.1 mg/kg as total uranium
^{232}Th	36 mg/kg (4 pCi/g)	–	Fly ash 17.9 mg/kg[a] (1.97 pCi) 19.9 mg/kg[b] (2.19 pCi)	–	8.64 mg/kg (0.95 pCi/g)	8.0 mg/kg as total thorium
^{226}Ra	4 ηg/kg (4 pCi/g)	Fly ash: 4.6 ηg/kg[a] (4.64 pCi/g) Bottom ash: 4.3 ηg/kg[a] (4.30 pCi/g)	–	–	1.08 ηg/kg (1.08 pCi/g)	–
^{40}K	2.1 mg/kg (15 pCi/g)	–	Fly ash: 2.27 mg/kg[a] (15.4 pCi/g) 0.65 mg/kg[b] (4.62 pCi/g)	–	1.41 mg/kg (10.0 pCi/g)	1.75 mg/kg[d]

[a] bituminous coal

[b] subbituminous coal

[c] lignite coal

[d] calculated from the mean concentration of potassium (1.46%) assuming that 0.012% is ^{40}K

When CCPs are placed in landfills or surface impoundments, there has been a concern that radionuclides may leach into surface and groundwater. Both laboratory and field studies have provided evidence that typical coal ash is not a significant source of radionuclides when the ash is stored in surface facilities. Uranium concentrations in field and lab studies were typically less than 1 pCi/L (e.g., Zielinski et al., 1999; EPRI, 2008). Batch leaching studies using pH in the typical environmental range found that less than 1% of the uranium and thorium present in the solid residue was water soluble under experimental conditions imposed. Moreover, field data suggested that ^{40}K is a major source of beta and gamma radiation in CCP leachate. Potassium-40 occurs in relatively large concentrations in many foods and drinks, and is a major source of natural radiation to the human body.

Radiological studies have been conducted to assess the dose of gamma radiation to workers when fly ash is placed in model landfills, road embankments, an ash pond, and a dry lagoon. Under these high-exposure occupational settings, the radiation exposure resulting from the presence of the coal ash was less than or equal to 10% when compared with the 2009 NCRP total natural background dose of 315 mrem/year. Exposure to the general public would be much less. In fact, the general public in the United States is exposed to an average of about 310 mrem/year by the health care industry.

Because CCPs contain radium, there has been concern that the use of fly ash in concrete and other building products could pose radiological risks from direct exposure and by enhanced radon production via the decay of radium. In 1983, the U.S. EPA concluded that the use of "typically-occurring fly ash [in the U.S.]" in concrete did not pose enhanced radiological risks (U.S. Federal Register, 1983). Since that time, additional studies have demonstrated that, although the amount of radon generated may be proportional to the amount of radium added to the concrete, the dense nature of concrete limits the amount of radon that diffuses into ambient air (e.g., USGS, 1997; Siegel et al., 2006).

Despite the enrichment of radionuclides from coal to ash, this critical review did not locate any published studies that suggested typical CCPs posed any significant radiological risks above background in the disposal scenarios considered, and when used in concrete products. These conclusions are consistent with previous assessments. The USGS (1997) concluded that "Radioactive elements in coal and fly ash should not be sources of alarm. The vast majority of coal and the majority of fly ash are not significantly enriched in radioactive elements, or in associated radioactivity, compared to common soils or rocks." A year later, the U.S. EPA (1998) concluded that the risks of exposure to radionuclide emissions from electric utilities are "substantially lower than the risks due to exposure to background radiation." In an extensive review of the health impacts of coal and CCP, Finkelman et al. (2002) concluded that "coals may concentrate uranium to a large degree [but] that these uraniferous coals are very rare and none are currently being used in the U.S."

Section 2: Introduction

Background

In the United States, 42% of the electricity generated from 2009 to 2013 was derived from coal (IEA, 2014), and the global demand for electricity is increasing. In 2012, the U.S. produced about 110 million short tons of CCPs including fly ash, bottom ash, and flue gas desulfurization (FGD) solids (American Coal Ash Association [ACAA], 2014). About 45% of this material was used beneficially. Fly ash comprised 52.1 million short tons (52%) of the CCP reported in the 2012 ACAA production and use survey. Of that amount, 23.2 million tons (45%) was used in concrete, concrete products, structural fill, waste stabilization, and other applications.

Coal is largely composed of combustible organic matter, but it also contains variable amounts of relatively refractory mineral matter such as clays and sulfide minerals. These minerals contain naturally occurring trace elements including radioactive elements such uranium, thorium, and radium. Uranium may also occur in the organic matter of coal. When coal is combusted, elements in both the organic fraction and mineral matter may be liberated and partition between the gaseous phases and the solid phases in the flue gases. The degree of partitioning between these phases is controlled by the volatility and chemical behavior of the individual element. Low-volatility radionuclides such as thorium and uranium are dominantly retained in the solid combustion products (USGS, 1997; Demir et al., 2001).

Objectives, Scope, and Approach

The purpose of this critical review is to present the current state-of-knowledge about radioactive elements in CCPs, and the potential radiological impacts associated with handling, disposal, and utilization of CCPs. The scope of this assessment is limited to the management of CCPs, and does not include an assessment of the radiological impacts of coal-fired power plants via air emissions of fly ash particles or radioactive gases from stack discharges. This review was developed by conducting computer-assisted literature searches for peer-reviewed journal publications, published symposia proceedings, final reports from sponsored research projects, publications by national and international agencies published before 2014, and resources made available by EPRI. Typical search terms included combinations of several terms such as *alpha, ash, beta, building materials, chemical, coal, combustion, concrete, contamination, dose, emanation, exhalation, exposure, extraction, flue gas, gamma, groundwater, health, ionizing,* *landfill, leaching, lignite, radium, radon, radioactive, radiation, radiological, radionuclide, residues, trace element, uranium,* and *uraniferous*. Information was also obtained from relevant textbooks and Internet sources. The review was intended to be comprehensive and up-to-date.

Radioactive Decay and Dose

During natural radioactive decay, charged and uncharged particles are emitted from the nucleus of the element, often in combination with energetic photons called gamma rays. Alpha radiation consists of positively charged helium nuclei: two protons and two neutrons bound together constitute one alpha particle. Beta radiation consists of high-velocity electrons or positrons that are ejected from a transforming nucleus. When a neutron is converted into a proton during radioactive decay, an electron is emitted. When a proton is converted into a neutron, a positron is emitted. Gamma radiation is a type of short-wavelength electromagnetic radiation emitted by the nuclei during radioactive decay. All the emissions from nuclear decay are called "ionizing radiation," because their energy is sufficient to break chemical bonds, i.e., to disrupt the forces that hold molecules together.

Because of their two units of electrical charge, alpha particles do not travel far in the environment; they lose energy rapidly in air, usually expending it within a few centimeters, and they cannot penetrate most matter they encounter such as paper or human skin (Figure 2-1). Alpha particles do not decay further, and once they have lost their energy, they pick up two electrons and become stable helium atoms (U.S. EPA, 2012a). Because alpha particles do not penetrate skin, external exposure is of less concern than internal exposure. When alpha emitters are inhaled, ingested, or absorbed into the blood stream, human tissue can be exposed to alpha radiation, increasing the risk of cancer. In particular, alpha radiation from elevated levels of radon-222 and its decay progeny is suspected to be the cause of some lung cancers in humans (ATSDR, 2012).

Beta particles, which carry a single charge, travel several feet in open air and are stopped by most thicknesses of solid materials (Figure 2-1). When a beta particle loses its energy, it becomes a free electron, which like any other free electron can be picked up by a positive ion. The speed of individual beta particles depends on how much energy they have, and varies over a wide range. For example, beta particles from tritium (^{3}H) decay have a peak energy of 0.0186 MeV, and beta particles from phosphorus (^{32}P) decay have a peak energy of 1.71 MeV. Beta particles with excess energy, in the form of speed, can cause harm to living cells by breaking chemical bonds and by creating ions and free radicals.

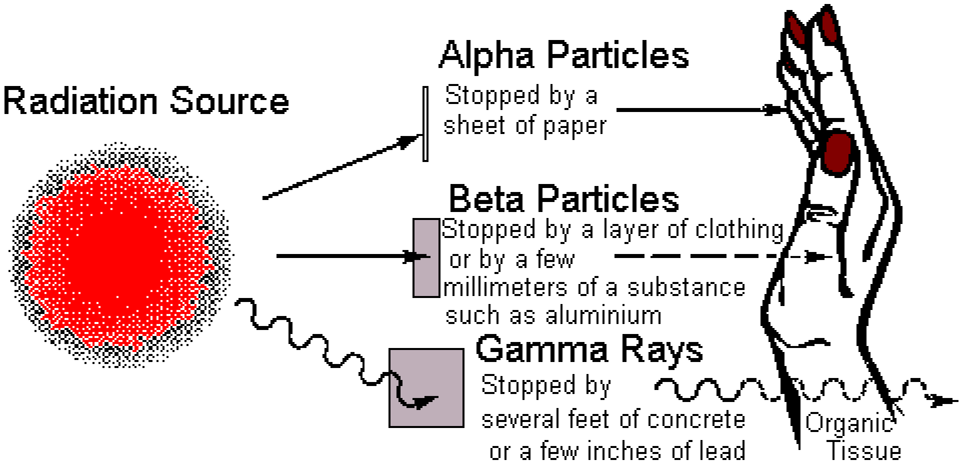

Figure 2-1
Relative depth of penetration of alpha, beta, and gamma radiation (from U.S. EPA, 2012a).

Direct exposure to beta particles from strong sources can redden or even burn the skin. However, emissions from inhaled or ingested beta particle emitters are the greatest concern because beta particles released directly into living tissue can cause damage at the molecular level, which can disrupt cell function. Because they are much smaller and have less charge than alpha particles, beta particles generally travel farther into tissues. As a result, the cellular damage is more dispersed. Some beta-emitters, such as potassium-40 and carbon-14, occur naturally in the body, and are widely distributed throughout it. Others, such as iodine-131 and strontium-90, accumulate in specific organs and can result in chronic exposure (U.S. EPA, 2012a).

Because gamma radiation consists of uncharged photons and is more energetic, it is able to penetrate materials that absorb and block alpha and beta particles (Figure 2-1). Because of this property, gamma radiation is the major source of external radiation exposure.

Alpha, beta, and gamma radiation can cause significant damage to DNA and can result in a wide array of biological effects. Radiation can also react with molecules other than DNA (such as lipids, proteins, and water) to produce free radicals, which can then go on to adversely react with the DNA molecule. DNA is the primary molecule of concern for effects from low-level radiation because DNA damage from radiation and from other sources is cumulative and can result in carcinogenesis or other adverse cellular events months or years after exposure (ATSDR, 1999).

A commonly used unit of radioactivity in the United States is the curie (Ci), which is defined as 3.7×10^{10} atomic disintegrations per second. The term "pico" means one-trillionth (10^{-12}). One picocurie (pCi) is equal to 2.22 disintegrations per minute. The SI (International System of Units) unit of radioactivity is the becquerel (Bq). One Bq is equal to 1.0 disintegration per second; one pCi is equal to 0.037 Bq.

When considering the entire electromagnetic spectrum, there are two types of radiation: non-ionizing and ionizing (Figure 2-2). Non-ionizing radiation does not carry enough energy to completely remove an electron from an atom or molecule. Visible light, radio waves, microwaves, and infrared are examples of non-ionizing radiation. Ionizing radiation can remove electrons from atoms and molecules. Both forms of radiation can be harmful to organisms, but ionizing radiation is far more harmful. During the reaction between ionizing radiation and a substrate, energy is absorbed by the material, and is called the absorbed dose, with units of the rad (radiation absorbed dose) or the SI unit gray (Gy). One Gy is equal to 100 rads. A rad is defined as a dose of 100 ergs of energy per gram of the given material.

However, the dosage level does not tell the whole story, because the potential biological harm from radiation depends both on the type of radiation (differentiated by a quality factor Q; alpha radiation [Q = 20] is more damaging than gamma rays [Q = 1]) and on the tissue sensitivity (differentiated by a tissue weighting factor; spleen tissue is more sensitive than brain tissue). Hence, health physicists calculate a dose equivalent that measures the biological effect to a living organism. The units for dose equivalents are the rem (roentgen equivalent in man) and the SI unit sievert (Sv). One Sv is equal to 100 rems. In radiological studies, dose is often reported as millirem (mrem) or micro (10-6) sievert (µSv). A listing of common unit conversion factors is included at the beginning of this report.

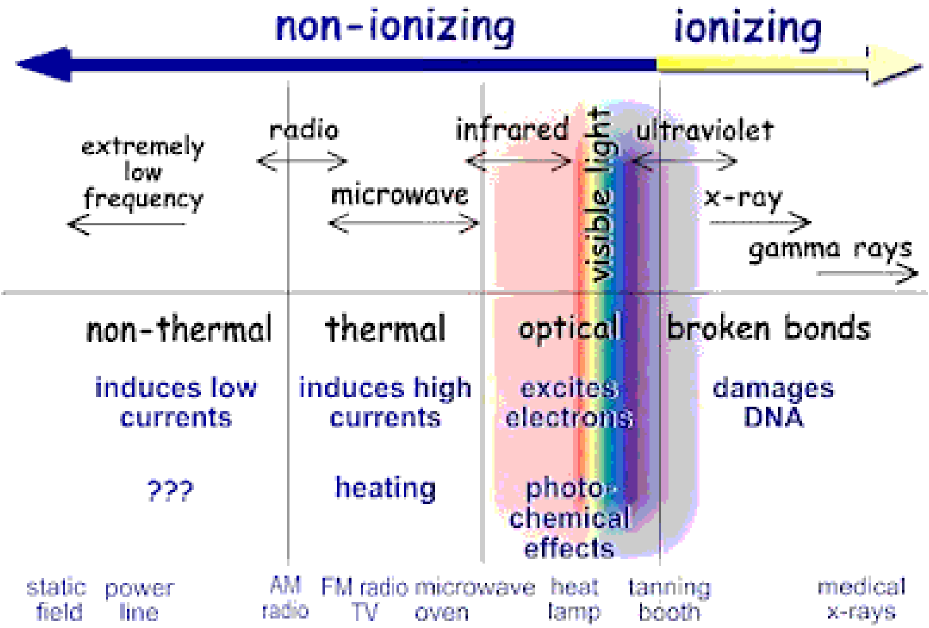

Figure 2-2
Types of radiation in the electromagnetic spectrum (from U.S. EPA, 2012a).

