

COAL SLURRY ASSESSMENT

Draft Final Report

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prepared by

**Alan Ducatman, M.D., MSc, Community Medicine and
Project Principal Investigator
Paul Ziemkiewicz, Ph.D, West Virginia Water Research Institute
John Quaranta, Ph.D., P.E., Civil & Environmental Engineering
Tamara Vandivort, M.S., West Virginia Water Research Institute
Ben Mack, M.S., West Virginia Water Research Institute
WEST VIRGINIA UNIVERSITY**

and

**Benoit VanAken, Ph.D., Civil & Environmental Engineering
TEMPLE UNIVERSITY**

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Foreword

This document summarizes public health concerns related to the injection of coal slurry into underground mine voids. This is Phase II of a two-part effort. The primary report data, Phase I, come from Raleigh, Boone, Kanawha, Nicholas, and Monongalia counties in West Virginia. The phase II report also seeks to identify and address data from other areas, and to be of use in consideration of potential public health implications of coal slurry injection more broadly.

In order to complete this document, several steps were necessary.

Evaluating exposure: The West Virginia University/Temple University research team started by reviewing the Senate Concurrent Resolution 15 (SCR-15) Phase I Report developed by the West Virginia Department of Environmental Protection (WVDEP) and provided by the West Virginia Department of Health and Human Resources (WVDHHR). The research team also solicited data from the U.S. Environmental Protection Agency (USEPA) Region III, U.S. Geological Survey (USGS), U.S. Department of Energy (USDOE), Pennsylvania Department of Environmental Protection, Kentucky Department of Environmental Protection, Virginia Department of Environmental Quality and other sources likely to have valid data including data submitted by researchers at one university (Wheeling Jesuit University), and historical data.

Evaluating health effects: This report focuses on public health and the evaluation is based on existing scientific data. To the degree possible, data gaps encountered by the research team were identified.

Developing recommendations: In this report, the research team outlines its conclusions regarding any potential health threat posed by the coal slurry injection sites selected for the SCR-15 Phase I environmental study, as well as other data that could be identified and acquired. This report attempts to make references regarding specific changes in water quality attributable to coal slurry injection, identifies limitations on such inferences because of substantial data gaps, and makes recommendations relating to information needed, as well as policy considerations in the current circumstances.

Soliciting community input: Two public meetings were held. These had two main purposes: (1) solicit data from stakeholders, and (2) understand stakeholder perspectives. A website was developed in order to post data that is appropriate for public review. (Any data that could violate personal health privacy is not posted.) The website also contains a place for community input, and the research team did respond to stakeholder questions as they were received.

The public was invited to attend meetings. Invitations were sent through personal invitation, when contacts were known, and by a media campaign including all print

media statewide. The public was invited to provide information/data at public meetings, via our website, via a posted e-mail address, or via post. A publicly available e-mail address was established to open lines of communication between the research team and the public.

If you have questions or comments about this report, we encourage you to:

Write: Program Manager
 Coal Slurry Study Research Team
 West Virginia Water Research Institute
 West Virginia University
 PO Box 6064
 Morgantown, WV 26506-6064

Or call: (304) 293-2867

List of Abbreviations

AEG	Ackenheil Engineers Geologists
ALMN	Allegheny and Monongahela River Basins fish community
AMD	Acid mine drainage
ATSDR	Agency for Toxic Substances and Disease Registry
BEN	Balkan Endemic Nephropathy
BLL	Blood lead levels
BMD	Benchmark dose: An exposure level that produces some measured change in response
BTEX	Benzene, toluene, and xylene
CCA	Chromate copper arsenate
CCR	Coarse coal refuse
CDC	Centers for Disease Control
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CI	Confidence interval
95% CI	Statistical testing provides a 95% chance that the true odds ratio (O.R.) is between the values shown
CKD	Chronic kidney disease
COMEST	Commission on Ethics of Scientific Knowledge and Technology
CSF	Cancer slope factor
CVs	Comparison values
DMR	Discharge monitoring report: A required monthly monitoring document submitted to WVDEP by an officially permitted well-injection owner. Since

many coal slurry injection sites have not been officially permitted, monthly reports are often not available.

DNA	Deoxyribonucleic acid
DSWB	Downstream Wet Branch
DWEL	Drinking water exposure level
DWS	Drinking water standard
FCR	Fine coal refuse
FISH	Fluorescent in situ hybridization
GFR	Glomerular filtration rate
HA	Health advisory
HAL	Health advisory level
IARC	International Agency for Research on Cancer
IDWHA	Interim drinking water health advisory
KXRF	X-ray fluorescence of the K shell. A clinical test for detecting lead in living humans
LOAEL	Lowest observed adverse effect level. (See NOAEL)
MCL	Maximum contaminant level (primary drinking water regulation)
MCLG	Maximum concentration limit goals (secondary drinking water regulation)
MRL	Minimum risk level
mRNA	Messenger RNA
MSHA	Mine Safety and Health Administration
NAMD	Neutralized alkaline mine discharge
NAS	National Academy of Sciences
NAWQA	National Water Quality Assessment Program

NHANES	National Health and Nutrition Examination Study
NIEHS	National Institute for Environmental Health Science
NOAEL	No observed adverse effect level. (See LOAEL)
NRC	National Research Council
NSDWR	U.S. EPA National Safe Drinking Water Standard
NTP	National Toxicology Program
OR	Odds ratio
OSM	Office of Surface Mining
PAH	Polycyclic aromatic hydrocarbon
PTWI	Provisional tolerable weekly uptake
RBC	Red blood cell
RCRA	Resource Conservation and Recovery Act
RDA	Recommended daily allowance
RdS	Subchronic Reference Dose
RfD	[USEPA Chronic] Reference Dose
RMEG	Reference Media Evaluation Guide
ROM	Run-of-mine
SCR-15	Senate Concurrent Resolution 15 (year 2007) mandated two reports, an environmental report to be followed by a health report. This document is the health report
SDWA	Safe Drinking Water Act
SDWR	Secondary drinking water regulations
SMCL	Secondary maximum contaminant levels

SMCRA	Surface Mining Control and Reclamation Act
SVOC	Semi Volatile Organic Compound
TCLP	Toxicity Characteristic Leaching Procedure
TDS	Total dissolved solids
TPH	Total Petroleum Hydrocarbons
UIC	Underground injection control: WVDEP regulatory program, including all types of injection wells (mine waste, septic, industrial, other). Mining-waste injection is administered by the Division of Mining and Reclamation
UL	Recommended upper intake level
UNESCO	United Nations Educational, Scientific and Cultural Organization
USDHHS	United States Department of Health and Human Services
USDOE	United States Department of Energy
USDW	Underground sources of drinking water
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USWB	Upstream Wet Branch
VOC	Volatile organic compound
WHO	World Health Organization
WJU	Wheeling Jesuit University
WVBPH	West Virginia Bureau for Public Health, the Division of the WVDHHR responsible for the Phase II report
WVDEP	West Virginia Department of Environmental Protection, responsible for the Phase I report
WVDHHR	West Virginia Department of Health and Human Resources

WVU West Virginia University, the state land-grant university, contracted by
WVBPH to perform this Phase II report

