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Groundwater Remediation of Inorganic Constituents at Coal Combustion Product Management Sites

Overview of Technologies, Focusing on Permeable Reactive Barriers

Technical Report

Groundwater Remediation of Inorganic Constituents at Coal Combustion Product Management Sites

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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

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CITATIONS

This report was prepared by

Natural Resource Technology, Inc.
23713 W Paul Road, Suite D
Pewaukee, WI 53072

Principal Investigator
B. Hensel

Southern Company Generation
Earth Science and Environmental Engineering
42 Inverness Center Parkway, Bin B426
Birmingham, AL 35242

Principal Investigator
J. Pugh

Powell and Associates
140 Pleasant Lake Drive
Waterford, MI 48327

Principal Investigator
R. Powell

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REPORT SUMMARY

This report reviews constituents that potentially may trigger groundwater remediation at coal combustion product (CCP) management sites and briefly summarizes various in situ and ex situ remediation technologies and their applicability to treat these constituents. The report provides a more detailed discussion for one potentially promising in situ remediation technology, permeable reactive barriers (PRBs).

Background

Relatively few instances of significant groundwater contamination at CCP disposal sites have required active remediation, and new designs make it unlikely that sites developed since about the mid-1990s will encounter problems. However, many older and closed sites pre-date current designs, and it is important that the industry develop remediation technologies to address groundwater issues if they arise.

Objectives

- To identify constituents most likely to trigger a groundwater remedial action at CCP management sites.
- To present an overview of remediation technologies for treating these constituents, focusing on in situ remediation in general and permeable reactive barriers in particular.

Approach

The project team identified potential constituents based on their concentrations in CCP leachate as listed in EPRI field and laboratory databases; their mobility as compiled by USEPA, EPRI, and other sources; their historical record in triggering remedial actions at CCP management sites; and interviews with utility environmental managers. The team then conducted a literature review to summarize technologies that may be applicable to remediating these constituents.

Results

Five primary constituents were identified: arsenic, boron, chromium, selenium, and sulfate. These constituents have 90th percentile concentrations greater than state or federal groundwater quality standards, can be mobile in groundwater under certain conditions, and have each triggered at least one known remedial action at a CCP management site. While these constituents are the focus of this technology review, it is important to note that they will not necessarily be present in leachate or groundwater at all CCP sites and that other inorganic constituents may require remediation at some sites.

Since all the constituents are inorganic and not subject to decay, remediation must focus on processes that will remove them from solution or cause them to become immobile in the subsurface. Ex situ and in situ processes summarized in the report include precipitation,

adsorption, membrane filtration, ion exchange, electrolysis, and phytoremediation. The effectiveness of these processes vary by constituent and environment. For example, arsenic can be treated using several different processes while boron, a key indicator of coal ash leachate, is only effectively removed from water by ion exchange and membrane filtration, with the latter only effective at high pH.

The report focuses on permeable reactive barriers as an in situ remediation technology for groundwater at CCP management sites. A PRB is a subsurface wall, gate, or container filled with a reactive media. As groundwater passes through the PRB under natural gradients, dissolved constituents in the groundwater react with the media and are immobilized. A variety of media have been used or proposed for use in PRBs. The most commonly cited medium is zero-valent iron (ZVI), which has been used to treat a wide variety of contaminants, including four of the five constituents identified for CCP sites—arsenic, chromium, selenium, and sulfate. Alternative media, or a combination of media, are needed to treat boron. The only documented PRB project at a CCP site, a pilot-scale test at a site in Canada, used a combination media consisting of ZVI, organic matter, and a boron-selective ion exchange resin to treat the groundwater. Results showed that the combination of media had potential for treating groundwater at CCP sites.

Permeable reactive barriers require further development for application at sites where the remedial objectives call for cleanup of the mixture of constituents typically present at CCP sites. A considerable amount of work has been done on arsenic, chromium, and cationic metals; but more research is needed on difficult to treat constituents such as boron, sulfate, molybdenum, and antimony and on the unique interactions that may occur in the CCP leachate matrix. Future research is recommended on removal effectiveness, long-term performance, and the cost of reactive media; innovative physical PRB configurations; and continued geochemical characterization of potential constituents of concern at CCP sites.

EPRI Perspective

Regulatory guidelines expected within the next few years will result in increased monitoring at both new and existing CCP sites. EPRI's groundwater remediation research, along with risk assessment studies currently underway, provides a framework for addressing groundwater issues when they arise. Additional bench- and pilot-scale research is planned to identify the most appropriate media to treat the constituents most commonly found at CCP sites. Other in situ approaches, including in situ fixation, will also be evaluated.

Keywords

Remediation
Groundwater
Arsenic
Boron
Chromium
Selenium
Sulfate
Permeable Reactive Barrier

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INTRODUCTION

There have been relatively few instances of significant groundwater contamination at coal ash disposal sites, and new designs make it unlikely that sites developed since about the mid-1990s will encounter problems. However, because of the large number of older and closed sites predating current designs, it is important that the industry has technologies available to address such needs should they arise.

This report addresses remediation technologies for the suite of inorganic constituents typically associated with coal combustion products (CCPs). Information is presented on these constituents related to their presence in CCPs, the likelihood they will be released to groundwater, and their fates in a subsurface system. The chemical properties of these constituents affecting their remediation are addressed, followed by a discussion of remediation systems that can use these properties to enhance removal. Physical removal techniques are briefly discussed, with regard to source elimination. Both ex situ and in situ groundwater remediation technologies are considered but the emphasis is on in situ approaches due to the known difficulties of efficiently and completely extracting groundwater contaminants for surface treatment. In particular, one in situ remediation approach that holds promise for a wide range of potential constituents is the use of permeable reactive barriers (PRBs).

Section 2 of this report provides a description of typical constituents found at CCP sites, and identifies those that are most likely to lead to a groundwater remediation action. Section 3 provides an overview of remediation technologies and their applicability to inorganic constituents of interest. In Section 4, PRBs are discussed in more detail; descriptions of the media used in PRBs are included in Appendix A, and summaries of several case studies of the application of PRBs to inorganic contaminants are included in Appendix B. Section 5 provides recommendations for research specific to the constituents identified as most important at CCPs.

2
IDENTIFICATION OF POTENTIAL CONSTITUENTS OF CONCERN

Coal Combustion Product Production and Reuse

The term *coal combustion products* refers to fly ash, bottom ash, boiler slag, and flue gas desulfurization (FGD) solids (Table 2-1). These materials are managed using a variety of methods including beneficial reuse, dry-management in landfills, and wet-management in impoundments. Bottom ash and boiler slag have a relatively low leachability and are widely used in a variety of use applications, including roadbeds, structural fills, blasting grit, and roofing granules, that are unlikely to result in groundwater contamination. Similarly, beneficial use of fly ash and FGD gypsum typically involves incorporation of the CCP into low-leachability materials such as concrete, wallboard, or stabilized soils with little potential to affect groundwater. The focus of this report is therefore on fly ash and FGD solids management in landfills and impoundments.

Table 2-1
Coal Combustion Product Production, Management, and Use for 2004

	Fly Ash	Bottom Ash	Boiler Slag	FGD Products
Total Production[2]	70.8	17.2	2.2	32.3
Percent Reused	40%	47%	90%	34%

[1] Source: American Coal Ash Association, 2004

[2] Production values in million short tons

Potential Constituents of Concern at CCP Management Sites

Many remediation technologies are designed to treat specific constituents. As a result, evaluation of remediation technologies requires knowledge of the potential constituents of concern (PCOC) in groundwater that may require treatment.

Most naturally occurring elements can be found in CCPs, but only a small subset of these elements and their compounds are found in leachate at concentrations high enough to be environmentally significant, and only a subgroup of these constituents has sufficient mobility in groundwater to potentially trigger a remedial action. Therefore, a multi-tiered approach was used to identify PCOCs at CCP management sites:

- Leachate data from a broad range of power plants and CCP management sites were compared to water quality standards to quantitatively determine constituents with the potential to leach to groundwater in significant concentrations.
- Generalized mobility data from USEPA and EPRI studies were reviewed to determine constituents that may be mobile in groundwater.
- Case studies of CCP remediation sites were examined to identify constituents that have triggered remedial actions.

This information was supplemented with qualitative interviews in which utility environmental managers were queried about constituents of concern to their operations.

Leachate Characteristics

In the event of a leachate release to groundwater, the potential for an exceedance of a groundwater quality standard is a function of the constituent's concentration in leachate relative to the relevant state groundwater quality standard, its mobility in groundwater (discussed later), and the hydrogeologic and chemical environment, which is not discussed because it is too site-specific for this broad-based assessment. Leachate quality was summarized based on two comprehensive studies covering a range of power plant and CCP management site conditions (Table 2-2):

- EPRI (1987b) lists results of hot-water leachate extracts on 94 unweathered CCP samples collected at 39 power plants.
- EPRI (2006a) reports on 81 field leachate samples collected from 29 CCP management sites.

Each study used consistent sample collection methods, and each study used a single laboratory for analysis, thereby eliminating these two possible causes of external variability.

The data were then compared to the federal maximum contaminant levels (MCLs) or secondary maximum contaminant levels (SMCLs), which are often used as the basis for state groundwater standards. For constituents with no MCL or SMCL, a representative state groundwater standard was used. A ratio less than 1.0 suggests that there is little likelihood of an MCL exceedance in groundwater for a given constituent in the event of a leachate release. A ratio greater than 1.0 suggests that an MCL exceedance is possible, but other factors, such as the hydrogeologic system and mobility of the constituent, must be considered.

The leachate data indicate that concentrations of antimony, arsenic, cadmium, chromium, selenium, and thallium were higher than health-based MCLs in at least 10 percent of the samples.[1] In addition, the 90th percentile concentrations of boron, lithium, manganese, molybdenum, sodium, sulfate, and vanadium were higher than alternative drinking water criteria. These constituents are more likely to trigger a remedial action in the event of a leachate release than constituents that typically have leachate concentrations lower than drinking water standards.

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[1] i.e., those samples with concentrations at or greater than the 90th percentile.

Table 2-2
Summary of Representative Laboratory and Field CCP Leachate Data

a. Constituents with Health-Based Maximum Contaminant Levels (MCLs)

Parameter[1]	Source[2]	Count	%BDL	Median	90th Percentile	Maximum	Standard	Ratio[3]
Antimony	Field	81	7%	0.002	0.020	0.059	0.006	**3.3**
	Lab	94	67%	BDL	0.114	0.752	0.006	**19.0**
Arsenic	Field	81	0%	0.026	0.178	1.380	0.010	**17.8**
	Lab	94	62%	BDL	0.340	14.040	0.010	**34.0**
Barium	Field	81	5%	0.089	0.250	0.657	2.000	0.1
	Lab	94	0%	0.160	0.677	2.990	2.000	0.3
Beryllium	Field	81	94%	BDL	BDL	0.009	0.004	NC
	Lab	0						
Cadmium	Field	81	10%	0.002	0.013	0.065	0.005	**2.6**
	Lab	94	73%	BDL	0.012	0.792	0.005	**2.3**
Chromium	Field	81	48%	0.001	0.025	5.100	0.100	0.2
	Lab	94	46%	0.014	0.212	5.320	0.100	**2.1**
Copper	Field	81	19%	0.003	0.021	0.494	1.300	<0.1
	Lab	94	64%	BDL	0.037	61.600	1.300	<0.1
Fluoride	Field	0						
	Lab	94	10%	0.163	1.312	8.850	4.000	0.3
Lead	Field	81	72%	BDL	0.0004	0.0080	0.0150	<0.1
	Lab	94	96%	BDL	BDL	3.7600	0.0150	NC
Mercury	Field	30	0%	0.000004	0.000029	0.000079	0.002000	<0.1
	Lab	0						
Nitrate	Field	0						
	Lab	90	9%	0.100	0.682	20.000	10.000	<0.1
Nitrite	Field	0						
	Lab	94	27%	0.015	0.077	5.800	1.000	<0.1
Selenium	Field	81	0%	0.018	0.181	2.360	0.050	**3.6**
	Lab	0						
Thallium	Field	81	53%	BDL	0.005	0.018	0.002	**2.6**
	Lab	0						

1. All concentrations in mg/L.

2. Field = EPRI (2006a) field leachate samples; Lab = EPRI (1987) hot water extracts.

3. Ratio is the 90th percentile divided by the standard.

4. NC indicates that the ratio was not calculated because the 90th percentile was below laboratory detection limits

5. BDL indicates that the median or 90th percentile was below laboratory detection limits.

Table 2-2
Summary of Representative Laboratory and Field CCP Leachate Data (Continued)

b. Constituents with Non-Health Based SMCLs or State Standards

Parameter[1]	Source[2]	Count	%BDL	Median	90th Percentile	Maximum	Alt. Standard[3]	Ratio[4]
Boron	Field	81	0%	2.6	14.0	112.0	0.5–2.0	**28.0**
	Lab	94	5%	1.4	7.8	82.4	0.5–2.0	**15.6**
Chloride	Field	80	0%	28	74	2,330	200–*250*	0.4
	Lab	94	0%	1	3	517	200–*250*	<0.1
Iron	Field	81	56%	BDL	0.05	25.60	*0.3*–5.0	0.2
	Lab	94	17%	0.01	0.03	39.40	*0.3*–5.0	0.1
Lithium	Field	81	14%	0.15	0.43	23.60	0.17	**2.5**
	Lab	94	0%	0.20	0.51	8.68	0.17	**3.0**
Magnesium	Field	80	9%	13	34	5,810	400	<0.1
	Lab	94	13%	1	3	143	400	<0.1
Manganese	Field	81	20%	0.060	0.202	4.170	*0.05*–0.15	**4.0**
	Lab	94	10%	0.004	0.043	3.080	*0.05*–0.15	0.9
Molybdenum	Field	81	2%	0.36	1.39	60.80	0.035–0.073	**39.7**
	Lab	94	27%	0.06	0.22	1.86	0.035–0.073	**6.3**
Nickel	Field	81	17%	0.005	0.014	0.597	0.1	0.1
	Lab	94	73%	BDL	0.011	8.520	0.1	0.1
Sodium	Field	80	0%	58	312	4,630	120	**2.6**
	Lab	94	0%	6	19	2,008	120	0.2
Strontium	Field	81	1%	1.2	3.9	16.9	4.6	0.8
	Lab	94	0%	0.8	2.5	23.7	4.6	0.6
Sulfate	Field	80	0%	485	1613	30,500	*250*–400	**6.5**
	Lab	94	0%	198	518	4,600	*250*–400	**2.1**
Vanadium	Field	81	6%	0.03	0.16	5.02	0.0045	**35.6**
	Lab	0						
Zinc	Field	81	48%	0.01	0.02	0.29	*5.0*	<0.1
	Lab	94	73%	BDL	0.01	121.20	*5.0*	<0.1

1. All concentrations in mg/L.
2. Field = EPRI (2006a) field leachate samples; Lab = EPRI (1987) hot water extracts.
3. The range of alternative standards is based on non-health based Federal SMCLs (italicized) and representative state drinking water standards and groundwater clean-up criteria (based on California, Illinois, Michigan, and Wisconsin).
4. Ratio is the 90th percentile divided by the *lowest* alternative standard.

Mobility

Chloride and sulfate are highly mobile in most natural groundwater environments. However, the mobility of most other inorganic constituents is dependent on site-specific conditions such as soil type (clay versus sand), redox environment (reducing versus oxidizing), pH, and the concentration of the constituent in groundwater. As a result, a constituent that may be mobile in groundwater at one site may be immobile at another site.

Mobility often is quantified by the linear distribution coefficient (K_d), which is a measure of the mass of a constituent dissolved in solution to the mass of constituent attached to the soil or rock matrix. When K_d is zero, the constituent migrates at the rate of groundwater flow; when K_d is greater than zero, the constituent interacts with the soil/rock matrix and migrates at a rate slower than the rate of groundwater flow. Therefore, the rate of migration, or mobility, of a constituent decreases as the K_d value increases. While many constituents have non-linear adsorption isotherms, linear K_d provides a useful comparison of relative mobility. For this assessment, ranges of linear K_d were compiled (Table 2-3) from the following sources:

- USEPA (1992): published ranges of K_d values for three pH conditions (pH 4.9, 6.8, and 9.0). For each constituent, the K_d range for the pH values likely to be encountered in groundwater at ash sites (6.8 and 9.0) was selected.
- USEPA (1996): used a geochemical model to calculate soil K_d values as a function of pH. The range of K_d values selected was for the pH range of 6.5 to 8.0 (the maximum pH value) expected in groundwater at CCP sites.
- EPRI has published reports listing mobility data for arsenic (EPRI, 2004), boron (EPRI, 2005a), and selenium (EPRI, 2006b). For boron, K_d is a function of concentration, and the range selected is for concentrations lower than 10 mg/L, which was the first reported concentration range below the 90th percentile boron concentration in CCP leachate. The arsenic and selenium ranges were based on field conditions reproduced for three CCP sites.

For purposes of evaluating inorganic constituents of interest in this study, a qualitative mobility ranking system was developed based on the K_d ranges in Table 2-3. A mobility ranking of high was assigned to any constituent where the lowest K_d was less than 2.0 L/kg. This value was selected because it is the approximate K_d where the constituent velocity is equal to one-tenth the groundwater velocity, and is also the approximate inflection point (shown in Figure 2-1) beyond which constituent velocity is very slow relative to groundwater velocity. A mobility ranking of moderate was assigned to any constituent where the lowest K_d was greater than 2.0 L/kg and less than 5.0 L/kg, and the overall range was less than 500 L/kg. A mobility ranking of low was assigned to all remaining constituents, which often had K_d ranges extending beyond 1,000 L/kg. It must be stressed that the K_d ranges are relatively large, and mobility can vary greatly for a given constituent. For example, in an EPRI study at three ash management facilities, the range of K_d values reported for arsenic is 5 to 50 L/kg for As(III), but 30 to 350 L/kg for As(V) (EPRI, 2004). This suggests that only As(III) is categorized as moderately mobile in this evaluation, and that even this species would not be categorized as moderate much of the time. There has been a significant amount of research on the adsorption of arsenic on pure mineral surfaces and soil particles that suggest a much larger range of arsenic K_d values (EPRI, 2000a).

Table 2-3
Mobility Assessment

	Kd (L/kg)			Potential Mobility
	USEPA (1992)	USEPA (1996)	Other*	
Antimony	4.2 – 126	45		Moderate
Arsenic	3.5 – 275	28 – 31	5 – 350	Moderate
Barium	13 – 1,442	37 – 52		Low
Beryllium	29 – 12,848	280 – 100,000		Low
Boron			0.4 – 3.0	High
Cadmium	8.6 – 2,818	52 – 4,300		Low
Chloride			0.0	High
Chromium	0.5 – 383	14 – 20		High
Copper	27 – 18,232			Low
Lead	48 – 432			Low
Lithium			0.03 – 0.25	High
Magnesium	57 – 1025			Low
Mercury		22 – 200		Low
Molybdenum			0.6 – 500	High
Nickel	8.3 – 1,675	50 – 1,900		Low
Selenium	0.1 – 66	2.2 – 6.1	2 – 500	High
Strontium			0.33 – 0.59	High
Sulfate			0.0	High
Thallium	20 – 430	66 – 96		Low
Vanadium		1000	13 – 500	Low
Zinc	14 – 3,989	51 – 530		Low

* Sources for other K_d values:

- Arsenic: EPRI, 2004
- Boron: EPRI, 2005a
- Molybdenum: USEPA, 2005a (literature search, pH range of 4 to 10 was greater than used here)
- Selenium: EPRI, 2006b
- Vanadium: USEPA, 2005a (literature search, pH range of 4 to 10 was greater than used here)
- Chloride: Considered conservative in groundwater
- Sulfate: Considered conservative in groundwater under most conditions, may not be conservative in strongly reducing environments
- Lithium and Strontium: confidential CCP site data for a sand aquifer at neutral pH (CCP Case Study Site 1, Table 2-4).

The potential mobility ranking shown in Table 2-3 indicates that boron, chloride, chromium, lithium, molybdenum, selenium, strontium, and sulfate are likely to be mobile in groundwater under the widest range of conditions, while arsenic and antimony may be mobile under certain conditions. The other listed constituents are less likely to be mobile in groundwater.

