Chemical Constituents in Coal Combustion Product Leachate: Beryllium

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EPRI Project Manager
K. Ladwig

ELECTRIC POWER RESEARCH INSTITUTE
3420 Hillview Avenue, Palo Alto, California 94304-1338 • PO Box 10412, Palo Alto, California 94303-0813 • USA
800.313.3774 • 650.855.2121 • askepri@epri.com • www.epri.com

CITATIONS

This report was prepared by

Southern Company Generation
42 Inverness Parkway Bin B 426
Birmingham, Alabama 35242

Principal Investigator
J. D. Pugh

University of Pennsylvania Medical Center
Pulmonary, Allergy and Critical Care Division
Hospital of the University of Pennsylvania
834 West Gates Building
Philadelphia, PA 19104-4283

Principal Investigator
M. Rossman

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ABSTRACT

Beryllium occurs naturally at low concentrations in environmental media. Ambient surface and groundwater concentrations are typically lower than the maximum contaminant level (MCL) of 4 μg/L, but may exceed the MCL under very acidic conditions. Low concentrations in water are attributable to its occurrence in solid media at low levels, and to its limited mobility. If released from solid media, beryllium's affinity for adsorption and (co)precipitation limits its mobility under most environmental conditions.

Average concentrations of beryllium in coal are similar to those in igneous rocks, shales, and United States soils (<5 mg/kg). Coal ash will generally contain from 2 to 11 times the concentration of the feed coal, and concentrations in both fly ash and flue gas desulfurization sludge are mostly less than 20 mg/kg. There is limited available data concerning the concentrations of beryllium in coal ash leachate, but existing data suggests that beryllium does not leach from coal ash under normal field conditions. Exceedingly high or low pH conditions may result in beryllium mobility, and field data have shown that beryllium is an indicator of groundwater impacts from coal storage piles that generate acidic runoff.

Beryllium resides in sparingly soluble phases in both coal and coal ash. Potential inorganic phases include chrysoberyl ($BeAl_2O_4$), phenakite (Be_2SiO_4), or beryllium hydroxide ($Be(OH)_2$). Concentrations in coal pile run-off and coal ash leachate appear to reflect the limited solubility of chrysoberyl, although a direct link has not been established. When present in solution, the most likely aqueous forms are Be^{2+}, $BeSO_4$, or BeF^+. Beryllium has a strong affinity for sorption, as reflected in its distribution coefficients. Beryllium sorption is pH-dependent, and reported K_d^{Be} values range from 23 L/kg at pH 1.36 to 100,000 L/kg at pH 8. Beryllium has an affinity for solids at pH 6 that is 10,000 times its affinity at pH 2.

Beryllium is considered a potential human carcinogen, although there is no evidence that suggests negative human health effects for any pathway other than inhalation. Oral ingestion of beryllium has not been associated with any human clinical disease. While lung cancer is probably associated with increased beryllium exposure from inhalation, the best data seem to indicate that the high exposures that occurred at beryllium processing facilities in the past were responsible and suggest that current practices greatly reduce the potential for exposure at cancer-causing levels.

Remediation of beryllium is readily accomplished by pH control. Most beryllium solid phases are insoluble at near-neutral to alkaline pH. Beryllium can be removed from solution by its high affinity for adsorption and its strong tendency to precipitate or coprecipitate in insoluble phases. Other successful remediation techniques include cementation/vitrification and cement-based grouting.

