

Evaluation of CCP Leachate Interactions with Mine Overburden

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INTRODUCTION

In 2000, the U.S. Environmental Protection Agency (EPA) determined that coal combustion products (CCPs) should not be regulated as hazardous waste. Since that time, EPA has conducted extensive evaluations of CCPs to determine if CCPs should be otherwise regulated.¹ Additionally, in 2006, the National Academy of Sciences (NAS) reported on a study of CCPs placed at coal mines. Although no instances of contamination at coal mines were discovered, NAS recommended that the placement of CCPs at coal mines be regulated.² The debate of regulating CCPs has more recently heated up because of increased regulatory scrutiny of CCP disposal practices. Moreover, since 2000, the appropriate method to evaluate the potential impact of CCP leachate on the environment has been debated with ongoing activities by ASTM International, EPA, and the academic arena.

The assessment of the proper method to evaluate potential CCPs leachate environmental impacts is now likely to accelerate. This is evidenced by EPA's recent Information Collection Requests to utilities to gather information regarding disposal practices at utility sites and by other activities at EPA and in Congress. However, utility sites are significantly different from mine placement sites, particularly with respect to geology and hydrology. One primary difference at surface coal mines is the millions and millions of tons of mine overburden materials that are removed and placed back in the mine pit as part of the reclamation process. The research described in this paper demonstrates and discusses some of the attenuation effects that are likely to occur as CCP leachate travels through the coal mine backfill material.

Previous research into the attenuation capacity of northern Great Plains sediments and later using sediments from other states indicated that the ability of certain sediments to retain trace elements was strong as well as variable.³⁻⁶ Reliance on leaching tests alone to determine potential for environmental impact tells only one small part of a much larger story. Leachate chemistry can and often does undergo significant changes in trace element concentrations as it moves through sediments. In the past, silty to sandy overburden-type deposits from coal mining regions were tested. In these tests, either actual leachates or synthetic mixtures prepared in the laboratory were mixed with

sediments in prescribed ratios. The purpose of these experiments was to determine the distribution coefficients of select trace elements of concern. The determination of distribution coefficients (K_d) is a laboratory method to determine the distribution of leachate constituents between the liquid and solid phases in a mixed system consisting of leachate containing select analytes and the sediment under question, after a predetermined equilibration time. In previous experiments, it was found that an iron oxide hydroxide mineral, goethite, was primarily responsible for trace element attenuation, likely through sorption. In earlier work, the presence of reactive or acid-forming pyrite in the sediment evaluated caused precipitation reactions that would be transient and variable over time and would result in the formation of additional acidic leachate.

The determination of K_d values or degree of attenuation for different leachate constituents is important from the standpoint of understanding what might happen at a compliance boundary, especially in areas where hydraulic conductivity is too low to allow for field studies in adequate time frames. Even if hydraulic conductivity is not low, the determination of K_d s can be valuable in determining the rate of transport of various constituents through the subsurface environment. The sediments through which leachate travels in the environment can separate analytes differentially because not all leachate constituents will travel at the same rates, which will be dependent on individual K_d s. Upon subsurface transport, analytes can be expected to move at different rates, and these rates are reflected by the K_d s or measured attenuation. Elements with a high K_d will travel slower than elements with a lower K_d because of their greater affinity for the solid geologic material through which they are traveling. For mine settings where large volumes of overburden are replaced in the mine, K_d s or measured attenuation has value in facilitating an understanding of trace element mobility at the site.

In recent work, six mine site sediments from two mine sites (three from each site) were evaluated. The sediments were characterized as unconsolidated sediments, sandstone, and massive or fissile shales. The mine sites are located within EPA Region 5.

EXPERIMENTAL

Batch experiments were set up to evaluate the trace element attenuation of the sediments. Select analytes for this set of experiments were As, B, Cd, Cr, Pb, Ni, and Se. The liquid-to-solid ratios used were 20:1, 100:1, and a blank containing no sediment. The sample containers were rotated at about 30 rpm for 72 hours, allowed to settle for 1 hour, and were then filtered through 0.45 μm filters. pH was taken on both filtered and unfiltered samples. The sediments were evaluated for reactive pyrite by reaction with dilute hydrogen peroxide solution. Concentrations of select analytes were chosen not necessarily on the basis of what would be found in naturally occurring ash leachate but rather were based on concentrations that would allow meaningful determination of attenuation. The starting concentrations of analytes are for the most part higher than what would be expected in CCP leachates, in some cases, much higher. In all cases, concentrations were chosen to be high enough to allow accurate quantitation at 90% removal through natural attenuation mechanisms. The analytes

chosen were selected based on elements that would be expected to occur in natural ash leachate and included elements that exist as metallic, nonmetallic, cations, anions, and oxyanions in aqueous solution. There were two different liquid-to-solid loadings chosen. These were 20:1 and 100:1 and were selected to demonstrate the difference that the amount of geologic material contacted would have on attenuation. It is generally accepted that a much lower liquid-to-solid ratio would be a better simulation of a real-world setting. To determine attenuation capacity with a much lower liquid-to-solid ratio (representing a higher amount of solid loading) would require a much greater concentration of analyte and would be problematic in a laboratory experiment with respect to the volume of recoverable liquid for subsequent analyses. It is generally expected that a higher liquid-to-solid ratio such as the 100:1 would exhibit less attenuation because of the smaller amount of geologic material than in the 20:1 case.