WWF Warm water fishery

Executive Summary

1. Coal slurry injection can have both positive and negative effects on mine pool water. Some aspects of alkaline mine pool water improve when slurry is injected. (Less is known about injection into acid pools.)
2. No public health problem, attributable only to coal slurry, can be documented from available data.
3. Literature review reveals theoretical and historic reasons, including examples cited in Federal documents, to believe that coal slurry injection does not always work as intended. Injection water does not always end up trapped below gradient. It can be a source of pollution.
4. The current regulatory framework incompletely describes the actual practice of coal slurry injection. In addition, current requirements do not address real time monitoring, so opportunities for early detection of quality assurance problems are not assured. The requirement that injection “will not cause, result in, or contribute to a violation of water quality standards or effluent limitations” is most meaningful in the context of a quality assurance program, which would include active monitoring.
5. To ensure that coal slurry injection worked as intended would require more consistent instrumentation of both intended receptacles and potentially impacted sites, including local wells and surface waters. A slurry-monitoring program should invoice the characteristics of the receiving mine area, including interconnections with other mines. It should include regular and repeated sampling with respect to chemistry, volume, and the proportion of liquid to solid fractions. Injection chemistry and flooded-area chemistry should be characterized.
6. We have stated that “No public health problem [is] attributable only to coal slurry.” However, the important limitations of the statement stem from the sparse quantity of available data, as well as the clear temporal limitations of available data.
7. These conclusions were based on data collected at four slurry injection sites: Southern Minerals, Loadout, Panther and Power Mountain. The data represent single sampling events. That prevented statistical testing to determine confidence intervals about the data points. However, the study was replicated across four sites and the consistency of the results suggests that they may be representative of slurry injection in southern West Virginia underground mines. In addition, our findings fundamentally agree with a similar study by Smith and Rauch (1987).

8. In order to better ensure against groundwater contamination, sufficient site characterization, modeling, before-and-after measurements, and ongoing instrumentation are needed to understand the environmental impact of a practice which deliberately puts coal slurry in a difficult-to-monitor environment.
9. Based on both available data and models, numerous chemicals to be reviewed are identified. The identification of chemicals to be reviewed does not mean that a health hazard has been detected in the past or present with certainty, it means that health hazards, past, present, and future, are plausible in this setting. The chemical of most health concern, from data available, is arsenic, based on low safety thresholds. However, no examples of arsenic or other concentrations above the current drinking water standards were unequivocally attributable to coal slurry injection. Chemicals to be reviewed will vary by site and can be predicted based on slurry measurements, mine-pool characteristics, and mass-balance models.
10. These recommendations are also potentially applicable to an easier-to-monitor but also potentially problematic environment, coal slurry impoundments. Use of data developed by ongoing monitoring can compare the effectiveness of practice alternatives.
11. Based on the mass of contaminants in the liquid fraction of the slurry and their estimated dilution by infiltrating groundwater, there was good agreement between the predicted occurrence of water quality standard exceedences and observations. This strongly suggests that the liquid fraction, not the solid fraction contaminants determines eventual water quality related to slurry injection.

Introduction

Historical and Legislative Background of the Phase II Report

Coal slurry injection is the practice of disposal of liquid or semi-liquid coal preparation wastes into underground voids, chiefly by drilling well entrances into abandoned underground coal mine deep spaces. There is a second usage of the term “coal slurry.” Finely ground, finished coal can be mixed with water and pumped over substantial distances to a coal-fired power generation station. This type of slurry is a commercial product, and would not normally be considered for purposes of injection into abandoned mines. Throughout this report, the term “coal slurry” will refer to the waste products of coal cleaning, and not to coal slurry used for power generation. Coal slurry contains suspended solid fine coal waste (<1.0 mm). Slurry injection began in 1958 or earlier and is most common in West Virginia’s southern, low-sulfur coal field.

The West Virginia Legislature adopted Senate Concurrent Resolution 15 (SCR-15) in February 2007, requiring a two-phase study of the environmental health impacts of coal slurry injection. Phase I investigated the hydrologic impacts of coal slurry practices and was performed by the West Virginia Department of Environmental Protection (WVDEP). It became publicly available the week of May 26, 2009. This document is the Phase II report, performed by faculty and staff at three colleges within West Virginia University (WVU) and one college at Temple University, under a contract with the West Virginia Bureau for Public Health (WVBPH). It addresses the human health effects of coal slurry injection. Appendices A and B contain all tables and figures

associated with this report, respectively. Appendix C features the names and credentials of principal contributors to this report.

Specific Tasks of the Legislative Resolution

SCR-15 required six tasks:

Phase I Tasks (covered in report developed by WVDEP)

1. An analysis of the chemical composition of coal slurry.
2. A hydrogeologic study of the migration of coal slurry into surface or groundwater.

Phase II Tasks (covered in this report)

3. An analysis of the known or predicted effects of coal slurry and its constituent contaminants on human health.
4. A study of the effects of coal slurry and its constituent contaminants on public health.

Tasks Pertinent to Phase I and Phase II

5. An environmental assessment of the effects on surface water (Phase I) and on aquatic systems (Phase II).
6. Any other considerations that the WVDEP and the WVBPH deem to be important. As part of their mission, WVU researchers requested and received contractual responsibility to seek and evaluate any reliable data about drinking water exposures, and their human health consequences, beyond the data available in the Phase I report. The WVBPH concurred, and that additional task is a report element. This includes review of data not in the Phase I report.

Specific Phase II Contract Tasks

Specific contract tasks articulated in the Phase II agreement between WVU and WVBPH include the following:

1. Review the Phase I report (received May 29, 2009)
2. Gather additional public health data from peer-review (and potentially non-peer-review) sources.
3. Create a website (www.coalslurry.net) for the purpose of receiving and hosting public health data.
4. Invite Federal, State, and local agencies, national foundations, and others to provide any human health effects data sources deemed important by the holder.
5. Make a news story available (hosted at www.coalslurry.net) to the central Appalachian media concerning the effort, also inviting others to contribute to the effort.
6. Visit State/Federal agencies and foundations (up to three) as needed for input into report creation.
7. Consult with Federal leaders for the purpose of selecting independent report reviewers. Appoint three to six independent report reviewers to critique the draft report before submission.
8. Create and present the draft and final report, including elements in the Center for Disease Control-Agency for Toxic Substances and Disease Registry (CDC-ATSDR) Public Health Assessment Manual format.

This list is not meant to be complete, as there are milestones and procedures in the contract. The list is intended to represent the most critical steps and intended outcome of a public product.

Regulatory Framework of the Permitting Process in West Virginia

The current regulatory framework in West Virginia classifies coal slurry injection wells as Class V. In this regulation, a Class V well is generally described by two conditions:

1. Class V wells inject non-hazardous fluid.
2. Class V wells inject into strata that do contain underground sources of potable water.

Coal slurry injections are intended to inject potentially hazardous fluids into underground spaces that are not intended to be in contact with potable water, but which have sometimes been in contact with potable water. Thus, the regulatory conditions do not precisely describe the coal slurry injection operating conditions as they pertain to drinking water. Mine pool water is also a potential source of drinking water, even when not currently used.

From a human health and aquatic environmental perspective, the public health outcome may be similar to the intent, so long as injection slurry does not degrade potable groundwater or surface water, and assuming that the mine pool water is not used in whole or part for replenishment of drinking water. Should contact with sources of potable water be sufficient to cause drinking water or surface water degradation, however, the Class V regulatory intent becomes a consideration. From a public health

perspective, the intended outcome of the current framework appears to be that surface water and potable water will meet regulatory standards.

1. The operator can inject into an underground mine only in the event that injection “will not cause, result in, or contribute to a violation of water quality standards or effluent limitations.”

A second pertinent requirement is not specific to slurry injections, but may still be applicable in the event that the first requirement is not met.