Radiation dose limits have been established for exposures to ionizing radiation for both radiation workers and the general public (Table 2-1). Of particular relevance to this study is the dose limit for the general public. The Health Physics Society "supports the establishment of an acceptable dose of radiation of 1 mSv/year (100 mrem/year) above the annual natural radiation background. At this dose, risks of radiation-induced health effects are either nonexistent or too small to be observed" (Health Physics Society, 2009). Sources of natural, background radiation are discussed in Section 3.

Also of particular relevance to CCPs are two terms: NORM and TENORM. NORM is an acronym for naturally occurring radioactive materials. NORM can be virtually any substance that contains radioactive elements that could expose people to radiation except radioactive materials that are regulated by the Atomic Energy Act of 1954. The elements in NORM are primarily potassium-40, and isotopes and decay products of uranium and thorium. The term TENORM means technologically enhanced NORM. In this case, the radioactive elements that were present initially in NORM have been concentrated by some anthropogenic process. Examples of TENORM are uranium mining wastes, oil and gas-well drilling wastes, and water-treatment wastes that contain a relatively large amount of radium-226 that was initially dissolved in untreated groundwater.

Table 2-1
Annual radiation dose limits (from ATSDR, 1999; U.S. DOE, 2010; and U.S. NRC, 2012).

Population	Type of exposure	Limit
Occupational/radiological worker. Total effective dose equivalent (TEDE)	Whole body (including internal and external sources of radiation)	5 rems
Occupational/radiological worker. Equivalent dose	Lens of eye	15 rems
Occupational/radiological worker. Sum of equivalent dose	Extremities (hands and arms below the elbow, feet and legs below the knees)	50 rems
General public and minors in a controlled area. TEDE	Whole body (including internal and external sources of radiation)	0.1 rem greater than background levels

Section 3: Radioactivity in Coal and Coal Combustion Products

Background Radioactivity

Radioactivity occurs naturally in the atmosphere, drinking water, soil, and in many foods. People are routinely exposed to radiation, and ingest naturally occurring radionuclides as part of everyday life. The National Council on Radiation Protection and Measurements recently concluded that if all of the natural and anthropogenic sources of background radioactivity are considered, the total effective dose is about 624 mrem/year (Figure 3-1). Natural sources account for about 50% of the background radiation, and medical applications account for 48% (NCRP, 2009). Consumer products account for the remaining 2%.

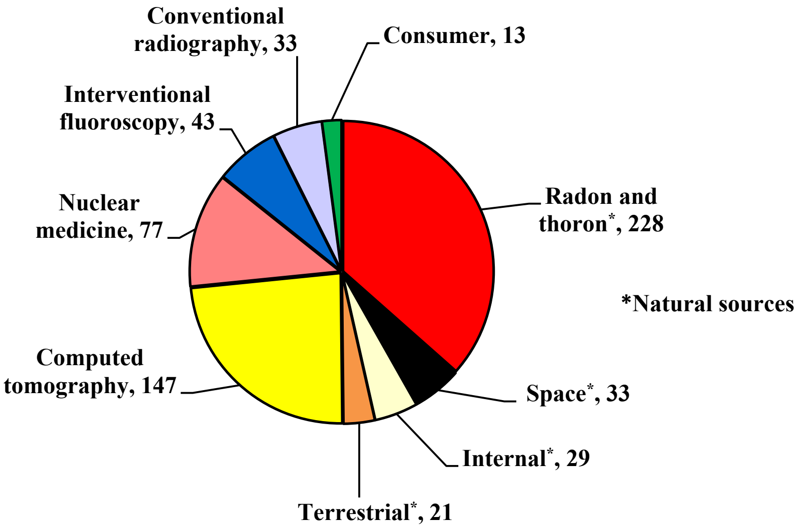

Figure 3-1
Distribution of the various background radiation sources in the United States (mrem/year) (derived from NCRP, 2009). Industrial exposure (0.3 mrem/year) and occupational exposure (0.5 mrem/year) were not included in this figure.

Among the manmade sources, medicinal applications are by far the largest source. Increased applications of X-ray computed tomography, conventional radiography and fluoroscopy, and interventional fluoroscopy since the early 1990s account for the largest increase in the previous estimated effective dose of 360 mrem/year (NCRP, 1994). Nuclear medicine (77 mrem/year) uses ^{99m}Tc in the diagnosis and treatment of cancers, and radionuclides such as ^{125}I and ^{89}Sr in pellets for in situ treatment of cancer. Consumer products (13 mrem/year) include older pottery, antique glass, bathroom tile, and jewelry in which uranium was used as a pigment. Other products include cigarettes, smoke detectors, brick masonry, granite countertops, and lawn fertilizer. Occupational exposure includes doctors, nurses, radiographers, dental hygienists, nuclear power plant workers, researchers, pharmacists, welders, and airplane and jet crews. This source also includes exposure during air travel, the dose depending on distance, altitude, and frequency of travel.

The total dose of natural radiation (which does not include medical or other man-made sources) varies with altitude, geographic location, and lifestyle. For example, the amount of cosmic radiation will increase from about 26 mrem/year at sea level to about 49 mrem/year at an elevation of 3,000 to 4,000 feet. Also, a person living on the Colorado Plateau will be exposed to an additional 67 mrem/year from terrestrial sources when compared to a person living along the Gulf Coast (see NCRP, 2009). A person who lives at an elevation of 600 feet in the Midwest may be exposed to natural radiation of about 315 mrem/year (see U.S. EPA, 2012b for details). The U.S. EPA provides an online calculator for radiation dose at http://www.epa.gov/rpdweb00/understand/calculate.html.

Among the natural sources, internal radiation (29 mrem/year) refers to the dose of radiation within the human body from radionuclides derived from food, water, and air. Many foods contain radioactive isotopes of common elements. Any food or drink that contains potassium will contain about 0.012% of the isotope ^{40}K, which is a beta-particle emitter. Common foods such as potatoes, chicken, and orange juice are all naturally radioactive. Milk, for example, contains about 2,000 pCi/L of ^{40}K. The body of an adult human male contains about 100,000 pCi of ^{40}K, which imparts a dose of about 18 mrem to soft tissues each year.

The largest single source of natural background radiation is from gaseous radon. The most stable isotope (^{222}Rn) is a source of alpha particles, and is a decay product from background levels of uranium (^{238}U) in soil and water. Thoron (^{220}Rn) is a decay product from thorium (^{232}Th). Radon can diffuse from the ground and accumulate in homes and buildings. Terrestrial sources (21 mrem/year) are all the naturally occurring radioactive elements in rocks, minerals, soil, fresh water, and sea water. Cosmic (space) radiation (33 mrem/year) is composed of high-energy particles from space and the sun. While the earth's atmosphere provides shielding from cosmic rays, they can also interact with the earth's upper atmosphere to produce a variety of radionuclides such as ^{14}C, ^{3}H, and ^{7}Be.

Radionuclides in Coal

Typical Coals in the United States

Coal contains naturally occurring radionuclides, and therefore it is a NORM. In general, however, the concentrations of radionuclides in coal are less than those in the earth's crust (UNSCEAR, 1982). The relative amount of uranium in coal depends on several geological and geochemical processes. Uranium may be incorporated into coal at all stages of the coal-formation process (Kolker and Finkelman, 1998). Dissolved uranium may be transported by surface or groundwater into the coal-forming swamps, and become sorbed by organic matter and sediments). Uranium may be taken up by organic matter during plant growth. In anoxic (oxygen-poor) waters where the aquatic environment is reducing, U(VI) will be reduced to U(IV), and the uranium will precipitate from solution as uraninite (UO_2) or coffinite ($U(SiO_4)_{1-x}(OH)_{4x}$). The major uranium-bearing minerals in coal are uraninite, zircon ($ZrSiO_2$), monazite, and xenotime (both rare-earth phosphates), which may also contain thorium (Kolker and Finkelman, 1998). Uranium and thorium may also be leached from sediments that cover the coal-forming organic material, or be derived from uranium-containing rocks and minerals that are near the depositional basin (digenetic). Eskenazy and Stefanova (2007) suggested that the uranium in subbituminous coals in Bulgaria was derived from volcanism that occurred near the coal-forming basin. Lastly, the distribution of uranium and thorium will be influenced by post-depositional fluid flow and mineralization of the coal during geologic time scales (epigenetic).

Natural uranium (^{nat}U) consists of three major isotopes: ^{238}U (99.27% natural abundance, by weight %), ^{235}U (0.72%), and ^{234}U (0.0054%). Because of its very long half-life (4.5 billion years), ^{238}U constitutes more than 99 percent of the mass of natural uranium, and is also the least radioactive per unit weight. Uranium-235 exhibits approximately 6.5-fold greater activity per unit mass, and ^{234}U is approximately 18,000 times more radioactive than ^{238}U. The specific activities of each of the isotopes of ^{nat}U are 0.34 pCi/μg (^{238}U), 2.2 pCi/μg (^{235}U), and 6,250 pCi/μg (^{234}U). The overall specific activity of ^{nat}U is therefore 0.69 pCi/μg.

The U.S. Geological Survey maintains a large coal quality database (COALQUAL) that contains analytical data for major, minor, and trace elements (USGS, 2006). Using this database, Kolker and Finkelman (1998) calculated that the mean concentration of uranium in all U.S. coals was 2.1 ± 16.0 mg/kg (0.69 ± 5.28 pCi/g as ^{238}U), based on 6,923 samples. Zielinski et al. (1999) also used the USGS database and reported that for 2,000 coal samples from the Western United States and about 300 coal samples from the Illinois Basin, the uranium concentrations ranged from less than 1 to 4 mg/kg (0.33 to 1.32 pCi/g as ^{238}U) in the majority of the coal samples. Both of these estimates are similar to the average amount of uranium in the earth's crust, which Earnshaw and Greenwood (1997) estimated as 2.3 mg/kg or as 0.76 pCi/g as ^{238}U (Figure 3-2).

Based on 6,866 samples from the COALQUAL database, Kolker and Finkelman (1998) also reported a mean concentration of thorium as 3.2 ± 3.0 mg/kg (0.35 ± 0.33 pCi/g as ^{232}Th) for all U.S. coals. Unlike uranium, it appeared that subbituminous coal contained more thorium than the bituminous samples (Figure 3-2), when compared using t-test, paired comparison ($p = 0.05$). According to Earnshaw and Greenwood's (1997) estimate, the crustal abundance of thorium is greater than the average thorium content of U.S. coals. However, a "world average lignite" compiled by Bouska and Pesek (1999) indicated that both the uranium and thorium content of some lignite coals may be more variable on a world-wide basis. Based on 2,503 lignite coal samples, the mean concentration of uranium was 6.06 ± 19.9 mg/kg (2.00 ± 6.55 pCi/g as ^{238}U) (Figure 3-2) and the thorium content (3.30 ± 3.70 mg/kg or 0.36 ± 0.41pCi/g as ^{232}Th) was similar to that in the COALQUAL database.

Focusing on about 2,100 western U.S. coal samples in the COALQUAL database, Zielinski and Affolter (1997) found that there was a weak relationship between ash content and uranium concentrations ($r = 0.47$) and between ash content and thorium levels ($r = 0.67$). Similarly, data given by Varinlioglu et al. (1998) suggested a weak relationship between ash content and uranium ($r = 0.56$) and thorium ($r = 0.69$). For coals in Spain, Alvarez et al. (1994, 1998) reported a strong correlation ($r \geq 0.9$) between uranium, thorium, and the ash content.

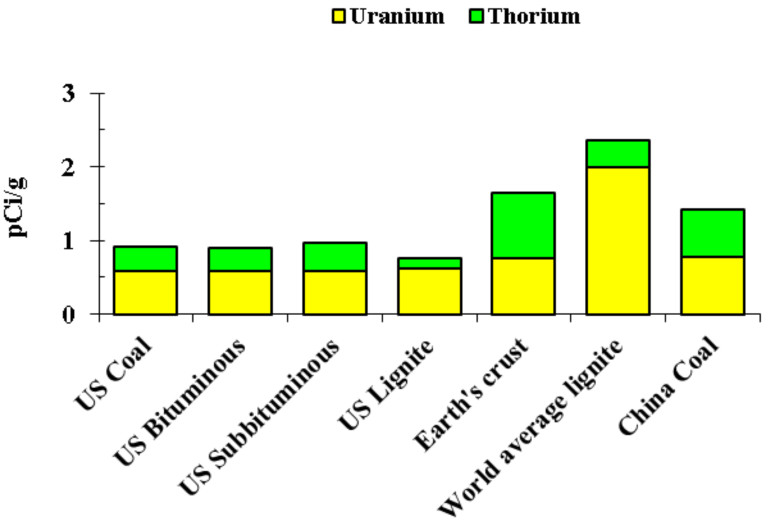

Figure 3-2
Mean concentration of uranium and thorium in coal and the earth's crust. The averages for all U.S. coal, bituminous, subbituminous, and lignite coal were calculated using the COALQUAL database. The earth's crust was based on Earnshaw and Greenwood (1997). World average lignite was given in Bouska and Pesek (1999), and "China coal" was given in Bai et al. (2007) as an average of 1,123 coal samples in China (see also Dai et al., (2012) for additional information about trace elements in Chinese coals).

High-Uranium Coals

United States Coal

Most coals in the eastern United States contain less than 10 mg/kg uranium (3.3 pCi/g as ^{238}U). Coal containing more than 20 mg/kg uranium is rare in the United States (USGS, 1997). However, some Cretaceous and Tertiary-age lignite coals in Wyoming and North and South Dakota contain from 0.1% to as much as 10% uranium by weight (Towse, 1957; Hurst 1981). Bisselle and Brown (1984) generalized, however, that most of these high-uranium coals occurred as relatively thin beds with a low BTU content, making them unsuitable for use in power plants.