RESULTS AND DISCUSSION

Results of pH measurements after treatment with 10% hydrogen peroxide (H₂O₂) solution are shown in Table 1. Addition of hydrogen peroxide facilitates the identification of the presence of acid-forming pyrite, usually present as framboidal pyrite, while avoiding the normal induction period required by pyrite in oxygenated water. Under other conditions, acid formation associated with the presence of pyrite may be slow, while with peroxide, this initial formation of sulfuric acid is greatly enhanced. It can be seen from the results in Table 1 that there is no significant activity that would lead to the production of acidic leachate, thus reactive pyrites were ruled out as a real consideration in the interpretation of results in these experiments. If reactive pyrites had been present, the pH would drop well into the acidic range.

Table 1. pH Determinations After Treatment using 10% Hydrogen Peroxide Solution

Sample	Initial pH	pH after treatment with H ₂ O ₂
Site 1 Unconsolidated Sediment	7.43	8.42
Site 1 Sandstone	7.89	7.17
Site 1 Massive Shale	5.96	6.17
Site 2 Unconsolidated Sediment	6.53	7.43
Site 2 Sandstone	6.54	7.80
Site 2 Fissile Shale	6.66	7.52

Sediments may have organic matter as a component of their composition, and these components have been shown to impact the capture of analytes in the attenuation process through sorption. These were not present in the samples evaluated in this study. Additionally, it is highly unlikely that organic constituents such as humic acids and related compounds from oxidized coals or residual organic material in overburden sediments were present. As reported in Table 2, the shale samples appeared gray, which was likely a result of reduced iron (Fe²⁺), while the unconsolidated sediment and

sandstone samples were brown, indicating the presence of oxidized iron (Fe^{3+}). The color noted is significant primarily with respect to determining if the geologic material came from an oxidizing or reducing environment. Brown coloration indicates oxidizing conditions, while blue/gray indicates reducing conditions with respect to iron.

Table 2. Results of Treatment of Sediments Using Dilute Hydrochloric Acid

Sediment	Description	Reaction with Dilute HCl
Site 1 Unconsolidated Sediment	Brown	Significant carbonate and sulfide present
Site 1 Sandstone	Brown	No H_2S or CO_2 given off
Site 1 Massive Shale	Gray	No H_2S or CO_2 given off
Site 2 Unconsolidated Sediment	Brown	No H_2S or CO_2 given off
Site 2 Sandstone	Brown	No H_2S ; a trace of CO_2 given off
Site 2 Fissile Shale	Gray	Some H_2S ; no CO_2 given off

The presence of sulfides is important with respect to trace elements such as nickel, which can form insoluble sulfides, while the presence of carbonates is important as a potential mechanism for providing alkalinity and carbonate ions, which can also be involved in the formation of insoluble carbonates of heavy metal elements such as lead and cadmium. Qualitative results indicated that most samples did not produce hydrogen sulfide or carbon dioxide on treatment with HCl as noted in Table 2. Only the Site 1 Unconsolidated Sediment produced significant releases, indicating the presence of sulfur and carbonate components.

A spiking solution containing the selected analytes (B, Cd, Cr, Pb, Ni, and Se) was prepared. Table 3 contains an analysis of the spiking solution. This solution was added to each of the six sediments in liquid-to-solid ratios of 20:1 and 100:1 to evaluate the attenuation of each element by the sediments.

The results of the attenuation experiments for the three samples from Sites 1 and 2 are shown in Tables 4 and 5, respectively. Included are the pH values of each attenuation experiment. Little can be said about exact mechanisms as many factors become involved in fairly complex systems as are provided when multielement samples are mixed with naturally occurring geologic materials.