2. The injection operator must replace the water supply used (by an owner) for “domestic, agricultural, industrial, or other legitimate use from an underground or surface source where such supply has been affected by contamination, diminution, or interruption proximately caused, unless waived by said owner.”

This requirement describes a remedy for when a goal of regulation (prevention of contamination above potable water standards) is not met. The presence of a remedy suggests an understanding that the goal will not necessarily always be met; the remedy pertains to an existing economic entity, and is most useful in the event of some economic and technical means to achieve rapid remediation. The remediation requirement does not specifically address the time scales of potentially persistent sources of water degradation. Also, the prevention requirement is not accompanied by defined requirements for ongoing quality assurance (measurements) which might detect failure to achieve the goal at the earliest opportunity.

A Sludge Safety Citizens’ Report (2005) questions whether slurry injection practice currently conforms to West Virginia regulation. Regulatory frameworks serve as

the background to risk assessments. The purpose of the risk assessment process is to provide data which may inform future regulatory processes.

Scope of the Slurry Injection Process in West Virginia

The estimated annual burden of slurry created annually in the United States is 70 to 90 million tons annually (NAS, 2002). In West Virginia, it is unknown how many tons are created annually. The Phase I report cited *Coal Age* magazine (2008) to suggest that about 15 percent of this burden is disposed of within underground mine works. In March 2009, there were 13 West Virginia sites depicted as active and approved for slurry injection (their activity may not have been uniform at the time of publication, however), 18 additional sites that were active after 1999 but not currently, and over 60 historic sites. The Phase I study methods limited site selection to approved, active sites. As the Phase I report makes clear, there are likely to be other sites; the Phase I report lists the known sites (Figure 3.3-1: UIC slurry sites, from Phase I: Environmental Investigation).

Appendix IIC of the Phase I report lists 237 chemicals accepted by West Virginia for underground injection; other injectates are illegal. However, there is no external monitoring system to ensure that only the legal substances are injected.

Summary Statement of Study Limitations, Including Data Gaps

The following introductory sections concern data gaps identified for purposes of this report, and summarized here. We are concerned that a discussion of data gaps could be interpreted as criticism of existing reports. That interpretation would be a misunderstanding. The purpose of research is often to characterize existing and needed

data. For coal slurry injection practices and outcomes, existing data gaps include (but need not be limited to):

- Absence of a good tracer for slurry inputs (identified as an issue in the Phase I report).
- Limited number of sites monitored, and local uniqueness of geography.
- Constrained time period of sampling, and limited periodic (not continuous) measures.
- Absence of pre-post slurry measurements at monitored sites.
- Inability to distinguish among different types of coal mining inputs to water quality from post hoc measurements.

While these data gaps pertain particularly to coal slurry injection in the context of this report, they are not unique to coal slurry injection. Similar data considerations may pertain to coal slurry impoundment practices and mine runoff more generally, or even to other non-mining disturbances to water quality.

It is important for readers to understand conclusions in the context of what we know, including data gaps which become targets for future knowledge. More detailed descriptions of these data gaps follow.

Coal Slurry Monitoring

The Phase I report emphasizes the technical difficulty of using post hoc measurements for the purpose of assessing intermittent problems in potable (or surface) water near slurry injection sites. A tracer substance was sought, but no satisfactory tracer was identified. The absence of a suitable tracer limits the ability to

track injected slurry and to detect problems or reliably confirm the absence of problems. Research into the use of iron has been suggested as a tracer, but it is not clear how well this works, especially in alkaline slurry environments. And, the presence of numerous metals in natural overburden implies that linking a finding to mining is problematic (Wigginton, et al., 2007). The inability to find a tracer is fully consistent with the current literature concerning slurry contents; it is not a unique attribute of any report. The following limitations stem from the absence of a unique trace substance: (1) It is not known where best to monitor post hoc in more detail. (2) It is not clear when or how long to monitor post hoc. (3) More than one and perhaps many potential contaminants are candidates for monitoring, increasing the difficulty and cost. (4) The effects of previous or present mining operations, in general, are not easily distinguished from the effects of current or past coal slurry mine injections if extensive pre-post operation data are not obtained.

Phase I Sites and Time Frames Selected for Study

Six sites were studied for the Phase I report, including four which were studied in depth. (Table 1 outlines the characteristics of these sites.) The actual number of coal slurry injection sites in West Virginia is unknown. An estimate is over 60 historic sites. Among known sites, a minority have gone through a formal permitting process. The Phase I study addresses four permitted sites with a hydrologic assessment and it addresses an additional two permitted sites for slurry constituents only. The sites selected for study were all formally permitted during or after the year 2000, and were intended to be representative of different regions and different kinds of conditions.

It is a statement of fact, rather than a criticism of any party, that the Phase I report could not address the following topics: non-permitted sites; geographies distinct from those chosen; longer time frames and temporal variations; pre- to post-injection measures. Furthermore, the topics of site or time frame limitations are not unique to this risk assessment and are not intended as a criticism of what is achievable in limited time frames with limited funding. Data limitations are addressed in risk assessment practice for reader comprehension. How well the selected sites represent other permitted or non-permitted sites, or the injection sites in different geographies, or any site at a different point in time, is unknown. As the primary legislative intent of the two-phased report may be a forward-looking evaluation of risk for future permitted sites, it is plausible (from a policy perspective) that the comparison with 13 active, permitted sites (at the time of the study) should be emphasized, and past practices at non-permitted sites considered less important. An opposite perspective could be that the effects of non-permitted sites deserve consideration as a matter of policy concerning adequacy of regulation and enforcement.

The Phase I study was unable to address data following injection into an acid mine pool (pools analyzed in the Phase I study were alkaline), or any site using a high-sulfur coal. It did not address sites outside West Virginia, nor the full range of different kinds of hydrologic conditions within the state. Study authors correctly acknowledged that downstream pollution sources, to the degree they existed, could have come from multiple sources. Importantly, pre-post injection measures do not and could not exist in the time frame of the Phase I report. A planning inference that could be made at the onset of the Phase I study is that water quality change potentially due to slurry injection

specifically will be difficult or impossible to detect post hoc. The Phase I report did not sample streams for microinvertebrates for this reason.

Inferences can be made from external data. In general, even fewer data points are available from other sources. A potential exception, water-quality concerns voiced by neighbors of one site, came from a site not addressed by measurements in the Phase I report. However, some measures pertaining to these concerns are independently available from work done at Wheeling Jesuit University. These additional measures are valuable for the further consideration of chemicals to be reviewed, and are discussed in this report. Thus, to the degree it relies on the Phase I report, the Phase II report concerning impacts upon benthic communities and human health is constrained by Phase I uncertainties about whether surface waters and drinking waters are actually affected. The additional data obtained from other sources such as Wheeling Jesuit University measurements have expected limitations as well, and did allow the research team to expand its consideration of chemicals to be reviewed.

Although one watershed area studied in the Phase I report, Wilderness Fork, associated with Loadout LLC, experienced a slurry “artesian event” in 2005, no discernible traces of this event could be detected by the time sampling was completed. This “black water” event is considered to have been substantial, but no flow rate or duration data exist. The interpretation of this incongruity can range from an absence of measurable impact to the inadequacy of the currently available data, suggesting a clear need to sample more frequently, over longer time periods, in more places. The Phase I report leaves open the possibility that the 2005 “artesian event” could have been the source of an earlier possible contamination of an artesian well. However, the actual

finding is that the Phase I report of that well does not reveal any residual slurry effects of the event at the time of sampling. Temporal limitations of the measurements relating to this event indicate the need for before-and-after as well as more frequent sampling. In the Phase I report, all sampling was done, by design, in a discrete time period (about one year), and no sampling site was continuously monitored. The Phase I part is constrained by the time period and the periodicity of sampling. This is not a criticism; it merely describes the extent of the effort requested and designed.