Worldwide Coal

High-uranium coals are more common outside of the United States. On a global scale, Mesozoic and Cenozoic lignite and subbituminous coals have the largest concentrations of uranium (Seredin and Finkelman, 2008). In most deposits, the uranium is thought to have been introduced into the coal by uranium-containing groundwater. Palmer et al. (2004) reported that low-rank coals in Turkey (lignite and subbituminous) are similar to lignite coal in the Gulf Coast and Fort Union regions in terms of major element composition. However, the concentrations of a variety of trace elements, including uranium, tended to be greater. Based on the analysis of 143 coal samples from Turkey, the average concentration of uranium was 13 ± 18 mg/kg (4.3 ± 5.9 pCi/g as ^{238}U) and ranged from 0.32 mg/kg to as much as 140 mg/kg (0.11 to 46 pCi/g as ^{238}U). The authors generalized that more than 75% of the Turkish coal samples contained more uranium than the average amount of uranium in Gulf Coast lignites (mean, 2.3 ± 1.7 mg/kg [0.76 ± 0.56 pCi/g as ^{238}U]) and Fort Union lignite (1.5 ± 1.9 mg/kg [0.50 ± 0.63 pCi/g as ^{238}U]). Crowley et al. (1997) reported that the mean concentration of uranium in lignite coals in east-central Texas was 2.6 mg/kg (0.86 pCi/g as ^{238}U). The source of the uranium in the Turkish coal samples was not discussed.

Papanicolaou et al. (2004) reported that the uranium content of Tertiary and Pleistocene-age brown coals in Greece depended on the geologic basin in which they formed. Samples of lignite coal from the Drama basin in northern Greece contained very large concentrations between 33 and 313 mg/kg uranium (10.9 to 103 pCi/g as ^{238}U). Samples from the Serres coal basin contained 98 to 563 mg/kg uranium (32.3 to 186 pCi/g as ^{238}U). Papanicolaou et al. (2004) suggested that the source of the anomalously large amounts of uranium was derived from magma and geothermal fluids that were associated with volcanic activity during the Upper Eocene and Oligocene. In contrast, lignite samples from the Olympia basin in southern Greece contained only 3 to 5 mg/kg uranium (1.0 to 1.7 pCi/g as ^{238}U). Lignite samples from the Megalopolis basin contained between 35 and 38 mg/kg uranium (11.6 to 12.5 pCi/g as ^{238}U) (Papaefthymiou et al., 2007).

Based on the analysis of 1,535 coal samples, Yang (2007) calculated a weighted mean uranium concentration of all coals in China as 2.31 mg/kg (0.76 pCi/g as ^{238}U), which is similar to U.S. coal. He noted, however, that there are coals in the southern part of China that contain anomalously large concentrations of uranium in the provinces of Guizhou, Guangxi, and Yunnan. For example, 40 coal samples collected from Heshan Coalfield in Guangxi contained 15 to 153 mg/kg uranium (5.0 to 50.0 pCi/g as ^{238}U). Heshan coals are high-sulfur, Upper Permian, bituminous coals that also contain relatively large amounts of molybdenum and tungsten in addition to uranium (Shao et al., 2003). Yang (2007) summarized that the source of the anomalous levels of uranium was likely derived from basaltic volcanic ashes that were emitted frequently during the Late Permian in the Guizhou province. Ren et al. (1999) reported that magma intrusions and related hydrothermal activity were widespread during the Mesozoic and Cenozoic Eras. The source of the relatively large concentrations of uranium in the Number 12 Coal in the Qinglong Coalfield in the Guizhou Province is thought to be an intrusive diabase (Yang, 2007).

Similarly, there are coal seams in southern Brazil that contain anomalously large amounts of uranium. As discussed by Depoi et al. (2008), the high-ash bituminous Figueira coal mined in the Permian-age Parana Basin may contain about 72 mg/kg uranium or 28 pCi/g as ^{238}U. Flues et al. (2007) noted that there is sandstone unit stratigraphically above the Figueira coal that contains 0.148% uranium. It has been speculated that uranium-rich waters may have enriched the coal during its formation (Depoi et al., 2008).

Uranium Decay Products and Potassium-40

Uranium (99.3% as ^{238}U) and thorium (100% as ^{232}Th) each decay into a series of daughter products. The uranium-238 decay series and the thorium-232 decay series yield a variety of daughter radionuclides that in turn decay into other radioactive species such as radium and radon (see Appendix A). Uranium in coal is in radioactive (secular) equilibrium with its decay products. In secular equilibrium, the rate of decay of uranium is equal to that of its decay product. Secular equilibrium occurs when the half-life of the daughter isotope is much shorter than the half-life of the parent isotope. For example, Zielinski and Budahn (1998) reported that six bituminous coal samples from Kentucky contained 0.64 ± 0.30 pCi/g ^{238}U, (1.94 ± 0.91 mg/kg), and it appeared to be in secular equilibrium with 0.67 pCi/g of ^{226}Ra (0.67×10^{-7} mg/kg ^{226}Ra). The concentration of ^{226}Ra was not significantly different (± 10 to 15%) from the parent ^{238}U in any sample.

Unrelated to either the uranium or thorium decay series, coal contains radioactive ^{40}K because coal contains potassium associated with sediments and clay minerals. Finkelman (1993) calculated the average amount of potassium in U.S. coals as 0.18%, based on 7,830 samples. Thus, a U.S. coal would contain about 0.216 mg/kg of ^{40}K, and yield about 1.53 pCi/g. The amount of ^{40}K in coal is the same order of magnitude of that in U.S. soil. UNSCEAR (2000) estimated that the concentration of ^{40}K in U.S. soils varies from 2.70 to 18.9 pCi/g (0.38 to 2.66 mg/kg).

Outside the United States, Lu et al. (2006) reported the average concentration of ^{40}K in bituminous coal samples in China as 2.7 pCi/g (0.38 mg/kg). Lignite coal samples in Greece contained 1.84 to 5.59 pCi/g of ^{40}K (0.26 to 0.79 mg/kg) (Simopoulos and Angelopoulos, 1987; Karangelos et al., 2004). Mishra (2004) reported that ^{40}K varied from 0.4 to 12 pCi/g (0.06 to 1.69 mg/kg) in subbituminous coal samples of India.

Radionuclides in Coal Combustion Products

Typical Coal Ash in the United States

According to the COALQUAL database, the average ash content of coal combusted in the United States is 10.06 ± 6.33%, based on 6,665 coal samples. Therefore, as a first approximation, the concentrations of uranium, thorium, and ^{40}K in coal ash (fly ash and bottom ash) can be estimated as 10 times that in the source coal, assuming no losses by volatilization and 100% capture by the ash. This approach was first used by the USGS (1997) who concluded that the uranium concentration of most fly ash is in the range observed in some shales and granitic and phosphate rocks (Figure 3-3). Based on the average concentrations of uranium, thorium, and potassium in all U.S. coals as reported by Finkelman (1993) and Kolker and Finkelman (1998), a typical coal ash would contain about 7 pCi ^{238}U/g, 4 pCi ^{232}Th/g, and 15 pCi ^{40}K/g (21 mg/kg ^{238}U, 36 mg/kg ^{232}Th, and 2.1 mg/kg ^{40}K). These estimates are in agreement with previous assessments. Based on the information available in the 1970s, the U.S. EPA (1984) calculated average estimates of 9 pCi/g for ^{238}U (27 mg/kg) and 4 pCi/g for ^{232}Th (36 mg/kg). Because the radionuclides initially present in the coal are concentrated by combustion, coal ash is considered a TENORM.

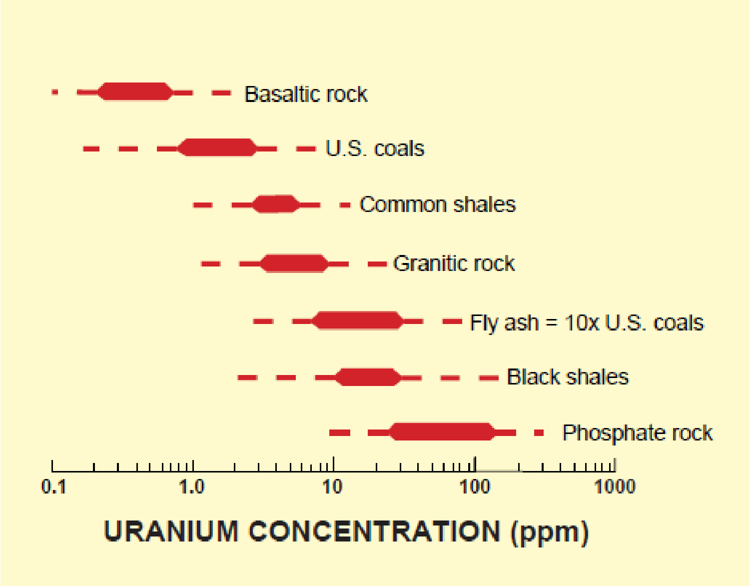

Figure 3-3
Typical range in uranium concentration in coal, fly ash, and a variety of common rocks (USGS, 1997).

Unlike the COALQUAL database, there is no analogous USGS dataset for coal ash. However, there are studies that indicate that the estimated radionuclide concentrations above are valid. For example, in a study conducted by Zielinski and Budahn (1998), the mean concentration of ^{238}U in 17 fly ash samples derived from bituminous coal in Kentucky was 4.67 pCi/g (14 mg/kg). The mean concentration of ^{238}U in 6 feed-coal samples was 0.64 pCi/g (1.94 mg/kg). The ratio of ash-to-coal was 7.3. The fly ash:coal ratio for ^{226}Ra was 6.9 and 9.2 for ^{210}Pb. Bottom ash samples contained 3.73 ± 0.96 pCi/g ^{238}U (11.3 ± 2.91 mg/kg), 4.26 ± 1.43 pCi/g ^{226}Ra (4.26 (± 1.43) x 10^{-3} µg/kg), and 2.17 ± 1.71 pCi/g ^{210}Pb (2.82 (± 2.22) x 10^{-5} µg/kg).

A study by Roper et al. (2013) provided activity measurements of ^{238}U, ^{232}Th, and ^{40}K in fly ash samples derived from eastern bituminous coals and western subbituminous coals (Table 3-1). The mean activities of ^{238}U and ^{232}Th in both types of fly ash were less than those predicted for a typical fly ash based on an ash content of 10%.

EPRI maintains a database (CPInfo) on the elemental composition of CCPs. This database indicated that the concentration of U varied from 3.15 to 30.4 mg/kg (1.0 to 10.0 pCi/g as ^{238}U) in fly ash, and from 2.40 to 17.6 mg/kg (0.8 to 5.8 pCi/g as ^{238}U) in bottom ash (Table 3-2). Thus, this database also suggests that 21 mg/kg (7 pCi/g of ^{238}U) is a reasonable, order-of-magnitude estimate for some types of coal ash, while it is an overestimate for others. The EPRI database also indicated that thorium ranged from 18 to 27 mg/kg (2.0 to 3.0 pCi/g as ^{232}Th) in 21 weathered subbituminous fly ash samples, and yielded a mean of 21.7 mg/kg (2.4 pCi/g). This mean was slightly less than the thorium content calculated for typical ash (36 mg/kg; 4 pCi/g).

Table 3-1
Summary of uranium, thorium, and potassium-40 activities in CCP samples[1] (as pCi/g).

Coal		^{238}U	^{232}Th	^{40}K
Bituminous	Mean	3.21 (9.72 mg/kg)	1.97 (17.9 mg/kg)	15.4 (2.27 mg/kg)
	Range	0.81 to 5.86 (2.45 to 17.8 mg/kg)	0.27 to 3.24 (2.45 to 29.5 mg/kg)	4.78 to 25.1 (0.67 to 3.53 mg/kg)
	Number of samples	n = 30	n = 30	n = 4
Sub-bituminous	Mean	3.11 (9.42 mg/kg)	2.19 (19.9 mg/kg)	4.62 (0.65 mg/kg)
	Range	1.94 to 5.64 (5.88 to 17.1 mg/kg)	1.43 to 2.97 (13.0 to 27.0 mg/kg)	2.35 to 8.18 (0.33 to 1.15 mg/kg)
	Number of samples	n = 9	n = 9	n = 9

[1] Derived from Roper et al. (2013)

Table 3-2
Summary of uranium concentrations in CCP samples[1] (as mg/kg).

CCP		Bituminous	Subbituminous	Lignite
Fly ash	Mean, standard deviation	11.2 ± 8.19	5.63 ± 4.37	4.14 ± 1.00
	Range	3.15 to 30.4	2.35 to 15.4	3.40 to 5.55
	Number of samples	n = 18	n = 9	n = 4
Bottom ash	Mean, standard deviation	7.89 ± 5.04	6.49 ± 7.99	3.88 ± 0.62
	Range	2.40 to 17.6	2.00 to 25.9	3.35 to 4.90
	Number of samples	n = 26	n = 7	n = 4

[1] EPRI 2012. Data from CPInfo Database

The ash content of the coal is a key factor influencing the levels of radionuclides in the fly ash and bottom ash. As the ash content increases, the enrichment factor (the ratio of the radionuclide in the ash to the radionuclide in the source coal) decreases (Figure 3-4). For example, Pires and Querol (2004) reported that the ratio of uranium in fly ash to a feed coal in Brazil was 1.8. The feed coal was a bituminous coal with an extremely large ash content of 49.7%. Using Figure 3-4, the predicted enrichment factor would be 2.0.

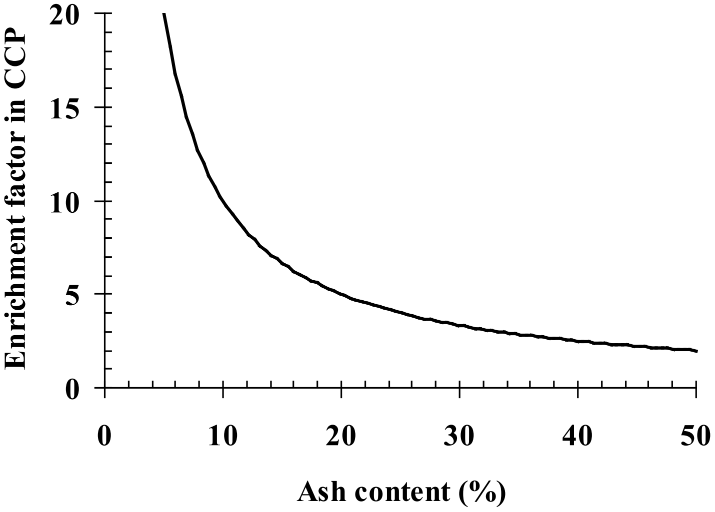

Figure 3-4
Enrichment factor (ratio of a radionuclide in CCP to the same radionuclide in the feed coal) as a function of ash content. The curve shown represents the degree of enrichment assuming that all of the radionuclide is captured in the ash and none of the radionuclide is lost by volatilization during combustion.