Table 3. Initial Concentrations of Elements in Spiking Solution, mg/L

Element	B	Cd	Cr	Pb	Hg	Ni	Se
Concentration	13	1.3	5.7	8.2	0.0018	5	0.11

Table 4. Results of Attenuation Experiments for Samples from Site 1, mg/L

Sample	Ratio	Spike	B	Cd	Cr	Pb	Hg	Ni	Se	pH
Unconsolidated Sediments	20:1	No	0.056	<0.0003	0.0007	0.0002	<0.0001	0.0005	0.004	8.09
	20:1	Yes	13	0.003	0.0049	0.005	0.0001	0.016	0.005	7.84
	100:1	Yes	13	0.0081	0.0004	0.001	0.0002	0.0087	0.001	7.90
Sandstone	20:1	No	0.247	<0.0003	<0.0001	0.0001	0.0002	0.0005	0.006	6.56
	20:1	Yes	13	<0.0003	0.088	0.016	0.0003	0.54	<0.0001	5.32
	100:1	Yes	13	1.04	0.0002	1.3	0.0006	3.8	0.013	4.42
Massive Shale	20:1	No	0.155	<0.0003	<0.0001	0.0001	0.0002	0.0019	0.012	7.36
	20:1	Yes	13	0.44	0.0009	0.13	0.0001	1.66	0.019	5.84
	100:1	Yes	13	1.2	0.0005	4.7	0.0002	4.6	0.016	4.51

Table 5. Results of Attenuation Experiments for Samples from Site 2, mg/L

Sample	Ratio	Spike	B	Cd	Cr	Pb	Hg	Ni	Se	pH
Unconsolidated Sediments	20:1	No	0.26	0.0004	0.034	0.0001	0.0002	0.0003	<0.0001	6.94
	20:1	Yes	12	0.035	0.48	0.004	0.0002	0.19	<0.0001	6.35
	100:1	Yes	13	0.0005	0.0002	0.11	0.0007	1.8	<0.0001	4.99
Sandstone	20:1	No	0.07	<0.0003	0.0006	<0.0001	0.0001	<0.0001	<0.0001	8.26
	20:1	Yes	12	0.0068	0.14	0.002	0.0003	0.01	<0.0001	7.67
	100:1	Yes	13	0.0008	0.09	0.13	0.0006	3.2	<0.0001	5.47
Fissile Shale	20:1	No	0.093	<0.0003	0.0016	<0.0001	0.0003	0.0002	<0.0001	7.94
	20:1	Yes	14	0.048	<0.0001	0.001	0.0008	0.29	0.01	7.15
	100:1	Yes	12	0.0007	<0.0001	0.13	0.0001	2.9	<0.0001	6.19

An evaluation of the data from the perspective of individual elements evaluated yielded the following observations:

- Cadmium was highly attenuated by all sediments evaluated in the experiments with the 20:1 liquid-to-solid ratio. Cadmium results are shown in Figure 1a. Cadmium attenuation was lower in the 100:1 liquid-to-solid ratio experiments. For the 100:1 experiments, the Site 1 sandstone and massive shale samples demonstrated much lower attenuation than the other sediments. Cadmium attenuation was interesting especially noting the difference between samples from Site 1 and Site 2. In samples from Site 1, the 100:1 loading of spiked solution to sediment produced a lesser attenuation as shown by higher concentrations of analyte compared to the concentrations of the 20:1 liquid-to-solid experiments, as would be expected. In samples from Site 2, a lower