Impact of Seasonality on Phase I Measures

Multiple times of sampling are important for understanding pollutants in surface water, groundwater, and ultimately in potable water. Flows vary by season and affect the entry of pollutants into receiving waters as well as the concentrations. Volatile organic compounds have a high vapor pressure. They are more likely to stabilize in cold water, and more likely to be detected in cold water samples. Some volatile organics, such as acetone, carbon disulfide, and benzene, have also been detected in some systems when stream flow increased. This may demonstrate a “flush-off” effect of heavy rains and snow melts, particularly when surfaces are relatively impervious due to freezing. These are some of many time-variable conditions which can affect the presence and detection of pollutants. These limitations are not unique to any study, but, they are important in constrained time periods.

The Phase I report was designed to be accomplished in a single year. A single year of sampling has potential limitations concerning the variability of weather, pollutant inputs, and pollutant migration into receiving waters.

Impact of Public Health Measurement Procedures on Available Data

Monitoring of potable water measures and current drinking water standards addresses a finite number of elements, chemicals, and indicators. These are national standards, not historically driven by consideration of all measurements that would be pertinent to contamination from coal slurry. In the appendices of this report, readers can compare primary and secondary water quality standards to data which has been provided by researchers independent of the Phase I report. (The Phase I report was not designed to measure pollutants in regional drinking water. This is not a criticism; it is a description of project scope.) Some but not all of the range of chemicals which are potentially significant pollutants in coal slurry, which might migrate into potable water following injection, are routinely and intermittently monitored in municipal potable water systems and rarely in private wells.

Confounding Impact of Historic Coal Activity

Surface waters and groundwater have been degraded by numerous mining activities throughout Appalachia for more than a century. (Table 2 provides historic estimates of trace elements in coal and coal refuse.) A logical problem faced by the Phase I report was the inability to distinguish water degradation due to coal slurry injection from simultaneous or pre-existing environmental footprints of all aspects of mining activity. Acid mine drainage (AMD) is the best known such impact.

Pyrite, or “fool’s gold,” occurs naturally in coal and in coal overburden. It is the major source of AMD. Combined with oxygen and water, pyrite gives rise to ferrous iron, sulfate, and acidity. A secondary outcome of the AMD then brings other constituents of

coal and overburden into acidified water solution. Examples include aluminum, arsenic, barium, cadmium, cobalt, copper, manganese, selenium, silver, strontium, and zinc. However, this general statement has many exceptions, and metals (or their absence) provide inferential rather than perfect data as a proxy of mining activity. The length of time that pollutants stay in solution and travel from the mining activity is highly variable. Sulfate itself tends to stay in contaminated mine drainage because it is highly soluble. Non-AMD is alkaline (by definition). However, non-AMD can also have elevated sulfate and can also carry heavy metals with it. Sulfate concentrations are typically highest in regions with the greatest historic mining activity, but what is typical has many exceptions. When water is degraded from mining activity, there is no universally accepted method to assign relative contributions to different places and specific areas by mining practices. This report will attempt to make best available inferences using available methods.

In a study of water quality of the Monongahela and Allegheny River basins, the presence of historic coal mining activity influenced the diversity of fish species (Anderson et al., 2000). Similar findings have been found for invertebrate species in the Kanawha-New River basin (Anderson et al., 2000). Mining activities are understood as able to affect groundwater quality after mining and reclamation have ceased. Sulfate, iron, manganese, and dissolved solids are more likely to exceed USEPA potable-water SMCL standards in mined, and even in coal-bearing areas, compared to non-coal geologic areas in the absence of mining activity (Anderson et al., 2000).

The Use of Predictive Models

Predictive models can be useful where measures are absent or insufficient. Predictive models of what will be in coal leachates are heavily influenced by volumes of water added and by pH (Heaton, 1981). Depending on the simulation method used, and the pH of the extraction, the metal content can be under- or overestimated compared to real-life conditions. (Note: The metals do not increase or go away. They will ultimately be in the coal, the leachate, or settled. However, the estimate of what will be in the leachate can vary with the method.) In general, historic predictive testing suggests that slurry could contain undesirable direct additions to drinking water for the following metals: cadmium, mercury, lead in some instances, arsenic and barium less often (Heaton, 1981). Similar considerations pertain to coal. Because industrial practices vary greatly, predictive models have not been developed for slurry-pertinent additives such as surfactants, solvents, cations, and flocculants.

Slurry Disposal Methods

Most slurry waste from coal preparation is created above ground in slurry impoundments where the slurry solids are left to settle. The discarded water in the impoundment can be recirculated within the preparation plant for some period of time. Impoundments can be consistently enlarged to receive greater volumes and to make up for the volume lost to settled solids or the impoundment water can be injected into underground voids. Impoundment water is contained, but it also migrates to some degree. Slurry impoundments are not designed to fully contain contents. To assist containment of solid particles, flocculants may be added to the process at one or more

points in slurry handling to hasten settling. A single preparation plant can generate millions of cubic feet of required storage.

Slurry impoundments present several challenges to the environment and to public health. The eventual potential for catastrophic releases is small at any time, yet over time such events have occurred resulting in drownings and in the release of toxic sediments which affect soil and water flows for miles. The best known catastrophic failure released an estimated 16.6 million cubic feet of slurry water, killed 125 people, and displaced an additional 4,000 people from their Logan County, West Virginia, homes (Davies, 1973). Other breakthroughs have occurred, including a recent vertical breakthrough from a slurry impoundment into underlying coal mines in Martin County, Kentucky, followed by pollution of local tributaries and flooded surface areas. Further, surface impoundments, when operated as intended, create an unusable terrain for years, and leave sediments behind, including settled toxins. The several problems of above-ground slurry disposal are not the point of this project, yet any discussion of the problems of slurry injection into mining voids lacks context in the absence of mention of the comparison to currently available alternatives that also carry potential risk for local water contamination, i.e., slurry impoundments.

To inject slurry into subsurface voids, preferably well below the local water table that connects to any regional drinking water supplies, may improve upon the problems associated with direct releases of impoundments. And, releasing cold water from underground sources has theoretical advantages including advantages for aquatic life over releases of warmer water from above-ground storage. However, the absence of research providing proof of principle concerning the theoretical superiority of this

practice has been noted for decades (Henton, 1987; NSF, 1975; Ackman, 1982; Smith, 1987). Just as slurry injection has some theoretical advantages over surface impoundments and releases, there are theoretical problems with slurry injection that do not pertain to slurry impoundments. Underground mine walls and bulkheads could sustain blowouts or ruptures if slurry injection raises a mine pool to the point that its weight is unsustainable within the current mine structure. Water saturation may degrade mine pillars, causing subsidence. Introduction of methane-forming products could add the risk of underground fires. Subsurface soil saturation may create pathways for water and suspended or dissolved toxicants to reach the surface or to contaminate nearby aquifers, even in the absence of blowouts or visible releases.

The suitability of an abandoned mine void for purposes of slurry injection is theoretically affected by a number of conditions. In order to work well, the void areas should be large and access to them unhindered. The ability to maintain access is advantageous for both the introduction of slurry into the intended area, and for the capability to monitor the outcome. If there are roof falls, the resulting floor rubble should be permeable so that pools do not build up unevenly.