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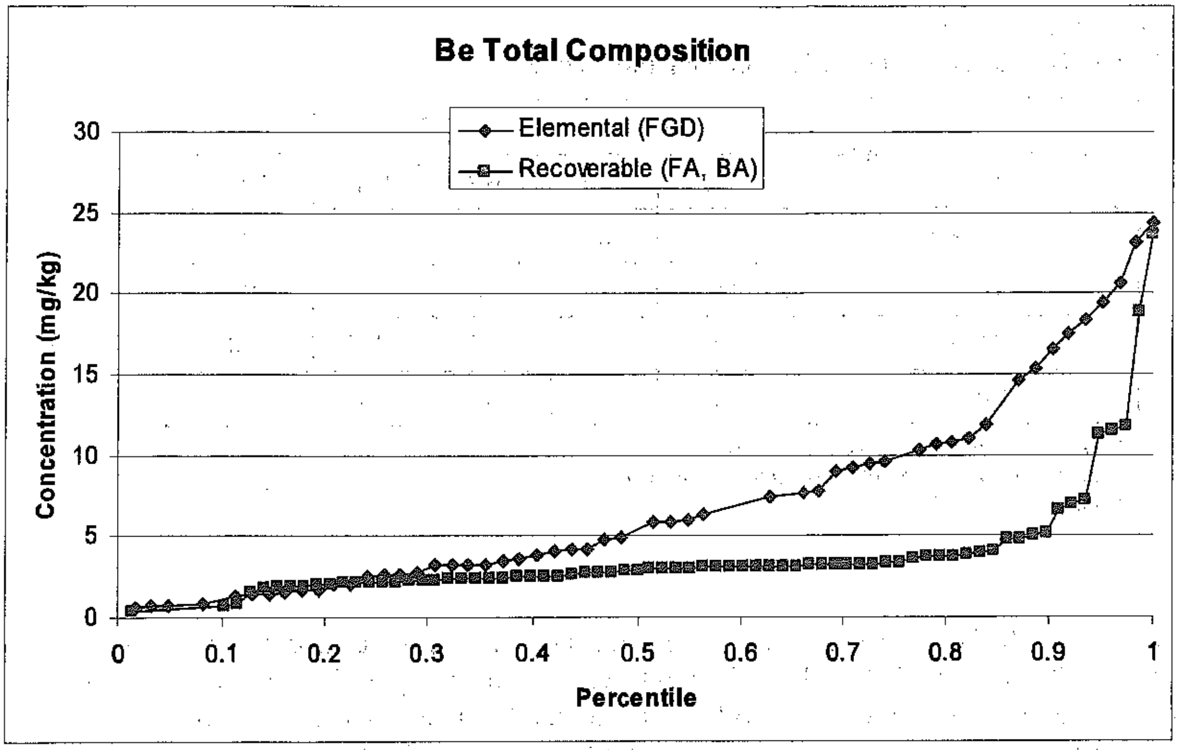

Figure 5-5
Solid composition data from ash and FGD solids (from EPRI CBEAS database)

Chemical Forms of Beryllium in Coal and CCPs

The chemical form of beryllium in coal and CCPs will have a large influence on its tendency to dissolve and be subsequently transported in solution. Many studies have investigated the chemical form of beryllium in coal, and most have concluded that beryllium is associated with the organic portion of coal. Some, however, suggest an inorganic affinity of beryllium in coal, while others have proposed an intermediate affinity (Xu et al., 2003).

The mineral forms of some trace elements in coal and coal ash were reported by EPRI (1999a). Beryllium was found to be associated with organics, oxides, silicates, and sulfides (Table 5-5). The authors reported that forms of beryllium in the silicate fraction may include beryllium aluminum silicate, beryllium aluminate, and beryllium oxides. However, they also noted that this fraction (determined by leaching with HF) could possibly represent beryllium that is associated with organic matter.

Table 5-5
Mode of occurrence of beryllium in coal and coal ash

Mode of Occurrence	Coal		Fly Ash		Bottom Ash	
	Bit	Sub	Bit	Sub	Bit	Sub
Organic	0	0	0	0	0	0
Oxides	50	20	0	0	0	0
Silicates	25	70	100	100	100	100
Sulfides	25	10	0	0	0	0

Bit = Bituminous, Sub = Subbituminous
Data reported as % of total Be content in sample
Source: EPRI (1999a)

Palmer et al. (2002) performed sequential chemical extractions on coal samples from eastern Kentucky. They found 50% of beryllium to be extractable by hydrofluoric acid (HF soluble), indicating an inorganic association with silicate minerals. The unleached fraction indicated an organic association. In another study, data from Palmer et al. (1998) suggested that 20-65% of beryllium in a subbituminous coal was organically-associated. On the other hand, Querol and Huerta (1998) found nearly all of beryllium in the same coal analyzed by Palmer et al. (1998) to be organically-associated based upon flotation experiments. Palmer et al. (2002) concluded that the reported association of beryllium in coal samples varies with selective extraction technique, and that the exact mode of occurrence of beryllium in coal and coal ash is unresolved.

Beryllium Leaching from Coal and CCPs

Ash Leachate Experiments: Laboratory and Field Conditions

Existing data suggests that beryllium does not leach appreciably from CCP solids. Three large-scale leaching studies were reviewed in which beryllium was included as a constituent:

- EPRI (1995) – Twenty-nine results are reported for TCLP and ASTM leaching tests performed on FGD solids. Only 3 of 29 results were detectable concentrations (detection level not reported), each resulting from ASTM leaching.
- EPRI (1998) – Fifty-four results are reported for TCLP and SPLP leaching tests performed on a variety of CCP samples. Seventeen of 27 TCLP results were above the detection limit, and only 3 of 27 SPLP results contained detectable beryllium. Detection levels were not reported, but results indicated that TCLP leaching is more likely to leach beryllium from coal ash than SPLP.
- EPRI (2006) – By far, the most representative cross-section of field data available comes from a recently completed EPRI study in which field leachate samples were collected from well-documented and well-described CCP management sites. Eighty-one field leachate