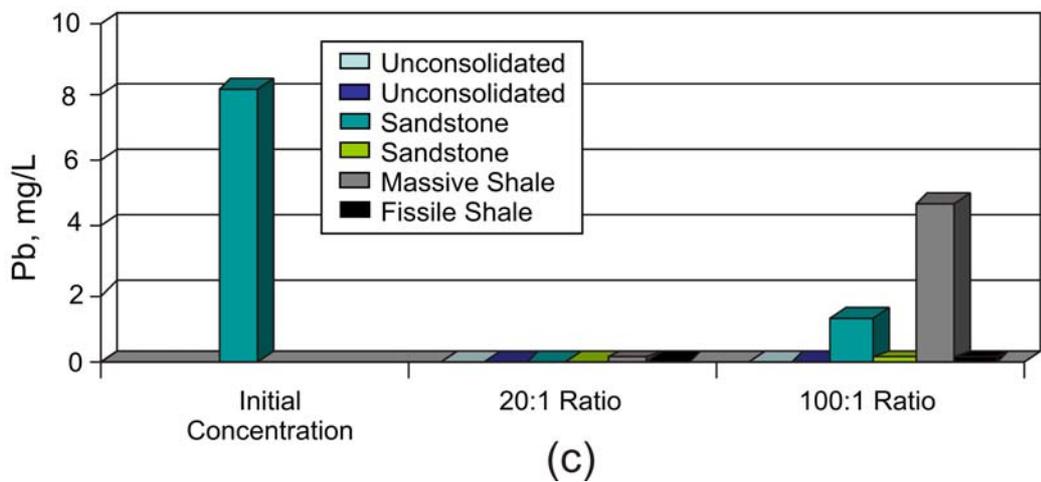
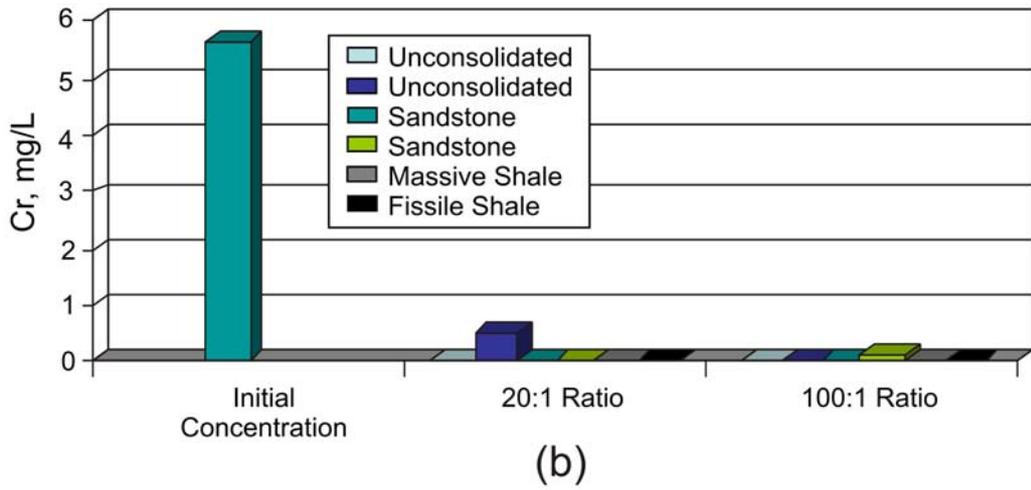
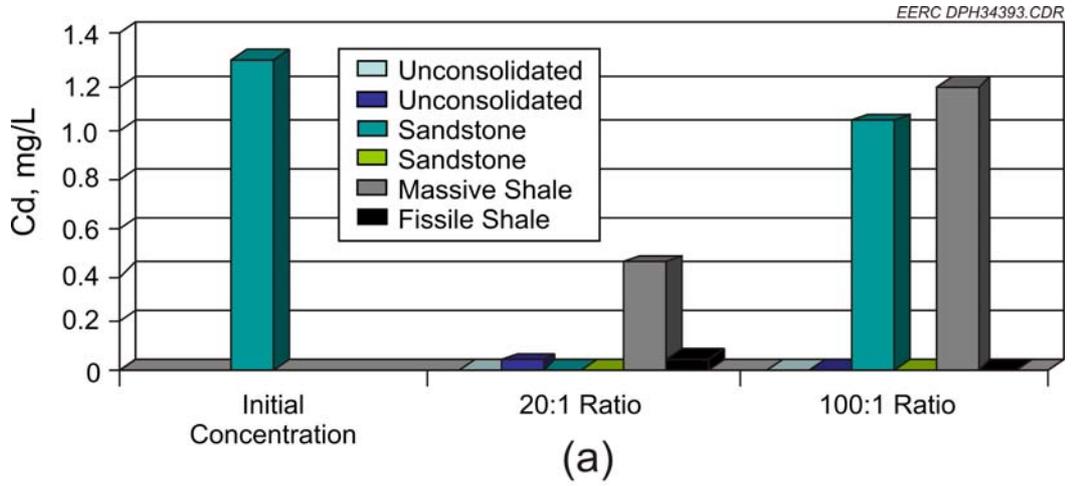


Figure 1. Attenuation results for a) cadmium, b) chromium, and c) lead.

loading of sediment (100:1) produced a lower concentration of analyte, which is contrary to expectations. This is possibly an artifact of pH. Even though the difference in pH values is small, it should not be ruled out as a factor influencing the attenuation results.

- Chromium was highly attenuated by all sediments evaluated and at both liquid-to-solid ratios. Results are shown in Figure 1b. The sandstone from Site 2 in the 20:1 experiment exhibited the lowest level of attenuation of chromium for the sediments in the sample set, yet the amount of chromium removed was nearly 92%, which is significant. The rest of the samples showed a removal of greater than 97.5%, with most showing removals of greater than 99.9%. Chromium produced the same sort of anomalous behavior for all samples as was seen in Site 2 for cadmium. In these cases, slightly higher attenuation was noted with exposure to lower amounts of geologic material. Normally, the presence of additional geologic material in the presence of the same amounts of analyte would be expected to produce lower levels of attenuation. This may be because of a pH effect, but in all cases, the degree of attenuation was high.
- Lead concentrations (Figure 1c) decreased more than 98% in 20:1 experiments as shown. Excluding the Site 1 massive shale results, the 20:1 experiments showed lead removal rates of greater than 99.8%. Lead attenuation increased when more sediment was present (20:1) except for the unconsolidated gray sediment from Site 1. Even in this case, interpretation of results is difficult as the concentrations were low in both the high and low sediment loadings.
- Mercury concentrations in all cases decreased by more than half as shown in Figure 2a. With the exception of the Site 2 Fissile Shale, the 20:1 experiments showed higher levels of attenuation for mercury than the 100:1 experiments. The demonstrated mercury attenuation is consistent with the general affinity of mercury to adhere to surfaces and be removed from solution. In these experiments, mercury was likely present in solution as HgCl_4^{2-} , the anionic form of Hg^{2+} in aqueous solutions with excess chloride ion. Previous experiments⁷⁻⁸ have shown that mercury is not easily mobilized from CCPs during leaching and would not be expected to be present in CCP leachate in measurable concentrations. Since mercury concentrations were all at near detection limits, it is likely that, if additional attenuation data are required, higher initial concentrations will be used and separate experiments run using analytical methods with lower detection limits.
- Nickel was relatively highly attenuated for all sediments at the 20:1 liquid-to-solid ratio; however, for the 100:1 liquid-to-solid ratio, the attenuation was lower for nickel as compared to most other elements tested. Nickel concentrations appeared to be slightly anomalous with respect to the unconsolidated gray sediment from Site 1 (Figure 2b). This difference may have been within the experimental deviation that could be expected in systems containing naturally