With unhindered entrance, the pool created by injections should, in theory, not require substantial treatment before it could be subsequently drained. All of these considerations, and others, are part of the intent of the permitting process.

Historic reports of contamination events from slurry injection do exist, so the potential problem to be addressed by environmental considerations leading to a valid permit is known to be practical rather than theoretical (Sludge Safety Citizens' Report, 2005) However, the specific conditions leading to problems are poorly characterized.

For example, in 1984 a large-scale slurry injection (250 gallons/minute) containing arsenic, barium, cadmium, chromium, lead, selenium, and mercury, all above then-current Safe Drinking Water Act standards, was investigated by the USEPA following a citizen's complaint. The subsequent USEPA evaluation concluded that site injections could endanger water quality and human health for 300 residents who used the pool as a source for drinking water (USEPA, 1985). In contrast to historic reports of slurry-injection contamination events, there are also some dilution improvements in alkaline mine-water-pool pH following the addition of slurry, noted in references that address this topic for alkaline receiving waters, such as ATSDR (2004).

Literature Review

Identification of Sources Being Used for the Investigation

Specific documentation about potential or reported health effects resulting from underground coal slurry injection is almost nonexistent. However, since coal slurry contains mostly coal-related substances, data about exposure to coal-related products and activities can be used. Also, coal mining and other mining activities share several potential health concerns with slurry injection, such as leaching of heavy metals. Health hazard data related to other mining activities was used for modeling purposes in this review. Extension of health effects reported below about coal and/or mining activities to the specific cases of underground coal slurry injection must be pursued with caution since potential leaching mechanisms and environmental and human exposure routes are likely to be different.

The present literature review focuses on health data related to the following key words and concepts:

- Exposure to coal, coal slurry, coal refuse, coal ash, coal waste, and coal processing products.
- Exposure to other substances resulting from diverse mining activities (e.g. toxic metals or breakdown products of flocculants, known to be in coal waste-processing streams).
- Exposure to hazardous substances detected in significant concentrations in coal slurry during Phase I of this investigation, or in data collected from Phase II researchers' request for public data.

Data reviewed are categorized as followed:

- Peer-reviewed published articles/proceedings obtained using search tools, such as the Web of Science, PubMed/MEDLINE, and Google Scholars. Within PubMed, the toxicology and environmental health sites including the TOXNET databases and linked resources were also accessed. For substances identified as chemicals to be reviewed, ATSDR reports and recent peer review literature from the national library of medicine were accessed.
- Public Health Assessments and Health Consultation previously conducted by ATSDR or other agencies related to the impact of coal mining/processing on community health, such as Martin County, Kentucky and Williamson, West Virginia (<http://www.atsdr.cdc.gov/HAC/PHA/index.asp>).

Reports on worker health and technical reports about processes which were unrelated to human health or water quality were excluded, unless there was a specific reason to include them in order to illustrate a point about human populations more generally. In the few instances in which workplace reports are referenced in order to illustrate a point potentially pertinent to wider populations, the authors have tried to be consistent to cite the workplace origin of the data. Reports which contained references to coal slurry and to human health, to coal slurry and water quality, or to coal slurry and policy recommendations which might reflect on public health, were included.

- Review and analysis of toxicology profiles (ATSDR) of contaminants detected in Phase I at “significant levels.”

Toxic Components of Coal, Coal Refuse, and Coal Combustion Products

Coal Slurry Composition

According to the Mine Safety and Health Administration (MSHA), there are more than 600 impoundments throughout the Appalachian region. Mined coal has impurities and small pieces unsuitable for use (“fines”) that are removed from coal by washing with water and flocculants, starches, or lime (ATSDR, 2006). Coal slurry typically consists primarily of coal fines, containing elemental carbon, hydrocarbons, including complex organic compounds, sulfur, silica, iron oxide, calcium oxide, sodium, and traces of metals (Landsberger et al., 1995; Hower et al., 1996). Genotoxicity and mutagenicity of coal, coal refuse, and coal ash can arise principally from two groups of compounds:

polycyclic aromatic hydrocarbons (PAH's) and salts of heavy metals (Griest et al., 1982; Liu et al., 2000; Manerikar et al., 2008).

Organic Contaminants

In contrast to metals, which are associated with coal, most of the hydrocarbons are intermittently and variably introduced. No one of these is predicted to be consistently present downstream of coal operations. Numerous hydrocarbon contaminants are neurotoxins, some are carcinogens, and none are known to be consistently found in water downstream from coal operations. This is not because hydrocarbons are absent from slurry. It is because the specific species vary and are unpredictable. When specific toxicants rather than total hydrocarbons are considered, benzene and toluene are sometimes featured. Shallow wells in close proximity to mining areas may have increased concentrations of benzene and toluene (USGS, 2006).

In addition, the slurry may contain traces of flocculent used to settle out the coal fines. Polyacrylamide flocculent used by coal preparation facilities also contains some hydrocarbons and traces of acrylamide (ATSDR, 2006). Acrylamide monomer is of concern because it is neurotoxic to mammals, including humans, and is also a suspected human carcinogen. Case reports substantiate the neurotoxicity, including but certainly not limited to two coal preparation workers from West Virginia (Mulloy, 1996). Acrylamide is a potential carcinogen. Population studies of acrylamide exposure have not shown a clear relationship to cancer, but evidence of exposure to acrylamide is present in the entire U.S. population (Vesper et al., 2010). Acrylamide biomonitoring is done by measuring adducts. The additional contribution of coal slurry to acrylamide

adducts in exposed populations has not been characterized by biological testing. The residual monomer is generally believed to be present in very small quantities in coal slurry settings; however, continuous-monitoring data to conclusively support this prevailing view are not available.

Polyacrylamides are known to bind strongly with soil particles, which are expected to reduce its mobility and bioavailability of a contaminant. On the contrary, acrylamide does not bind to soil and is highly mobile in soil. However, acrylamide is rapidly degraded by microbes in soil (ATSDR, 2006).

Oils and alcohols are added during the coal cleaning process to agglomerate and separate the coal.

Metal and Inorganic Contaminants in Coal Beds

Presence of toxic metals in coal beds has been investigated in order to characterize the potential release of toxic metals from coal handling and combustion. Hower et al. (1997) analyzed Middle Pennsylvanian Breathitt Formation (Westphalian B) Pond Creek and Fire Clay coals from active coal mines in 22 localities (Pike and Martin Counties, Kentucky). Two metals, arsenic and lead, included in the 1990 Clean Air Act Amendments were analyzed. Findings showed levels as high as 4000 ppm arsenic (ash basis). Most of arsenic compounds (and lead) were associated with pyrite, which is largely removed by coal processing and likely to be found at even higher levels in coal slurries. High levels of arsenic and lead are found in coarse pyrite, enter into coal slurries, raising the problem of coal refuse disposal (Hower et al., 1996; Hower et al., 1997).

Although data about potentially toxic organic compounds in coal are very scarce, there have been several reports suspecting a link between coal organic compounds and human disease. For instance, Balkan endemic nephropathy (BEN) is today hypothesized to be related to long-term exposure to PAHs and other toxic organic compounds leaching from low rank coals (lignite) into drinking water sources (Tatu et al., 1998). Bunnell et al. (2006) investigated the relationship between chemicals and pathogens associated with low rank coal (lignite) and renal pelvis cancer rates in northwestern Louisiana. The authors analyzed samples from private drinking water wells in northwestern Louisiana likely to have been in contact with lignite. Water samples were analyzed for organic compounds, and nutrient and anion concentrations. Significant associations were revealed between the cancer rates and the presence in drinking water of organic compounds, nutrients (phosphate and ammonia), and 13 chemical elements. This study suggests possible linkages between aquifers containing chemically reactive lignite deposits, hydrologic conditions favorable to leaching of toxic organic compounds, and cancer risk. Although these examples illustrate the potential toxic character of various forms of coal, there is no lignite in West Virginia and this particular case is, therefore, not an issue for human health in the state.