Alleman et al. (1998) collected coal, fly ash, and bottom ash samples from 16 power plants distributed throughout the state of Indiana. The feed coal used at each plant was likely from the Illinois Basin. The emphasis of the study was on the major sources of gamma radiation from CCPs: ^{228}Ac, ^{212}Pb, ^{212}Bi, and ^{208}Tl (from the ^{232}Th decay series), ^{226}Ra, ^{214}Pb, and ^{214}Bi (from the ^{238}U decay series), ^{235}U, and ^{40}K. Alleman et al. found that the major gamma source in both bottom and fly ash was ^{40}K, and when compared with coal samples, the enrichment factors were 8.4 and 9.9, respectively. When the average concentration of each gamma source was compared, the fly ash samples tended to contain larger amounts of each radionuclide than the bottom ash samples (Figure 3-5). Figures 3-6, 3-7, and 3-8 provide detailed depictions of the distribution of ^{226}Ra, ^{40}K, and ^{235}U, respectively. It also appeared that ^{228}Ac was in secular equilibrium with ^{212}Pb in the coal, bottom ash, and fly ash samples (Figure 3-9, for example), and ^{226}Ra appeared to be in secular equilibrium with ^{214}Pb and ^{214}Bi (Figure 3-10) in all three groups of samples.

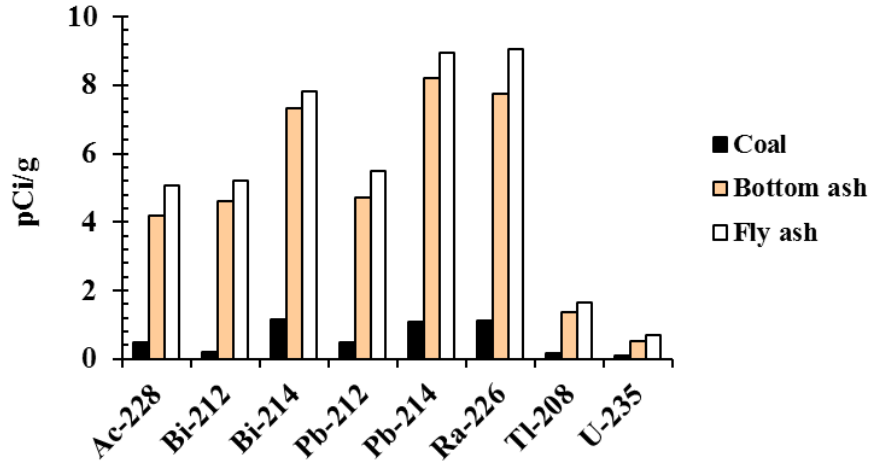

Figure 3-5
Mean concentrations of gamma-radiation sources in 21 samples of coal, bottom ash and fly ash (derived from Alleman et al., 1998).

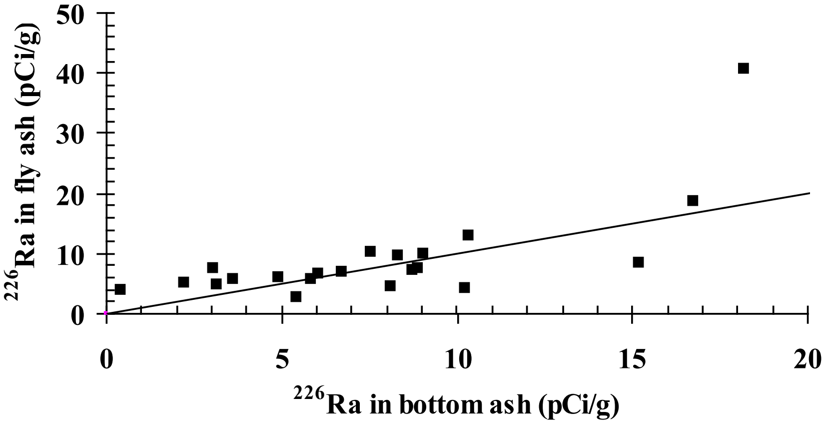

Figure 3-6
Comparison of the concentration of ^{226}Ra in 21 bottom ash samples with 21 fly ash samples. The line represents 1:1 agreement (data from Alleman et al., 1998).

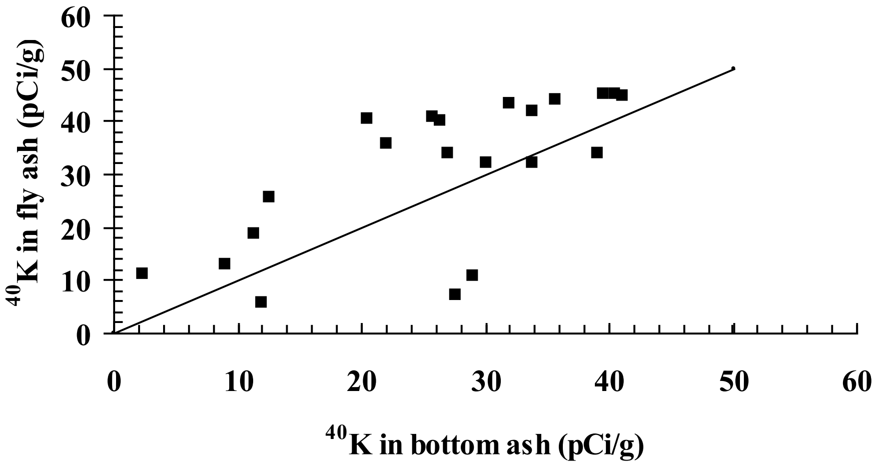

Figure 3-7
Comparison of the concentration of ^{40}K in 21 bottom ash samples with 21 fly ash samples. The line represents 1:1 agreement (data from Alleman et al., 1998).

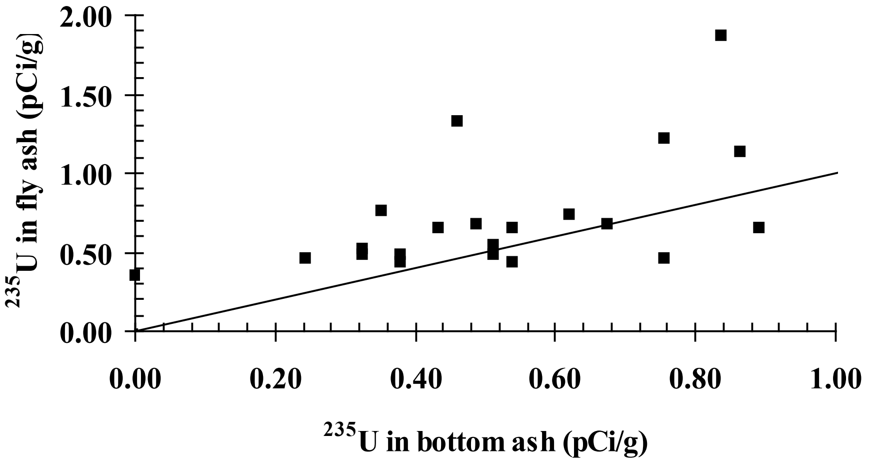

Figure 3-8
Comparison of the concentration of ^{235}U in 21 bottom ash samples with 21 fly ash samples. The line represents 1:1 agreement (data from Alleman et al., 1998).

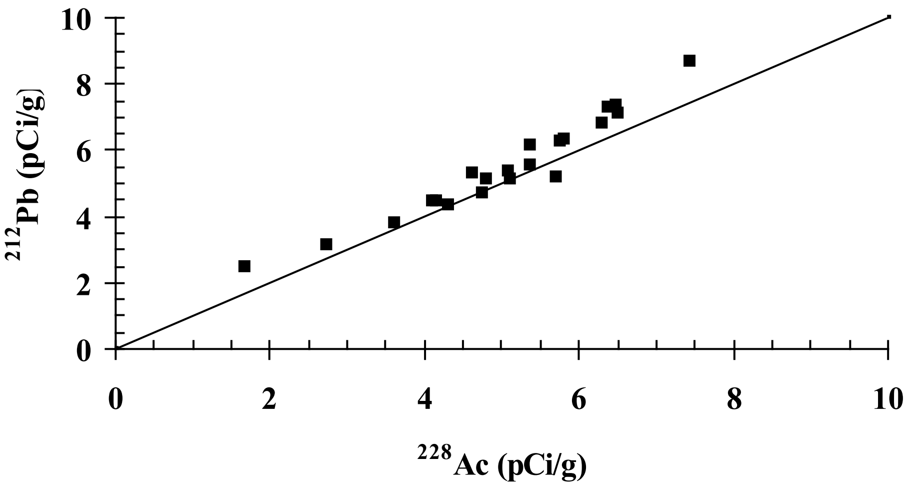

Figure 3-9
Concentrations of ^{228}Ac and ^{212}Pb in 21 fly ash samples. The line represents secular equilibrium (data from Alleman et al., 1998).

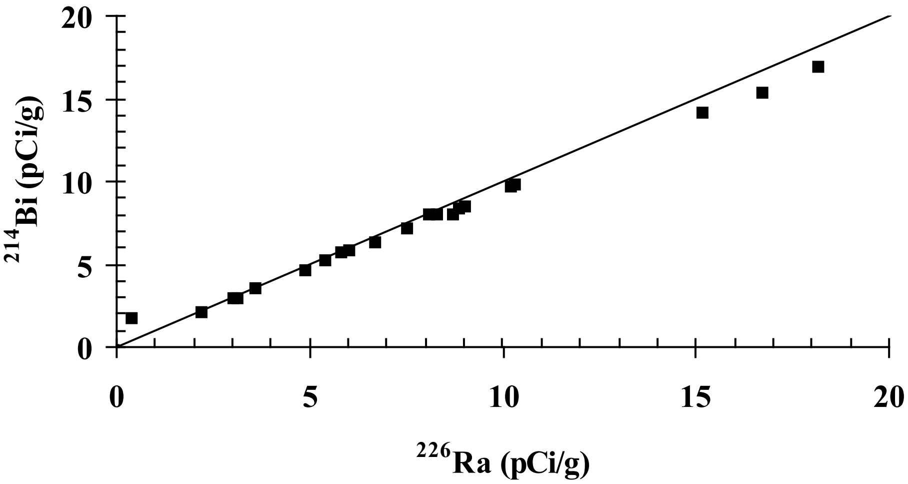

Figure 3-10
Concentrations of ^{226}Ra and ^{214}Bi in 21 bottom ash samples. The line represents secular equilibrium (data from Alleman et al., 1998).

Krysiak (1995) conducted a field-scale site characterization study of radionuclides in an ash landfill in Ohio. Krysiak used a 500 x 500 square foot grid to collect 67 surface samples of bottom ash mixed with fly ash. The ash was relatively heterogeneous with respect to the radionuclides measured; ^{40}K, for example, varied from 0.54 to 8.83 pCi/g (0.08 to 1.24 mg/kg). Radium-226 ranged from

1.13 to 7.65 pCi/g. No information was provided about the source coal, and the ash landfill was operated from 1945 to 1991. Therefore, the CCP samples could have been subjected to leaching prior to sampling.

The concentration of radionuclides in ash may also depend on the particle size of the material. In fly ash, the uranium is more concentrated in the finer-sized particles (USGS, 1997). However, no obvious evidence of surface enrichment of uranium has been found in the hundreds of fly ash particles examined by USGS researchers. Lead-210 is sometimes enriched in fly ash relative to other decay products. Tadmor (1986) suggested that some of the more volatile daughters of ^{238}U are preferentially mobilized during combustion, then condense on particle surfaces as they cool while moving in the flue gases away from the furnace. Support for a volatilization-condensation mechanism is the observation that ^{226}Ra and ^{210}Pb are found in larger concentrations in smaller (< 10 μm) particles relative to the bulk ash. Polonium-210 has also been reported to be associated with fine (< 1μ) particles (Roeck et al., 1987).

High-Uranium Coal Ash

United States Coal Ash

As previously noted, no high-uranium coals are used for electricity production in the United States. However, some of the thin-bed high-uranium lignite coals in South Dakota were tested for uranium content in the ash. Breger et al. (1955) described an uraniferous lignite coal bed in South Dakota that contained 180 mg/kg of uranium. When samples were ashed under laboratory conditions, the resulting ashes contained about 0.12% uranium. Although these high-uranium coals are not used for electricity production, some were once mined as a low-grade ore of uranium. From 1963 to 1967, there were two facilities in North Dakota that heated the coal to concentrate the uranium. The coal was initially burned in pits at the source mines, then sent to the either the Belfield or Bowman (sometimes referred to as Griffin) facility where the ash would be heated in a rotary kiln, then sent by rail to uranium mills. The Belfield facility produced between 60 to 100 tons of ash per day from 1964 to 1966, then ceased production. The Bowman site produced between 80 to 90 tons per day. Unfortunately, no information was located on the concentrations of uranium in the ash. Hurst (1981) reported that about 283,000 pounds (128 metric tons) of uranium were produced from the Williston Basin coals before all the mining operations ceased because of diminishing uranium reserves, economic barriers, and the discovery of contaminated soil and groundwater at the ashing facilities.

Worldwide Coal Ash

As noted previously, coal at the Figueira power plant in Brazil contains anomalously large amounts of uranium (72.2 to 108 mg/kg or 23.8 to 35.8 pCi/g as ^{238}U). Flues et al. (2006) reported that the uranium content of fly ash samples was between 119 and 425 mg/kg (39.4 and 140 pCi/g as ^{238}U). Bottom ash samples contained between 133 and 192 mg/kg (44.1 and 63.5 pCi/g) of uranium. Flues et al. also reported that the radium-226 content varied from 39 to

102 pCi/g (0.04 and 0.10 µg/kg) in the fly ash samples, and between 37 and 98 pCi/g (0.04 and 0.10 µg/kg) in the bottom-ash samples. In a later study, Depoi et al. (2008) reported that the fly ash generated at the Figueira power plant contained 609 mg/kg uranium (201 pCi/g as ^{238}U), while ash samples collected at four other Brazilian power plants contained from 5.65 to 11.8 mg/kg (1.9 to 3.9 pCi/g as ^{238}U) uranium.