occurring materials. Attenuation was lower with a lower sediment loading in all other cases.

- Selenium concentrations decreased to detection limits or near detection limits with sediments from Site 2, while sediments from Site 1 generally showed greater than 80% removal (Figure 2c).
- Boron remained quite mobile in all experiments, as would be expected. Boron mobility is not expected in cases of highly alkaline material or in the presence of sediment or soil containing high amounts of organic material. Neither of these conditions existed in this set of experiments, so the lack of attenuation of boron was consistent with the nature of the materials evaluated. The primary conditions for attenuation of boron in CCP systems are the formation of ettringite or ettringite-like compounds. Ettringite is a calcium aluminate sulfate hydroxide hydrate that only forms at between pH 11.5 and 12.5. These conditions clearly did not exist in any of our experiments. Some organic materials can also sorb boron.

Attenuation capacity of the sediments evaluated is indicated in Figures 3–8. The results indicate:

- The Unconsolidated sediments strong attenuation of all elements except boron at both liquid-to-solid ratios.
- Sandstones exhibited strong attenuation of all elements except boron at 20:1, but lower attenuation capacity at 100:1.
- Massive Shale exhibited moderate attenuation capacity at 20:1, but attenuation was variable at 100:1
- Fissile Shale generally exhibited a high attenuation capacity at both liquid-to-solid ratios except for mercury in the 20:1 experiment and nickel in the 100:1 experiment.

CONCLUSIONS

All of the geologic materials, which consisted of various types of mine spoils and overburden, provided high retardation or removal of outside analytes with boron being the only exception. The chemistry-related mechanisms can vary but include:

- Precipitation and coprecipitation.
- Sorption.
- Ion exchange.