A recent USEPA report characterized coal refuse and determined that mining rejects have a higher concentration of mercury than normal coals (USEPA, 2008). For instance, in West Virginia and Pennsylvania, gob has 3.5-4 times more mercury than bituminous coal. Also, Pennsylvania culm and gob have about four times more chromium and three times more lead, and high levels of arsenic as compared to coal.

Metals Added During Coal Processing

Magnetite (iron) can be added during coal cleaning processes (beneficiation). Most can be recovered, some adheres to the coal product, and some is lost to waste and appears later in slurry. For practical purposes of public health considerations, magnetite is indistinguishable from the iron that may enter into slurry from the overburden or the mine drainage.

Metal and Nonmetal Electrolytes in Coal Mining

Sodium chloride and magnesium chloride can be used as electrolyte solutions to assist the flotation aspect of coal cleaning operations. The solution may then become part of the slurry. A variety of simple salts may also be present in overburden; the most notable of these are sulfates. Coal mining activities can increase the electrolyte content of surface waters downstream. These increases can lead to variations in the electrolyte content and specific conductance of drinking water.

Toxicity and Environmental Impact of Coal and Coal-Related Compounds

Generality

Coal contaminants from numerous stages of coal mining, cleaning, transport, and waste can enter waste streams. Influential health advocacy groups point out that contaminants can potentially affect all major body organ systems, leading to major causes of mortality in the U.S., such as heart disease and cancer (Lockwood et al., 2009). Although such reports generally consider exposure by inhalation of particles and gases generated by coal combustion, authors also observed that each step of coal processing, from mining to waste disposal, including coal washing can potentially

impact human health. Besides other environmental and health threats, the authors pointed out that coal washing generating coal slurry can release arsenic, barium, lead, and manganese, and contaminate nearby wells and local water supplies.

Environmental and Health Effect of Coal Mining Activities

Intensive Appalachian coal mining has caused extensive surface and groundwater contamination. These are contamination problems which precede any history of coal slurry injection, and which can occur independently of coal slurry injection, yet coal slurry injection may contribute to them. Surface and underground coal mining exposes pyrite and marcasite (iron disulfides) naturally occurring in coal to weathering processes, leading to AMD. AMD results from geochemical and bacterial reactions that occur when pyrite is exposed to air and water. The reactions generate dissolved ferrous iron that precipitates in the form of insoluble ferric hydroxide. Acidic water then also dissolves other coal and overburden metals such as, aluminum, arsenic, barium, cadmium, cobalt, copper, manganese, and zinc. These metals may enter the water table or surface water, affect wildlife, and render drinking water unfit for consumption (USGS, 2000). Mining activity can also generate neutralized or alkaline mine drainage (NAMD) containing elevated concentrations of sulfate, iron, manganese, and other constituents. The USEPA has established Secondary Maximum Contaminant Level (SMCL) of 250 mg/L for sulfate. Besides taste and odor problems, high sulfate concentrations in water may cause diarrhea in sensitive populations. Concentrations of sulfate are, on average, five times greater in coal mine-impacted stream basins than in unmined basins. As reported in a study conducted on the Allegheny and Monongahela

River Basins fish community (ALMN), a difference in fish abundance and diversity of species was observed between streams receiving mine drainage as compared to those in unmined basins (USGS, 2000). Similarly, a study conducted on aquatic invertebrates (insects, worms, crustaceans, and mollusks) showed an inverse relationship between sulfate concentrations and the diversity for three groups of sensitive insect species (mayflies, stoneflies, and caddisflies).

A recent USGS report compared groundwater quality in mined and unmined areas in the northern and central Appalachian coal regions of Pennsylvania and West Virginia (USGS, 2006). Groundwater in the mined high-sulfur coal region (northern Appalachian coal region) has higher concentrations of sulfate, hardness, calcium, and specific conductance as compared to the unmined high-sulfur coal region (and to both mined and unmined areas in the low-sulfur coal region). This phenomenon is explained by the transport of pyrite-oxidation products from the mined site and subsequent neutralization reactions by calcareous materials at the mine site or along the flow path. These mine-drainage constituents generally exceeded background concentrations only in the close vicinity of mined sites (<500 ft). Concentrations of sulfate, hardness, and TDS were higher in shallow groundwater (50-150 ft) and generally less than background concentrations in deeper groundwater. Also, concentrations of iron, manganese, and aluminum were reported higher than background concentrations in many shallow wells. The USGS report also presents data about the analysis of volatile organic compounds (VOCs) measured in mined and unmined areas in the northern Appalachian coal region (30 and 15 wells, respectively). Of the 86 compounds analyzed, seven compounds were detected in mined areas only and eight compounds were detected in unmined areas.

The detected chemicals included benzene, toluene, and xylene (BTEX), halogenated alkanes and alkenes, ketones, tetrahydrofuran, and carbon disulfide. Detection frequencies of benzene and toluene were greater in mined areas than unmined areas.

Environmental Contamination by Coal Slurry Impoundments

In an attempt to assess well and drinking water contamination by the coal slurry impoundment failure in Martin County, Kentucky, in 2000, Wigginton and coworkers analyzed water samples collected from hot water tanks in the affected area (Wigginton et al., 2007). The hypothesis for this sampling strategy was that hot water tanks indicate previous contamination from the water supply because sediment and precipitates accumulate in the tanks. (Technical constraints of this strategy include but need not be limited to the independent contributions of the tank, and its anode, valves, and fittings, as well as any biofilms and their contributions. In addition, the time course over which precipitates accumulate and flush has not been modeled. These data gaps represent potential constraints upon the interpretation of collected hot water tank precipitates data as it may reflect long term concentrations of the measured contaminants in water.) Results obtained show that samples taken from affected and reference area hot water tanks often exceeded USEPA drinking water guidelines including arsenic, cadmium, chromium, copper, iron, manganese, and lead. Barium, mercury, and selenium did not exceed USEPA limits in any samples. The report also showed strong correlations among metal concentrations for arsenic, barium, cadmium, chromium, cobalt, and iron, indicating that these metals may accumulate proportionally. Importantly, the authors did not find any clear relationship between metals in the hot water tanks and at the current

water source, as sampled from the cold-water tap, which may be explained either by the high efficacy of hot water tanks to concentrate metals from source water, or by the historic presence of more metals in source water than at present, or by limitations of the sampling strategy. The authors pointed out that accumulated copper, iron, and lead may come from water system pipes and plumbing.

An unpublished study investigated the water quality of 15 wells collected within 2 air miles of the Sprouse Creek Slurry Impoundment (Stout and Papillo, 2004). The study focused on seven heavy metals regulated by USEPA primary drinking water standards and five metals regulated by secondary standards. Results indicated that primary drinking water standards were exceeded for lead, arsenic, barium, beryllium, and selenium. Secondary drinking water standards were exceeded for iron, manganese, aluminum, and zinc. A comparison of water quality during low flow versus high flow events showed the detection of arsenic and lead at a higher frequency during high flow. Comparing well water in the Williamson area with neighboring counties of southern West Virginia and eastern Kentucky indicated that Williamson area wells had the poorest water quality in the coalfield region.