High-uranium CCPs are currently being considered as a viable commercial source of uranium outside the United States. As noted previously, some coal seams in the Yunnan Province of China contain anomalously large amounts of uranium. Sparton Resources Inc. announced that the fly ash pile at the Xiaolongtang Power Plant contains between 160 and 180 mg/kg of uranium (53 and 59 pCi/g) (World Nuclear News, 2007). Sparton extracted an ash sample with sulfuric acid and produced yellowcake, which is an intermediate product in the production of nuclear fuel. No recent information was located about the current status of uranium production.

Leaching of Radionuclides from Coal Ash

United States Coal Ash

Since the early 1980s, many laboratory and field-scale studies have been conducted to investigate the leaching behavior of the major, minor, and trace elements associated with coal ash. These studies have addressed the extent of leaching, leaching kinetics, and solid-phase equilibria of ash-water systems. While the leaching behavior of potential groundwater contaminants such as arsenic, boron, lead, and mercury have been studied in detail, there have been relatively few studies on the leaching of radionuclides.

It is possible to make some predictions about the leachability of uranium from CCP based on its physicochemical form. With increasing exposure to combustion temperatures, fly ash is largely composed of solid glassy spheres, hollow spheres (cenospheres), and filled spheres (plerospheres) in addition to solid, iron-rich spheres. Zielinski et al. (1999) suggested that the distribution of uranium within the glassy spheres was uniform, with no apparent enrichment of uranium on particle surfaces. If uranium is evenly distributed in the glassy or amorphous phases of most CCPs, then the extent and rate of leaching may be limited by the rate of dissolution of the relatively insoluble glassy particles when in contact with water.

Zielinski et al. (1999) conducted short-term batch extractions with 36 fly ash samples that were collected from a power plant in Ghent, Kentucky. The uranium content of the fly ash samples ranged from 10 to 20 mg/kg (3.3 to 6.6 pCi/g as ^{238}U). Leaching tests were performed using deionized water at a 1:20 solid:liquid (S/L) ratio and mixing for 18 hours. The pH of the suspensions ranged from 3.4 to 11.9. The authors found that the amount of uranium in solution was greatest under acidic ($pH < 5$) conditions. At a pH of about 3.4, the maximum amount of uranium in solution represented about 10 to 20% of the amount of uranium in the ash. In the pH range of 6 to 11.9, the solution concentrations were less than 1 µg/L, suggesting that less than about 0.2% of the matrix uranium was soluble under these conditions. Zielinski et al. (1999) also conducted limited column leaching tests with aged fly ash samples that were collected from an on-site pond. Although the experimental procedure was not described in detail, the results indicated that the amount of uranium in solution was generally less than 1 µg/L. The uranium content of the aged samples was not given.

Worldwide Coal Ash

Georgakopoulos et al. (2002) conducted both 18-hour batch extractions and column leaching experiments with fly ash generated by the combustion of Greek lignite coal. The fly ash sample contained 40.6 mg/kg (13.4 pCi/g) uranium and 34.0 mg/kg thorium (3.7 pCi/g as ^{232}Th). The authors applied the Synthetic Groundwater Leaching Procedure (SGLP) with a 1:20 S/L ratio. The column experiment consisted of a gravity-fed column containing 100 grams of sample at a rate of 2 mL/hour. The ash sample yielded an alkaline reaction (pH 11.9). Regardless of the procedure used, Georgakopoulos et al. found that less than 0.1% of the mass of either uranium or thorium leached from the samples.

The leaching of uranium and thorium from fly ash was investigated by Moreno et al. (2005) under controlled, laboratory conditions. In this study, 23 fly ash samples from coal-fired power plants in Europe were subjected to 24-hour batch-type extraction using a S/L ratio of 1:10 with distilled water. The power plants were in Spain, the Netherlands, Greece, and Italy. The type of coals used ranged from lignite to anthracite. The amount of thorium in the 23 ash samples ranged from 17 to 55 mg/kg (1.9 to 6.1 pCi/g as ^{232}Th). The pH of the short-term extracts varied from 6.40 to 12.54. The amount of thorium that leached from the solid material ranged from 0.01 to 0.06%. The amount of uranium in the ash samples varied from 5 to 29 mg/kg (1.7 to 9.6 pCi/g as ^{238}U). The amount of matrix uranium that was extracted into solution ranged from less than 0.01% to 0.16% of the total uranium. These results suggested that thorium and uranium were in physicochemical forms that were not readily leachable. Similarly, an earlier study, Querol et al. (2001), reported that 0.19% of the matrix uranium in four fly ash samples collected in Spain leached into solution. The samples were leached in both dilute batch systems and by the use of columns.

Pires and Querol (2004) conducted 2-hour and 24-hour batch extraction procedures and a relatively simple column experiment to study the leachability of uranium and thorium from fly ash samples derived from a high-ash (49.7%) bituminous coal in Brazil. The fly ash samples yielded an acidic reaction when in contact with water. There was no apparent enrichment of uranium or thorium in the fly ash: the fly ash samples contained 6.0 and 21 mg/kg (2.0 pCi/g as ^{238}U and 2.3 pCi/g as ^{232}Th) uranium and thorium. The application of the short-term extractions indicated that less than 1.3% of the matrix amounts of uranium and thorium were in extracts. The column experiment suggested that after 1,000 mL had been passed through a 2-gram sample of fly ash, about 9.5% and 1.9% of the matrix uranium and thorium had leached into solution.

Environmental Chemistry and Field Studies

The environmental chemistry of radionuclides can yield insights about their fate and movement in saturated-water systems after they have leached from ash. Many radionuclides will occur as cations in solution that can be retained or sorbed by suspended sediments or subsurface materials such as clay minerals, organic matter, and iron oxides. Sorption is a physicochemical process in which ions become concentrated at solid-liquid interfaces. The extent of sorption of many metals in solution increases with an increase in pH. In pH neutral and alkaline solutions, some metals precipitate to form solid phases.

For example, radium occurs as Ra^{2+} over a wide range of pH and Eh, and may be removed from solution by negatively charged clay surfaces, which retard the movement of radium relative to the velocity of surface or groundwater. The concentration of radium in solution can be controlled by the solubility of radium sulfate and carbonate minerals (ATSDR, 1990). It can also precipitate with calcium, strontium, and barium sulfate phases.

In neutral and relatively aerobic solutions, uranium can occur as U(VI) in the forms of UO_2^{2+} and UO_2OH^+, and in more alkaline systems such as some ash leachates, uranium can occur as various anionic hydroxyl complexes (Garrels and Christ, 1965). In anaerobic systems such as groundwater, uranium can occur as U (IV), and the amount in solution may be controlled by the solubility of uraninite (UO_2).

Thorium occurs only in the +4 oxidation state in nature. In natural waters, the concentrations of thorium are typically less than 0.002 mg/L (Vandenhove et al., 2009). Thorium can form complexes with dissolved carbonate, phosphate, and nitrate ions, which will increase the amount of thorium in solution. The maximum concentration of thorium in aqueous systems, however, may be controlled by the solubility of hydrous thorium oxide (Ryan and Rai, 1987).

Tracy and Prantl (1985) collected a limited number of water samples at an on-site storage lagoon for CCPs generated by the Nanticoke Thermal Generating Station in Ontario, Canada. The concentrations of ^{238}U, ^{226}Ra, and ^{210}Pb were all less than 3 μg/L. The authors concluded that leaching of radionuclides from CCP was not likely to be a serious concern.

In a review of U.S. coal fly ash, the USGS (1996) concluded that the uranium in fly ash particles was uniformly distributed throughout the glassy particles. It follows then that the release or leaching of uranium would be limited by the relatively slow rate of dissolution of the glassy-host particles. The USGS (1996) also proposed that, because fly ash leachate typically contains relatively large concentrations of sulfate, the concentration of radium released by fly ash particles would be limited by the solubility of radium sulfate.

In EPRI (2008), 18 leachate samples were collected from a total of three CCP management facilities in the Midwest. The samples were collected from impoundments and landfills, and analyzed for a comprehensive list of alpha and beta sources. Of all the alpha-radiation sources measured, the frequency of detection was ^{238}U > $^{233/4}$U > ^{226}Ra. Both ^{238}U and $^{233/4}$U were less than 1 pCi/L in all of the samples. Radium-226 was detected in 20% of the samples, but at concentrations that were also less than 1 pCi/L. Thorium-228 was detected in one sample (0.55 ± 0.26 pCi/L), but was not detected in any other sample. The alpha sources ^{212}Bi, ^{230}Th, ^{232}Th, and ^{235}U did not occur at levels greater than the minimum detectable concentrations. Potassium-40 was found to be the major source of the beta radiation. Of the beta-radiation sources investigated in the study, ^{40}K occurred most frequently, and in substantially larger concentrations (32.7 to 546 pCi/L) than the other beta sources. Radium-228 was detected in 67% of the samples, yielding a median of 0.76 pCi/L. Lead-214 was detected in three samples, ranging from 8.6 to 11.6 pCi/L. Other potential beta sources such as ^{137}Cs ^{208}Tl, ^{212}Pb, ^{212}Bi, ^{212}Bi, and ^{243}Th were not detected at concentrations greater than the minimum detectable concentrations. Additional information about the mobility of radionuclides in groundwater is given in EPRI (2008).

EPRI maintains the CPInfo database on the chemical composition of CCP leachate. Based on 50 leachate samples collected at either landfills or impoundments, the concentration of uranium reported as ^{238}U varied from 0.004 to 20.1 pCi/L (0.01 to 59.1 µg/L) in samples collected from lysimeters, leachate collection systems, leachate wells, impoundments, sluice water, and pore waters. However, the concentration of ^{238}U in 66% of the samples was between 0.004 and 1.0 pCi/L (Figure 3-11), yielding an overall median of 0.43 pCi/L. Values greater than 10 pCi/L appear to be outliers in the EPRI dataset.

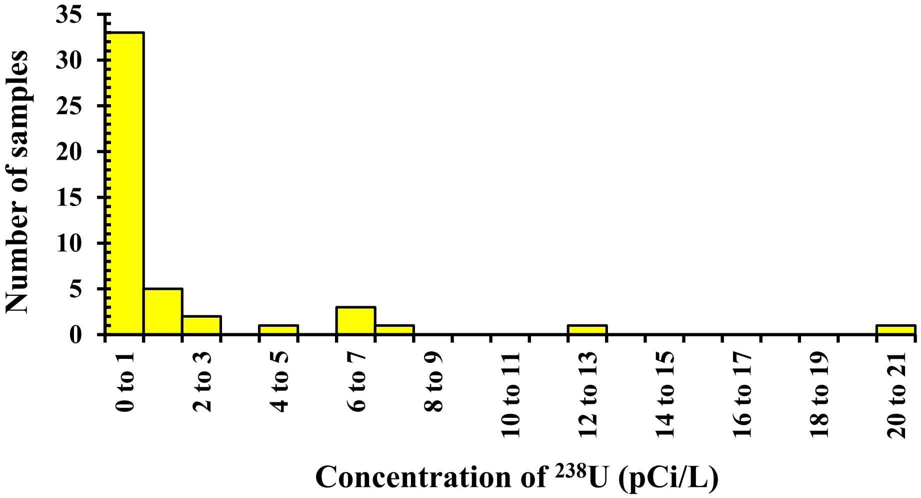

Figure 3-11
Concentration of ^{238}U in 50 leachate samples collected from 18 CCP management facilities (data from the EPRI CPInfo Database).

Mljac and Krizman (1996) presented field data suggesting that coal ash, derived from lignite coal in Slovenia, may have been a source of elevated concentration of ^{226}Ra in surface water adjacent to an unlined ash basin. The ash contained an average of 8.9 pCi/g of ^{226}Ra (0.01 µg/kg). A shallow lake that was adjacent to the ash basin contained 1.3 to 1.9 pCi/L of ^{226}Ra (1.3 to 1.9 x 10^{-6} µg/L), and discharged into a river. The one-time sampling study of the water and sediments in the river suggested that ^{226}Ra was increased in both media, but that the extent of influence was relatively limited downstream from the source (Figure 3-12). It appeared likely that sediments sorbed a fraction of the dissolved radium from solution. The variability of the background concentrations was not known.

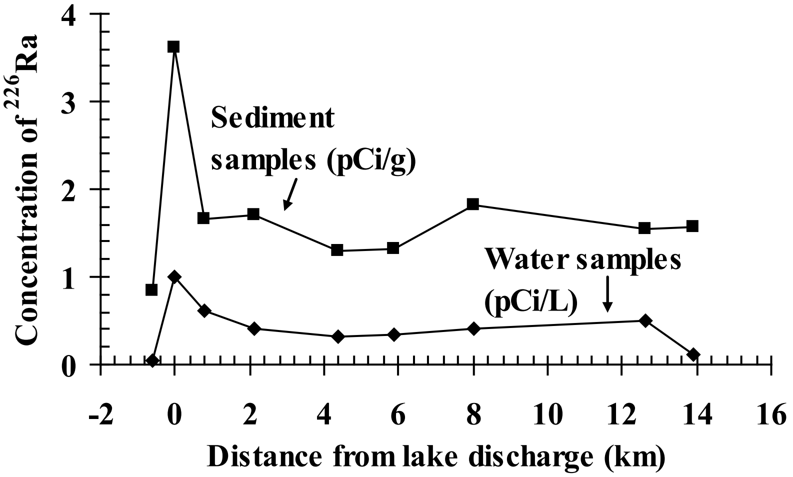

Figure 3-12
Concentration of ^{226}Ra in water and sediment samples collected downstream from a lake in an ash-disposal site (derived from Mljac and Krizman, 1996).

Vukovic et al. (1996) conducted a study on the impact of lignite ash on groundwater quality in Yugoslavia. The ash had been stored in a pond, and the authors collected shallow groundwater samples in and near the pond. Both gross alpha and beta measurements of the groundwater samples were less than 10 pCi/L. The concentrations of ^{238}U in the water samples were less than 1.2 pCi/L (3.52 µg/L). The authors concluded that the ash lagoon was not a significant source of uranium and thorium to groundwater.