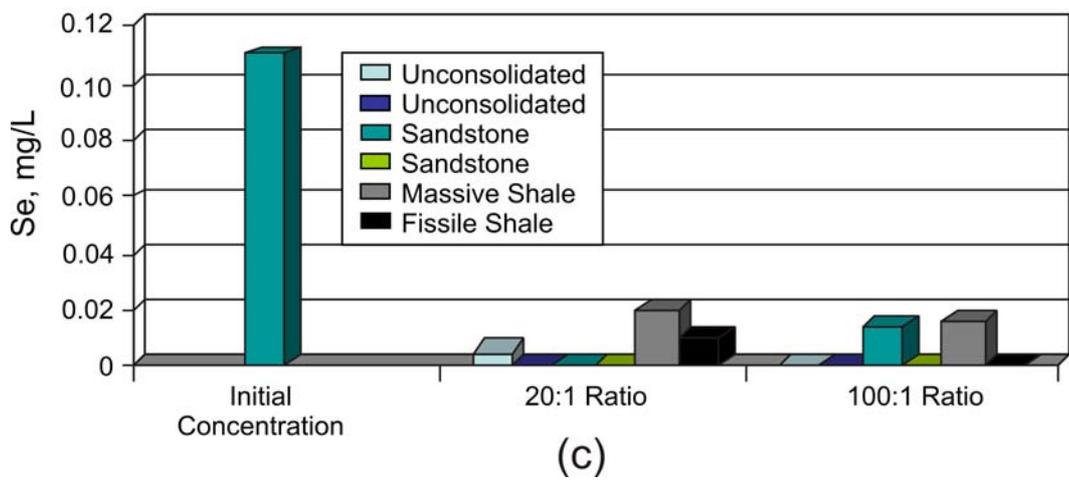
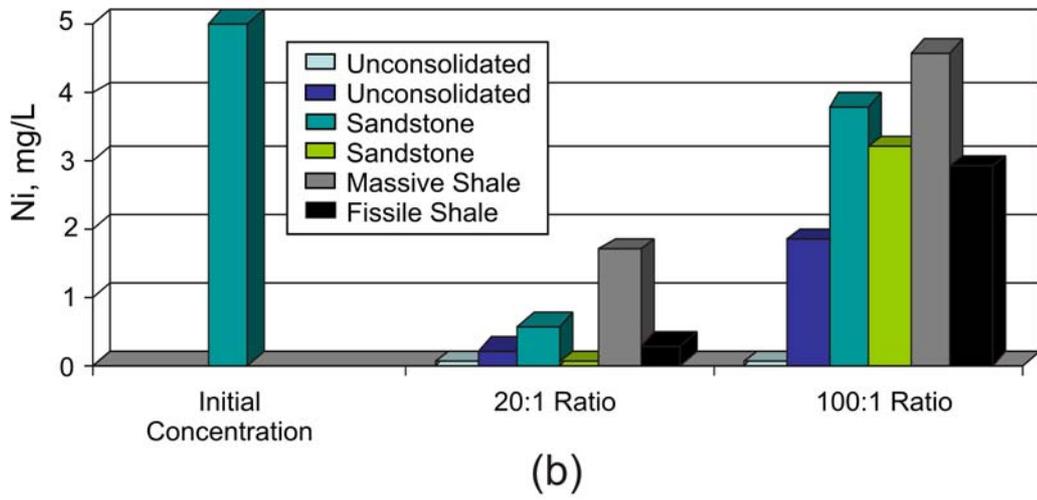
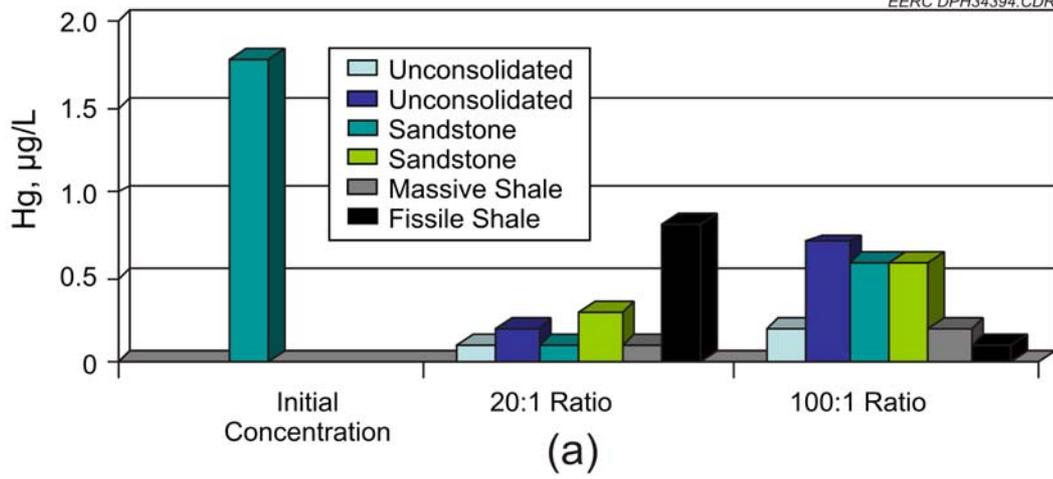


Figure 2. Attenuation results for a) mercury, b) nickel, and c) selenium.

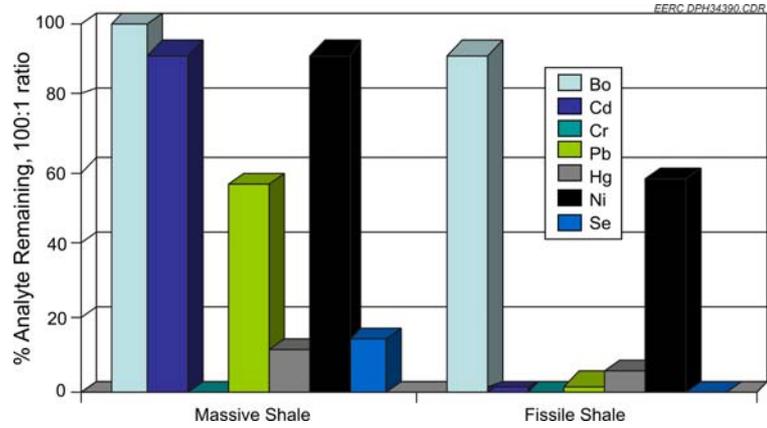


Figure 3. Attenuation results for shale samples in 100:1 experiments.