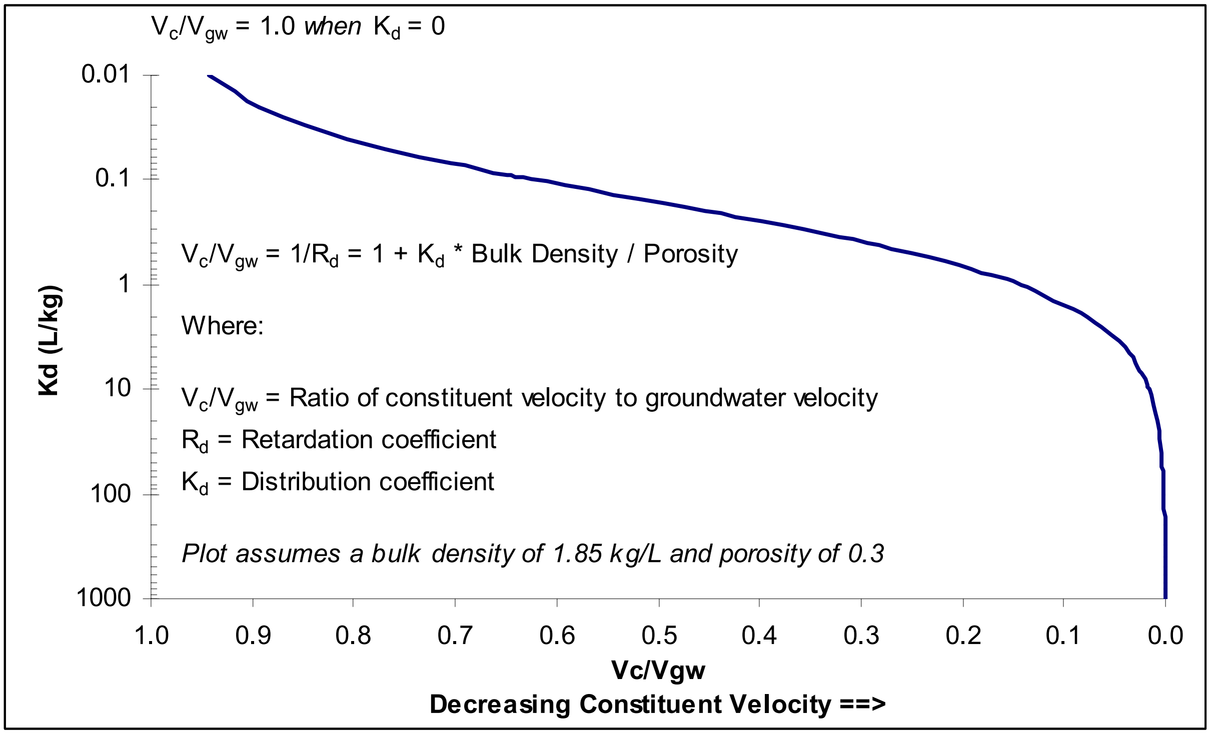

Figure 2-1
Constituent Velocity Relative to Groundwater Velocity as a Function of the Distribution Coefficient

Utility Interviews

Eight utility environmental managers were interviewed to determine constituents of significance to their CCP management programs. The respondents were asked to rank the constituents in order of significance to their sites. Twenty-two constituents were mentioned at least once, and 13 different constituents were ranked among the top three in importance. Five constituents were ranked among the top three by at least half of the respondents: arsenic, boron, chromium, selenium, and sulfate; although no constituent was ranked among the top three by all respondents.

Remediation Case Studies at CCP Sites

Table 2-4 summarizes CCP management sites where groundwater remedial actions have been performed. This list is not all-inclusive, but is representative of documented remedial actions performed by the industry. The list includes primary parameters, meaning the parameters that triggered remedial actions, other parameters that were prominently mentioned in site documentation, remedial actions performed to date, and references, if publicly available.

Table 2-4
CCP Management Sites Requiring Remedial Action

Site Code	Site Type[1]	Primary Parameters	Other Parameters	Remedial Actions	Published Reference
1	LF	B, Se, Li	SO_4, Mn, Sr	Closed; fully-encirculating barrier wall with gradient control; soil cap	Confidential
2	I	Se, B	Sb, Li	Groundwater extraction	Confidential
3	I	As, B, Li	SO_4, Fe	Natural attenuation (for As); barrier wall with gradient control	Confidential
4	I	B	SO_4, Mn	Closed; soil cap	EPRI 1005165 (2001a)
5	I	B, SO_4		Closed	EPRI 1005165 (2001a)
6	I	B, SO_4	TDS, Mn, Fe	Closed	EPRI 1005165 (2001a)
7	I	B	SO_4, Fe, Mn, pH	Closed; portions excavated	Confidential
8	LF	B, SO_4	Se	Groundwater extraction; PVC cap	EPRI 1005214 (2001b)
9	LF	SO_4, B, Mo	Se, Cr	Closed; HDPE cap	EPRI 1005262 (2002)
10	LF	B, SO_4	Mo	PVC cap; alternative water supply; excavation of small area with saturated ash	Confidential
11	I	B, SO_4	Mn, TDS	Closed; will be capped	Confidential
12	LF	B, SO_4	As, Se	Interceptor trench; cap TBD	Confidential
13	LF	Se, SO_4	V	Alternative water supply, soil/clay caps, groundwater extraction/gradient control	http://www.epa.gov/epaoswer/other/fossil/sandgrav.pdf
14	LF	B, Mo		Alternative water supply; cap TBD	http://www.epa.gov/region5/sites/pines/
15	LF	As, B, Cr, Mo, Se, V	SO_4	Permeable reactive barrier (demonstration project)	McGregor et al. (2002)
16	I	B, SO_4	Fe, Mn, TDS, pH	Capped with synthetic liner for new impoundment (with leachate collection)	Confidential

1. I = impoundment; LF = landfill

All of these landfills and impoundments sites were unlined. In some cases, the leachate chemistry may have been influenced by comanagement of pyrite with coal ash, a practice that has since been addressed by the industry (EPRI, 1999a). Most of the sites either closed as part of the remedial action, or were already closed or inactive. Remedial actions included the following:

- Closure of seven sites;
- Caps at nine sites (three synthetic, two soil or clay, and five yet to be determined);
- One site was "capped" by constructing a new ash impoundment with a synthetic liner and leachate collection over the top;
- Hydraulic controls (groundwater extraction or interceptor trenches) at four sites;
- Excavation of saturated ash at one site;
- Partial excavation (for a new lined impoundment) at one site;
- Two barrier walls with hydraulic gradient control to assure inward flow of groundwater;
- Three remediation programs included provision of alternative water supplies;
- A permeable reactive barrier was constructed at one site (see PRB case study 1, Appendix B).

The primary constituents driving remediation were boron (15 of 16 sites), sulfate (10 sites), selenium (4 sites), arsenic (2 sites), lithium (2 sites), molybdenum (2 sites), and chromium (1 site).

Compilation of PCOCs

A listing of leachate constituents, and an evaluation of whether or not they are PCOCs from a remediation perspective, based on the leachate data, mobility data, and case studies, is presented in Table 2-5. A constituent was listed as a potential remediation constituent (√) based on leachate data if the ratio of 90th percentile leachate concentration to MCL was greater than 1.0. Mobility was categorized as potentially high if a K_d value of 2.0 L/kg or lower was listed in Table 2-3, or moderate if a K_d value between 2.0 and 5.0 L/kg was listed. The potential remediation constituents identified for the case studies were those that were listed in Table 2-4 as primary drivers for remediation.

Selenium and chromium have three unqualified check marks in Table 2-5 and are therefore included in the list of potential constituents of concern for CCP management sites. Several other constituents had two unqualified check marks and one qualified check mark: arsenic, boron, lithium, molybdenum, and sulfate. Arsenic, boron, and sulfate were each listed as one of the three most important constituents by at least half of the utility interview respondents, while lithium and molybdenum were not prominently mentioned; therefore, arsenic, boron, and sulfate are grouped with selenium and chromium as the primary PCOCs for CCP management sites. Lithium, molybdenum, and antimony (the only constituent with two check marks) are considered secondary PCOCs.

Table 2-5
Potential Remediation Constituents in CCP Leachate

	Leachate Data	Mobility	Case Studies
Antimony	√	(√)	-
Arsenic	√	(√)	√
Barium	-	-	-
Beryllium	-	-	-
Boron	(√)	√	√
Cadmium	√	-	-
Chloride	-	√	-
Chromium	√	√	√
Copper	-	-	-
Fluoride	-	**	-
Iron	-	**	-
Lead	-	-	-
Lithium	(√)	√	√
Magnesium	-	√	-
Manganese	(√)	**	-
Mercury	-	-	-
Molybdenum	(√)	√	√
Nickel	-	-	-
Nitrate	-	**	-
Nitrite	-	**	-
Selenium	√	√	√
Sodium	(√)	**	-
Strontium	-	√	-
Sulfate	(√)	√	√
Thallium	√	-	-
Vanadium	(√)	-	-
Zinc	-	-	-

√ denotes potential remediation constituents identified within each category.

(√) indicates that leachate concentration for this constituent exceeds a SMCL or state standard, rather than a MCL, or that mobility is moderate.

\- indicates constituents with low potential to trigger a remedial action.

** denotes constituents not rated because mobility data were not available.

3

OVERVIEW OF GROUNDWATER REMEDIATION TECHNOLOGIES

Treatment/Removal Processes for Dissolved Inorganic Constituents

Inorganic constituents vary widely in their removal from aqueous systems by treatment processes. In some cases, the properties that make a constituent mobile in groundwater also make it difficult to remove using a cost-effective treatment approach. There are a variety of approaches that are used to remove inorganic constituents from water, but only a few basic processes that are implemented by these approaches. These include:

- Precipitation/Co-precipitation
- Adsorption
- Membrane Filtration
- Ion Exchange
- Electrolysis
- Phytoremediation

Precipitation/Co-Precipitation

Precipitation occurs when a constituent exceeds its solubility limit in water. This can occur for a variety of reasons including a simple increase in the concentration of the constituent, or a change in pH, Eh (oxidation/reduction potential), temperature, or ionic strength. Co-precipitation is the removal of a contaminant by precipitation of another constituent that is typically present in higher concentrations, usually Fe(III) or Al(III) salts (often added as coagulants in water treatment systems). The constituent of concern is removed by trapping within or adsorption to the precipitates as they form. Ex situ precipitation/co-precipitation via pump and treat technologies allows separation of the aqueous phase from the precipitate with subsequent disposal/recovery of the material. Precipitation/co-precipitation in situ can be a viable groundwater treatment strategy provided that conditions are sufficiently stable that re-dissolution and remobilization do not occur.

Adsorption

Adsorption is a surface-chemical phenomenon wherein accumulation of a constituent occurs at the interface between the aqueous phase and solid materials in contact with the aqueous phase. This process can also be used in treatment systems implementing a variety of substrates as the solid phase (zeolites, granular activated carbon, etc.), whether in situ or ex situ.

Adsorption of inorganic contaminants and metals involves either complexation of the contaminants on the surfaces by bond formation or electrical (coulombic) interactions between the contaminant and the surfaces. Adsorption can be either relatively weak (reversible) or relatively strong (often irreversible) depending on whether outer-sphere or inner-sphere complexation has occurred, respectively. Outer-sphere complexes involve electrostatic attraction whereas inner sphere complexes have covalent bonding and ionic bonding characteristics. Therefore, outer-sphere bonds are less stable than inner-sphere bonds. The chemistry of adsorption is very complex and beyond the scope of this document except to say that pH, ionic strength, and other chemical aspects of the system can affect adsorption.

Membrane Filtration

Membrane filtration is a physical process that uses a semi-permeable membrane to separate the contaminants. The water is passed through the membrane via pressure, which allows low molecular weight chemicals to pass and blocks contaminants with high molecular weight. Various membrane filtration techniques can be used to meet very distinct liquid separations. Examples of membrane filtration processes include microfiltration, ultrafiltration, nanofiltration, and reverse osmosis. Reverse osmosis is the most effective membrane filtration process and results in water with very low total dissolved solids concentrations. The typical membranes used for reverse osmosis are synthetic (TFC - thin film composite) or organic (CTA - cellulose triacetate) and have pores that are less than 0.001 micron in size. The reverse osmosis process is known to remove dissolved inorganic compounds such as sulfate, arsenic, boron (at high pH), chromium, and selenium. Given current technology, membrane filtration is not amenable to in situ remediation.

Ion Exchange

Ion exchange is a common water treatment and is widely used in homes to eliminate problems with hard water and other trace constituents. It is the replacement of one adsorbed, readily exchangeable ion on the surface of a supporting substrate with another ion. This involves the concept of outer-sphere complexes discussed previously for adsorption. When the exchange medium becomes saturated with the ions that are being removed from the system, the medium can be replenished and reactivated by soaking it in a concentrated solution of K^+ or Na^+, thus desorbing the Ca^{2+}, Mg^{2+}, or other constituents to a waste stream. The relatively low cost and simplicity of ion exchange processes has made this approach a popular choice for ex situ treatment of water. In situ usage in groundwater is less well developed, partially due to the fact that the predominant concentrations of major dissolved ions, such as Ca^{2+}, can out-compete the contaminants for adsorption sites because the contaminants have much lower concentrations. The adsorption of major ions can deplete the ion-exchange capacity of some media; however recently developed adsorbents are more constituent-specific.

Electrolysis

Electrolysis is the application of an electric current through a liquid using at least two electrodes, one of which is positively charged, and the other of which is negatively charged. The current results in the migration of ions in the liquid to the electrode of opposite charge. Metallic ions and metalloids will precipitate or “plate out” onto the surfaces, or in the vicinity of the surface, of the electrode. Electrolysis has been a classical technique in chemistry laboratories but such separation of trace metals from the aqueous phase tends to function most efficiently in relatively pure, low ionic strength solutions. In groundwater systems, the presence of fairly high concentrations of dissolved ionic species, which will themselves migrate to and plate out on the electrodes, can cause passivation of the electrodes and rapid decreases in the removal efficiency of the contaminants of interest. Additionally, these approaches have been very difficult and expensive to implement and maintain in situ.

Uptake by Plants/Phytoremediation

Phytoremediation is a process that uses vegetation to remove, transfer, stabilize, or destroy contaminants in groundwater (or soil and sediment). Various plants and trees are used for this process depending on the type of phytoremediation application, the contaminants of concern, the depth of the contaminants to be addressed, and the media to be addressed. Dissolved inorganics can be treated by adsorption or precipitation onto plant roots or absorption into plant roots. The constituent may remain on the root, within the root, or be taken up and translocated into other portions of the plant, depending on the constituent, its concentration, and the plant species, for example, Cr(III) and As(V) can sorb to plant roots (GWRTAC, 1997a). Phytoremediation of dissolved inorganics is generally applicable at relatively low concentrations.

Constituent Properties Affecting Remediation

Properties of the most significant PCOCs for remediation of CCP sites (arsenic, chromium, selenium, boron, and sulfate) are described in this section, and the chemical treatment/removal processes effective on each are summarized in Table 3-1.

Table 3-1
Potential Constituents of Concern and Removal Processes

Constituent	Removal Processes
Arsenic	Adsorption, best with As(V) Reductive Precipitation Co-Precipitation Ion Exchange Membrane Filtration
Chromium	Adsorption, best with Cr(III) Reductive Precipitation Co-Precipitation Ion Exchange, primarily Cr(VI) Membrane Filtration
Selenium	Adsorption Reductive Precipitation Ion Exchange Membrane Filtration
Boron	Ion Exchange Membrane Filtration (at high pH)
Sulfate	Adsorption Reductive Precipitation Ion Exchange Membrane Filtration

Arsenic

Arsenic is a metalloid that is very redox-labile and, as such, can exist in several different valence states (-3, 0, +3, +5) and a wide variety of species in the environment. In natural aqueous systems, such as surface and ground waters, arsenic occurs primarily as an oxyanion, usually as arsenate [As(V), $As0_4^{-4}$] and arsenite [As(III), AsO_3^{-3}]. Arsenic concentrations in CCP field leachate range from 1 to more than 1,000 µg/L (EPRI, 2006a) with a median of 26 µg/L and a 90th percentile concentration of 178 µg/L (Table 2-2). The dominant species in CCP leachate is usually arsenate (EPRI, 2006a). Arsenite is typically more toxic, more soluble in water, and more mobile in groundwater than arsenate. Arsenic can be removed from water by a variety of processes, including adsorption, precipitation, and co-precipitation, often with conversion of any arsenite to arsenate prior to treatment.

Boron

Boron compounds tend to be soluble, mobile in the subsurface, and difficult to remediate. Boron has the highest concentration of minor and trace elements in coal ash leachate, ranging from 0.2 to more than 100 mg/L (EPRI, 2006a), with a median concentration of 2.6 mg/L and a 90th percentile concentration of 14 mg/L (Table 2-2). Boron typically occurs as a neutral boric acid species and is not readily removed by common water treatment procedures. EPRI (2005a) reports that boron can be removed from water using boron-selective ion exchange and boron-selective solvent extraction. Reverse osmosis is not effective at acidic or near-neutral pH, but is effective at high pH (>9.24). Other removal mechanisms have been proposed, but none have been fully developed.

Chromium

Chromium is less commonly found in CCP field leachate than the other PCOCs discussed here, as 48 percent of the field leachate samples were below the detection limit of 0.2 µg/L. The median field leachate concentration was 1 µg/L, and the 90th percentile was 25 µg/L, although concentrations as high as 5,000 µg/L were observed at one site (Table 2-2). When detected, Cr(VI) typically predominates in CCP leachate (EPRI, 2006a). In groundwater, Cr(VI) is mobile as an oxyanion, chromate (CrO_4^{2-}), which is also its more toxic form. Like arsenic, chromium can be removed from water by a variety of processes (Table 3-1).

Selenium

Selenium is considered by some to be non-metallic and by others to have metallic properties (Irwin, 1997), with behavior somewhat similar to sulfate (EPRI, 1994a). Like arsenic, selenium is generally present in predominantly two oxyanion forms in natural waters: Se(IV) as selenite ion SeO_3^{-2}, and Se(VI) as selenate ion SeO_4^{-2}. Selenium concentrations in CCP field leachate range from less than 1 to more than 2,000 µg/L (EPRI, 2006a), with a median concentration of 18 µg/L and a 90th percentile concentration of 181 µg/L (Table 2-2). Selenite tends to dominate in impoundment settings when the source coal is bituminous or a mixture of bituminous and subbituminous, while selenate tends to predominate in landfill settings and when the source coal is subbituminous/lignite (EPRI, 2006a). Selenate is generally soluble and mobile, and is readily taken up by organisms and plants. Selenite is less soluble and mobile than selenate, therefore reductive precipitation/co-precipitation of selenium could serve as a viable remediation approach. However, re-oxidation is a potential problem. Phytoremediation has also been reported and adsorption has been used.

Sulfate

Sulfate is naturally present in many minerals and its occurrence in groundwater is ubiquitous. It also has the highest concentration of any constituent in CCP leachate (EPRI, 2006a), with a median concentration of 485 mg/L in field leachate samples and a 90th percentile concentration of 1,613 mg/L (Table 2-2). Sulfate is mobile in groundwater except under strongly reducing conditions, where it is reduced to sulfide. Sulfate is typically removed from water by precipitation or by reductive processes. For precipitation to occur, concentrations of precipitating cations (e.g., Ca^{2+}, Ba^{2+}, etc.) must be present in sufficient quantity and under the right pH conditions to lower the sulfate concentration via precipitation as $BaSO_4$ or $CaSO_4$. The reduction of sulfate to elemental sulfur (S) and hydrogen sulfide (H_2S) is microbially mediated and the presence of organic matter is required. Sulfate reducing conditions do not typically occur in surficial sand and gravel alluvial aquifers typical of those present beneath most CCP management sites because these aquifers tend to be mildly oxic.

Remediation Technology Descriptions

There are many technologies that can be used individually or in combination to minimize the release of contaminants into groundwater or attempt to remediate groundwater once a release has occurred. Minimizing the potential release of contaminants to groundwater is clearly preferable to remediating contaminated groundwater, because remediation often requires allocation of resources for prolonged periods of time and is expensive. Approaches for minimizing the potential for releases from CCP sites are dependent on site-specific attributes such as underlying geology, climate, and the management method utilized (wet or dry); and can vary from dry-stacking with an eventual evapotranspirative cap to liners with leachate collection systems.

The focus of this report, however, is on remedial technologies applicable after a release to groundwater has occurred from a CCP management unit. Remediation technologies can be broadly grouped into source control, ex situ remediation, and in situ remediation. In source control, the CCP source is physically or chemically removed or constrained such that the release cannot extend beyond the applicable boundary of the CCP management unit. Ex situ remediation consists of removal of groundwater for treatment at the land surface, while in situ remediation consists of in-place treatment of a groundwater plume as it migrates downgradient from the source.

Source Control

Controlling an active source of groundwater contamination can reduce remedial costs by shortening the time that remedial processes have to be maintained. In some cases, source control coupled with monitored natural attenuation is all that is required at a site. Source control options can be particularly beneficial for CCP sites due to the long leaching time of these materials; however, the range of feasible options at CCP sites is often limited due to their large size.

Capping

Capping is usually performed to prevent or reduce infiltration of water into CCPs, which subsequently reduces the volume of leachate generated. Caps can be installed on both legacy and recently filled CCP sites. Depending on climatic conditions, designs can range from barrier caps utilizing low permeability materials such as PVC, to evapotranspirative caps that utilize soil sequencing and vegetation to promote runoff and evaporation of water. Caps are not effective when CCP is filled below the water table, because groundwater flowing through the CCP will generate leachate even in the absence of vertical infiltration through the CCP.

Caps can be effective for relatively long-term mitigation of source contaminant intrusion into the subsurface when properly installed and maintained, and when the CCP is above the water table, but their installation may not be sufficient as a complete remedial solution once a groundwater plume has formed. More than half of the remediation case studies listed in Table 2-4 included capping as a component, and in at least two cases (sites 4 and 9) the cap and closure approaches have resulted in documented significant decreases of PCOC concentrations.

Removal/Excavation

Source removal is an effective, but often impractical, method of contaminant source control. Due to the large areal and vertical extent of most CCP disposal sites, excavation, removal, and alternative disposal of the materials can be either impossible or at least cost prohibitive when risk and alternative approaches are considered. However, there are scenarios where excavation of some material can be both technically feasible and cost effective. For example, in CCP case study 10 (Table 2-4), review of historical aerial photos revealed that the area of greatest groundwater impact was downgradient of a low area (pond) that existed at the site prior to filling with CCP. Groundwater fate and transport modeling showed that excavating the saturated ash filled in this area would enable remediation without implementation of a groundwater extraction system, and economic analysis showed the cost of excavating this 2-acre (0.8-ha) area, even though it was below 35 feet (11 m) of unsaturated ash, would be lower than in situ stabilization or implementation of a long-term groundwater extraction system. The final remedial approach therefore included: 1) removal and stockpiling of overlying unsaturated CCP; 2) excavation of saturated CCP and refilling of the excavation with clean sand below the water table; 3) replacement of the unsaturated CCP; 4) placement of a PVC cap; and 5) provision of alternative groundwater supplies to users within the plume area.

Barriers

When excavation or removal is impractical and the source materials are in the groundwater or infiltration from these materials cannot be mitigated, it is sometimes possible to contain the source by the implementation of physical or hydraulic barriers. Barriers are installed to either surround the source or to divert groundwater around and away from the source.