Flue Gas Desulfurization Solids

Wet flue gas desulfurization (FGD) solids are the residue generated by removing sulfur dioxide from the exhaust gases of a coal-fired power plant. An alkaline source such as limestone or lime is added as a spray into the exhaust gas, where it reacts with SO_2 in the flue gas and is collected as a calcium sulfate or calcium sulfite slurry. Nearly all wet FGD systems in the United States collect fly ash prior to the FGD absorber, so the FGD solids contain little or no ash. Therefore, the sources of radionuclides in FGD will be the radionuclides initially present in the limestone or lime, and those associated with the small amount of fly ash carryover.

Because radionuclide concentrations in FGD solids are expected to be small, they are often not measured, and only limited data are available. The radionuclide content of FGD samples is provided in Table 3-3. Limited data for FGD samples suggest that the uranium content can vary from 1.8 to 3.2 pCi/g (5.5 to 9.7 mg/kg), and that ^{226}Ra is in secular equilibrium with the uranium as evidenced by the similar (activity) concentrations. It is difficult, however, to interpret these few data because no information was given about the type and age of the scrubber system, the type of coal used, and the ash content of the FGD samples.

The concentrations of uranium and thorium in spray dryer absorber (SDA) solids are summarized in Table 3-4. SDA is a dry FGD material, and may contain a large percentage of fly ash, depending on the type of collection system used. As shown in Table 3-4, the concentrations of both radionuclides were less than 21 mg/kg.

Table 3-3
Summary of radionuclide concentrations in FGD samples (as pCi/g).

Sample	^{238}U	^{226}Ra	^{210}Pb	^{210}Po	^{232}Th	^{214}Bi	^{208}Tl
"scrubber output"[1]	1.1 to 3.2	0.9 to 3.0	1.0 to 6.4	0.5 to 8.4	0.4 to 1.2	0.9 to 2.8	0.3 to 1.2
scrubber slurry[2]	1.8 to 2.8	2.1 to 2.7	2.9 to 6.2	1.4 to 3.6	0.4 to 1.3	-	-
scrubber sludge[3]	2.9	2.6	3.4	-	0.5	-	-

[1] Wagner et al. (1980).

[2] Wagner and Greiner (1982).

[3] Also reported ^{40}K as 5.6 pCi/g (Beck and Miller, 1980)

Table 3-4
Summary of uranium and thorium concentrations in SDA samples[1] (as mg/kg).

Radionuclide		
U	Mean, standard deviation Range Number of samples	7.14 ± 1.57 3.9 to 9.2 n = 8
Th	Mean, standard deviation Range Number of samples	16.11 ± 4.00 9.1 to 20.5 n = 8

[1] EPRI 2012. Data from the CPInfo Database

It is possible to make order-of-magnitude estimates of the concentrations of radionuclides in FGD solids by considering what is known about uranium in limestone and coal ash. Limestone and lime will contain uranium and its decay products. The mean concentration of uranium in sedimentary rocks is about 3 mg/kg (1 pCi/g) (ATSDR, 1999). In a study by Lasemi et al. (2008), fine-grain (0.84 to 4.76 mm) limestone samples were collected from 36 representative quarries in Illinois. The purpose of this study was to identify limestone sources for use as sorbents for desulfurization. The concentration of uranium in the limestone samples ranged from < 0.1 to 4.6 mg/kg (< 0.03 to 1.5 pCi/g as ^{238}U) with a mean of 1.39 mg/kg. If it is assumed that ^{226}Ra is in secular equilibrium with uranium, then the mean concentration of ^{226}Ra in the limestone samples would be 0.46 pCi/g (4.6 x 10^{-4} μg/kg).

The term "FGD gypsum" refers to FGD solids that are produced in wet FGD units that use forced oxidation to convert any calcium sulfite to calcium sulfate. FGD gypsum is used in commercial wallboard, and in agricultural applications. There has been some concern that wallboard produced using FGD gypsum may be source of indoor radon from the decay of radium.

Wallboard-grade FGD gypsum in particular contains very little fly ash (< 1%). As discussed earlier, the average fly ash is estimated to contain about 7 pCi/g (21 mg/kg) of uranium. If secular equilibrium is assumed, then the model fly ash would also contain 7 pCi/g of ^{226}Ra (7 x 10^{-3} μg/kg). Assuming that all of the radium initially present in the limestone remained in the FGD solids, and a 1% fly ash content, the total amount of ^{226}Ra in the FGD gypsum would be 0.53 pCi/g (5.3 x 10^{-4} μg/kg). Of that amount, 84% of the radium would be derived from the limestone. This result suggests that the concentration of radium—the parent radionuclide of indoor radon—in wallboard made from FGD gypsum should be close to background levels for radium because of the relatively low ash content of the material. This expectation was supported by a recent study by Roper et al. (2013) in which the activities of ^{238}U, ^{232}Th, and ^{40}K were measured in 20 FGD gypsum samples derived from eastern bituminous and western subbituminous coals. The mean activities of each radionuclide were less than 0.40 pCi/g. The activity of uranium was very low, ranging from 0.03 to 0.65 pCi/g.

EPRI also maintains a database on the chemical composition of FGD leachate. Based on 10 leachate samples collected at either landfills or impoundments, the concentration of uranium (reported as ^{238}U) varied from 0.007 to 16.5 pCi/L (0.02 to 48.5 μg/L) in samples collected from leachate collection systems, leachate wells, impoundments, and sluice water. However, the largest concentration appeared to be an outlier; the concentration of ^{238}U in 60% of the samples was less than 1.0 pCi/L (Figure 3-13), yielding an overall median of 0.27 pCi/L (0.79 μg/L), which is similar to the median for ash leachate (0.43 pCi/L). Both values are comparable to or less than the natural concentrations of uranium in surface and groundwater (EPRI, 2008), which underscores the fact that typical CCPs are not a significant source of soluble uranium.

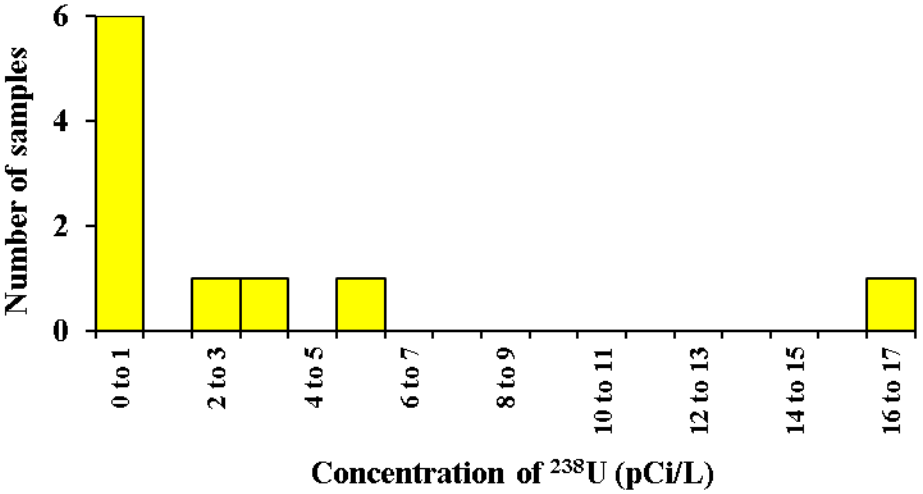

Figure 3-13
Concentrations of ^{238}U in FGD leachate samples collected from 5 CCP management facilities (data from the EPRI CPInfo Database).

Section 4: Radiological Exposure Assessment of Coal Combustion Products

Radiological Exposure

The occurrence of naturally occurring radionuclides in coal ash has been the impetus for assessments conducted to determine whether the radiation from the ash could pose a significant radiological hazard to occupationally exposed workers or to members of the public. There are a number of potential pathways by which radioactivity may be released from a CCP management facility or when used in building materials:

1. When stored in piles or surface impoundments, CCPs may be a source of external radiation to facility workers.

2. Inhalation and incidental ingestion of fugitive ash particles blowing from piles and lagoons may be another pathway.

3. The deposition of fugitive ash particles off-site from CCP facilities and their subsequent uptake by plants can also give rise to external exposure of the general public to radiation, inhalation and ingestion of ash particles, and ingestion of plants containing radionuclides.

4. When placed in landfills and impoundments, there is a potential for radionuclides to leach from CCPs and be transported to drinking water supplies, which can expose the general public via ingestion of water and inhalation of radon.

5. When added to building materials, CCPs have the potential to expose the public to external radiation and the inhalation or radon.

Common to most studies, the combined dose of gamma radiation from each radionuclide was calculated for an occupational-exposure scenario. Occupational exposures would be significantly greater than exposures to the general public, and as such represent worst-case exposure conditions.

Alleman et al. (1998) conducted a study to determine whether gamma radiation from coal ash would pose a significant radiological hazard to highway workers if the material was used as fill in highway embankments in Indiana. Coal, fly ash, and bottom ash samples were collected from 16 power plants distributed throughout the state of Indiana. The feed coal used at each plant was likely from the Illinois Basin. Each sample was analyzed using a germanium-crystal detector system, and the results were presented previously (Figure 3-5). Alleman et al. (1998) calculated the equivalent dose gamma radiation that a highway worker would be exposed to during a 2,000-hour work year by an embankment of uncompacted coal ash without any soil or asphalt cover. It was also assumed that the model embankment was infinite in both area and depth, and that the critical organ location of the worker was one meter above the surface of the embankment.

Using the analytical results derived from the ash samples, the gamma-ray flux from the ash was calculated for each gamma source, and silicon was used to represent ash to account for mass attenuation by the ash. Mass attenuation by the air above the embankment was also taken into account. Then the dose rate to human tissue was calculated for each gamma source using the appropriate mass absorption coefficient for soft human tissue. The results were summed to yield a total dose rate, which was in turn converted to a dose equivalent rate using a quality factor of 1.0 for gamma rays. The calculated dose equivalent rates for bottom ash ranged from 8.09 to 37.5 mrem/year, and from 7.90 to 59.1 mrem/year for fly ash.

Alleman et al. (1998) concluded that some of the ash samples yielded more gamma radiation than traditional construction materials such as sand, brick, clay, and limestone. However, if the average gamma radiation for the fly ash and bottom ash samples is compared with background levels (Figure 4-1), the levels measured from the CCP sample were generally less than both cosmic and terrestrial sources (as defined in Figure 3-1). Therefore, under an occupational exposure during a 2,000-hour work year to an average, uncovered fly ash embankment, the results represent an average of about 4% of the 2009 NCRP total natural background dose of 315 mrem/year, or the medical applications dose of about 310 mrem/year. Infrequent exposure to the general public would be significantly less. Alleman et al. concluded that gamma radiation from CCPs used in highway embankments presents a negligible radiological risk to the public.

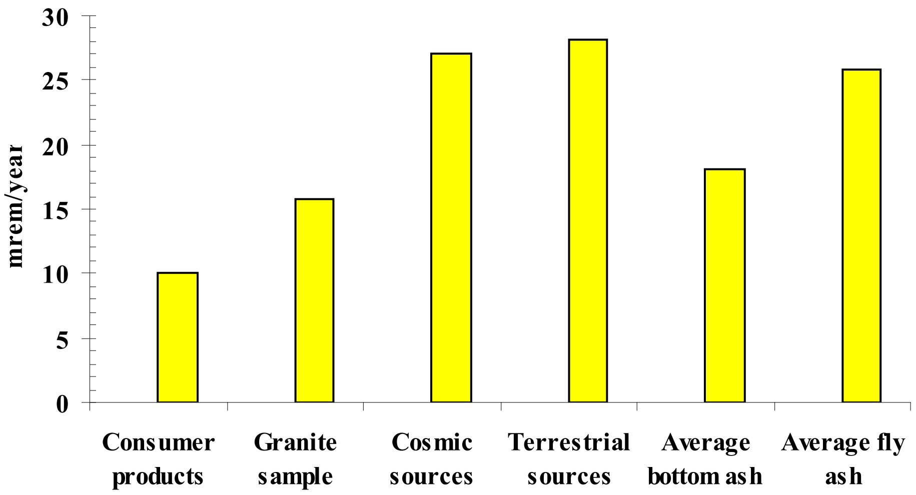

Figure 4-1
Comparison of the average dose equivalent to a highway worker from 21 fly ash and bottom ash samples with three background sources and a sample of granite (derived from Alleman et al., 1998).

Corbett (1983) estimated that coal ash in a landfill in the United Kingdom that contained typical concentrations of ^{40}K, ^{232}Th, ^{238}U, and ^{235}U would yield 9 mrem of gamma radiation per year to an exposed worker. This estimated equivalent dose is insignificant when compared with the 2009 NCRP total natural background dose of 315 mrem/year (Figure 3-1). Such an increase is insignificant in relation to natural variations in dose by geographic locations (Murray, 2003).

Smith et al. (2001) estimated the dose from direct radiation from a model ash placed in a landfill in the United Kingdom to landfill workers. It was assumed that the landfill workers were exposed for 50 hours per year, and that the mass of ash placed in the landfill was 10^8 kg (100,000 metric tons) per year. Smith et al. predicted that the maximum effective dose to landfill workers would be about 0.5 mrem/year. Of that dose, ^{238}U, ^{235}U, and the daughter products of both contributed 0.28 mrem/year and ^{232}Th and its daughters accounted for 0.19 mrem/year. The worker would be exposed to the equivalent of 0.2% of the 2009 NCRP total natural background dose of 315 mrem/year. Again, such an increase is a small fraction of the natural background variations in dose by geographic locations and elevation.

The gamma radiation from fly ash in a dry lagoon in Hong Kong was estimated by Tso and Leung (1996) by summing the mean activity of ^{226}Ra, ^{228}Th, and ^{40}K. They estimated the maximum absorbed dose rate in the air 1.0 meter above the center of the dry lagoon as 0.14 rad/year, which was slightly greater than the of local background dose (0.07 rad/year) in Hong Kong (Leung et al., 1990). During a 2,000-hour work year, a landfill worker standing on the dry lagoon would be exposed to an equivalent dose of about 33.0 mrem, which represents about10% of the total natural dose of 315 mrem per year.