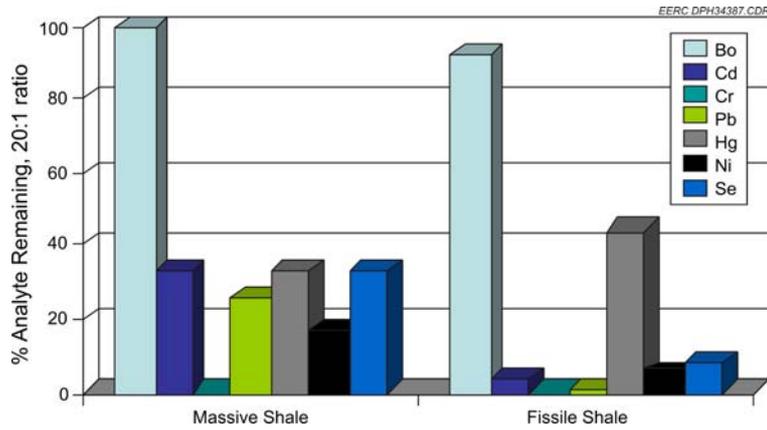


Figure 4. Attenuation results for shale samples in 20:1 experiments.

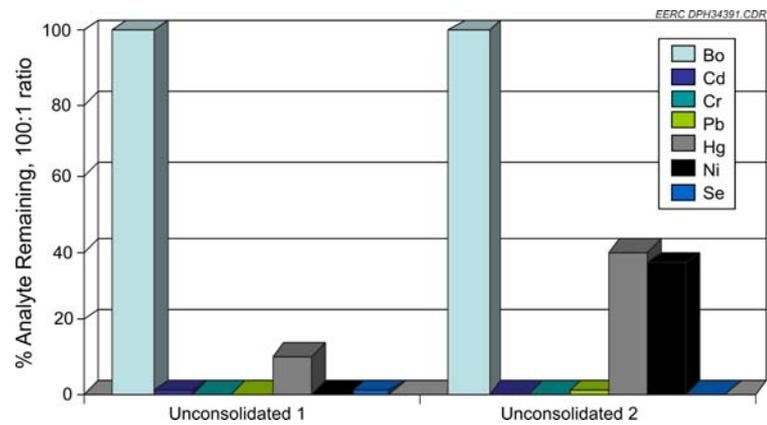


Figure 5. Attenuation results for unconsolidated soil samples in 100:1 experiments.

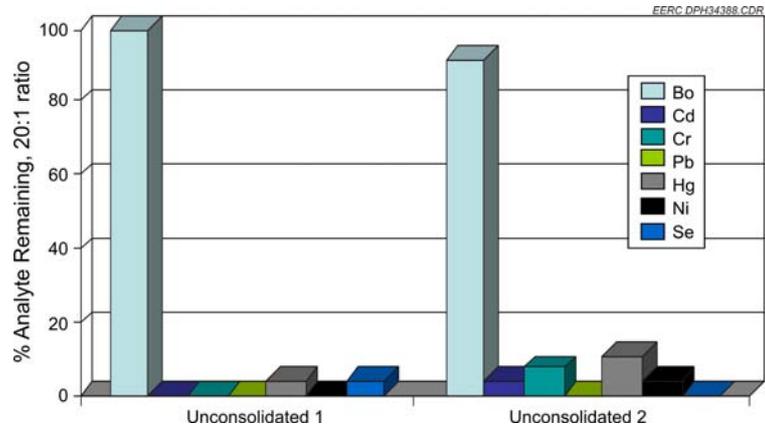


Figure 6. Attenuation results for unconsolidated soil sample in 20:1 experiments.

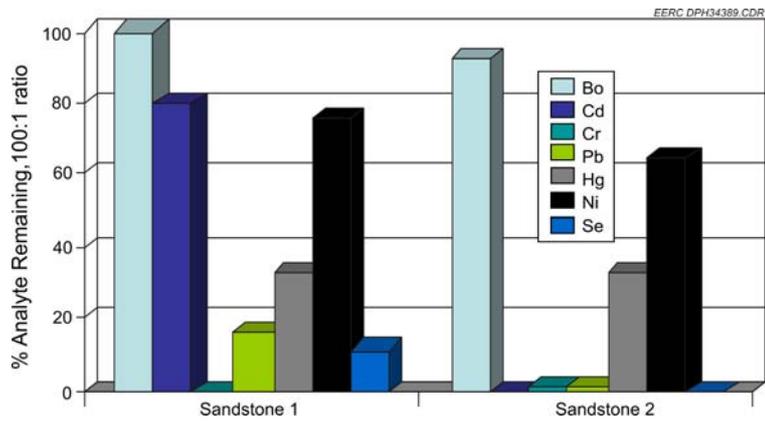


Figure 7. Attenuation results for sandstone samples in 100:1 experiments.