Coal Combustion Residues

Although they are not coal or coal slurry *per se*, coal combustion residues illustrate chemicals/elements that are found in coal and coal slurries (Elmogazi et al., 1988), especially the inorganic contaminants.

Intentional or accidental releases of coal combustion residues result in deleterious effects to aquatic environments (Gupta et al., 2002; Reijnders, 2005). Metals

and trace elements present in combustion residues have accumulated in aquatic organisms to reach very high concentrations, sometimes much higher than concentrations detected in contaminated water (Rowe et al., 2002). Biological effects were observed in both vertebrates and invertebrates, including histopathological, behavioral, and physiological (reproductive, energetic, and endocrine) effects. Release of coal combustion products has resulted in fish kills and extirpation of sensitive species, with indirect effects on the entire ecosystem due to changes in resource abundance or quality (Rowe et al., 2002). Recovery of impacted sites can be extremely slow due to cycling of elemental contaminants, even in sites that have been exposed for short periods of time. Many studies have focused biological effects of exposure to selenium because of associated teratogenic and reproductive toxic effects. The complex mixture of metals and trace elements characteristic of coal combustion residues suggests that a large variety of inorganic compounds enter sediments, water, and organisms, including terrestrial, semiaquatic, and avian species that live at or visit impacted aquatic sites (Rowe et al., 2002).

Brieger and coworkers (1992) reported on 48 plant species, 18 terrestrial animal species, and 7 aquatic animal species collected on a coal fly ash slurry impoundment site and a dry deposit site. These were analyzed for the presence of metals using neutron activation analysis. Based on phytotoxicity levels found in the literature, the authors concluded that, in general, plants did not accumulate toxic levels of metals; one plant exhibited high levels of cadmium and sixteen had excessive levels of selenium concentrations (>5 ppm). (The ability of plants to concentrate cadmium is a specific health concern. Because inhaled cadmium is well absorbed, tobacco plants can be a

significant source of cadmium, and the presence of cadmium in crop soil is a seldom considered additional public health concern where tobacco is planted.) Yet, trace metal concentration in terrestrial animals was generally in between that of control animals and that of the fly ash itself. Zinc was concentrated in all the terrestrial animals to levels higher than in fly ash. Crickets concentrated high levels of chromium, selenium, and zinc, and all animal species studied accumulated high levels of selenium.

Selenium was also found to accumulate into aquatic organisms, such as observed in a selenium-contaminated lake (Lake Macquarie, Australia); *Marphysa sanguinea* and *Spisula trigonella* accumulated significantly more selenium when exposed to contaminated sediment than when exposed to uncontaminated sediments. Most of the selenium in mollusc tissues was found to be associated with the protein fraction as selenomethionine (Peters et al., 1999)

Research on responses of aquatic organisms to exposure to coal combustion residues suggests that disposal methods which prevent an aquatic slurry phase may limit environmental risks (Rowe et al., 2002).

Genotoxicity and mutagenicity of coal, coal refuse, and coal ash arise principally from two groups of compounds: PAHs and salts of heavy metals (Griest et al., 1982; Liu et al., 2000; Manerikar et al, 2008). Chakraborty and Mukherjee (2009) investigated the toxicity of leachate from ash ponds used for disposal of coal ash slurry near power stations. Elemental analyses of leachate showed predominance of sodium, silicon, potassium, calcium, magnesium, iron, manganese, zinc, and sulfur. Ames *Salmonella* mutagenicity assay revealed that the leachate was mutagenic, even though sterilization by autoclaving rendered it non-toxic, presumably because of the removal of metals by

precipitation. However, based on Comet assay, the leachate was found to be directly mutagenic and induced significant ($P < 0.05$) concentration-dependent increases in DNA damage in whole blood cells, lymphocytes, and *Nicotiana* plants. These results indicate that leachate from fly ash dump ponds has genotoxic character, potentially leading to adverse effects on plants, animals, and human health (Chakraborty and Mukherjee, 2009).

Underground Backfilling of Coal-Related Waste

A USEPA report was published in 1999 on Class V underground injection wells to evaluate the risk posed to underground sources of drinking water (USEPA, 1999). This study was conducted to develop background information the Agency can use to evaluate the risk that these wells pose to underground sources of drinking water (USDWs). The report reviewed here (USEPA, 1999), volume 10, covers Class V mining, sand, or other backfill wells. Although the report concerns various kinds of mine backfilling materials, it also includes coal cleaning waste and other coal-related waste. Mine backfill wells are used to inject a mixture of water and other materials, including sand, mine tailing, coal combustion ash, coal cleaning wastes, AMD treatment sludge, and/or flue gas desulfurization sludge, into mined out portions of underground mines. Mine shafts and pipelines in an underground mine, as well as more conventional drilled wells, used to place slurries and solids in underground mines are considered mine backfill. In a summary statement that applies to all kinds of mine backfills, the document reports that, even though the physical and chemical characteristics of the injected materials vary widely, data from leaching tests of backfill materials indicate that

concentrations of heavy metals (e.g., antimony, arsenic, barium, beryllium, boron, cadmium, chromium, lead, mercury, molybdenum, nickel, selenium, thallium, sulfate, and zinc) frequently exceed primary maximum contaminant levels (MCLs) or health advisory levels (HALs), while concentrations of aluminum, copper, iron, manganese, TDS, and sulfate, as well as the pH, frequently exceed secondary MCLs. However, the report indicates that no incidents of contamination of a drinking water supply have been identified that are directly attributable to injection into mine backfill wells. The report also mentions that groundwater contamination is common at mining sites, making it difficult to identify the specific causes. The likelihood of groundwater contamination from backfill injection is dependent on site conditions, including mine mineralogy, site hydrogeology, backfill characteristics, and injection practices. Based on this report, approximately 5,000 documented mine backfill wells and more than 7,800 wells are estimated to exist in the U.S., with 401 known in West Virginia only (USEPA, 1999).

Constituent properties of backfill-wells material that may affect drinking-water supplies are toxicity, persistence, and mobility. Constituents frequently exceeding health-based standards in Toxicity Characteristic Leaching Procedure (TCLP) or other leachate from backfill material include antimony, arsenic, barium, beryllium, boron, cadmium, chromium, lead, mercury, molybdenum, nickel, selenium, thallium, and zinc. In addition, aluminum, copper, iron, manganese, TDS, sulfate, and pH have been frequently measured above secondary MCLs in TCLP or other leachate. The persistence of constituents that leach from mine backfill depends on complex solution-mineral equilibria that are determined by site-specific conditions such as leachate and groundwater characteristics, host rock characteristics, and oxygen availability in the

mine workings and surrounding formation (USEPA, 1999). For injected backfill, mobility of metals in the mine environment is primarily dependent on their tendency to dissolve, which generally increases as pH decreases. Precipitation can also occur as a result of oxidation when reducing environment is exposed to oxygen supply, although the same phenomenon can also result in dramatic pH reduction, therefore, increasing metal solubility. Injection of backfill material often occurs at sites where low pH water is present and in contact with the backfill injection zone. At these sites, mobility of most metals present in the backfill will be greater than if injection occurred under neutral or alkaline pH conditions. However, backfill injection under these conditions can also result in a decrease in metal mobility by reduction of water flow rates through the mine if the backfill eliminates direct air contact with pyrite or other sulfide minerals, which will greatly reduce acid generation and metal solubility and mobility (USEPA, 1999). In other words, mine backfill can improve water quality. When this occurs, the specific contribution of coal slurry is unknowable among the constituents.