Similarly, Mandal and Sengupta (2003) estimated the absorbed dose rate of gamma radiation above a subbituminous ash pond at the Kolaghat Thermal Power Plant in India. They estimated the maximum dose rate in the air 1.0 meter above the center of the dry lagoon as 0.13 rad/year. This calculated dose was made by summing the mean activities of ^{238}U, ^{232}Th, and ^{40}K multiplied by their respective dose-conversion factors (in units of rad-year/pCi-g) that were published in UNSCEAR (1988):

Absorbed dose (rad/year) =

$$0.0138(^{238}\mathrm{U}(\mathrm{pCi/g})) + 0.0215(^{226}\mathrm{Th}(\mathrm{pCi/g})) + 0.0014(^{40}\mathrm{K}(\mathrm{pCi/g})) = \qquad \textit{Eq. 4-1}$$

$$0.0138(2.7) + 0.0215(4.01) + 0.0014(7.20) = 0.13\ \mathrm{rad/year} \qquad \textit{Eq. 4-2}$$

During a 2,000-hour work year, a landfill worker standing on the dry lagoon would be exposed to an equivalent dose of about 30.1 mrem, which represents about 10% of the total natural dose of 315 mrem/year.

Based on the average concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in fly ash samples derived from lignite in Turkey, Cevik et al. (2007) estimated the absorbed dose rate of gamma radiation in the air 1.0 meter above the ash (in a hypothetical ash pond) as 0.095 rad/year. During a 2,000-hour work year, a landfill worker standing on the dry lagoon would be exposed to an equivalent dose of about 21.7 mrem, which represents 7% of the total natural dose of 315 mrem per year. Using the same three radionuclides in fly ash derived from lignite in Turkey, Turhan et al. (2010) estimated the total annual effective doses of external gamma radiation, inhalation, and ingestion by adult members of the public living near a hypothetical fly ash pile or landfill in a scenario described in European Commission (2002). The adult is, for example, assumed to spend 6,000 hours per year (68% of the year) in a house that is located 25 meters from the edge of the fly ash pile/landfill. Based on fly ash samples that were collected from 15 power plants in Turkey, Turhan et al. (2010) estimated that the mean effective annual dose was 7.7 mrem/year, which was insignificant when compared with the annual natural dose.

Occupational Exposure Assessment

An assessment of occupational exposure to a model fly ash pile was conducted using the "outdoor worker scenario." This scenario was derived from the U.S. EPA's Preliminary Remediation Goals for Radionuclides (see U.S. EPA, 2012c). The exposure routes were incidental ingestion of soil (ash) particles, inhalation of ash particles, and external exposure to radiation from the ash. Radon exposure was considered as only that emanating from the ash particles inhaled by the outdoor worker. In this scenario, a worker is exposed for 225 days for 8 hours per day (1,800 hrs/yr). It was envisioned that the employee was a heavy machine operator who worked in an ash storage area, and was exposed to the radiation from ash stored at a coal-fired power plant. An ash-particle emission rate of 1.36×10^9/kg was used. An air inhalation rate of 60 m^3/day and an ash inhalation rate of 100 mg/day were assumed. The ash inhalation rate is 5 times greater than would be used for the "resident scenario," which reflects why occupational exposures are greater than those for the general public.

As discussed previously, a typical fly ash contains about 7 pCi/g of uranium. For this assessment, it was assumed that ^{238}U was in secular equilibrium with its long-lived daughter products plus radon (Table 4-1). It was also assumed that the typical fly ash contained 4 pCi/g of ^{232}Th and that it was in secular equilibrium with its decay products. Potassium-40 was also included in the model ash. When the calculated doses were added together, the total effective dose from this model fly ash was about 3.3 mrem/year. Potassium-40 contributed about 76% of this calculated dose. This estimate of occupational exposure represents only 1.0% of the 2009 NCRP total natural background dose of 315 mrem/year. For comparisons, when the mean concentrations of ^{238}U, ^{232}Th, ^{226}Ra, and ^{40}K for all U.S. soils from UNSCEAR (2000) were used in the same type of assessment, the total effective dose was 0.31 mrem/year.

Table 4-1
Summary of a typical fly ash model and the calculated effective dose in an "outdoor worker soil" scenario.

Isotope	Concentration (pCi/g)	Half-life	Mode of decay, and specific activity	Calculated dose (mrem/year)
^{238}U	7	4.468 x 10^{9} years	α, 3.4 x 10^{-7} Ci/g	0.027
^{230}Th	7	80,000 years	α, 0.020 Ci/g	0.125
^{226}Ra	7	1,602 years	α, 1.00 Ci/g	0.201
^{222}Rn	7	3.823 days	α, 160,000 Ci/g	<0.001
^{214}Pb	7	27 minutes	β, 3.3 x 10^{7} Ci/g	<0.001
^{214}Bi	7	20 minutes	β, 4.5 x 10^{7} Ci/g	<0.001
^{210}Pb	7	21 years	β, 77 Ci/g	0.281
^{210}Po	7	138.4 days	α, 4,500 Ci/g	0.015
^{232}Th	4[a]	1.4 x 10^{10} years	α, 1.1 x 10^{-7} Ci/g	0.078
^{228}Ra	4	5.8 years	β, 280 Ci/g	0.077
^{40}K	15[a]	1.3 x 10^{9} years	β, 7.1 x 10^{-6}Ci/g	2.510
TOTAL				**3.32**

[a] See the subsection "Typical Coal Ash in the United States" in Section 3.

Radiological Impacts of Using Fly Ash in Building Materials

Fly ash is used as a partial replacement for portland cement. About 23% of the fly ash generated in the United States in 2012 was used in the production of concrete, concrete blocks, precast concrete products, and mortar (ACAA, 2014). Ash is used as a direct replacement for about 15 to 30% of the portland cement in concrete, and can be as much as 50% in some applications. In 2012, about 12 million tons of fly ash in the United States were used in concrete.

The radiation levels in buildings made with concrete containing ash may be enhanced by increased direct exposure, and by inhalation of radon, formed by the radioactive decay of ^{226}Ra:

$$^{226}\text{Ra} \rightarrow {}^{222}\text{Rn} + \alpha \qquad (^{222}\text{Rn half-life of 3.82 days}) \qquad \textit{Eq. 4-3}$$

Radon emanation is the process by which radon is transported from the edge of a solid particle, such as ash, to the gas-filled or liquid-filled pore spaces between the ash particles. Radon exhalation is the process of the actual release of radon from the pore space by diffusion and advection, and its subsequent movement to the ambient air (ATSDR, 2012). The radon emanation coefficient is the fraction of the amount of radon produced by radium decay that escapes from the solid particles and diffuses into the pores of the medium compared with the amount of radon that remains in the solid. The radon emanation coefficient is a dimensionless parameter and is represented as either a fraction or as a percentage. The radon exhalation rate (Q) is related to the emanation coefficient (Kovler et al., 2005a) as

$$Q\,(\text{pCi/m}^3\text{-sec}) = \lambda C_{Ra}\, \rho(\varepsilon/p) \qquad \textit{Eq. 4-4}$$

where λ = 2.1×10^{-6}/sec, the radon decay constant
C_{Ra} = ^{226}Ra activity/mass (Bq/kg)
ρ = density of the material (kg/m^3)
ε = radon emanation coefficient
p = porosity of the material

The addition of fly ash to concrete as a substitute for portland cement will likely increase the amount of radium in the final product, but the amount of radon that escapes from the concrete into the atmosphere may or may not be proportionally greater. An early study conducted in Norway (Stranden, 1983) measured the exhalation of ^{222}Rn from crushed concrete cubes. About 25% of the portland cement was replaced with fly ash. He reported that the addition of 5% fly ash by weight to “ordinary Norwegian concrete” yielded a product that produced less radon than the concrete alone. Another early study (Ulbak et al., 1984) reported that the replacement of as much as 30% of portland cement with fly ash by weight in Danish concrete did not seem to result in a significant increase in the radon exhalation rate. The average exhalation rate of 14 fly ash-concrete samples was 2.06 pCi/g-year. Four concrete samples without ash ranged from 2.94 to 4.38 pCi/g-year.

After reviewing the available studies, the U.S. EPA published its final rule on the use of fly ash in concrete (U.S. Federal Register, 1983). Relevant to this report are three conclusions (paraphrased from Federal Register, 1983, p. 4248):

2. "Although the rate at which radon is created is directly related to the radium content, other factors may inhibit radon emanation . . . Because fly ash . . . has a glassy structure [that] keeps most of the radon from escaping. The emanation [coefficient] has been measured at no more than a few percent. In contrast, typical soil and soil-like materials tend to have an emanation [coefficient] in the neighborhood of 20 percent." [Radon emanation coefficients for soils have ranged from 12% to 70% (see Nazaroff et al., 1988)].
3. "[The] EPA believes that the use of typically-occurring fly ash in concrete does not constitute a significantly different radiation risk than the risk from the cement it replaces, and neither of these is significantly different from the radiation risk posed by common soil."

Similarly, the USGS (1997) concluded that "the radioactivity in a typical fly ash is not significantly different from that of more conventional concrete additives or other building materials such as granite or red brick." Furthermore, the USGS (1997) concluded that the increased dose from fly ash-concrete in a residence would be no more than 3% as compared to natural background radiation, and that emanation of radon from fly ash is less than natural soil that contains the same amount of uranium.

Research conducted since the U.S. EPA's rule has provided additional insight into radon coefficients and exhalation rates. Siegel et al. (2006) re-examined the work of Stranden (1983) and Ulbak et al. (1984) and others. When exhalation rates were plotted as a function of the amount of ^{226}Ra in fly ash, it appeared that there was a linear relation between ^{226}Ra and the amount of radon generated by the decay of radium (Figure 4-2). However, Siegel et al. concluded that the occupants of a residence with a typical air exchange rate are unlikely to be exposed to a significant increased health risk from concrete containing fly ash.

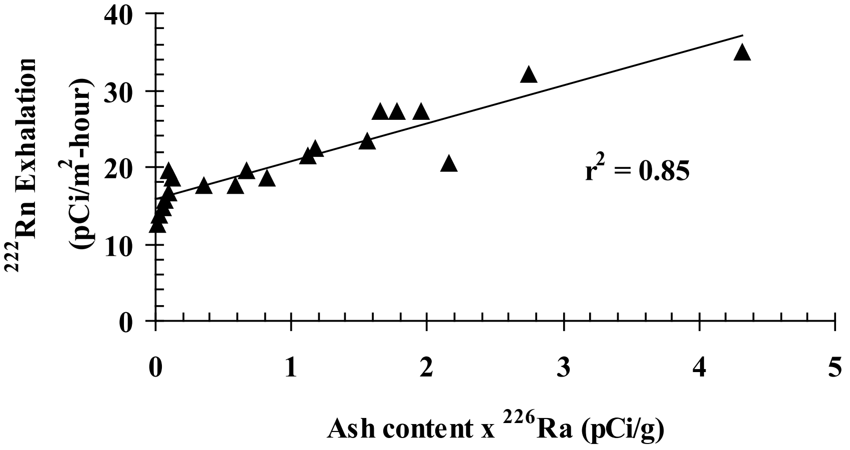

Figure 4-2
Relationship between the amount of ^{226}Ra in fly ash versus the ^{222}Rn exhalation rate (derived from Siegel et al., 2006).

Kalkwarf et al. (1985) and Barton and Ziemer (1986) reported that the radon emanation coefficient of fly ash increases with a decrease in the particle size of the ash and that the radon emanation coefficient is dependent on the moisture content of the ash. For example, when the moisture content of the fly ash sample was greater than 20%, the radon emanation coefficient decreased. Yu (1994) measured the radon exhalation rate from conventional concrete blocks, and compared the rates measured with concrete blocks in which 15% of the portland cement was substituted with fly ash The proportion of cement used in the concrete blocks was not given. Based on four concrete blocks without fly ash, each measured in triplicate, the average radon emanation rate was 0.266 ± 0.015 pCi/m^2-sec. The ash-containing samples yielded a rate of 0.284 ± 0.018 pCi/m^2-sec. Yu (1994) concluded that the addition of 15% fly ash to concrete would not result in a significant increase in radon exposure. Yu et al. (1996) also provided experimental evidence that the radon exhalation rate from concrete-containing ash blocks decreased with time. As the concrete ages, the densification of the microstructure of ash-containing concrete may also reduce radon exhalation (Kovler et al., 2005a, b).

Smith et al. (2001) conducted a dose assessment resulting from the use of fly ash in building materials in the United Kingdom. They chose 5% as the best estimate of an emanation coefficient. Both external radiation from radionuclides in concrete and concrete blocks containing ash (referred to as cinder blocks in the United States and New Zealand), and the dose resulting from the inhalation of both ^{220}Rn and ^{222}Rn were considered. A model ash contained radionuclide activities that were based on the averages of published sources. It was assumed that both the cinder blocks and the concrete contained 30% ash, which was regarded as fairly typical in the United Kingdom. Their results (Table 4-2) suggested that the additional dose to a resident in a model home with 30% ash by weight in the building material as a replacement for cement in the blocks and concrete would be about 20 mrem/year. This value represents 6% of the 2009 NCRP total natural background dose of 315 mrem/year.

Table 4-2
Predicted effective dose (mrem/year) from concrete to a resident living in a home with and without an ash component (derived from Smith et al., 2001).

Scenario	External exposure	Inhalation of radon	Total dose
Dose from building materials not containing ash	75.8	50.8	126.6
Dose from concrete and building blocks containing 30% ash	89.3	57.4	146.7
Additional dose using 30% ash	13.5[1]	6.6	20.1

[1] The additional external dose resulted from 34% ^{238}U, 27% ^{232}Th, and 39% ^{40}K.

It should be noted that most building materials contain naturally occurring radionuclides (Table 4-3). For example, Pavlidou et al. (2006) reported that the average concentrations of ^{226}Ra, ^{232}Th, and ^{40}K in concrete in the United Kingdom are 0.51, 0.30, and 4.94 pCi/g, respectively. Bricks made in Hungary contain ^{226}Ra in concentrations of 0.81 to 4.0 pCi/g (Trevisi et al., 2012). Granite countertops also contain naturally occurring radionuclides. Myatt et al. (2010) estimated the annual dose from spending 4 hours per day in a hypothetical kitchen containing granite countertops as 0.5 to 18 mrem/year, depending on the source of the granite. The authors concluded that granite countertops present a negligible risk to human health. Lu et al. (2012) assessed the radioactivity of building materials in Xianyang, China, and concluded that the annual effective dose of each material was less than 100 mrem/year.