Physical barriers are constructed from a variety of materials (cement, bentonite, sheet piling) and installed using widely differing techniques (jetting, trench and fill, pile driving). In order to be effective, there must be a low-permeability lower confining layer into which the barrier can be keyed, and it must be at a technically feasible depth. Furthermore, if the barrier fully surrounds the site, some form of gradient control is typically needed to avoid a build-up of head within the barrier. However, since an inward gradient can be maintained within the wall at relatively low pumpage rates, it may be possible to close such a site with a simple soil cap, which results in savings in short term construction costs, relative to an engineered cap, and potentially enables more options for future site development. A remediation approach utilizing this technology was used at CCP case study site 1 (Table 2-4).

Hydraulic barriers are used to contain leachate discharging from a site or to change hydraulic gradients such that the plume can be managed on site. Containment is accomplished by groundwater extraction wells or trenches that intercept all groundwater flowing from a CCP unit. Depending on the concentration of PCOCs in the extracted groundwater, it may be possible to route the extracted groundwater to an existing treatment system, either for plant production water, as was done at CCP case study site 2 (Table 2-4), or to a sanitary sewer.

Chemical in Situ Source Treatments

The in situ treatment of contaminant sources is a relatively recent approach to source control. Most in situ source treatment has been focused on organic chemical contaminants such as chlorinated hydrocarbons and petroleum hydrocarbons. These systems have included:

- Cosolvent/surfactant flushing
- Thermal stripping
- Air sparging
- Steam enhanced extraction
- Surfactant flushing with enhanced bioremediation
- Chemical fixation/in situ oxidation

A few in situ source treatments have been attempted for metals and inorganics. At the U.S. Coast Guard Air Support Center (Elizabeth City, NC), sodium dithionite was injected into a high concentration Cr(VI) source zone, directly below an old chrome plating shop, to reduce the chromate to Cr(III) and immobilize it. The process of in situ chemical fixation using ferrous sulfate has been evaluated in the laboratory for arsenic-contaminated soils at utility substation sites (Donahoe, 2006a). As a result of successful laboratory studies, ferrous sulfate was injected into soil contaminated by arsenic-containing herbicides to mitigate release of arsenic to groundwater. The arsenic is immobilized by co-precipitation with, or adsorption onto, iron precipitates (Redwine, 2001).

Whereas most treatments for organic contaminants depend upon actual destruction or removal, either oxidizing the materials to CO_2 and water or increasing the vapor pressure to enhance volatilization, inorganic contaminants and metals are typically immobilized by reduction or oxidation followed by precipitation or adsorption; or, less commonly, the contaminants may be intentionally mobilized to facilitate capture and removal.

Some key issues for in situ source remediation are:

- Locating the source
- Source dimensions
- Source contaminant mass
- The ability to comingle the contaminants and reactants in the subsurface
- Competing subsurface reactions (that consume added reactants)
- Hydrologic characteristics of the source and subsurface vicinity
- Delivery options for the cleanup procedure(s)
- Capture of any contaminants mobilized by the procedures
- Long term stability of any immobilized contaminants

Stabilization/Solidification

Stabilization/solidification (S/S) reduces the mobility of organic and inorganic substances through both physical and chemical means by addition of binder materials to the soil and groundwater. In stabilization, chemical reactions are used to reduce the leachability of a waste product, while solidification encapsulates the waste, decreasing the available surface area from which leaching can occur.

The typical binder materials are cement-based (i.e., cement or blast furnace slag) and can be added ex situ or in situ. Cement-based S/S reduces the mobility of inorganic compounds by formation of insoluble hydroxides, carbonates, or silicates; substitution of the metal into a mineral structure; sorption; and physical encapsulation in a stabilized monolith. The process also reduces the hydraulic conductivity of the material, which limits the contact between the transport fluid and contaminants. Because it reduces hydraulic conductivity, there may be cases where it will be advantageous to use S/S technology to construct a barrier wall. For in situ applications, the binder material is mixed using vertical augers, conventional equipment such as backhoes, or injection grouting (Redwine, 2001).

Cement-based S/S involves a complex series of reactions and there are many potential interferences that can prevent attainment of S/S treatment objectives for physical strength and leachability. Treatment of arsenic and chromium with cement-based S/S is not always effective because the high pH of the cement may inhibit formation of insoluble precipitates (USEPA, 1997).

Ex Situ Groundwater Remediation

Historically, ex situ remediation, such as pumping groundwater followed by treatment at the surface (pump and treat), was the standard approach to managing groundwater plumes. In recent years, the emphasis has shifted to in situ technologies as limitations of the pump and treat approach, as described below, became apparent. However, there will continue to be applications where pump and treat and other ex situ technologies are the optimal remedial approach.

A dedicated treatment system is not always necessary for ex situ remediation at CCP sites, depending on the PCOCs present, their concentration, and the availability of alternative water management options. For example, it may be possible to discharge extracted groundwater that contains relatively low concentrations of inorganic constituents to a storm sewer, sanitary sewer, or water treatment system used by the power plant.

Groundwater Extraction

Pumping groundwater to the surface and treating it to remove contaminants has a long history of use as a plume control and remedial technology. Numerous surface treatments have been devised to remove virtually any contaminant from the water, including those found in CCP leachate.

Surface treatment of inorganics results in materials that must be subsequently disposed or recycled. Unlike organic compounds, which can be completely destroyed by certain treatments, inorganics persist and are concentrated by the treatment processes and must be managed within the treatment train. Examples of these residues are sludges resulting from reductive precipitation, concentrated “reject” water from reverse osmosis, depleted resins or backflush water from ion exchange, and plated electrodes from electrolysis.

Treated water must also be managed. Management options include but are not limited to:

- Reinjection to groundwater if the treated water meets groundwater clean-up criteria and if allowed by state regulation;
- Discharge to surface waters or storm sewers if available and if the treated water meets surface water effluent limits;
- Discharge to sanitary sewers if the only available option or if the treated water does not meet surface water effluent limits. Depending on the concentration of the extracted groundwater, it may be possible to discharge groundwater from a CCP site directly to sanitary sewers, thereby avoiding treatment costs. This approach was used at CCP case study site 1 (Table 2-4).

Pump and treat approaches can be effective at lowering contaminant concentrations, but they require long-term operation and maintenance for every aspect, from pumping the groundwater to operating the treatment train and ultimately disposing of the residuals. The expenditures of energy and money for operating pump and treat systems may, in and of themselves, be acceptable if cleanup to remedial goals is attainable within a reasonable time frame. However, pump and treat systems do not always perform as designed. It has been repeatedly observed that rebound of contaminant concentrations sometimes occurs when pump and treat systems are turned off (Keeley, 1989). This is due to processes such as slow diffusion of sorbed/adsorbed contaminants from the mineral surfaces and high contaminant concentrations contained in restricted pore spaces of the aquifer materials that gradually diffuse/bleed/pinch off into the surrounding groundwater. Another potential problem is deterioration of extraction wells, as occurred at CCP case study site 8 (Table 2-4), where the groundwater extraction system was eventually abandoned due to decreasing well efficiency (Figure 3-1), and an alternative remedial approach (a cap upgrade) was subsequently implemented.

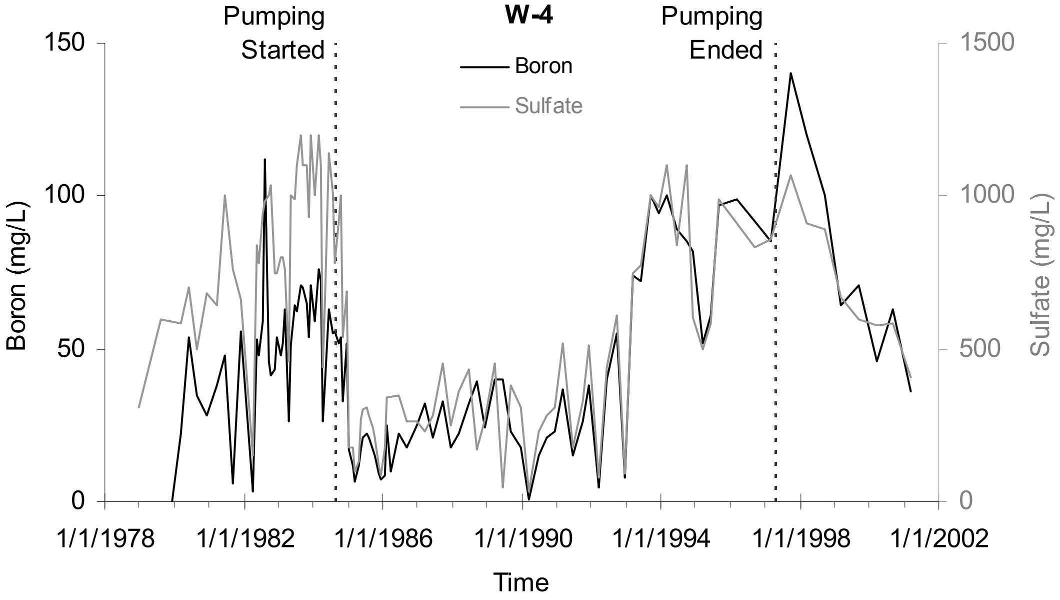

Figure 3-1
Concentration Plot Showing Decreasing Effectiveness of Groundwater Extraction at CCP Case Study Site 8 (from EPRI, 2001b)

Remediation times for pump and treat systems can be very long (some sites have reported periods of 50-100 years). The National Research Council (1994) has listed the processes responsible for affecting pump and treat cleanup times. These are:

- Mixing of clean groundwater with contaminated groundwater (inevitable during pump and treat remediation), resulting in much larger quantities of water requiring treatment.
- Geologic heterogeneities (difficulties flushing low permeability zones, contaminant diffusion limited cleanup).
- Non-aqueous phases (the presence of NAPLs and their slow dissolution—not an issue for CCP sites).
- Sorbed contaminants (desorption rate limited cleanup processes—a potentially significant issue for CCP sites).
- Leachate from remaining contaminant sources (remaining source terms).

The NRC has also stated the situations in which it thinks pump and treat can be used as a viable treatment technology. These are:

- May be able to restore the water to health-based standards at relatively simple sites;
- May be able to clean up the dissolved portion of the contaminant plume at more complex sites while either additional pumping or other methods contain the remaining contamination.

Most sites are not geologically homogeneous and isotropic, but instead vary widely with regard to complexity over short distances. Containment of the remaining contaminants by active technologies (e.g., pumping) is also not generally a cost-effective long-term management strategy. These issues have driven research into and adoption of in situ remediation strategies that are less impacted by pumping limitations.

Interception/Drainage Trenches

For shallow plumes, interception or drainage trenches might be a viable alternative to groundwater extraction wells. The trenches are similar to a French drain except that the captured water originates in the subsurface rather than on the surface. Generally, the trench is excavated to intersect groundwater perpendicular to the flow path and to a depth within the zone of contaminant migration. Contaminated groundwater then flows into this trench. A variety of methods may be used to remove the water from the trench and into a treatment system (gravity flow, pumps, etc.). These systems are generally limited to relatively shallow depths, and issues such as trench stability, etc., are important to an effective design.

In Situ Groundwater Remediation

The conceptualization and initial development of in situ remediation approaches for groundwater contamination began about 15 to 20 years ago, and have gained impetus during the last decade. Most early efforts at in situ remediation were via bioremediation, i.e., using microorganisms to alter or eliminate the groundwater contaminants, initially focusing on plumes of dissolved hydrocarbons. More recently, these technologies have been applied to plumes containing inorganic constituents; an area of continuing research.

Bioremediation

Most efforts at bioremediation have been for the remediation of organic contaminants, notably petroleum hydrocarbons and chlorinated ethenes. Some success has been attained using microbial processes for inorganic compounds as well, especially using the ability of certain microorganisms to create reducing environments under the proper conditions. One example is the reduction of sulfate concentrations by sulfate reducing bacteria with the concomitant removal of metals as sulfide precipitates (e.g., PbS, CdS). Potential bioremediation processes for inorganics include (Bolton and Gorby, 1995):

- Oxidation
- Reduction
- Methylation
- Demethylation
- Metal-organic complexation
- Ligand degradation
- Precipitation
- Bioaccumulation
- Biosorption

Biological processes are always present in soils and aquifer materials, sometimes including those processes that serve to remove contaminants from the water migrating through these materials. Occasionally these processes are sufficiently active, and receptors of concern are sufficiently distant that contaminant removal to below regulatory requirements will occur by natural processes. This is the premise of monitored natural attenuation. When the natural processes are not sufficient, conditions are not in the right ranges (pH, Eh, nutrients, etc.), the native microorganisms are not appropriate, or downgradient receptors are too close, then enhanced bioremediation might be required.

Enhanced bioremediation processes have been extensively investigated since the 1980s and have included the evaluation of numerous modifications to subsurface environments in an attempt to improve contaminant removal/transformation by microorganisms. Typically these have involved the additions of electron acceptors (e.g., oxygen, peroxide, sulfate) and/or electron donors (e.g., readily oxidizable organic matter), carbon sources, and nutrients by injection and infiltration. They have occasionally included the addition of non-native bacterial species or microbial consortia as well, when the native microbes did not have the needed capabilities. Certain oxidized metals and inorganic species can serve as electron acceptors in the subsurface, themselves becoming reduced in the process. If the reduced species are more readily adsorbed, decreased in toxicity, or precipitated because of this reduction in oxidation state, then this approach can be used for in situ remediation of these constituents. Oxidized species of PCOCs sometimes found in CCP leachate that may be amenable to bioreduction and immobilization include chromate, sulfate, selenate, and molybdate. Other constituents, however, may become more mobile if converted to a more reduced state, arsenic being a notable example. For the near-neutral pH range of 6.0 to 8.5 typical of groundwater (Hem, 1989), As(III) is more toxic, has higher solubility, and is more mobile than As(V).

Another important consideration when evaluating potential for bioremediation at CCP sites is the effect of iron and sulfate reactions. Fe(III) is a potential electron acceptor but tends to precipitate as hydrous iron oxides or oxyhydroxides. When subsurface conditions are such that Fe(III) becomes the favored electron acceptor (anoxic environment) and appropriate microbial populations or consortia are present, the Fe(III) forms can be reduced to Fe(II), which tends to remain in solution as an aquo complex. If groundwater containing Fe(II) migrates to an oxic zone, then the Fe(II) can reoxidize and precipitate, which can cause coprecipitation of other metallic constituents present in the water. Microbial reduction of sulfate can remove divalent metal aquo complexes by precipitation of the metal as a sulfide, e.g., CdS, FeS, PbS.

Phytoremediation

Plants are able to remove, transfer, stabilize, or destroy contaminants in groundwater (or soil and sediment). One of the mechanisms used to remove dissolved inorganic contaminants from water is rhizofiltration, which involves the adsorption or precipitation of contaminants onto plant roots or the absorption into the roots of contaminants that are in solution surrounding the root zone. This mechanism is primarily used on extracted groundwater or surface water, although it can also be used as an in situ treatment. When used ex situ, the extracted groundwater is pumped to an ex situ engineered tank system with plants grown under hydroponic conditions whereby the water must come into contact with the roots. The plants are harvested and disposed as the roots become saturated with contaminants. When used in situ, the tanks would be placed in a downstream or downgradient location where the water can enter and exit by gravity drainage.

Phytovolatilization is a phytoremediation mechanism that can be used for in situ remediation. It involves contaminant uptake by the plant, transpiration, and eventual release to the atmosphere of a volatile contaminant, a volatile degradation product of the contaminant, or a volatile form of an initially non-volatile contaminant. For effective phytoremediation, the degradation product or modified volatile form should be less toxic than the initial contaminant. An example includes transformation of selenate to the less toxic dimethyl selenide gas (USEPA, 2001).

The primary limitation for in situ phytoremediation of groundwater is the depth of the plume. It is limited to shallow depths in unconfined aquifers in which the plume is accessible to the plant roots.

Phytoremediation can also be used as a hydraulic control measure to influence the movement of groundwater through the uptake and consumption of large volumes of water (typically associated with plantations of poplar or willow trees) (EPRI, 1999b). This mechanism may be used as a supplement to another groundwater remediation technology as a containment measure or as a means to draw water from one location to another.

A considerable volume of research has been performed on phytoremediation including:

- The U.S. Army Corps of Engineers: http://el.erdc.usace.army.mil/phyto/
- USEPA: http://www.epa.gov/ORD/NRMRL/lrpcd/rr/phytores.htm
- ITRC: http://www.itrcweb.org/gd_Phyto.asp
- EPRI:
  - The Tennessee Valley Authority Constructed Wetland at Widows Creek: Role of Vegetation in the Removal of Toxic Trace Elements, TR-114220, 1999
  - Improvement of Plants for Selenium and Heavy Metal Phytoremediation Through Genetic Engineering, TR-114219, 11/09/1999
  - Phytoremediation of Trace Elements by Wetland Plants, 1005185, 08/23/2001
  - The Allegheny Power Service Constructed Wetland at Springdale: The Role of Plants in the Removal of Trace Elements, 1006504, 11/05/2001
  - Phytoremediation at an Arsenic Contaminated Site, 1011760, 2005

Electrokinetics

Electrokinetic techniques use low voltage direct current to separate and extract metals and other contaminants from groundwater. The goal of electrokinetic remediation is to effect the migration of subsurface contaminants by developing an electrical potential between electrode pairs that have been implanted in the ground on each side of the contaminated area. The charged particles are mobilized toward the electrodes by the current. Upon their migration to the electrodes, the contaminants may be removed by electroplating, precipitation/co-precipitation, pumping near the electrode, or complexing with exchange resins. In situ electrokinetic remediation has been developed largely to enhance contaminant removal in low permeability soils (GWRTAC, 1997b). This technology has been used on arsenic in soils at a utility substation (EPRI, 2000b) and at an MGP site (EPRI, 1994b). Results from the utility substation pilot test suggested that electrokinetic remediation of arsenic was not cost-competitive with competing technologies (EPRI, 2000b).

Chemical Injection to Promote in Situ Immobilization

This approach covers a broad range of technologies where liquid or gaseous reactants are injected into the substance to cause immobilization of dissolved inorganic constituents. Examples of reactants that have been used or are in development include:

- **Ferrous sulfate ($FeSO_4$•$7H_20$):** Ferrous sulfate has been used for in situ remediation of chromium-contaminated sites. The oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) is proposed to reduce Cr^{6+} to Cr^{3+}. A field application of ferrous sulfate to treat chromium at the Townsend Saw Chain site in Pontiac, South Carolina, showed that, despite ultimate reduction of chromium concentrations in the aquifer, initial concentrations of chromium increased due to displacement of adsorbed chromium by excess sulfate ions (USEPA, 2000). Due to the strong adsorption affinity of arsenic for iron oxyhydroxides, it is likely that ferrous sulfate can also be utilized to remediate arsenic-contaminated groundwater.
- **Nanoscale zero-valent iron:** This ultrafine "nanoscale" iron powder is injected into a plume as a slurry and flows with the groundwater to remediate contaminants in situ. The nanoscale iron particles are 10 to 1000 times more reactive than conventional iron powders because their smaller size gives them a much larger surface area. An oxidation/reduction reaction occurs with the iron that reduces the dissolved metals to an insoluble form that remains in place (Zhang, 2003).
- **Organo-phosporus nutrient mixture (PrecipiPHOS™):** The PrecipiPHOS™ method involves injection of a carbon feed source and a gaseous organo-phosphorus nutrient mixture to promote the growth of microbes that in turn produce inorganic phosphates as a by-product.[2] The inorganic phosphates immobilize the metals through precipitation, co-precipitation, or adsorption.
- **Sodium dithionite:** Sodium dithionite is a strong reductant that is injected into the subsurface to reduce dissolved metal species, such as Cr(VI) to Cr(III), which then precipitate. Sodium dithionite solutions can also be injected into a plume to reduce natural ferric iron-bearing minerals to ferrous iron-bearing minerals. The ferrous minerals then reduce oxidized species dissolved in passing groundwater. This technology was applied at a site in Washington state as described in PRB case study 17 (Appendix B).

Permeable Reactive Barriers

Among the most promising of the innovative in situ remediation technologies are permeable reactive barriers (PRBs). Permeable reactive barriers have been defined as:

> *An emplacement of reactive materials in the subsurface designed to intercept a contaminant plume, provide a flow path through the reactive media, and transform the contaminant(s) into environmentally acceptable forms to attain remediation concentration goals downgradient of the barrier (Powell and Powell, 1998; Powell et al., 1998).*

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[2] http://www.epa.gov/superfund/programs/aml/tech/news/precipip.htm

The concept of PRBs resulted from the observation of chlorinated hydrocarbon concentrations during investigations of well casing material effects on groundwater sampling (Reynolds et al., 1990). It was realized that halocarbon concentrations decreased when exposed to iron and steel casing materials. From this, researchers at the University of Waterloo derived the concept of using reactive media emplaced in the subsurface to intercept plumes of contaminants and transform them to harmless by-products.

Initial experiments to test the hypotheses of contaminant removal were done using scrap iron (e.g., iron filings and granules) in batch and column tests in the laboratory, followed by pilot-scale field demonstrations and full-scale remedial implementations. Initially the focus was on the remediation of chlorinated hydrocarbons via successive dechlorination reactions, e.g.:

$$PCE \rightarrow TCE \rightarrow DCE \rightarrow VC \rightarrow Ethene \rightarrow Ethane$$

Realization that a reductive process was occurring resulted in the application of the process to inorganic contaminants as well.