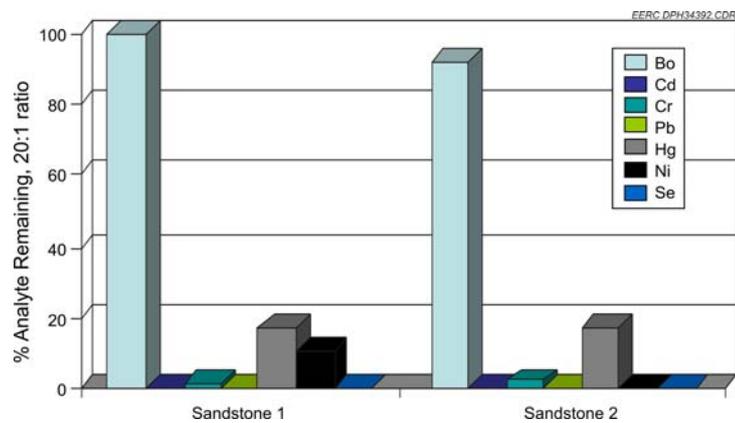


Figure 8. Attenuation results for sandstone samples in 20:1 experiments.

In addition to removal through chemical processes, there is also the possibility for changes in concentration in natural systems related to several physical processes which include:

- Dispersion
- Diffusion
- Dilution

These last three attenuation mechanisms all involve nonsorptive processes and are active for any constituent introduced into groundwater from a point source.

The experiments described in this report were designed to evaluate the relative attenuation of select trace elements through interaction of synthetic leachate with samples of overburden and mine spoils.

The important factor is that the sediments exhibited a high degree of attenuation as determined through reduction of concentration of select analytes after exposure to two levels of each sediment for all of the elements tested, with the exception of boron. Low boron attenuation was to be expected since the pH did not raise high enough (pH 11.5 to 12.5) to incorporate boron into secondary hydrated phases and little if any organic materials were contained in these materials. With the exception of boron, decreases in concentration in excess of 90% were the rule. Higher degrees of attenuation would be expected with much higher solid-to-liquid ratios such as would be encountered by leachates moving through overburden and mine spoils of the type used in these experiments. Exact mechanisms are difficult to determine but likely include sorption on amorphous iron oxide hydroxides, which are difficult to directly identify but can be present at significant concentrations in brown-colored sediments as determined in previous research.³⁻⁶ Amorphous iron oxide hydroxides such as goethite are important since they can have very high sorptive properties. They can, however, lose some of their strength as they age, thus the type of materials as well as their simple presence is important. Similar experiments are under way for arsenic and for selenium utilizing higher concentrations in the simulated CCP leachate.

REFERENCES

[1] U.S. Environmental Protection Agency. Federal Register 40 CFR Part 261. Notice of Regulatory Determination on Wastes from the Combustion of Fossil Fuels. Vol 65, No. 99, May 2000.

[2] National Research Council. Managing Coal Combustion Residues in Mines. Advance National Research Council, Washington, DC, 2006; 227 p.

[3] Hassett, D.J., Groenewold, G.H. Attenuation Capacity of Western North Dakota Overburden Sediments; Final Report for U.S. Department of Energy Contract No. DE-AT18-80FC10120; Bulletin No. 86-04-MMRRI-01; 1986; 105 p.

- [4] Hassett, D.J., Groenewold, G.H. Trace Element Attenuation by Western North Dakota Overburden Sediments. Presented at 9th Annual Madison Waste Conference, Madison, WI, Sept 9–10, 1986, 16 p.
- [5] Hassett, D.J., Schmit, C.R., Groenewold, G.H. Trace-Element Attenuation Capacity of Sediments from Typical Coal-Conversion Solid-Waste Disposal Sites in Texas. In Proceedings of the 10th Annual Madison Waste Conference; Madison, WI, Sept 29–30, 1987; pp 579–589.
- [6] Hassett, D.J., Daly, D.J., Groenewold, G.H., Schmit, C.R. Attenuation Capacity of Shallow Geologic Materials with Respect to Trace Elements, Powder River Low-Rank Coal Region. In Proceedings of the 3rd AIRM Western Regional Conference on Precious Metals, Coal, and Environment, Black Hills Section, K.N. Han and C.A. Klilche Eds, Rapid City, SD, Sept 23–26, 1987, pp 256–262.
- [7] Hassett, D.J., Heebink, L.V., Pflughoeft-Hassett, D.F., Buckley, T.D., Zacher, E.J., Xin, M., Gustin, M.S., Jung, R. Mercury and Air Toxic Element Impacts of Coal Combustion By-Product Disposal and Utilization, Final Report (Jan 23, 2003 – Dec 31, 2006) for U.S. Department of Energy National Energy Technology Laboratory Cooperative Agreement No. DE-FC26-02NT41727, North Dakota Industrial Commission Agreement No. FY03-XLVIII-117, Duke Energy, Great River Energy, Utility Solid Waste Activities Group, and Electric Power Research Institute, EERC Publication 2007-EERC-10-03, Energy & Environmental Research Center: Grand Forks, ND, Oct 2007.
- [8] Sanchez, F., Keeney, R., Kosson, D., Delapp, R. Characterization of Mercury-Enriched Coal Combustion Residues from Electric Utilities Using Enhanced Sorbents for Mercury Control, Contract No. EP-C-04-023, Work Assignment 1-31, EPA-600/R-06/0008, Feb 2006.