Table 4-3
Summary of ^{226}Ra, ^{232}Th, and ^{40}K concentrations in building materials (IAEA, 2003 and Lu et al., 2012).

Material	**^{226}Ra**	**^{232}Th**	**^{40}K**
Concrete	0.03 to 6.75 pCi/g (0.03 to 6.75 ηg/kg)	0.03 to 5.13 pCi/g (0.25 to 46.6 mg/kg)	0.14 to 42.4 pCi/g (0.02 to 5.97 mg/kg)
Cement	0.19 to 4.86 pCi/g (0.19 to 4.86 ηg/kg)	0.19 to 6.48 pCi/g (1.72 to 58.9 mg/kg)	0.65 to 23.0 pCi/g (0.09 to 3.23 mg/kg)
Clay (red) bricks	0.03 to 5.40 pCi/g (0.03 to 5.50 ηg/kg)	0.03 to 5.40 pCi/g (0.25 to 49.1 mg/kg)	1.62 to 54.0 pCi/g 0.23 to 7.61 mg/kg)
Limestone	0.16 to 1.35 pCi/g (0.16 to 1.35 ηg/kg)	0.03 to 0.81 pCi/g (0.25 to 7.36 mg/kg)	0.14 to 18.9 pCi/g (0.02 to 2.66 mg/kg)
Tiles (glazed and unglazed)	0.81 to 5.40 pCi/g (0.81 to 5.40 ηg/kg)	0.54 to 5.40 pCi/g (4.91 to 49.1 mg/kg)	4.32 to 38.1 pCi/g (0.61 to 5.36 mg/kg)
Natural gypsum	< 0.03 to 1.89 pCi/g (< 0.03 to 1.89 ηg/kg)	< 0.03 to 2.70 pCi/g (< 0.25 to 24.6 mg/kg)	0.19 to 7.56 pCi/g (0.03 to 1.06 mg/kg)
Roof tile	1.10 to 1.44 pCi/g (1.10 to 1.44 ηg/kg)	1.58 to 2.10 pCi/g (14.3 to 19.1 mg/kg	18.4 to 21.p pCi/g (2.59 to 3.01 mg/kg)
Hollow brick	1.18 to 1.39 pCi/g (1.18 to 1.39 ηg/kg)	1.50 to 1.74 pCi/g (13.7 to 15.8 mg/kg)	17.5 to 20.5 pCi/g (2.46 to 2.88 mg/kg)

Taylor-Lange et al. (2012) conducted Monte Carlo simulations of radon emanation from hypothetical fly ash-concrete mixtures, based on published sources. A 5% emanation coefficient was used in each simulation. The investigators found that concrete floors made of 25% fly ash by weight as a replacement for cement in a simulated home resulted in an annual effective dose of ≤ 9.8 mrem/year. A dose of 9.8 mrem/year represents an increase of about 4% to the effective dose of 228 mrem/year resulting from the inhalation of both ^{222}Rn and ^{220}Rn and their decay products in the United States. Taylor-Lange et al. (2012) concluded that the magnitude of this increase would pose little risk to human health. In a recent study, Taylor-Lange et al. (2014) measured the concrete emanation fraction of four concrete mixtures in which 25% by weight of the cement was replaced with fly ash samples generated in Texas. The concentration of uranium in fly samples was greater than in the cement, but the emanation fraction was either about the same as or less than that from the concrete control (containing no fly ash). Sakoda et al. (2011) summarized a large number of studies on radon emanation fractions for a wide range of materials including fly ash.

Roper (2012) also conducted Monte Carlo simulations to estimate the total effective dose from ^{222}Rn and external (^{238}U + ^{232}Th + ^{40}K) sources to a person standing in the center of a hypothetical room composed entirely of concrete mixed with fly ash. The amount of fly ash was varied from 0% to 25% by weight as a substitute for cement. Roper also varied the size of the room, the age and gender of the occupant, the type of fly ash, and the amount of time spent in the hypothetical room. The radionuclide activities used in the simulations were taken from Roper et al. (2013). Of all the combinations used, the largest dose (136 mrem/year) was calculated when an adult female remained in a small (6 x 12 x 8 ft^3) room (such as a prison cell) 100% of the time when the concrete contained 25% fly ash as a substitute for cement, and the fly ash was derived from bituminous coal. Under the same conditions, however, the concrete without fly ash yielded a total dose of 102 mrem/year. This estimated dose represented an increase of 11% to the 2009 NCRP total natural background dose of 315 mrem/year. Roper (2012) concluded that the total doses estimated from the fly ash-concrete mixtures were insignificant when compared to background levels from routine and medical radiation exposure (290 mrem/yr), even under this extreme exposure condition.

Concerned with fly ash utilization in Israel, Kovler (2012) summarized studies that had shown that the presence of fly ash in concrete can increase, decrease, or have no impact on the rate of radon exhalation rate from ash-concrete mixtures. He proposed that a lack of standardized protocols at the international level could have created the inconsistent results. Kovler (2011, 2012) recommended that a systematic study be conducted to determine all of the factors that influence the release of radon from concrete-ash mixtures.

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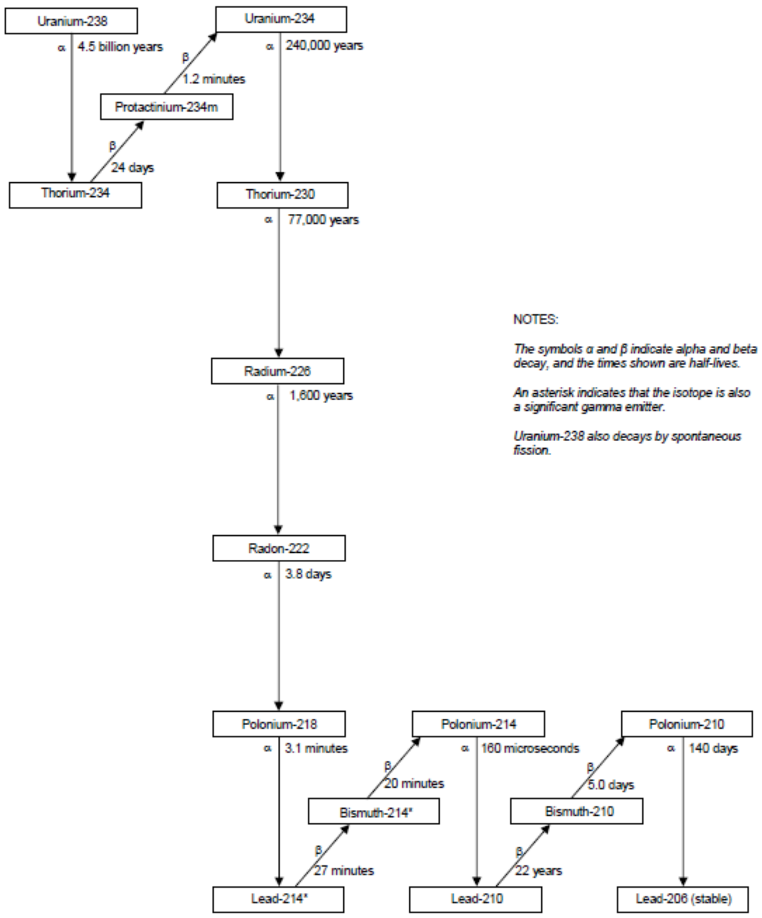
Appendix A: Uranium-238, Uranium-235, and Thorium-232 Decay Series

Uranium-238 Decay Series. Reproduced with permission from Peterson, J., M. MacDonell, L. Haroun, F. Monette, R. D. Hildebrand, and A. Taboas. 2007. Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas. Argonne National Laboratory, Environmental Science Division.



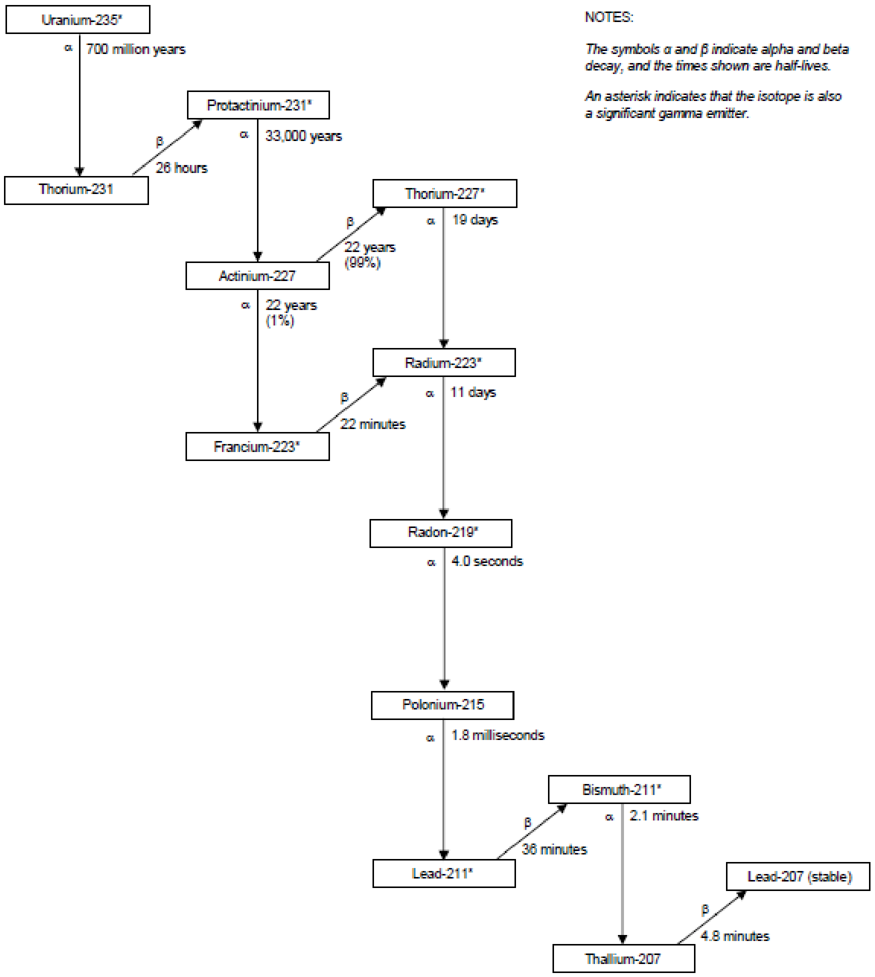
NOTES:

The symbols α and β indicate alpha and beta decay, and the times shown are half-lives.

An asterisk indicates that the isotope is also a significant gamma emitter.

Uranium-238 also decays by spontaneous fission.

Uranium-235 Decay Series. Reproduced with permission from Peterson, J., M. MacDonell, L. Haroun, F. Monette, R. D. Hildebrand, and A. Taboas. 2007. Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas. Argonne National Laboratory, Environmental Science Division.

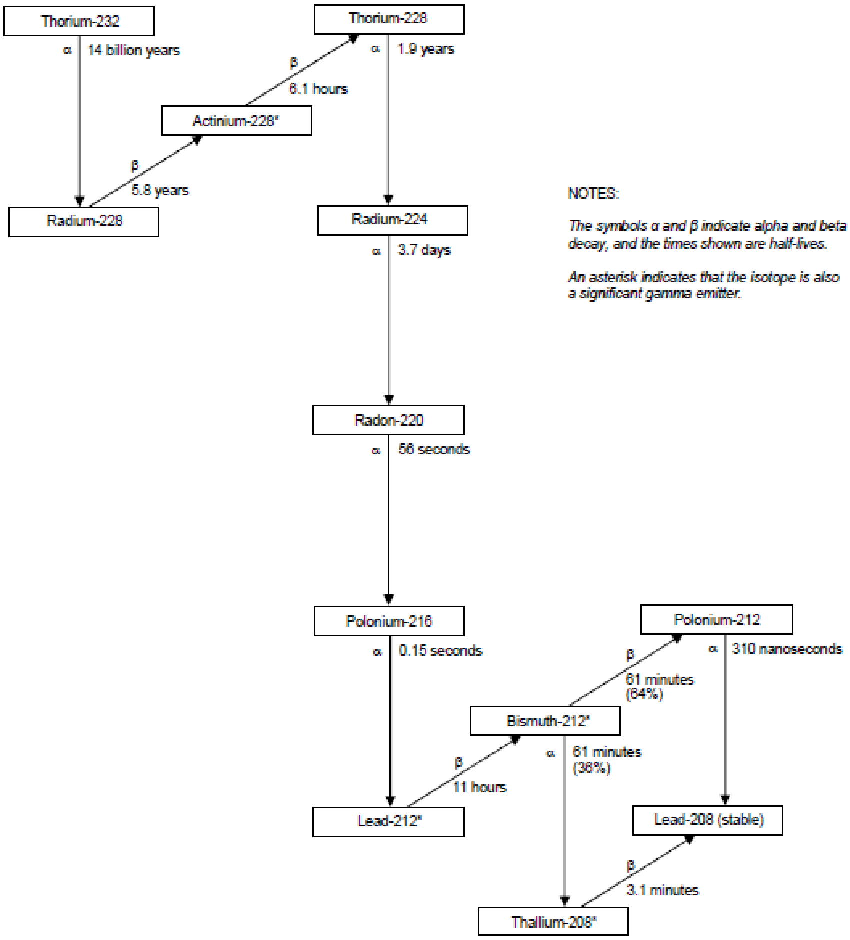


NOTES:

The symbols α and β indicate alpha and beta decay, and the times shown are half-lives.

An asterisk indicates that the isotope is also a significant gamma emitter.

Thorium-232 Decay Series. Reproduced with permission from Peterson, J., M. MacDonell, L. Haroun, F. Monette, R. D. Hildebrand, and A. Taboas. 2007. Radiological and Chemical Fact Sheets to Support Health Risk Analyses for Contaminated Areas. Argonne National Laboratory, Environmental Science Division.



NOTES:

The symbols α and β indicate alpha and beta decay, and the times shown are half-lives.

An asterisk indicates that the isotope is also a significant gamma emitter.

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