The remediation of reducible contaminants by iron metal is based on the corrosion of the iron metal itself. Corrosion occurs because zero-valence iron, or Fe(0), such as the metallic iron chips, filings, and granules used in most PRBs, are thermodynamically unstable and can serve as electron donors for the reduction of oxidized species, themselves becoming oxidized in the process while the contaminants are reduced. Zero valence iron (ZVI) is unstable in the natural environment and has to be created using high temperature metal refining processes (Evans, 1960; Sculley, 1975; Snoeyink and Jenkins, 1980). It tends to revert to a form that is more thermodynamically stable; for example, iron metal oxidizes to Fe_2O_3 in the earth's oxygen-rich atmosphere. At low temperatures, the rate of atmospheric oxidation of iron and steel is negligible due to the oxide surface films that form and inhibit further surface exposure. However, when the iron is immersed in an aqueous salt solution, as would be the case for a reactive barrier of iron chips or filings in groundwater, an electrochemical corrosion mechanism will occur.

Electrons are given up by the metal in one area (the anodic region) forming soluble cations of the metal, and taken up by oxidized species that become reduced, at another part of the metal surface (the cathodic region). The instability of the iron itself can provide the necessary energy for oxidation-reduction reactions without external energy input, provided suitable coupled electron-accepting reactions can occur with reducible species at the cathode. Typically, dissolved oxygen is the preferred oxidant, or electron acceptor, during aerobic corrosion processes. These systems can, however, become anoxic or anaerobic if oxygen is depleted by the reactions. When present, inorganic contaminants such as chromate (CrO_4^{2-}), selenate (SeO_4^{2-}), or highly halogenated organic compounds such as PCE and TCE can serve as the oxidants, accept electrons, and become reduced. Protons (H^+) can also be reduced and paired to form hydrogen (H_2). As long as electron acceptors are present, corrosion processes and electron transfer within the metal can continue.

In addition to metallic iron, numerous other reactive materials have been investigated for use in PRBs for remediation of a variety of metals, inorganics, and organic contaminants. These have included bimetallic media (such as platinum, palladium, nickel, or copper-coated iron), organic matter to promote biological reactions (leaf litter, sphagnum peat, etc.), crushed limestone, phosphate rock (and fishbone), scrap iron, tin, aluminum, zeolite, pyrite, iron oxides, zinc, stainless steel, copper, brass, biotite, vermiculite, and others. The mechanisms of contaminant remediation by these materials vary widely and include bioreduction, adsorption, precipitation, and molecular sieves. A number of inorganic contaminants are now known to be amenable to remediation using PRB technology and the appropriate selection of reactive media. These include chromium, sulfate, selenium, nickel, lead, uranium, technetium, iron, manganese, copper, cobalt, cadmium, zinc, molybdenum, nitrate, phosphate, and arsenic. Notably, four of the five primary PCOCs for CCP sites are known to be treatable by PRB technology, and research has been performed for the other constituent, boron (McGregor et al., 2002).

PRBs are discussed in more detail in Section 4.

Monitored Natural Attenuation

Monitored natural attenuation (MNA) is a relatively new approach to subsurface/groundwater management that is not an active remediation but is also not a "no action" approach. MNA relies on natural physical/biological processes being sufficient to protect potential receptors and regulated boundaries downgradient of the source/plume. To ascertain that the processes are sufficiently protective requires:

- thorough site characterization,
- a conceptual model of the biogeochemical behavior of the contaminants over time in this milieu,
- careful calculation of distances, travel time, source mass/concentration,
- determination of removal or degradation rates, and
- ongoing monitoring of dissolved contaminant concentrations and geochemical indicators.

The concept of MNA initially developed from observations that certain contaminant plume dimensions did not increase in size (or did not increase at the expected rate) even when an ongoing source term was present. Plumes that decreased in volume without advancing were also noted. The process was referred to as natural attenuation or intrinsic bioremediation until the importance of the monitoring aspects of the approach were fully realized, at which time it became generally redesignated as monitored natural attenuation. As with PRBs, the concept was originally applied to plumes of organic contaminants, in this case petroleum hydrocarbons, and subsequently considered for chlorinated hydrocarbons and inorganic contaminants. MNA differs from active bioremediation because, in general, no additions are made to the subsurface to alter the geochemical or microbiological environment, with the possible exception of the removal of the source term whenever practical.

The mechanisms that result in the natural attenuation of metals and inorganics along a plume flow path are generally the same used for active remediation processes, as listed previously. These include sorption, adsorption, precipitation, ion exchange, biodegradation, surface complexation, oxidation/reduction reactions, etc. In addition to these, the physical processes of dispersion and dilution can also contribute to natural attenuation. MNA of inorganic constituents differs from MNA of organic constituents in that the constituents are not degraded—rather they disperse, or remain in an immobilized form as a precipitate or adsorbed to the solid matrix.

Monitoring for MNA may be more extensive than for other remedial approaches, possibly including a series of wells along the length, and often breadth, of the plume. This allows observation of whether or not the plume size is increasing, is at a pseudo-steady state, or is diminishing in volume. In addition to simple observation, it is possible to use these data to get at least approximate rate values for this increase or decrease (usually calculated as pseudo-first order rate constants) and a travel time estimate should the plume be advancing in spite of naturally attenuating processes. Additionally, understanding the geochemistry and microbiology along the flow path can yield information on whether or not the attenuating processes will continue, become depleted, increase, or decrease in rate downgradient of the current plume boundaries.

USEPA is currently developing a framework document for the assessment of MNA for inorganic constituents. Key elements of the framework are that 1) immobilization is the primary viable process for MNA of non-radioactive inorganic constituents, and that two "plumes" must be managed—the liquid plume (immobilization) and solid phases (so they do not remobilize) (Puls, 2006). The document will provide a framework for evaluating whether or not MNA is viable, and guidance for determining rates of attenuation, long-term stability, and establishment of a monitoring and contingency plan. Although MNA is now often proposed as a stand-alone approach to management of contaminant plumes, it can also be evaluated adjunctive to other remediation technologies.

Groundwater Remediation Alternatives at CCP Sites

The optimal groundwater remediation alternative for a given CCP site will depend on a variety of factors such as:

- **The location of the site and PCOCs present in groundwater.** A site leaching selenium to an aquifer with nearby downgradient receptors may require a higher level of effort (such as active downgradient remediation and/or provision of alternative water supplies) due to health-based water quality issues, than a site leaching sulfate with no downgradient receptors.
- **Whether the CCP was managed wet or dry.** If managed wet, the readily leachable fraction of some constituents may have been largely removed during sluicing and the remaining mass may only leach low concentrations. Case studies have shown that in some hydrogeologic environments, it may be possible to remediate groundwater at a CCP impoundment by closing and dewatering the impoundment (CCP case study sites 4 and 5, Table 2-4).
- **Whether the CCP lies above the water table.** In many cases, an engineered or evapotranspirative cap will effectively remediate a CCP source if the CCP is above the water table (CCP case study sites 8 and 9); while a cap alone may not be effective at sites where CCP was filled below the water table.
- **The remaining capacity of the site.** It may be more advantageous to install an active downgradient remediation at sites with a large amount of remaining capacity than to prematurely close the site.
- **Hydrogeologic conditions.** A permeable reactive barrier is potentially feasible in a non-lithified aquifer when the plume is within the limits of PRB trenching technology (currently 40 to 50 feet, 12 to 15 m). A different alternative, such as groundwater extraction, may be necessary or more cost effective in lithified (rock) aquifers, and when the plume extends deeper than the limits of PRB trenching technology.

- **Sensitive environmental areas.** It may not be feasible to excavate trenches for barrier walls or permeable reactive barriers through environmentally sensitive areas downgradient of some CCP sites. This restriction factored into the selection of the groundwater extraction system installed at CCP case study site 2.

The case studies listed in Section 2 list the following general approaches to remediation:

- Closure
- Capping
- Excavation
- Barrier walls with hydraulic gradient control
- Provision of alternative water supplies
- Groundwater extraction
- Permeable reactive barrier
- Monitored natural attenuation

The first five approaches are fairly standard applications. The sixth approach, groundwater extraction (with or without ex situ treatment), is a relatively mature technology, and has limitations, but may be the only viable alternative in some cases. The last two alternatives are forms of in situ remediation, a topic of developing interest for CCP sites.

In situ remediation approaches, which allow the plume to follow its natural flow path to treatment, are very attractive, relative to groundwater extraction with ex situ treatment, because they:

- require no energy/financial expenditure to control the groundwater flow;
- minimize the treatment of clean groundwater along with the contaminated;
- reduce or eliminate the need to dispose of treatment by-products;
- eliminate the need to manage extracted groundwater; and
- reduce potential for cross-media contamination (groundwater to air, surface water, or land).

The next section in this report describes the potential for application of one particular in situ remediation technology at CCP management sites: the permeable reactive barrier. The PRB shows promise because it can be used to treat a variety of inorganic constituents. Furthermore, this technology is still being actively researched, and there are multiple pilot scale and field applications; therefore, there is a sizeable body of published research on the topic.

4

PERMEABLE REACTIVE BARRIERS

Introduction

Permeable reactive barriers (PRBs) have potential to provide cost-effective, passive, in situ treatment of groundwater contamination. Remediation is achieved as contaminated groundwater passes through a reactive subsurface zone that either removes the constituent of concern from groundwater or facilitates its transformation into a less toxic form. The implementation of PRBs has resulted primarily from the recognized ability of reactive materials (e.g., zero-valent iron) to remediate organic compounds. The favorable oxidation kinetics of zero-valent iron result in effective dechlorination of organic solvents such as TCE by reductive processes. The success of zero-valent iron in passively remediating organic contaminants has led to more recent advances in every aspect of PRB technology. These advances include design and construction techniques, reactive media development, application to inorganic constituents, and increased understanding of PRB economics and long-term performance.

Comprehensive descriptions of PRB design, installation, and monitoring have been published by:

- The Interstate Technology & Regulatory Council: http://www.itrcweb.org/gd_PRB.asp
- USEPA Office of Research & Development: http://www.epa.gov/ada/pubs/reports.html

Additional PRB references, including case studies, studies of specific reactive media, and links to other organizations can be found at:

- USEPA CLU-IN web site: http://clu-in.org/conf/itrc/prb/resource.htm
- USDOE: http://www.gjo.doe.gov/perm-barr/
- The United Kingdom's Engineering and Physical Sciences Research Council (EPSRC): http://www.prb-net.org/
- The University of Waterloo has been a leader in PRB research and holds several patents on the technology: http://www.science.uwaterloo.ca/research/ggr/PermeableReactiveBarriers/PermeableReactiveBarriers.html

This section summarizes the application of PRB technology for remediation of inorganic constituents typically associated with CCPs in groundwater. It does not attempt to reproduce all of the information that can be obtained from the above-listed sources, as well as other sources, but instead serves as a primer to familiarize the reader with the general concepts of PRBs as they may be applied to CCP sites, and to identify areas of potential CCP-focused research.

Intellectual Property

Many of the technologies discussed in this summary report are protected intellectual property, including design (e.g., U.S. patents 5,362,394 and 5,514,279; Canadian patent 2,062,204), installation techniques (e.g., U.S. patent 6,357,968 for a jet-grouting approach to injecting PRB material), and reactive media (e.g., U.S. patent 5,876,606 for a media composed of basic oxygen furnace oxides or slag). Patented material (for example, many reactive media are patented) can be researched online at http://www.uspto.gov/patft/index.html (for United States patents) and http://patents1.ic.gc.ca/intro-e.html (for Canadian patents).

Design and Construction

Design Criteria

Permeable reactive barriers must be engineered with appropriate reactive media, effective residence time of contaminated water in the reactive media, and strategic location to passively capture the entire extent of the plume. Various design configurations have been constructed, including continuous barriers, funnel-and-gate systems, in situ deep slurry injections, and in situ reactive vessels (ITRC, 2005). Important design considerations include:

- Characterization of site hydrogeology, including delineation of the plume—which provides necessary data for feasibility analysis and the physical design of the PRB.
- Site constraints such as buildings and major overhead or underground utilities that will affect PRB positioning and construction methods.
- Characterization of the chemical composition and redox environment of the plume and background groundwater—which is needed for feasibility analysis and evaluation of reactive media.
- Regulatory acceptance: will the design feature an unusual physical configuration or new reactive media, such that a high degree of performance monitoring will be required?

Site Characterization Considerations for the Installation of a PRB

Although a good site characterization is needed for any type of groundwater remediation scenario, it is especially important for the installation of a PRB. This is because no active pumping of the water (i.e., flow control) will occur for a typical installation. The site characterization must be sufficient to allow a thorough understanding of the contaminant plume in three dimensions, groundwater flow directions and flow rates, and, if possible, the mass of the contaminant source term. The PRB must lie directly in the flow path of the plume and its design and construction must be such that the plume cannot bypass the treatment system by flowing over, under, or around the distal ends of the PRB. This means that the PRB must have a cross-sectional area (including funnels if so designed) sufficient to more than encompass the cross-sectional area of the advancing plume. The PRB must also contain an adequate volume of reactive media and the constituents of interest must have a residence time within the media (based on flow rate and media thickness) that is long enough to accomplish the remediation concentration goals. These issues are addressed in greater detail in publications such as Powell et al. (1998).

The surface characteristics of a site (e.g., buildings, utility lines, property boundaries, and a variety of other considerations) may also impact the design and construction approach for PRB installation. In most cases, it has not been possible to actually locate the PRB in front of the advancing plume. Typically, the PRB is installed in a manner that transects the plume, as near its leading edge as possible, ahead of the zone with highest concentrations. Of necessity, this leaves the leading edge of the plume downgradient of the PRB; however, it may be possible to treat this portion of the plume using MNA.

PRB Configurations

Continuous

In a continuous PRB, the reactive media extends across the entire path of the contaminant plume (Figure 4-1). For shallow applications, the PRB is typically trenched. When plumes are too deep to feasibly excavate a trench, it may be possible to use injection methods such as jet-grouting or hydrofracturing to place the reactive media.

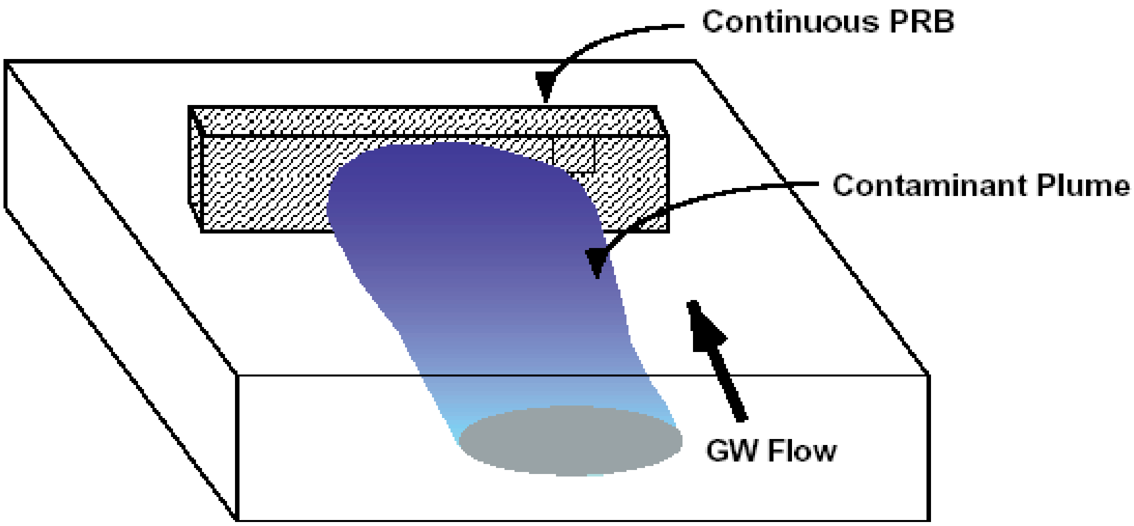


Figure 4-1
Continuous Reactive Barrier (from USEPA, 1998)

Keyed PRBs are installed such that the bottom of the PRB is keyed into a layer of relatively low hydraulic conductivity, such as clay, to reduce the potential for contaminant migration under the barrier. Hanging PRBs are not keyed into a zone of low hydraulic conductivity—these must be carefully designed to assure that groundwater will preferentially flow through, rather than below, the PRB. Very long PRBs might have hanging and keyed sections, dependent upon the stratigraphy. At least one installation has had an additional PRB installed downgradient of the primary PRB, a multiple installation (PRB case study 15, Appendix B).

Funnel-and-Gate

In funnel-and-gate systems, barrier walls are installed to control groundwater flow through a permeable gate containing reactive media (Figure 4-2). The walls are usually constructed using sealed-joint sheet piling, or by excavating a trench and installing bentonite or other low-permeability media (see PRB case studies 2, 12, and 22 in Appendix B). Walls must be keyed into a layer with low hydraulic conductivity to assure that the plume is directed toward the gate rather than flowing beneath the wall. Several gate configurations have been developed, including a baffled design that forces water to flow up and down through reactive media to increase residence time.

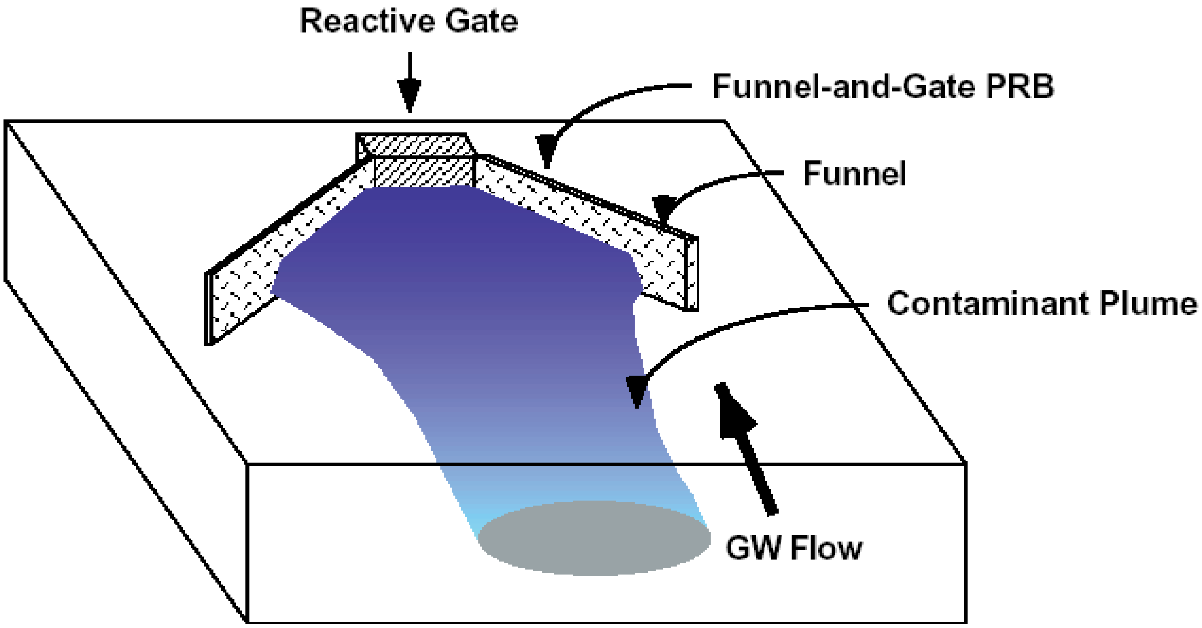
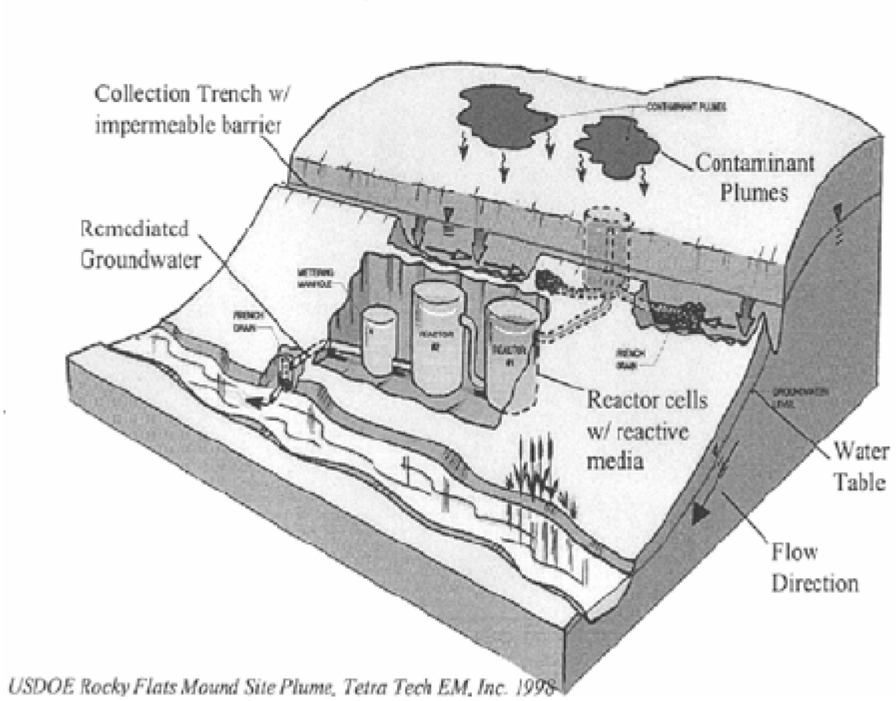


Figure 4-2
Funnel-and-Gate System (from USEPA, 1998)

In Situ Reactive Vessels

These installations use funnels and/or collection trenches to capture a plume and pass the water through one or more reactive vessels (Figure 4-3). The vessels can be located within the contained area, within the funnel, or at a distance downgradient from the plume (ITRC 2005). These systems use gravity or hydraulic head to pass groundwater through the treatment vessels. This configuration is designed to facilitate reactive media replacement. A patent-pending in situ reactive vessel design (GeoSiphon™) is currently in use at the Savannah River site (PRB case study 3, Appendix B; Phifer et al., 2005). The Y-12 site at Oak Ridge also utilized reactive vessels (PRB case study site 5, Appendix B).



USDOE Rocky Flats Mound Site Plume, Tetra Tech EM, Inc. 1998

Figure 4-3
In Situ Reactive Cell Design (from ITRC, 2005)

Reactive Media

The main considerations in selecting reactive media are as follows (Gavaskar et al., 1998):

- **Reactivity**: The media should be of adequate reactivity to immobilize a contaminant within the residence time of the design.
- **Hydraulic performance**: The media should provide adequate flow through the barrier, meaning a greater particle size than the surrounding aquifer materials. Alternatively, gravel beds have been emplaced in front of barriers to direct flow through the barrier.
- **Stability**: The media should remain reactive for an amount of time that makes its use economically advantageous over other technologies.
- **Environmentally compatible by-products**: Any by-products of media reaction should be environmentally acceptable. For example, iron released by zero-valent iron corrosion should not occur at levels exceeding regulatory acceptance levels.
- **Availability and price**: The media should be easy to obtain in large quantities at a price that does not negate the economic feasibility of using a PRB.

Of these considerations, the most important criterion for media selection is its ability to immobilize the PCOCs or convert them to non-toxic forms. Immobilization is the most important control for the PCOCs encountered at CCP sites, while conversion is of interest for remediation of plumes containing organic compounds. Some constituents are immobilized by pH control, while others rely on redox transformation, precipitation, sorption, or biological transformation.

Chemical Mobility Controls

EPRI (1984) identified major factors influencing chemical attenuation of constituents found in CCPs (Table 4-1). The major processes are the combinations of adsorption/desorption and precipitation/dissolution.

Table 4-1
Major Chemical Attenuation Mechanisms for Constituents in CCPs

Mechanisms	Important Factors
Adsorption/Desorption	Only uncomplexed rather than complexed ions are effectively adsorbed (e.g., $CdCl_2^0$ is not adsorbed, but Cd^{2+} is adsorbed). Hydrous oxides of Al, Fe, and Mn, amorphous aluminosilicates, and organic carbon are important sorbents. Oxyanions (e.g., As, Cr, Se, Mo, V, SO_4) adsorb most strongly at low pH and cations (e.g., Pb, Cd, Ni) adsorb most strongly at high pH. Competing ions and complexing ligands generally reduce adsorption (e.g., phosphate effectively competes with arsenate). Specific adsorption (strong, inner sphere adsorption) predominates at lower concentrations for most elements.
Precipitation/Dissolution	Precipitation is the primary attenuation mechanism for Fe, Al, and Mn. Solubility-controlling carbonate and hydroxide phases of Cd, Pb, Cr, and Cu have been observed in alkaline conditions. Formation of Fe-containing solids may be an important attenuation mechanism for both cationic and anionic elements. Precipitation of solid solutions [e.g., $(Fe,Cr)(OH)_3$, $(Ca,Cd)CO_3$] is expected to be very important.

Some potential reactive media, such as zero-valent iron, promote both adsorption and precipitation of a broad range of constituents, while others, such as hybrid ion exchange resins, specifically promote one reaction to target a single or narrow range of constituents (Table 4-2).

Table 4-3 summarizes aqueous species that may exist in either pure water or in a hypothetical groundwater (EPRI, 1984; USEPA, 2004). The species that exist are primarily a function of pH, Eh, and overall ion composition of groundwater. Aqueous speciation changes as conditions of Eh, pH, and ion composition change. Potential solubility controls for various elements are summarized in Table 4-4.

Table 4-2
Immobilization Mechanisms of Potential Reactive Media

Constituents*	Mechanism	Media	Comments
Oxyanions (e.g., As, Se, V, Cr, Sb, Mo, SO_4)	Adsorption	Zero-valent iron (ZVI) Surfactant modified zeolites Basic oxygen furnace slag Amorphous ferric hydroxide Neutralized red mud Diatomaceous earth Ferrous sulfate (HFO) Activated alumina Hybrid ion exchange resin Rare earth elements Kanchan™ arsenic filter Granular Ferric Hydroxide™ Clays	Neutral-to-acidic pH is optimal Rare-earth or Fe-doping improves adsorption capacity High levels of sulfate may depress adsorption
	Precipitation	ZVI Ferrous sulfate (Cr) Sodium dithionite (Cr) Organic carbon	Obtained by chemical reduction or as solid solutions with Fe
Cations (e.g., Fe, Mn, Cd, Pb, Ni, Be, Ba, Tl)	Adsorption	ZVI Humasorb™ Ferrous sulfate (HFO) Zeolites Clays	Neutral-to-alkaline pH is optimal
	Precipitation	Phosphates Limestone ZVI Organic carbon Neutralized red mud Oxygen sparging	May include sulfides, sulfates, carbonates, oxides, and hydroxides

* The listed reactive media will not treat all constituents listed, nor will a reactive media necessarily treat any one constituent in all groundwater environments.

Table 4-3
Probable Aqueous Species in Pure Water and with Common Complexes

Element	Valence States	Oxidized (Pure Water)	Reduced (Pure Water)	Other*
As	5+, 3+, 0	$HAsO_4^{2-}$	$H_3AsO_3^0$	Thio(S)-species
B	3+	$B(OH)_3$,$B(OH)_4^-$	$B(OH)_3$,$B(OH)_4^-$	**BF_4^-
Ba	2+	Ba^{2+}	Ba^{2+}	$BaSO_4^0$, $BaCO_3^0$
Be	2+	Be^{2+}	Be^{2+}	BeF^+, $BeSO_4$
Cd	2+	Cd^{2+}	Cd^{2+}	$CdSO_4^0$, $CdCO_3^0$
Cr	6+, 3+	CrO_4^{2-}	Cr^{3+}, $Cr(OH)_3(s)$	CrF^{2+}
Fe	2+, 3+	Fe^{3+}	Fe^{2+}	FeF^+, $FeSO_4^0$
Mn	4+, 3+, 2+	Mn^{4+},Mn^{2+}	Mn^{3+}, Mn^{2+}	$MnSO_4^0$
Mo	6+, 5.33+, 5+, 4+	$HMoO_4^-$	MoO_2^+, $Mo_3O_8(s)$, $MoS_2(s)$	NA
Ni	2+, 3+	Ni^{3+}, Ni^{2+}	Ni^{2+}	$NiHCO_3^+$, $NiSO_4^0$
Pb	2+	Pb^{2+}	Pb^{2+}	$PbCO_3^0$, $Pb(CO_3)_2^{2-}$
S	4+, 6+, 2-	SO_4^{2-}, SO_3^{2-}	HS^-, H_2S	$CaSO_4^0$
Sb	5+, 3+, 0	$Sb(OH)_6^-$	$Sb(OH)_3$, $Sb(s)$	NA
Se	6+, 4+, 0, 2-	SeO_4^{2-}	SeO_3^{2-}, $Se(s)$, HSe^-	NA
Tl	4+, 3+, 1+	Tl^{4+}, Tl^{3+}	$Tl_2O(s)$, Tl^+	NA
V	5+, 4+, 3+	$H_2VO_4^-$, HVO_4^{2-}	VO_2^{2+} , $V(OH)_3^0$	NA

NA = Not applicable

Data from USEPA (2004) and EPRI (1984)

* Species listed under "Other" only form under specific circumstances, for example under a specific redox condition *when* a certain ion is present

**EPRI (2005a) – BF_4^- included as boron species

Reactive Media Summary

A summary of reactive media that have been used in PRBs for inorganic constituents is provided in Table 4-5. Table 4-6 contains a listing of other media, primarily sorbents, that have been tested for water treatment and may have potential application as a component of a reactive media used in a PRB. A listing of different reactive media options for the PCOCs identified in Section 2 is presented in Table 4-7. Media descriptions are provided in Appendix A.

By far, the most commonly used reactive media for inorganic constituents has been zero-valent iron. This media can immobilize four of the five most likely PCOCs identified for CCP sites (arsenic, chromium, selenium, and sulfate). It is also proven effective for immobilization of molybdenum; however, it has not been proven for boron, antimony, and lithium.

Table 4-4
Potentially Important Solubility and Sorption Controls

Element	Solids	Sorbents	Key Factors
As	$FeAsO_4$, AsS, As_2S_3, ettringite*	Clays, Fe-/Al-oxides	As(V) adsorbs best at acidic pH under oxidizing conditions; can form a sulfide under reducing conditions.
B	Hydroxyborates, Ca-borate, ettringite*	Fe-oxides, clays, Al-/ Mg-hydroxides	Sorption maximums on Fe-oxide observed at pH 8-10.
Cr	$Cr(OH)_3$, $FeCr_2O_4$, $(Fe,Cr)(OH)_3$, ettringite*	Fe-oxides, Mn-oxides, clays, organic matter	Adsorbs at pH < 8 under oxidizing conditions or precipitates as $Cr(OH)_3$ under reducing conditions.
Se	Se(s), metal-selenides, ettringite*	Clays, Fe- and Al-oxides	Adsorbs at acidic pH under oxidizing conditions; insoluble as Se(s) when reduced.
S	$CaSO_4$, $Al_4(OH)_{10}SO_4 \bullet 5H_2O$, $KAl_3(SO_4)_2(OH)_6$, ettringite*	Fe-oxides, amorphous aluminosilicates	Can be sequestered in sulfides under reducing conditions; adsorbed under oxidizing conditions at acidic pH; forms sulfate solids.
Mn	$MnCO_3$, Mn-oxides	NA	Precipitation is key to immobilization.
Mo	$PbMoO_4$, $FeMoO_4$, $Fe_2(MoO_4)_3$, MoS_2, ettringite*	Fe-oxides, amorphous aluminosilicates	Highly mobile in oxidized systems at pH >7; adsorbed at pH <7 under oxidizing conditions; forms sulfide at low Eh.
Sb	$Sb(OH)_3$	Amorphous Mg- or Al-hydroxides	Only precipitates at or above 26 μg Sb L^{-1}; adsorbed at acidic pH.
Ba	$BaSO_4$	Clays	Barite solubility ~ 32 μg/L; precipitation is likely solubility control.
Be	$Be(OH)_2$	Al-oxides	Sparingly soluble above pH 6; pH control is major factor.
Cd	$CdCO_3$, $Cd_3(PO_4)_2$, CdS	Fe-oxides, Mn-oxides, clays	Immobilized at alkaline pH by adsorption and precipitation; forms a sulfide under reducing conditions.
Fe	$Fe(OH)_3$, $Fe_3(OH)_8$, $FeCO_3$, FeS_2	NA	Immobile under oxidizing or very reducing conditions; wide pH stability range as $Fe(OH)_3$.
Ni	NiS, $NiFe_2O_4$	Fe-oxides, Mn-oxides	Adsorbs at alkaline pH; will form a sulfide under reducing conditions.
Pb	$Pb(OH)_2$, $PbCO_3$, $Pb_3(PO_4)_2$, $Pb_4O(PO_4)_2$, $Pb_5(PO_4)_3OH$, PbS	Fe-oxides, Mn-oxides, clays	Immobilized at alkaline pH by adsorption and precipitation; forms a sulfide under reducing conditions.
Tl	Tl_2O_3, $Tl(OH)_3$, TlS (only above pH 12)	MnO_2, clays	Immobile as Tl-oxide under all but highly reducing conditions; only forms sulfide under highly reducing conditions and pH >12.
V	$Fe_2(VO_3)_2$, $VO(OH)_2 \bullet H_2O$, ettringite*	Fe-oxides	Easily reduced and mobilized by organics; adsorbed at acidic pH under oxidizing conditions.

After USEPA (2004) and EPRI (1984)

* Formation of ettringite occurs at pH >11, which is greater than the pH of most groundwaters. However, if formed, ettringite may sequester of variety of oxyanions (As, B, Cr, Se, SO_4, Mo and V) (Hasset et al., 2003)

Table 4-5
Field-Tested PRB Reactive Media for Inorganic Constituents

Media	Treated Inorganics[1,2]	Cost[3]	Field Applications[4]
Zero-valent iron (Fe^0 or ZVI)	***As, Cr***, ***Se***, ***SO$_4$***, *Mn*, *Mo*, Ba, Ni, Pb, U, Tc, Fe, Cu, Co, Cd, Zn, NO$_3$, PO$_4$, Hg, V	\$350-400/ton (USEPA, 1998)	1. CCP Landfill, Ontario, Canada (McGregor et al., 2002; Blowes et al., 2006) 2. Former DOE Mill Site, Monticello, UT (Morrison et al., 2002) 3. Savannah River Site TNX Area, Aiken, SC (Phifer et al., 2005) 4. Haardkrom Site, Kolding, Denmark (Kjeldson and Fuglsang, 2000) 5. Y-12 Site, Oak Ridge National Laboratory, Oak Ridge, TN (Watson et al., 1998) 6. U.S. Coast Guard Support Center, Elizabeth City, NC (Puls et al., 1998) 7. Fry Canyon Site, UT (Feltcorn and Breeden, 1997) 8. Bodo Canyon, Durango, CO (http:www.rtdf.org) 9. Rocky Flats Environmental Technology Site, Golden, CO (http:www.rtdf.org) 20. Newport Superfund Site, DE (Bronstein, 2005) 22. Uranium Mill, Canon City, CO (USDOE, 2005) 23. Columbia Nitrogen Site, Charleston, SC (Bronstein, 2005)
Organic matter	***As***, ***Se***, ***SO$_4$***, NO$_3$, Cd, Pb, Co, Cu, Ni, Zn, Fe, PO$_4$	NI	1. CCP Landfill, Ontario, Canada (McGregor et al., 2002; Blowes et al., 2006) 9. Rocky Flats Environmental Technology Site, Golden, CO (http:www.rtdf.org) 10. Nickel Rim Mine Site, Sudbury, Ontario, Canada (Benner et al., 2000) 12. Public School, Langdon, Ontario, Canada (Baker et al., 1998) 23. Columbia Nitrogen Site, Charleston, SC (Bronstein, 2005)

Table 4-5
Field-Tested PRB Reactive Media for Inorganic Constituents (Continued)

Media	Treated Inorganics[1,2]	Cost[3]	Field Applications[4]
Phosphates (Bone char/Apatite II™)	***As***, ***SO_4***, *Mo*, Mn, Pb, Cd, Ni, Ba, U, Zn, NO_3	$350/ton (Conca and Wright, 2006)	7. Fry Canyon Site, UT (Feltcorn and Breeden, 1997) 18. Success Mine and Mill Site, Idaho (Conca and Wright, 2006)
Ion exchange resin	***B***	NI	1. CCP Landfill, Ontario, Canada (McGregor et al., 2002; Blowes et al., 2006)
Limestone, hydrated lime, dolomitic limestone	***As***, ***Se***, ***SO_4***, *Mo*, Cd, Pb, U, Cu, Ni, Zn	$95/ton (USGS, 2006)	11. Tonolli Superfund Site, Nesquehoning, PA (USEPA, 2005b) 12. Public School, Langdon, Ontario, Canada (Baker et al., 1998) 19. Cyprus AMAX Minerals Company, Carteret, NJ (Bronstein, 2005)
Zeolites and surfactant-modified zeolites	***Cr***, Ba, Sr	$20/ton (SMZ = $425/ton) (Ott, 2000)	1. CCP Landfill, Ontario, Canada (McGregor et al., 2002; Blowes et al., 2006) 13. Chalk River Laboratories, Ontario, Canada (http:www.rtdf.org) 14. LEAP Permeable Barrier Demonstration (http:www.rtdf.org)
Basic oxygen furnace slag (BOF)	***As***, ***SO_4,*** Pb, Zn	$4 to $7/ton (USGS, 2006)	15. DuPont Site, East Chicago, Indiana (Wilkens et al., 2003)
Sodium dithionite/ calcium polysulfide	***Cr***	NI	17. 100D Area, Hanford Site, WA (Naftz et al., 2002; Bronstein, 2005) 21. Universal Forest Products, Inc., Granger, IN (Ott, 2000)
Neutralized red mud (Bauxsol™, Viromine™, Acid-B Extra™)	***As***, ***Cr***, ***SO_4***, *Sb*, Cd, Co, Cu, Pb, Fe, Mn, Ni, Zn, NO_3	NI	16. Gilt Edge Mine, SD (McConchie et al., 1999)

1. The list of constituents for each media may be incomplete; furthermore, a reactive media that successfully treated a constituent in one application may not necessarily be successful in another application due to differences in environmental conditions.
2. The most likely PCOCs for CCP Leachate (***As***, ***B***, ***Cr***, ***Se***, and ***SO_4***) are indicated by ***bold italics***; additional PCOCs determined in Section 2 (*Li*, *Mo*, *Sb*) are indicated by italics.
3. NI = information not available
4. Numbers indicate case studies listed in Appendix B.

Table 4-6
Other Potential PRB Reactive Media for Inorganic Constituents

Media[1]	Treated Inorganics[2,3]	Mechanism	Reference
Humasorb™	***As***, Hg, Pb, Al, Cu, Cd, Fe, Ni, Zn,	Adsorption	http://www.arctech.com/
Surfactant-modified zeolites	***As, B, Se(VI)***, *Mo*, V	Adsorption	Donahoe (2005, 2006b)
Amorphous ferric hydroxide (AFO)	***As, Se***, U	Adsorption	Feltcorn and Breeden (1997)
Dissolved oxygen	***As***	Precipitation	US Patent 6,254,786
Diatomaceous earth/ HFO impregnated diatomite	***As***	Adsorption	Jang et al. (2005)
Activated alumina	***As***	Adsorption	McRae et al. (1999)
Hybrid ion exchange resins (ArsenX^{np})	***As, Cr***, *Mo*, V, P, Ra, U, F, possibly *Sb*	Adsorption	http://www.purolite.com/
Titanium oxide (ADSORBSIA™)	***As***, Pb	Adsorption	http://www.dow.com/liquidseps/prod/pt_as.htm
Mg-Al oxide (SORBPLUS™)	***Cr***, Cu, Co, Ni	Adsorption	Evanoff et al. (1992)
Ferrous sulfate	***As, B, Cr***, *Mo*, Ni, and V	Reductive precipitation; adsorption	USEPA (2000), Donahoe (2006b)
Forager™ Sponge	***As***, Pb, Cu, Cd	Adsorption	http://www.dynaphore.com/
Rare earth elements	***As, Se***	Adsorption	Tokunaga and Hakuta (2002), Harck et al. (2004), Zhang et al. (2005)
Kanchan™ Arsenic Filter	***As***, Fe	Adsorption	http://www.irc.nl/page/25176
Granular Ferric Hydroxide™	***As, Se, Cr***, *Sb*, Cu, PO_4,	Adsorption	http://www.usfilter.com/en/Product+Lines/General_Filter_Products/General_Filter_Products/general_filter_gfh.htm

1. The authors were unable to locate field application data for the reactive media listed in this table; however, that does not necessarily mean that these media have not been used in field applications. Check with the listed vendors or references (see also Appendix A) for information on bench, pilot, or field-scale applications.

2. The list of constituents for each media may be incomplete; furthermore, a reactive media that appears successful in one application may not necessarily be successful in another application due to differences in environmental conditions.

3. The most likely PCOCs for CCP Leachate (***As***, ***B***, ***Cr***, ***Se***, and ***SO_4***) are indicated by ***bold italics***; additional PCOCs determined in Section 2 (*Li*, *Mo*, *Sb*) are indicated by italics.

Table 4-7
Potential Reactive Media by Constituent

Constituent[1]	Reactive Media with PRB Case Studies	Other Potential Reactive Media
As	ZVI, organic matter, phosphates, limestone, BOF, red muds	Humasorb™, surfactant-modified zeolites, AFO, diatomaceous earth, activated alumina, hybrid ion exchange resin, Ti oxide, ferrous sulfate, Forager™ sponge, rare earth elements, Kanchan™ filter, Granular Ferric Hydroxide™, clay minerals
B	Boron ion exchange resin	Surfactant-modified zeolites, ferrous sulfate
Cr	ZVI, zeolites, sodium dithionite, red muds	Hybrid ion exchange resin, Mg-Al oxide, ferrous sulfate, Granular Ferric Hydroxide™
Se	ZVI, organic matter, limestone	Surfactant-modified zeolites (Se(VI) only), AFO, rare earth elements, Granular Ferric Hydroxide™
SO_4	ZVI, organic matter, phosphates, limestone, BOF, red muds	
Li	none	
Mo	ZVI, phosphates, limestone,	Surfactant-modified zeolites, hybrid ion exchange resin, ferrous sulfate
Sb	Red muds	Hybrid ion exchange resin, Granular Ferric Hydroxide™

1. The lists of reactive media for each constituent may be incomplete; furthermore, a reactive media that successfully treated a constituent in one application may not necessarily be successful in another application due to differences in environmental conditions.

The only proven reactive media for boron is a boron-specific ion exchange resin, although ferrous sulfate and, to a lesser extent, surfactant modified zeolites have shown potential in laboratory experiments. Neutralized red muds have been demonstrated to immobilize antimony, and granular ferric hydroxide and hybrid ion exchange resins have potential for immobilization of antimony. No reactive media for lithium were identified during this review; it is unknown whether this is due to a lack of need to remediate for lithium, or due to difficulties in precipitating or adsorbing this constituent.

Treatability Testing

Treatability testing is performed during the design of a PRB to evaluate the potential effectiveness of a reactive media in a bench-scale hydrogeological environment comparable to that expected in the field. This is a critical portion of the design process because environmental factors such as pH, Eh, and competing ions in the groundwater will affect the ability of various media mixtures to immobilize the PCOCs present in site groundwater, as well as the rate at which a media may degrade due to clogging and due to reactions with constituents that are not targeted PCOCs.

Laboratory studies using samples of site groundwater are needed to determine the effectiveness of the selected reactive media at the site. Two types of studies are usually carried out: batch studies and column studies. Batch studies are usually a “first cut” type of study in which samples of groundwater from the site and different mixtures of reactive media are concurrently shaken or mixed for a specified period, and then analyzed to see if contaminant removal has occurred and to what extent. Column studies are more sophisticated one-dimensional flow studies that are used to determine rates of removal for the best performing mixture(s) determined during the batch study. A column is filled with the selected reactive media and site groundwater is pumped through the saturated media at a flow rate scaled to that of the groundwater flow rate at the site. Samples are taken down the length of the column periodically to assess the degradation/removal rate. The zone wherein most of the reactions are occurring can also be observed as it moves gradually down the length of the column. The benefits of column testing following batch testing are as follows (Gavaskar et al., 2000):

- Design parameters are determined under dynamic flow conditions. Installation of intermediate sampling points along the length of the column allows measurement of changes in contaminant concentrations through the barrier media.
- Non-linear sorption to non-reactive sorption sites is better simulated in columns.
- Reaction products may accumulate in batch reactors, but could be washed away in columns, depending on porosity of the geologic material.

Construction Methods

A variety of construction methods are available for PRB emplacement. Selection of the most-appropriate method will vary depending on the configuration and depth of the PRB, as well as on the soil type and on the availability of materials. Construction methods are described in detail in Gavaskar et al. (2000), and summarized below.

Excavated PRBs

Excavated PRBs are built using traditional soil excavating techniques and are subject to the same limitations, e.g. water intrusion, collapse of the excavation walls, etc. Some PRBs have been constructed where only excavation dewatering was required but most excavated PRBs have required supports. Some trenches have been constructed using sheet piling as supports. More recently, dense biodegradable polymer solutions, such as guar gum, have been used to support the trench while the reactive media is emplaced. At least three excavation methods have been used, with low relative cost (compared to injected PRBs) that increases with depth:

- Backhoes and clamshell excavators remove the soil in one operation and then fill once the excavation has reached design depth. Backhoe excavations are limited to relatively shallow depths (30 feet, 9.1 m), while clamshell excavators are capable of depths greater than 100 feet (30 m); although maximum depth in both cases is dependent on the ability to keep the trench from collapsing before the reactive media is placed.
- Trenching machines have been built that are able to excavate the aquifer materials and soils with immediate replacement of the solids by reactive media within the cut (see PRB case example 6). Trenching machines used for PRB installations have been limited to depths of about 40 feet (12 m) (ITRC, 2005); although there are trenching machines used for barrier wall applications capable of excavating to depths of 100 feet (30 m) or more.

- Caissons can be driven, while excavating material within, to construct PRBs to depths of 50 feet (15 m) or more. A potential disadvantage of this approach is that removal of the caisson can be difficult due to friction with native soil on the outside of the caisson and friction with the reactive media on the inside (Gavaskar et al., 2000).

Direct Placement PRBs

With injected PRBs, reactive media is placed in the subsurface without prior excavation. Injection methods allow placement of reactive media at depths greater than is feasible by excavation, although cost is higher. Depth and relative cost data are from Gavaskar et al. (2000).

- Mandrels/Tremie Tubes are essentially hollow tubes (typically rectangular) with drive shoes on the bottom. They are driven to the desired depth, filled with reactive media, and then the tubes/mandrels are withdrawn. Maximum reported depth using this method is 50 feet (15 m), and cost is moderate—a factor of about 2 higher than excavation.
- Augered/deep soil mixing techniques use augers to drill vertical boreholes and mix in reactive media. Overlapping boreholes are used to create the PRB. This method is capable of achieving depths up to 150 feet (46 m), but cost is high.
- High pressure jetting approaches were developed from the construction industry where grouts are injected to increase soil stability. Under extremely high pressure, the reactive media is jetted into the subsurface, displacing the native soils/aquifer materials. A linear configuration of the media results if the jets are not rotated. Rotation of the jets produces thicker cylindrical media zones. This method can install PRBs to depths of 200 feet (61 m). Cost is relatively high—a factor of 5 to 10 greater than excavation.
- Hydraulic and sand fracturing are rarely-used high-pressure PRB installation techniques that induce fractures in sand or force reactive media into existing bedrock fractures. Achievable depths up to 120 feet (37 m) have been reported and cost is high.

PRB Costs

The most reliable and thorough cost information has been obtained from sites using zero-valent iron as the reactive media. Where information is available, costs are usually reported in terms of two categories: 1) capital costs and 2) operation and maintenance. The cost-benefit of PRB technology over other remediation technologies (e.g., pump-and-treat) is realized in reduced operation and maintenance. The extent of operation and maintenance that is required will depend largely on the longevity of the reactive media.

Capital Costs

Capital costs for PRB implementation at CCP sites include:

- **Site characterization**: hydrogeologic, geotechnical, and geochemical assessments;
- **Design**: treatability studies, modeling, data collection, licensing fees, cost evaluation, cost comparisons, and work plan development;
- **Construction**: media, mobilization, emplacement, waste disposal, health and safety, and site restoration.

Documented capital costs for PRB applications ranged from \$0.09 million to \$1.45 million (Table 4-8). The largest portion of capital expenses associated with installing PRBs is related to construction. Emplacement costs will be determined by the following (Gavaskar et al., 1998):

- **Plume and aquifer depth**: Greater depths increase both emplacement and media costs.
- **Plume width**: Wider barriers increase both emplacement and media costs.
- **Geotechnical considerations**: Boulders, rocks, or highly consolidated material increase the difficulty of emplacement.

Table 4-8
Major Capital Costs Associated with PRBs (After USEPA, 2002b)

Site#	PRB/ Media Length (Feet)+	Depth (Feet)	Site* Characterization	Design*	Construction*	Total*	Primary Stated Cost Source
USCG Support Center	152/152	24	\$150,000	\$145,000	\$500,000	\$795,000	RTDF (2000)
Moffet Federal Airfield	50/10	25	\$100,000	\$175,000	\$332,375	\$607,375	RTDF (2000)
Dover AFB, DE	68/8	39	\$165,000	\$200,000	\$296,000	\$661,000	RTDF (2000)
Kansas City Plant, MO	130/130	30	\$150,000	\$100,000	\$1,200,000	\$1,450,000	RTDF (2000)
Aircraft Maintenance, OR	650/100	29	\$350,000	\$35,000	\$700,000	\$1,085,000	RTDF (2000)
Nickel Rim, Ontario	50/50	14	\$25,000	\$30,000	\$35,000	\$90,000	RTDF (2000)
Pease AFB, NH	150/150	33	\$400,000	\$200,000	\$500,000	\$1,100,000	Gavaskar et al. (2000)

Nickel Rim reactive media consists of organic matter, all others are ZVI.

+ First number is total PRB length, second is reactive media length, which may be less than the total PRB length for funnel and gate systems.

*Costs adjusted from primary stated cost sources by USEPA (2002b) to reflect cost by category. Costs are not adjusted to present-day dollar amounts and should be used only as indications of relative categorical expenses.

Although highly site-specific, the installation costs will be determined mostly by the length and depth of installation. However, the costs of other factors, such as media unit costs, should not be overlooked when selecting a design. The unit cost of the media will depend on the type of media selected. Total reactive media cost, however, is also driven by the amount of reactive material that is required. The following considerations will determine how much media should be used in a specific PRB (Gavaskar et al., 1998):

- **Type and concentrations of contaminants**: Those with slower reactivities with selected media will require a PRB design that includes a greater volume of media.
- **Regulatory criteria**: More stringent regulatory criteria may require a greater treatment volume, depending on the reactivity of the contaminant with selected media.
- **Groundwater velocity**: Higher groundwater velocity will require a greater barrier thickness, requiring a greater volume of media.
- **Groundwater flow and contaminant distribution**: Heterogeneous flow and contaminant distribution may lead to inefficiencies in barrier design, resulting in "wasted" media.
- **Geochemical and biogeochemical conditions**: Biofouling and mineral precipitation can substantially reduce the effective treatment surface area of barrier media. These processes can reduce efficiencies or even clog the media over time.

Operation and Maintenance

The most important operation and maintenance (O&M) costs include the following (Gavaskar et al., 1998):

- **Compliance monitoring**: This will vary from site to site, depending on local regulatory requirements.
- **Long-term performance monitoring**: Monitoring objectives will determine the value and frequency of long-term performance monitoring.
- **Replacement/rejuvenation of the reactive media**: This will vary, depending on site-specific geochemical, biological, and hydrogeological factors.

Operation and maintenance costs for PRB systems are not well-defined due to the fact that PRBs are a relatively new technology with little history of recorded cost data. However, O&M costs of PRBs have been compared to other remedial technologies. PRB construction costs can be relatively high, particularly when costly reactive media, such as granular iron, are used. Conversely, groundwater extraction and treatment systems tend to have lower construction costs than PRBs, with higher O&M costs. The only annual O&M cost for a typical PRB system is routine monitoring to ascertain that it is functioning properly ($30,000 to $90,000 per year for the sites listed in Table 4-8; EPA, 2002b). Groundwater extraction systems, with or without on-site treatment, have O&M costs for the wells, pumps, treatment system or water management, *and* monitoring.

More difficult to quantify is the replacement cost of reactive media, if necessary. This is because the technology is relatively new and the industry has little real experience with replacement of reactive media. However, should the reactive media become depleted or an impediment to flow due to precipitate blockage, causing a need for replacement, then a large maintenance cost will result. Research is ongoing into methods for treating the upgradient surfaces of PRBs to disrupt any precipitate blockages that might impede the groundwater flow.

According to Battelle (2002), a PRB system will be more cost-effective than a pump-and-treat system if the reactive media functions for greater than 10 years without the need for rejuvenation or replacement. If the media functions for only 5 years or less before rejuvenation or replacement, then pump-and-treat remediation may be more cost-effective. ITRC (2005) suggests that a general rule for iron-based reactive media is to expect some form of maintenance every 10 years at a cost of approximately 25 to 30 percent of initial construction costs. However, very recent data are beginning to suggest that this 10-year rule of thumb may be overly conservative, and that some PRBs may be effective for more than 10 years, and possibly as long as 30 years (Blowes et al., 2006; Puls, 2006; ITRC, 2005).

Long-Term Performance

Monitoring of PRBs

Two types of monitoring may be used for PRB remediations:

- Compliance Monitoring
- Performance Monitoring

Compliance monitoring is used to determine whether or not regulatory concentration goals are being met at the compliance boundary, e.g., at agreed upon downgradient monitoring wells, property boundaries, etc. These monitoring approaches are usually regulated as part of the facility's operating/closure permit or as part of the remedial action plan.

Performance monitoring is used to ascertain that the PRB itself is meeting its design goals. PRBs may be performance monitored in several locations relative to the PRB itself, e.g.:

- Immediately upgradient of the PRB
- Immediately downgradient of the PRB
- At the distal ends of the PRB
- Occasionally within the reactive media of the PRB itself

PRB performance monitoring is typically done using small diameter wells (as small as ¾-inch i.d. or even bundled tubes with short screens less than 1 foot in length), using low flow and semi-passive purging and sampling techniques (Powell and Puls, 1997). The concept of performance monitoring is to provide a performance baseline for the PRB for later comparison; therefore, it should be implemented shortly after PRB completion. It should accomplish a number of objectives, including the determination of:

- Short-circuiting of contamination through or around the PRB
- Changes in reactivity
- Decreases in PRB permeability
- Changes in upgradient contaminant concentration, etc.

As the number of PRB installations has increased to over 100, there has been decreasing emphasis on highly detailed performance monitoring other than at research sites or other sites incorporating new configurations, reactive media, etc. This is due to the increased confidence in the performance of the PRBs.

PRB Longevity and Maintenance

PRB longevity has been a much debated and researched topic. Early lifetime estimates for PRBs with ZVI as the reactive media were for 5 to 10 years. Many of these early PRBs have now been successfully operating, with little sign of deterioration or plugging by precipitates, for more than 5 years, and recent estimates have been revised upwards to somewhere between 10 to 20 years, if not longer (ITRC, 2005). Less information is available for the longevity of other reactive media, such as organic matter (which may still be from 5 to 10 years).

Geochemical, biogeochemical, and biological processes can have significant effects on the long-term hydraulic and reactive performance of PRBs. Permeable reactive barriers remove not only contaminants from groundwater, but also aqueous species that are not necessarily targeted for removal, such as inorganic carbon, calcium, magnesium, nitrate, and silica. These species are removed by mineral precipitation, adsorption, and biochemical transformations. In zero-valent iron barriers, the major geochemical, biological, and biogeochemical processes that occur are iron metal corrosion, microbial sulfate and nitrate reduction, adsorption, gas production, and mineral precipitation (USEPA, 2003).

Importance of Iron Metal Corrosion

The major consequences of iron corrosion are (USEPA, 2003):

- the production of OH^- ion (pH increases to pH 9-11 in the wall),
- decreases in oxidation-reduction potential (Eh sometimes <-500 mV),
- increases in hydrogen concentration (under anaerobic conditions),
- release of ferrous iron (under anaerobic conditions), and
- precipitation of iron-bearing minerals.

The rate of iron corrosion is significantly affected by the anion composition of groundwater. It is expected that corrosion rates will be faster in chloride-rich water than in bicarbonate- or sulfate-rich water. This is because the tendency of ferrous iron to form complexes with anions follows the order $Cl > HCO_3 > SO_4 > OH$ (USEPA, 2003). CCP leachate is usually dominated by sulfate, suggesting lower iron corrosion rates than in alkaline or chloride dominated waters.

The anion composition will also dictate the types of mineral precipitates that will form in iron PRBs (Table 4-9). If minerals form as surface coatings on reactive iron surfaces, reactivity may be reduced or enhanced, depending on the contaminant. For example, the uptake rate of chromium is increased over time, likely due to an increase in available sorption sites. However, excess precipitation may eventually result in long-term porosity and permeability loss. Li et al. (2005) performed reactive transport simulations to assess the impact of mineral fouling on the hydraulic behavior of continuous-wall PRBs that employ zero-valent iron in a carbonate-rich alluvial aquifer. They found that only subtle changes in hydraulic behavior occur during the first ten years, and that significant changes do not occur until at least thirty years of operation. However, they noted that water with high TDS can increase the rate of fouling, and decrease the time necessary for changes to occur. The Elizabeth City, NC PRB (PRB case study 6, Appendix B) has experienced minor mineral accumulation because of the low-TDS groundwater at the site. Studies have shown that volume loss in iron barriers results from the formation of precipitates containing carbon, sulfur, and iron (USEPA, 2003).

Table 4-9
Mineral Precipitates in Zero-Valent Iron PRBs (from USEPA, 2003)

Precipitate Type	Mineral
Oxides and Hydroxides	Ferrihydrite – $Fe(OH)_3$ Lepidocrocite – FeOOH Goethite – FeOOH Hematite – Fe_2O_3 Maghemite – Fe_2O_3 Green rust 1 – $Fe_6(OH)_{12}CO_3 \cdot xH_2O$ Magnetite – Fe_3O_4
Carbonates	Calcite – $CaCO_3$ Aragonite – $CaCO_3$ Iron carbonate hydroxide – $Fe_2(OH)_2CO_3$ Siderite – $FeCO_3$
Sulfides	Mackinawite – $Fe_{1+x}S$ Greigite – Fe_3S_4 Pyrite – FeS_2

Microbial Activity

Microbial activity will have significant effects on iron-based PRB performance. Metallic iron is a major energy source for microorganisms, and will be utilized as such in natural environments. Gu et al. (2002) investigated the microbial population at the Oak Ridge Y-12 Plant site (PRB case study 5, Appendix B) and found that concentrations of biomass within the ZVI media were one to three orders of magnitude greater than that found in adjacent aquifer material. Similar results have been found at the Elizabeth City (PRB case study 6) and Denver Federal Center[3] sites (USEPA, 2003).

Negative effects of microbial activity include changes in PRB hydraulic conductivity, masking of active sites, removal of active chemical species, mineral precipitation, production of gas bubbles, and competition for reducing equivalents (USEPA, 2003).

It has been reported that the release of ferrous iron may not be detrimental to PRB performance. For example, if the targeted contaminant can be reduced by either Fe^0 or Fe^{2+}, then the zone of reactivity is essentially increased beyond the surfaces of Fe^0. Additionally, if sulfate-reducing bacteria begin to proliferate, then constituents such as arsenic, antimony, molybdenum, cadmium, nickel, and lead may be immobilized by metal sulfide precipitation.

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[3] Not listed in Appendix B because this PRB was designed to treat organic compounds.

The presence and utilization of dissolved hydrogen can result in bacterial growth and biofilm formation. Biofilm growth in a porous medium such as an aquifer or reactive wall may cause reductions in total pore volume, but quantification of pore volume reductions is difficult (Taylor et al., 1990; Thullner et al., 2002). USEPA (2002c) suggests that while the overall growth of biomass in a barrier may seem insignificant, the localization of these growths can lead to significant heterogeneities in barrier hydraulic performance.

Combining PRBs with Monitored Natural Attenuation

Because it is not always possible to locate a PRB downgradient of the advancing front of a plume, PRBs are sometimes constructed to transect the plume. This approach manages the upgradient plume as it impinges the PRB but does little other than eliminate the ongoing source for the aquifer downgradient of the PRB. Given this situation, there are several possible options for managing the downgradient plume:

- In some instances, regulators have been content with simple monitoring to ascertain that the downgradient contamination is gradually decreasing.
- If necessary, the rates of natural attenuation can be evaluated in the downgradient portion and an assessment of the travel times and concentrations that will reach downgradient receptors can be made. Should natural processes be sufficient, nothing more is needed. This is monitored natural attenuation in combination with the PRB.
- If neither simple monitoring nor monitored natural attenuation is sufficient to satisfy stakeholders and regulators, then it might be necessary to actively treat the downgradient water.

If treating the downgradient water is necessary then one approach is to pump the downgradient water and reinject it upgradient of the PRB. This must be done at a withdrawal/injection rate that is not disruptive to the PRB goals (i.e., avoid significantly enhancing the flow rate through the PRB; contaminant residence time is important). If it is known that remediation of the downgradient waters will be required, this should be factored into the PRB design. At some point the downgradient waters, having no source term, should be sufficiently low in concentration to allow the pump(s) to be turned off.

Another possibility for combining PRBs with MNA is to rely on MNA to complete the cleanup that was mostly accomplished by the plume passing through the PRB (ITRC, 2005). In this case the PRB could be deliberately designed in such a manner that:

- The PRB is not expected to remove 100 percent of the contaminant,
- Contaminant breakthrough could occur because multiple contaminants are present in the plume and the PRB has been designed primarily to remove those of greatest concern, or
- Some unexpected breakthrough has occurred.

If it can be shown that MNA is sufficient to avoid impacts on sensitive downgradient receptors and protect human health and the environment, then a strong argument can be made that the remediation is sufficient.

Applicability of PRBs for Remediation of Groundwater at Coal Combustion Product Management Sites

Only one of the 23 PRB case studies compiled for this technology review was performed at a CCP site (PRB case site 1, Appendix B). Eight of the sites were mining or metal refining sites, three were metal plating sites, and 11 were of miscellaneous use. PRB case study 1 demonstrated a promising approach for remediating boron and other PCOCs in groundwater using a mixed media approach that included ZVI, organic matter, and a boron-selective ion exchange resin. However, this was a pilot scale application—the trench was only 42 feet (13 m) long—and cost data for the mixed media were not available, so cost effectiveness relative to other remedial technologies could not be evaluated.

Despite the limited application of this remediation technology at CCP sites to date, permeable reactive barriers appear to be a viable alternative if remedial objectives require groundwater restoration, either with or without source control. There are a variety of PRB configurations and reactive media currently available that can be employed for targeted remediation of PCOCs that may exceed health-based standards, such as arsenic, selenium, and chromium. One of these media is zero-valent iron, for which there is a considerable amount of case-study application data. However, other media also show potential for application in mixtures at CCP sites; cost and compatibility in mixtures with other media to immobilize boron will determine media selection.

This technology requires more development for application at sites where the remedial objectives call for clean-up of the mixture of constituents typically present at CCP sites. A considerable amount of work has been done on arsenic, chromium, and cationic metals, but more research is needed on difficult to treat elements such as boron, sulfate, molybdenum, and antimony, and unique interactions that may occur in the CCP leachate matrix.

5

RESEARCH ISSUES AND RECOMMENDATIONS

PRB Research Needs and Recommendations for Application at CCP Sites

A review of relevant published literature regarding permeable reactive barrier technology has identified a variety of short-term and long-term research needs. In the context of CCP management sites, the most important future research needs relate to reactive media selection and long-term media performance. With respect to remediation designs and remedial alternatives, the least known variables relate to media life expectancy.

Short-term research needs include:

- **Media selection:** Evaluation of reactive media mixtures that target utility PCOCs (specifically oxyanions and boron). Media such as ZVI, organic matter, ion-exchange resins, surfactant-modified zeolites, ferrous sulfate, red muds, and Granular Ferric Hydroxide™ show promise for remediation of utility constituents. Overall, performance and cost data are needed for a wide range of constituents, and for varying mixtures of these constituents.
- **PRB configurations:** Related to media selection, research on innovative PRB configurations, such as sequential PRBs designed to treat different PCOCs, may yield an alternative that will be effective for all PCOCs likely to be encountered in groundwater at CCP sites.
- **Geochemical characterization:** Methods of geochemical characterization of a site should be targeted to a wide range of utility constituents. For example, selenium and arsenic are both redox-sensitive, and valuable information can be derived from knowledge of elemental redox states. Advanced field and laboratory methods as they pertain to utility constituents should be compiled and used as site characterization guidance.

Long-term research needs include:

- **Long-term performance:** Laboratory experiments designed to simulate long-term media life expectancy should be performed on a variety of media, including predictive modeling of geochemical and biogeochemical reactions that occur in field settings. Experiments should address the potential for biofouling and the resulting permeability and reactivity loss.
- **Media rejuvenation:** Improved methods of in situ and ex situ media replacement and rejuvenation may result in procedures to reduce future operation and maintenance costs.
- **Innovative applications:** Additional cost-benefit may result from innovative methods of incorporating reactive media into construction of CCP storage sites; for example, reactive liners.

6
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A
PRB REACTIVE MEDIA DESCRIPTIONS

Field Tested Reactive Media

Zero-Valent Iron

The most commonly used barrier medium is zero-valent iron (ZVI) (ITRC, 2005). The iron used in most PRBs is comprised of a mixture of ductile and cast iron cuttings and borings that can be obtained from a number of industries. Originally used for its ability to degrade organic compounds, the material has become increasingly utilized for its ability to immobilize a wide range of inorganics.

Oxidation of Fe^0 to Fe^{2+} is a thermodynamically favorable reaction under most environmental conditions and forms the basis for the technology. The Fe^0 donates the electrons necessary for other reduction reactions to occur, such as reductive dechlorination of chlorinated solvents and chemical alteration of redox sensitive inorganics such as Cr, As, Se, and U. In the presence of sulfur, some metals may form metal-sulfides. Others may be immobilized by adsorption onto oxidized iron surfaces such as magnetite.

Morrison et al. (2002) report successful treatment of uranium, selenium, arsenic, molybdenum, vanadium, and nitrate with a ZVI PRB in Monticello Canyon, Utah. Manganese was not treated successfully. Groundwater pH within the PRB increased from a maximum of 6.8 in the influent to 10. Laboratory column tests using ZVI have shown that arsenic can be successfully reduced to levels below the detection limit (limit not reported) from concentrations as high as 10 mg/L (Bain et al., 2002).

Organic Matter

Organic matter is commonly used to degrade organic contaminants such as perchlorate (Craig, 2004). Several different materials have been used, including activated charcoal (GAC), cottonseed meal, peat moss, lignite, humite, compost, wood chips, leaves, molasses, and whey. The purpose is to promote biological activity that will act to destroy a contaminant (organics) or create conditions that are optimal for contaminant immobilization (inorganics).

A common method of metal stabilization uses sulfate reducing bacteria (SRB) to reduce available sulfate (SO_4^{2-}) to sulfide species (HS^- or S^{2-}):

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO_3^-$$

$$Me^{2+} + H_2S \rightarrow MeS + 2H^+$$

Bicarbonate (HCO_3^-) is also formed, which acts to buffer pH. The species S^{2-} is able to react with metals to form metal sulfide solids. These solids are usually less soluble than a metal's hydroxide phase, which makes the technology attractive in remediation designs.

A combination of municipal compost, leaf compost, and wood chips has been used at the Nickel Rim Mine Site in Ontario, Canada to remediate nickel, iron, and sulfate in groundwater (Benner et al., 1997).

Phosphate-Based Precipitation

Biogenic apatite, known as Apatite II™, has been used in a PRB application at Success Mine, Idaho (Wright and Conca, 2002). The material is mostly porous amorphous hydroxyapatite (calcium phosphate), and is soluble enough to release phosphate ions at concentrations exceeding the solubility limit of many metal-phosphate phases. The media is also proposed to reduce contaminant concentrations by three other processes: 1) cations can substitute for Ca, 2) oxyanions can replace structural PO_4^{3-}, and 3) anions F^- and Cl^- can exchange with OH^-.

The affinity for cations is proposed as:

$$UO_2^{2+} > Pb^{2+} > Th^{4+} > Cd^{2+} > Mn^{2+} \sim Zn^{2+} > Cu^{2+} \sim SbO^{+} \sim Hg^{2+} > Ni^{2+} > Sr^{2+} > Ba^{2+}.$$

Removal of oxyanions has proven less successful, but follows the approximate order of preference:

$$VO_4^{3-} > MoO_4^{2-} > SeO_3^{2-} > AsO_4^{3-} > CrO_4^{2-} > TcO_4^{-}.$$

The method, termed phosphate induced metal stabilization (PIMS), has been demonstrated to immobilize Cd, Zn, Pb, U, and Pu by precipitating stable metal-phosphate phases or other low-solubility phases. Major effects of the barrier include substantial downgradient reductions of Cd, Zn, and Pb, accompanied by a shift in pH from ~4.5 upgradient to 7 downgradient (Bostick et al., 1999).

Limestone and Hydrated Lime

Limestone ($CaCO_3$) has been used to treat a variety of contaminants due to its ability to buffer pH and to provide a ligand (CO_3^{2-}) for solid formation. Limestone materials have been used extensively for reducing the effects of acid mine drainage (USEPA, 2002a). Buffering of pH is a beneficial by-product of using limestone because some contaminants are effectively immobilized by hydroxide formation (e.g., $Be(OH)_2$). Others, such as lead, can form insoluble carbonates. Hydrated lime, $Ca(OH)_2$, can raise pH so that metal hydroxides such as $Be(OH)_2$ are more effectively precipitated.

A mixture of limestone, organic matter, and sand was used at the Nickel Rim Mine Site in Ontario, Canada. The limestone provides a pH buffer, the organic matter stimulates microbial activity, and the sand provides increased permeability.

Zeolites and Surfactant-Modified Zeolites

Zeolites are hydrated aluminosilicates with cage-like structures that are commonly used as sorptive substrates due to their large surface areas and high cation exchange capacities. Hydraulic characteristics make zeolites extremely effective filtration materials. The predominantly negative surface charge of zeolites makes them much more selective for cations than for anions (Haggerty and Bowman, 1994). Adsorption onto zeolites and surfactant-modified zeolites is pH-dependent.

Surface charge of zeolites can be altered with cationic surfactants to promote sorption of anions, in addition to cations. Hexadecyltrimethylammonium (HDTMA) is a common and low-cost surfactant that is commonly used for this purpose. Field demonstrations have utilized zeolites for removal of Sr-90, and some zeolites have been suggested as an immobilization mechanism for boron (McGregor et al., 2002). Recent experiments at the University of Alabama have shown that HDTMA-treatment of clinoptilolite greatly improves adsorption of As, Cr, Mo, Se, and V, reduces adsorption of Ba, K, Na, and Sr, and slightly improves B adsorption (Donahoe, 2005, 2006b). However, another study showed a decrease in Cr immobilization effectiveness for a HDTMA modified zeolite after flushing a column with 400 pore volumes of clean water (Li, 2006). Based on this decrease, the author suggested that caution should be exercised when using SMZs in a PRB.

Basic Oxygen Furnace Slag

Basic oxygen furnace slag (BOF) is a mixture of material ranging in grain size from silt to fine gravel and is the nonmetallic waste by-product of steel production generated at several steel plants. It contains various oxides and silicates of iron, calcium, magnesium, and aluminum. It is commonly used as aggregate in roadbed and other construction projects. The material has a high sorptive capacity and can buffer pH from acidic to alkaline conditions (ITRC 2005).

BOF has been used in a PRB to treat arsenic-impacted groundwater at an industrial site in Chicago in 2002. Data from the first two years of operation indicate removal of arsenic from concentrations greater than 1 mg/L to less than 0.001 mg/L within the barrier (Wilkens et al., 2003). BOF is also capable of removing zinc, lead, and sulfate from solution (Blowes et al., 2006)

Sodium Dithionite (NaS_2O_4) and Polysulfide Compounds

Sodium dithionite is a chemical reductant that is capable of converting ferric oxides and hydroxides in soils to ferrous iron ($Fe^{3+} \rightarrow Fe^{2+}$). The re-oxidation of ferrous iron to ferric iron has the ability to reduce other metal contaminants to immobile forms. Laboratory experiments have shown that the effectiveness of this technology is limited to easily reducible metals, such as uranium (Gavaskar et al., 1998). Amonette et al. (1994) and Cummings and Booth (1997) have demonstrated sodium dithionite to be an effective treatment to reduce aqueous chromium concentrations.

Polysulfide compounds (S_3^{2-}, S_4^{2-}, S_5^{2-}, S_6^{2-}) are also capable of chemically reducing inorganic pollutants such as Cr^{6+}. The reduced sulfur compounds are readily oxidized by means of reducing Cr^{6+} to Cr^{3+}. Calcium polysulfide (CASCADE®) has been shown to effectively reduce chromium concentrations at a wood treatment facility in Ukiah, California (Thomasser and Rouse, 1999).

Bauxsol™, Viromine™, Acid-B Extra™

Bauxsol™, marketed by Virotec, is a manufactured dry red solid composed of different minerals, including hematite, boehmite, gibbsite, sodalite, quartz, cancrinite, brucite, calcite, diaspore, ferrihydrite, gypsum, hydrocalumite, hydrotalcite, p-aluminohydrocalcite, portlandite, minor aragonite, and other trace minerals (Clark, 2000; McConchie et al., 1999). Mixtures of sand and Bauxsol™ have been tested in column experiments for their ability to remove metal contaminants (Munro et al., 2004), indicating metal removal by $M(OH)^+$ precipitation and other processes such as sorption. Viromine™ and Acid-B Extra™ are also marketed by Virotec as sorbents for contaminants.

Other Proposed Reactive Media for Inorganic Constituents

Humasorb™

Humasorb™, developed by ARCTECH, Inc., is a water insoluble lignite-derived humic acid with the ability to sorb metal cations, organic contaminants, and radionuclides (USEPA, 1999a).

Amorphous Ferric Oxide

Amorphous ferric oxide (AFO) has been tested at pilot scale for uranium removal at the Department of Energy Fry Canyon, Utah site (Feltcorn and Breeden, 1997). It was shown to be less effective at uranium treatment than zero-valent iron and bone char. Amorphous ferric oxide has been shown in laboratory studies to remove large amounts of arsenic and selenium from solution by adsorption. It is likely that AFO can sequester large amounts of various trace elements in a barrier application, and that the effectiveness will be pH-dependent (ITRC, 2005).

Dissolved Oxygen Barriers

Certain redox-sensitive elements may be successfully immobilized by an oxidizing zone, rather than a reducing zone. For example, it is well-documented that As(III) is poorly sorbed to aquifer material compared to As(V). In aquifers that are mildly reducing or only weakly oxidizing, it may be appropriate to create an oxidizing zone that will convert less reactive species such as As(III) to the more reactive form.

There are limitations to this concept. An aquifer with abundant organic material may consume any oxygen that is introduced at a faster rate than it can be replenished. Additionally, replenishment of oxygen is an added maintenance and expense that is preferably avoided in passive treatment systems. The best use of this technology may involve an aquifer with an oxygen consumption rate that will not readily scavenge dissolved oxygen. Slow-release technologies are available (ORC®) that allow continued release of dissolved oxygen over extended periods of time. Other possibilities include the direct introduction of oxygen through a sparging system.

Diatomaceous Earth

Diatomaceous earth is a fossilized mineral, formed from the accumulation of silica-based diatom skeletons. Jang et al. (2005) have shown that hydrous ferric oxide (HFO) impregnated diatomite showed better arsenic removal capacities than ZVI or granular activated carbon.

Activated Alumina

Activated alumina is produced as a porous, dehydrated alumina oxide. It has a surface complexation affinity for cations and anions, greater than basic oxygen furnace slag. McRae et al. (1999) found that a mixture of 10 percent basic oxygen furnace slag, 20 percent activated alumina with agricultural limestone, and silica sand had a high capacity to remove arsenic from groundwater in column experiments.

Ion Exchange Resins

A hybrid ion exchange material is prepared by modifying a traditional ion exchange resin. Iron oxide nanoparticles are impregnated into the surface of the ion exchange resin. The newly created surface has unique properties for adsorbing contaminants from water. For example, one ion exchange resin, marketed under the name ArsenX^{np} by Purolite, can adsorb both As(III) and As(V), and a number of other constituents including P, V, Ra, U, F, Cr, Mo, Se(VI), and possibly Sb (Sylvester et al., 2006). The same manufacturer manufactures another ion exchange resin (S-108) designed to immobilize boron.

ADSORBIA™ (Titanium Oxide-Based Adsorbent)

ADSORBIA™ is a titanium-based media produced by DOW that is marketed for its ability to adsorb arsenic. According to the manufacturer, it removes both arsenate and arsenite over a wide range of pH without the need for pretreatment.

SORBPLUS™ Adsorbent (Mg-Al oxide)

SORBPLUS™ is a Mg-Al oxide sorbent developed by ALCOA for removal of chelated nickel, copper, cobalt, hexavalent chromium, and metal-complexed cyanides from waste streams. Evanoff et al. (1992) found that chromium concentrations in chemical film rinse water could be reduced from as much as 20 mg/L to consistently less than 0.2 mg/L by the sorbent.

Ferrous Sulfate

Ferrous sulfate ($FeSO_4 \cdot 7H_20$) has also been used in chromium remediation designs. The oxidation of ferrous iron (Fe^{2+}) to ferric iron (Fe^{3+}) is proposed to reduce Cr^{6+} to Cr^{3+}. A field application of ferrous sulfate to treat chromium at the Townsend Saw Chain site in Pontiac, South Carolina, showed that, despite ultimate reduction of chromium concentrations in the aquifer, initial concentrations of chromium increased due to displacement of sorbed chromium by excess sulfate ions (USEPA, 2000).

Ferrous sulfate heptahydrate has been used successfully by Southern Company Services, Inc. to treat arsenic-contaminated soils (Redwine et al., 2004). It has been shown that ferrous iron precipitates as ferrihydrite in the subsurface and strongly adsorbs arsenic that would otherwise be mobile. Batch tests, column tests, and a field scale demonstration have proven that newly formed iron compounds and adsorbed arsenic are stable over time.

Ferrous sulfate has been tested as an additive to ash sluice water, and preliminary experimental results have suggested that it can reduce the leaching potential of As, B, Cr, Mo, Ni, and V from coal fly ash samples (Donahoe, 2006b).

FORAGER™ Sponge

Dynaphore, Inc. has developed a cellulose sponge by the name of FORAGER™ Sponge that is open-celled cellulose containing iminodiacetic acid groups that chelate metal cations. The sponge polymer also contains tertiary amine salt groups that can bind anionic contaminants. According to Dynaphore, Inc., it can be designed for site-specific needs, such that a contaminant of interest can be targeted for removal. For example, the sponge can be pre-loaded with ferric iron to facilitate precipitation of ferric arsenate.

The technology was demonstrated at the National Lead Industry Site, Pedricktown, NJ, in a mobile pump-and-treat system (Ott, 2000). The demonstration found that reductions in contaminants were observed for Cu (>94% removal), Cd (~89% removal), and Pb (~96% removal), but not for Cr (~32% removal).

Rare Earth Elements

Rare earth elements, particularly of the lanthanide series, have been studied for their ability to remove arsenic and selenium from solution. Tokunaga and Hakuta (2002) found that salts and oxides of lanthanum and cerium were effective in immobilizing arsenic in soil. Tokunaga et al. (1999) reported that lanthanum ions outperformed salts of aluminum, polyaluminum chloride, calcium, and ferric iron for removal of pentavalent arsenic from solution. Harck et al. (2004) have patented a process for removing arsenic and selenium from solution using a concentrate of lanthanum oxide and various oxides (U.S. Patent 6,800,204, issued 2004). Because of their high costs, these elements are used mostly as minor additives to an iron-based sorbent. Lanthanum- and cerium-doped iron oxide minerals exhibit high sorptive capacity for both arsenic and selenium, but Zhang et al. (2005) report that Fe-Ce exhibited the highest removal capacity for arsenic over the widest pH range (pH 3 to 7).

Kanchan™ Arsenic Filter

The Kanchan™ Arsenic Filter has the ability to remove arsenic, iron, and pathogens from water through filtration. It is constructed of PVC pipes, iron nails, brick, sand, and gravel. Arsenic is removed by adsorption to rusted iron nails inside the filter. Solubilized iron and pathogens are then removed by physical straining in a fine sand layer. The average arsenic removal efficiency is between 90 and 93 percent. Modifying the use of iron nails may be an effective and cheap media for PRB emplacement. The filter is jointly implemented by the Massachusetts Institute of Technology (MIT), the Nepal-based non-governmental organization Environment and Public Health Organisation (ENPHO), and the Rural Water Supply and Sanitation Support Programme.

Granular Ferric Hydroxide®

USFilter has developed a ferric iron based media called GFH® (Granular Ferric Hydroxide®) that can remove arsenate, arsenite, phosphate, antimony, selenium, copper, and chromium from solution. According to the supplier, this media is currently being tested for water supply wells in Phoenix, AZ and has successfully removed arsenic to levels below 10 ppb.

B

PRB CASE STUDIES

The following pages present, in no particular order, summaries of PRB case studies from around the world that involve remediation of inorganic constituents. PRB case study 1 is the only example involving a CCP site. Note that some case studies describe applications that were unsuccessful in remediating one or more constituents. Most case studies can be found on the internet. References are given as sources of supplemental information.

CCP Landfill, Ontario, Canada

Reference: McGregor et al., 2002; Blowes et al., 2006

Site background: An unlined CCP landfill is underlain by a thick sand and gravel aquifer. The landfill covers an area of 19 acres (7.7 Ha). Groundwater velocity in the aquifer ranges from 23 to 165 ft/yr (7 to 50 m/yr). A plume containing As (up to 0.42 mg/L), B (35 mg/L), Cr (0.19 mg/L), Mo (0.97 mg/L), Se (1.75 mg/L), V (1.0 mg/L), and SO_4 (2,000 mg/L) was mapped downgradient from the site heading in the direction of a lake.

Contaminants: As, B, Cr, Mo, Se, and V

Reactive media: A) Wood chips, bottom ash, surfactant modified zeolite, ZVI, and boron ion-exchange resin; B) ZVI, surfactant modified zeolite, bottom ash, and boron ion-exchange resin; and C) ZVI, surfactant modified zeolite, and bottom ash.

Demonstration: A PRB was installed in a trench 42 feet (13 m) in length, 6 feet (2 m) wide, and 12 feet (4 m) deep. The trench was divided along its length into three treatment zones, each containing a different mixture of reactive media. All of the zones contained a surfactant modified zeolite, which was hypothesized to have potential for immobilizing boron, and two of the three zones contained a small percentage of boron ion-exchange resin. The final hydraulic conductivity of the barrier was approximately 3 x 10^{-3} cm/s, a factor of 10 to 15 greater than the surrounding aquifer.

After nearly four years of monitoring the following observations were made:

- Reactive media mixture A was very effective in reducing concentrations of As, B, Cr, Mo, and V, and moderately effective for Se.
- Mixture B was less effective than mixture A for arsenic and boron.
- Mixture C was less effective than mixture A for arsenic, and ineffective for boron.
- None of the mixtures reduced sulfate concentrations appreciably, although sulfate was not a focus of this study.

The authors concluded that the boron ion-exchange resin was more effective than surfactant modified zeolite in immobilizing boron, and suggested that the adsorption surfaces of the zeolite may have become saturated after only seven pore volumes.

Former DOE Mill Site, Monticello, UT

Reference: Morrison et al. (2002); http://www.rtdf.org

Site background: The former Monticello mill site was built in 1942 and operated as a uranium and vanadium ore-processing mill. Beneath the repository, two aquifers exist—a perched alluvial aquifer and the regional Burro Canyon aquifer beneath the alluvial aquifer. The perched aquifer was contaminated by mill tailings prior to construction of the repository.

Contaminants: U, Se, V, As, Mn, Mo, Fe

Reactive media: ZVI

Demonstration: A funnel-and-gate system was constructed downgradient of the contaminant plume. Two slurry walls funnel the contaminated plume through the gate, containing a PRB of zero-valent iron. The south slurry wall is 240 feet (73 m) long and the north wall is 97 feet (30 m) long; both are constructed of a bentonite and soil slurry mix. The barrier was built by driving steel sheet piling into the bedrock, forming a box approximately 100 feet (30 m) long by 8 feet (2.4 m) wide. The soils were replaced by ZVI and gravel. A downgradient gravel pack 2 feet (0.6 m) wide contains an air sparging system designed to remove Mn and Fe if concentrations become too high.

Concentrations of As, Se, U, and V have been reduced to non-detectable levels (detection level not reported). Concentrations of Fe increase as groundwater passes through the barrier, although Fe concentrations are lower than expected and are well within acceptable risk ranges.

Savannah River Site TNX Area, Aiken, SC

Reference: Phifer et al. (2005); http://www.rtdf.org

Site background: The TNX Area at the Savannah River Technology Center was used for pilot-scale testing and evaluation of various chemical processes associated with the Savannah River Site. Contamination has been detected in the water table aquifer. This aquifer is approximately 35 to 40 feet (11 to 12 m) thick and is comprised of interbedded sand, silty sand, and relatively thin clay layers. The aquifer has a horizontal hydraulic conductivity of 65 ft/d (2.3×10^{-2} cm/s), a vertical hydraulic conductivity of 30 ft/d (1.1×10^{-2} cm/s), an effective porosity of 0.15, a pore velocity of 3 ft/d (0.9 m/d), and a horizontal gradient of 0.007.

Contaminants: NO_3

Reactive media: ZVI

Demonstration: The TNX GeoSiphon™ Cell is a large-diameter (8 feet, 2.4 m) well containing ZVI. The cell passively induces flow using a siphon to the nearby Savannah River. So far, effective treatment of nitrate has been observed.

Haardkrom Site, Kolding, Denmark

Reference: Kjeldsen and Fuglsang (2000); http://www.rtdf.org

Site background: The site formerly hosted an electroplating facility. The plating process involved the use of chromium, nickel, zinc, and TCE. Contaminants of major concern are Cr^{6+} and TCE, and concentrations range from 8-110 mg/L and 40-1,400 µg/L, respectively. Due to aquifer heterogeneity, concentration levels vary significantly from point to point. The aquifer is less than 6.6 feet (2.0 m) below ground surface and is not continuous through the site. The upper 6.5 to 10 feet (2.0 to 3.0 m) consists of a low permeability, heterogeneous mixture of sandy and clayey loam interspersed with local lenses of sandy layers.

Contaminants: Cr, TCE

Reactive media: ZVI

Demonstration: Laboratory experiments showed chromate reduction capacities of 1 to 3 mg Cr^{6+} per g Fe^0. The designers accordingly set the dimensions of the trench and barrier to accommodate all of the Cr^{6+} in the contaminant plume. A continuous trench system PRB was installed. The PRB is 164 feet (50 m) long, 3.3 to 9.8 feet (1.0 to 3.0 m) deep, and 3.3 feet (1.0 m) thick. Bypass trenches and recirculation pipes were installed to increase water flow through the low permeability, heterogeneous aquifer. Results suggest the design is not effectively controlling the uneven distribution of Cr, and the chromate removal capacity has been exhausted due to heterogeneous loading of the PRB.

Y-12 Site, Oak Ridge National Laboratory, Oak Ridge, TN

Reference: Watson et al. (1998); http://www.rtdf.org.

Site background: Originally this site was a disposal pond for a DOE laboratory from 1952 to 1981. The area was capped in 1983, but both the groundwater and surface water are considered to be contaminated. The site has a very low permeability and the soil is mostly unconsolidated clay with overlying fractured shale. It is approximately 10 to 15 feet (3 to 5 m) to groundwater, where the aquifer is approximately 10 to 20 feet (3 to 6 m) thick.

Contaminants: HNO_3, U, Tc

Reactive media: ZVI

Demonstration: This system consists of two separate PRBs. The first PRB was installed in November of 1997 and consists of a continuous trench system 225 feet (69 m) long, 2 feet (0.6 m) wide, and 22 to 30 feet (6.7 to 9.1 m) deep. It is filled with approximately 80 tons of zero-valent iron and emplaced parallel to groundwater flow. The second PRB is a funnel-and-gate system designed to direct groundwater flow into a concrete vault to test treatment with different kinds of media. The total cost for the system was approximately $1,000,000.

The system was enhanced in 1999 to improve treatment efficiency by extending the trench system by approximately 100 feet (30 m). This served to increase the groundwater treatment zone to other affected areas on the site. This enhancement was also an excellent deterrent to changes in groundwater flow that resulted in PRB bypass.

U.S. Coast Guard Support Center, Elizabeth City, NC

Reference: Puls et al. (1998); http://www.rtdf.org

Site background: A groundwater plume containing hexavalent chromium and TCE exists near a former electroplating shop that operated until 1984.

Contaminants: Cr(VI), TCE

Reactive media: ZVI

Demonstration: The PRB is a continuous wall design with dimensions of 150 feet (46 m) in length, 24 feet (7.3 m) deep and 2 feet (0.6 m) thick. It was installed using a continuous trencher method and filled with a ZVI reactive material. Continued monitoring of the site showed total chromium removal within the first six inches of the wall.

Fry Canyon Site, Fry Canyon, UT

Reference: Feltcorn and Breeden (1997); http://www.rtdf.org

Site background: Fry Canyon Site, UT, is an abandoned uranium upgrader site. The water table is located 8 to 9 feet (2.4 to 2.7 m) below ground surface. The shallow aquifer is comprised of colluvial material, with a groundwater flow rate of approximately 1.5 ft/d (0.5 m/d).

Contaminants: U

Reactive media: ZVI, AFO, PO_4

Demonstration: Field-scale demonstration is underway, testing performance of three funnel-and-gate barriers: ZVI, AFO, and PO_4. Objectives of the demonstration include: 1) hydrologic and geochemical characterization of the site, 2) design, installation, and operation of the three barriers, and 3) evaluation of barrier performance.

Each barrier is 7 feet (2.1 m) wide, 3 feet (1.0 m) thick, and 4 feet (1.2 m) deep. Approximately 110 ft^3 (3.1 m^3) of material was used in each barrier. Groundwater velocities through the barriers are approximately 4.5 ft/d (1.4 m/d). The ZVI and PO_4 barriers are removing over 99 percent of U, but the AFO reached uranium breakthrough after about 1,000 pore volumes.

Bodo Canyon, Durango, CO

Reference: http://www.rtdf.org; Bronstein, 2005

Site background: Uranium mill tailings were relocated to the Bodo Canyon disposal cell in the fall of 1990. Contaminated seeps developed downgradient shortly after construction.

Contaminants: As, Mo, Se, U, and V

Reactive media: ZVI, copper wool, steel wool

Demonstration: Four PRBs were installed in Bodo Canyon as a pilot-scale demonstration to treat contaminated groundwater and test the efficiency of PRBs for remediation of metals and uranium. In order to compare different designs, four PRBs were installed near the retention pond, each containing a form of zero-valent iron media.

Results:

- As reduced from up to 186 µg/L to 2.2 µg/L
- Mo reduced from 1180 µg/L to 359 µg/L
- Se reduced from 337 µg/L to 5.9 µg/L
- Gasses (H_2 and CH_4) built up in PRB and required venting

Rocky Flats Environmental Technology Site (Solar Ponds Plume), Golden, CO

Reference: http://www.rtdf.org.

Site background: At the Rocky Flats Environmental Technology Site in Golden, CO, past waste storage practices have resulted in groundwater contaminated with nitrate and uranium. The Solar Ponds were drained and sludges removed by 1995, but contaminated groundwater has migrated downgradient to a nearby stream.

Contaminants: NO_3, U

Reactive media: ZVI and wood chips

Demonstration: Bench scale studies were conducted at the University of Waterloo. The groundwater collection system extends approximately 1,100 feet (340 m). Excavations were performed at variable depths between 20 to 30 feet (6 to 9 m) below ground surface and approximately 10 feet (3 m) into underlying clay. The barrier consists of HDPE panels. The concrete treatment cell is divided into two sections. Treatment media occupies the lower 10 feet (3 m) of each section. The first cell contains a mixture of sawdust and leaf mold with 10 percent ZVI by weight. The second cell is filled with ZVI. Water exiting the treatment cell typically contains less than 5 mg/L nitrate (from 140-170 mg/L) and less than 1 pCi/L uranium (from 20-28 pCi/L).

Nickel Rim Mine Site, Sudbury, Ontario, Canada

Reference: Benner et al. (2000); http://www.rtdf.org

Site background: Nickel Rim was an active mine from 1953 to 1958. The contamination has resulted from 40 years of oxidation of a tailings impoundment on site. The site is underlain by an aquifer 10 to 26 feet (3.0 to 7.9 m) thick composed of glacio-fluvial sand. The aquifer is confined to a narrow valley, bounded on both sides and below by bedrock. Groundwater velocity is estimated to be 49 ft/yr (15 m/yr).

Contaminants: Ni, Fe, and SO_4. Initial concentrations were 2,400-3,800 mg/L SO_4, 740-1,000 mg/L Fe, and up to 10 mg/L Ni.

Reactive media and construction: Organic carbon (mixture containing municipal compost, leaf compost, wood chips, and pea gravel to increase hydraulic conductivity) as a continuous barrier.

Demonstration: A continuous PRB was installed in August 1995 using a cut and fill method. The reactive barrier is 50 feet (15 m) long, 14 feet (4.3 m) deep, and 12 feet (3.7 m) wide, for a total of 8,400 ft^3 (240 m^3) of media. Coarse sand buffer zones were installed upgradient and downgradient of the reactive material, and the PRB was capped with 12 in. of clay to minimize entry of surface water and oxygen. Remediation was accomplished by sulfate reduction and metal sulfide precipitation.

Nine months after installation, sulfate concentrations had decreased to 110-1,900 mg/L and iron concentrations decreased to <1-91 mg/L. Dissolved Ni decreased to <0.1 mg/L within and downgradient of the PRB. Groundwater pH increased from 5.8 to 7.0 across the barrier, and the PRB converted the aquifer from acid-producing to acid-consuming. Significant hydraulic heterogeneities exist in the barrier, probably due to poor mixing of the media, and/or air pockets from installation.

Tonolli Superfund Site, Nesquehoning, PA

Reference: USEPA, 2005b

Site background: The Tonolli Corporation operated a battery recycling plant and a lead smelting plant at the site from 1974 until 1986. Elevated levels of dissolved metals are attributed to both waste sources and anthropogenic sources, including dumping of battery acid and acid mine drainage effect from spoil piles. The contaminants are located in a coal mine spoil at 0 to 19 feet (0 to 5.8 m) and in alluvium from 74 to 113 feet (23 to 34 m). Maximum concentrations of these contaminants encountered were 328 µg/L of Pb, 77 µg/L of Cd, 313 µg/L of As, 1,130 µg/L of Zn, and 140 µg/L of Cu.

Contaminants: Pb, Cd, As, Zn, and Cu

Reactive media: Limestone

Demonstration: In 1998, a continuous trench PRB was installed. A trackhoe was used to excavate a trench, approximately 3 feet (1 m) wide, 20 feet (6 m) deep, and 1,100 feet (340 m) long. Trench boxes were installed parallel to a creek. Lead concentrations are being reduced to less than performance standards (not reported). As and Sb have shown increases in concentration downgradient of the landfill.

Public School, Langton, Ontario, Canada

Reference: Baker et al. (1998); http://www.science.uwaterloo.ca/research/ggr/PermeableReactiveBarriers/Phosphate_Treatment/Phosphate_Treatment.html

Site background: Not reported.

Contaminants: PO_4, NO_3

Reactive media: Fe/Ca oxides, limestone, wood chips

Demonstration: This funnel-and-gate PRB was installed on a septic system on school property to remove nitrates and phosphates. After six years of operation, decreases in both contaminants were noted in samples from downgradient wells.

Chalk River Laboratories, Ontario, Canada

Reference: http://www.rtdf.org

Site background: In the early 1950s, a pilot plant was operated at Chalk River for the purpose of decomposing and reducing the volumes of ammonium nitrate solutions that contained mixed fission products. Some of these solutions were released into pits lined with crushed limestone. In 1998, Atomic Energy of Canada, Ltd. installed a wall and curtain PRB to remove Sr-90 from groundwater. The site is underlain by sands derived from granitic gneiss. The saturated thickness of sandy aquifer ranges from 16.4 to 42.6 feet (5.0 to 13 m).

Contaminants: Sr-90

Reactive media: Clinoptilolite (Zeolite)

Demonstration: The PRB is a steel cut-off wall, a curtain of zeolite to treat the water, and a subsurface bypass drainage system for non-contaminated, overlying groundwater. A granular curtain of 153.4 yd^3 of 14x50 mesh clinoptilolite (zeolite) is positioned in front of the cut-off wall. The curtain is 6.6 feet (2.0 m) long, 36.1 feet (11 m) wide, and 18 feet (5.5 m) deep. The PRB cost a total of $300,000.

Groundwater outflow meets Canadian drinking water standards and the PRB has retained 100 percent of the contaminant since 1998. The wall and curtain have exhibited good performance chemically and physically and require almost no cost for routine monitoring of performance and to adjust capture zone dimensions.

Large Experimental Aquifer Program (LEAP) Demonstration Facility, Portland, OR

Reference: http://www.rtdf.org; Haggerty and Bowman (1994); USEPA (1999b)

Site background: The LEAP facility is a PRB demonstration facility, located in Portland, OR.

Contaminants: Cr(VI), PCE

Reactive Media: Surfactant modified zeolites (SMZ)

Demonstration: The barrier construction is a hanging barrier in a perforated metal frame. This site was created and intentionally contaminated for research purposes. Overall, the retardation factors for each contaminant were on the order of 50. The system was designed for a sorption method of remediation.

DuPont Site, East Chicago, IN

Reference: Wilkens et al. 2003; ITRC, 2005

Site background: DuPont purchased the site from Grasselli Corp. in 1928. The site is 440 acres (180 ha) and was a diversified chemical manufacturing facility. This site is the first full-scale permeable reactive barrier site to remove arsenic from groundwater using basic oxygen furnace slag.

Contaminants: As (1-2 mg/L)

Reactive media: Basic oxygen furnace slag (BOF)

Demonstration: In 2002, a full-scale PRB was installed that consisted of 100 percent BOF slag. The continuous trench PRB is 2,000 feet (610 m) long and 35 feet (11 m) wide, consisting of two parallel trenches to achieve desired width. Results have shown a decrease from 1 to 2 mg/L to <0.001 mg/L in the effluent.

Gilt Edge Mine, SD

Reference: McConchie et al. (1999)

Site background: The Gilt Edge Mine site is an open pit, cyanide heap leach gold mine, developed in both oxidized and highly sulfidic ore bodies. Mining operations for gold, copper, and tungsten were conducted since 1876. Currently the site hosts 150 million gallons of acidic, heavy metal-laden water in three open pits and millions of cubic yards of acid-generating waste rock.

Contaminants: As, Cd, Co, Cu, Pb, Zn, NO_3, and SO_4.

Reactive media: Viromine™ Acid-B Extra™ mixed as 10 percent (weight) with waste rock.

Demonstration: A trial was conducted for waste rock remediation. A series of 200-L drums were filled with waste rock and Acid-B Extra™ mixture (10%, 5%, and 2%) to determine effective treatment at the lowest possible application rates. Results from the drum trial show that 6 to 7 percent is the optimal addition rate for the reactive media. Leachate pH was raised from 1.92 to 7.21, arsenic was reduced from 23,000 µg/L to <5 µg/L, iron was reduced from 19,000,000 ppb to 33 ppb, and concentrations of other trace metals (Sb, Cd, Cr, Pb, and Ni) were all reduced to near or below detection limits (limits not reported).

A shallow lined trench containing about 20 cubic meters of waste rock mixed with 10 percent (weight) Acid-B extra reagent was constructed. The leachate was sampled monthly, but monthly data was not available. Ongoing three-year results from the trench trial are shown below. Data is reported from Virotec, and has been validated by CDM Federal Programs Corporation.

- Leachate pH was raised from 1.93 to 7.9
- As was reduced from 35,000 µg/L to <4 µg/L
- Fe from 21,000,000 µg/L to 210 µg/L
- Sb from 500 µg/L to <10 µg/L
- Cd from 630 to <10 µg/L
- Cr from 390 µg/L to <10 µg/L
- Pb from 390 µg/L to <10 µg/L
- Mn from 34,000 to <10 µg/L
- Ni from 1,600 to <10 µg/L

100 D Area, Hanford Site, Benton County, WA

Reference: Naftz et al., 2002; Bronstein, 2005; http://www.rtdf.org/public/permbarr/prbsumms/profile.cfm?mid=43

Site background: The Hanford Site created plutonium from 1943 until the 1980s as part of the Manhattan Project. The site has been divided into four separate NPL sites, one of which is named the 100 D Area. A hexavalent chromium plume was detected in groundwater, which is about 85 feet (26 m) below ground surface. Average groundwater velocity is approximately 1 ft/day (0.3 m/d).

Contaminants: Cr(VI)

Reactive media: Sodium dithionite injection

Demonstration: Not truly a PRB, because no solid media is used, this demonstration utilizes "in situ redox manipulation" to create a reducing zone in the area of injection. In 2003, sodium dithionite with a potassium carbonate/potassium bicarbonate buffer was injected into the hexavalent chromium plume. The redox zone was created by 65 injection wells over a length of 2,000 feet (610 m). The zone is located parallel to the Columbia River. Chromium concentrations in 59 of 66 wells are below the detection limit (0.008 mg/L). Performance monitoring is complicated by seasonal fluctuations associated with the river and preferential flow paths created by well installations.

Success Mine and Mill, Wallace, ID

Reference: Conca and Wright, 2006; Bronstein, 2005

Site background: The Success Mine and Mill site, located in Northern Idaho, was the largest metals loader in the Ninemile Creek drainage area of the Coeur d'Alene mining district. Groundwater contamination results from drainage of a tailings/waste rock pile that is 1,200 feet (370 m) long and 150 feet (46 m) high. Hydraulic conductivity of the sand and gravel aquifer is 1.7×10^{-3} ft/s (5.2×10^{-2} cm/s). A shallow bedrock (quartz monzonite) aquifer exists below the sand and gravel aquifer and has a hydraulic conductivity of approximately 5.6×10^{-5} ft/s (1.7×10^{-3} cm/s).

Contaminants: Pb, Zn, Cd, SO_4, and NO_3

Reactive media: Apatite II™

Demonstration: Phosphate induced metals stabilization (PIMS) was used at this site in the form of a 13.5 feet (4.1 m) high, 15 feet (4.6 m) wide, and 50 feet (15 m) long PRB. The PRB is constructed of two cells, each measuring 8.0 feet (2.4 m) high, 6.5 feet (2.0 m) wide, and 45 feet (14 m) long. One cell contains 100 percent Apatite II™, and the other contains 50 percent Apatite II™ and 50 percent gravel. The PRB was keyed into underlying bedrock. A hydraulic drain was installed upgradient of the PRB to direct flow into the cells. Cadmium concentrations were reduced from 0.436 mg/L upgradient of the wall to <0.002 mg/L downgradient, Pb from 0.658 mg/L to <0.005 mg/L, and Zn from 68 mg/L to 0.034 mg/L. pH is buffered from 4.9 to 6.9 through the wall.

After 3.5 years, less than 40 percent of the media has been spent and the wall remains effective. The PRB is anaerobic and creates conditions optimal for sulfate reducing bacteria. The wall is expected to provide treatment for Cd and Pb for up to 30 years, but only a few years for Zn. Zinc is currently being attenuated in sulfide phases.

Cyprus AMAX Minerals Company/AMAX Realty Development, Inc., Carteret, NJ

Reference: Bronstein, 2005

Site background: This site is a former copper smelting facility. Groundwater is contaminated with Cu, Ni, Se, and Zn. The groundwater discharges into a nearby estuary.

Contaminants: Cu, Ni, Zn

Reactive media: Dolomitic limestone and powdered sodium carbonate

Demonstration: A 685-foot (209-m) long and 45-foot (14-m) deep trench was installed in 1993, and extended by 200 feet (61 m) in 2000. The trench was filled with 2,600 tons of dolomitic limestone and 20 tons of sodium carbonate. Downgradient wells have shown increases in Ni and Zn since barrier emplacement. Selenium concentrations have decreased slightly from 2.5 mg/L, and no results have been reported for Cu.

E.I. DuPont, Newport Superfund Site, DE

Reference: Bronstein, 2005

Site background: The site is currently occupied by a paint pigment production facility, a chromium dioxide production facility, two industrial landfills, and a baseball diamond. The site was added to the NPL list in 1990 after elevated concentrations of barium, cadmium, cobalt, lead, manganese, nickel, zinc, and volatile organic compounds were found in the 1970s and 1980s.

Contaminants: Mn, Ba, Cd, Cu, Ni, Pb, and Zn

Reactive media: Sand, calcium sulfate, ZVI, and magnesium carbonate

Demonstration: Batch scale studies revealed that a mixture of sand, calcium sulfate, ZVI, and magnesium carbonate would decrease concentrations of Zn, Mn, and Ba. A field demonstration PRB measuring 2,200 feet (670 m) long, 18 inches (46 cm) wide, and 20 feet (6 m) deep was installed in 2002. Barium concentrations were reduced from 8,000 to 1,000 µg/L; Zn concentrations were reduced from 1,000 to <9 µg/L, and Mn concentrations were reduced from 26,000 to 900 µg/L or less. Manganese concentrations remained elevated due to reducing conditions created inside the PRB. The lifetime of the PRB has been estimated at 600 years. Projected savings in comparison to pump-and-treat have been estimated at $13 million.

Universal Forest Products, Inc., Granger, IN

Reference: Ott, 2000

Site background: Spills and leaks from a wood treatment plant contaminated local groundwater with Cr(VI), Cu, and As. Pump-and-treat was used for off-site contamination. No on-site remediation was implemented, creating the need for further remedial action.

Contaminants: Cr(VI), Cu, and As

Reactive media: Calcium polysulfide

Demonstration: A combination of pump-and-treat and PRB technologies was implemented in 1995. Groundwater was pumped from a recovery well and treated with 29 percent calcium polysulfide in a series of pipes, then discharged to a bag filter. Cr(VI) is reduced to Cr(III) and precipitated from solution as $Cr(OH)_3$. Treated water was then reinjected by a horizontal infiltration pipe. The site remediation has been completed after five years and two months of remediation. No results are reported for Cu or As.

Cotter Corporation Uranium Mill, Canon City, CO

Reference: USDOE, 2005

Site background: Groundwater at this former uranium-ore milling site is locally contaminated with molybdenum and uranium at concentrations of approximately 4.8 mg/L (Mo) and 1.0 mg/L (U). Groundwater flows through unconsolidated sand, gravel, and silt. Bedrock consists of claystone, sandstone, and coal. The groundwater flux is estimated at 1 gallon per minute at the site.

Contaminants: Mo, U

Reactive media: ZVI

Demonstration: A 30-foot (9.1-m) wide, 7-foot (2.1-m) high funnel-and-gate PRB was installed in June 2000. The PRB consists of approximately 80 tons of ZVI. Part of the barrier was excavated in 2004 because of deteriorating performance. The ZVI was clogged with precipitates, including calcium carbonate, iron oxides, and sulfide minerals. Performance deterioration was indicated by groundwater mounding at the upgradient side of the barrier and increased concentrations of Mo within the barrier over time. It was recommended to install a pretreatment zone composed of gravel and ZVI.

Columbia Nitrogen Site, Charleston, SC

Reference: http://www.epa.gov/ada/research/waste/research_01.pdf; Bronstein, 2005; Puls, 2006

Site background: Oxidation of pyrite cinders has contaminated groundwater with arsenic and other heavy metals. The spent pyrite resulted from extensive phosphate fertilizer production between 1905 and 1972.

Contaminants: Pb, Cd, As, acidic pH

Reactive media: Organic carbon (30%), ZVI (20%), limestone (5%), and pea gravel (45%)

Demonstration: A pilot-scale PRB was constructed on site in 2002. The PRB measures 30 feet (9.1 m) long, 12 feet (3.7 m) deep, and 6 feet (2 m) wide. The study is designed to assess the performance of organic carbon and ZVI in treating arsenic and other heavy metals, the longevity of organic carbon-based systems, and the long-term reactivity and hydraulic performance of the barrier. Two years of sampling revealed effective removal of Pb, Cd, and As, and buffering of pH from <4 to >6.

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