Injection of Coal-Cleaning Waste

The USEPA report (USEPA, 1999) includes also a distinct section specifically dedicated to the injection of “coal-cleaning waste” that is of special relevance for our review. “Coal-cleaning waste,” the results from the wet cleaning of raw coal, is defined as extremely fine solids, including coal particles and coal associated minerals, suspended in water. The report indicates that the chemical composition of the injected material depends primarily on the characteristics of the coal, associated bedrock, and water used in the cleaning process. For instance, the injected slurry of a Colorado mine

(New Elk Mine) was shown not to exceed the relevant primary or secondary MCLs or HALs for the constituents tested, with the exception of arsenic and total suspended solids. On the other hand, cleaning waste slurry and slurry leachate from an Indiana mine (Kindall mine) exceeded the primary MCLs for arsenic, cadmium, and lead, and the secondary MCLs for TDS, sulfate, and manganese.

A 1987 study assessed the injection of coal slurry wastes from coal preparation and sludge from treatment of AMD into underground coal mines in West Virginia (Smith and Rauch, 1987) In some cases (7 mines), slurry injection was found to improve the already degraded water quality by increasing alkalinity and pH, and decreasing concentration of iron and manganese, even though sulfate concentration was shown to increase. Only minor changes in trace element concentrations were detected that did not appear to be a concern for drinking water. Sludge injection at other sites (3 mines) appeared to increase alkalinity, pH, sulfate, and total suspended solids. Generally speaking, injection into mines with high pH water resulted in lower iron and manganese concentrations and injection into mines with low pH resulted in increase of iron concentrations, although most changes in other trace element concentrations were negligible, with the possible exception of arsenic.

Transport and Mobility of Coal-Associated Contaminants

General Considerations

For many years, coal fly ash produced by thermal power plants has been hydraulically placed openly in impoundments in the form of wet slurry. There is evidence that leaching of trace toxic metals from these impoundments has occurred that

contaminate both surface and groundwater. Wasay (1992) investigated leaching of chromium (III), chromium (VI), mercury (II), and arsenic from fly ash at various pH levels through monitoring wells surrounding a dumping site and designed for studying these metals in groundwater. It was estimated that at pH 7.0, about 40% of these toxic elements were leachable and susceptible to contaminate groundwater.

A report from Krishnan et al. (1992) studied leachability of the toxic elements, cadmium, arsenic, mercury, and selenium from various solid wastes, including coal fly ash. The results concluded that cadmium displayed the greatest leachability in all waste types (up to 76%). Leachability and bioavailability of metal in ashes appeared to be mainly determined by the volatility of the element.

Based on the history of selenium pollution in a lake (Lake Macquarie, Australia), the authors observed major selenium contamination in the last 30 years, due to a fly ash dam associated with nearby electric power generation plants (Peters et al., 1999). Changing redox condition in lake sediments resulted in a release of selenium under oxidizing conditions and immobilization under reducing conditions. The sediment-bound selenium was associated with organic/sulfide fraction under reducing conditions, and, as the redox potential increased, it moved into more exchangeable iron/manganese oxyhydroxide phases.

A USEPA study was conducted between 1975 and 1979 at an abandoned sand pit near Boguszowice, Poland to determine the extent of groundwater deterioration due to coal mine refuse disposal (USEPA, 1983). Groundwater and leachates were monitored and laboratory testing was conducted. Leaching experiments revealed that pollutants may be divided into three groups: most easily leached (chloride, sulfate,

sodium, potassium), medium leachability (copper, zinc, mercury, strontium, cadmium, manganese, molybdenum, cyanide), and slowest leaching (magnesium, aluminum, chromium, arsenic, lead, ammonia, calcium). Colloidal sediments were shown to be flushed from the coal waste. This report concluded that coal refuse disposal in an abandoned open pit in contact with an underlying aquifer deteriorated groundwater quality at the site. The report also pointed out that the level of groundwater contamination depends on the leachability of the wastes, the amount of precipitation, and the self-sealing of the disposal site bottom by the fine clays washed out from the waste. Also, it was observed that significant pollution occurred only in the direction of the greatest declination in the groundwater table. Finally, the report divided coal waste into two subgroups: dry and wet wastes, of which the wet waste has a greater potential for groundwater contamination because of its fine granulation.

Regarding underground coal slurry injection, it is noteworthy that chemical models predict that the high pH associated with coal slurries would prevent acid leaching of toxic metals by precipitation of metal oxides, hydroxides, and carbonates. In addition, underground injection of coal slurry is likely to result in reducing conditions due to consumption of oxygen by chemical reactions and metabolism of heterotrophic microorganisms. Reducing conditions will further contribute to the immobilization of metals by formation of insoluble sulfides.

Coal Slurry Injection Considerations

Very little information is available regarding potential contamination of groundwater by organic compounds from coal slurry. Madsen et al. (1996) investigated

the transport of naphthalene from buried subsurface coal tar and observed a 400-m migration via groundwater to an organic matter-rich seep area. Using laboratory analyses, the authors determined that neither toxicity nor nutrient limitation was the cause of naphthalene persistence. They suggested that oxygen limitation was the most probable cause for lack of naphthalene biodegradation, even though diffusion or sorption reactions might also play a role.

Even though leaching of organic compounds from coal slurry is an understudied phenomenon, evidence is accumulating that sorption of organic chemicals to carbonaceous materials, including coal and kerogen, may exceed absorption in amorphous organic matter by a factor of 10 to 100. Presence of such carbonaceous materials can explain that sorption of organic materials to soils and sediments is up to two orders of magnitude higher than expected on the basis of sorption to organic matter only. Also, higher sorption of organics on carbonaceous materials may explain low observed biota to sediment accumulation factors and limited potential for microbial degradation (Cornelissen et al., 2005).

Microbiology of Coal-Related Compounds

Bioleaching of toxic metals, such as aluminum and iron from coal fly ash, is known to be mediated by acidophile bacteria such as *Thiobacillus thiooxidans* (Johnson and Hallberg, 2003). Laboratory-scale studies of the interactions between bacteria, metabolic coal fly ash particles, and metal leaching, Seidel et al. (2001) showed that coal could mitigate metal leaching through the release of alkaline components that

causes a rise in the pH and inhibition of bacterial growth by attachment of the cells to both sulfur particles and coal ash particles.

Bacteria isolated from selenium-contaminated Lake Macquarie, Australia sediment were able to transform selenite to elemental selenium. While most isolates grew on media containing selenate, no elemental selenium was formed from this species (Peters et al., 1999).

Prokaryotes, including bacteria and archaea, are known to play potentially important roles on the chemistry of coal and coal refuse (Faison, 1991). Heterotrophic aerobic microbes are expected to use abundant organic material as electron donors, which results in oxygen depletion and anoxic conditions. In the absence of oxygen, heterotrophic anaerobes use alternate electron acceptors, such as sulfate, which generate toxic sulfides (Stoner et al., 1993).

The overall effect of microbial activity on underground coal slurry injection is unpredictable in the absence of comprehensive, specific investigation. Some beneficial effects can be considered, including immobilization, sequestration, and biodegradation of toxic organic contaminants (Fakoussa and Hofrichter, 1999; Filcheva et al., 2000).

It has been shown that various hydrocarbons are efficiently degraded under anaerobic conditions by bacteria using a variety of electron acceptors (Foght, 2008). Aromatic hydrocarbons enter the environment through various human activities, including crude oil spillage, fossil fuel combustion, and coal mining and coal refuse dumping. Aromatics (such as benzene and toluene), PAHs (such as naphthalene and pyrenes), and numerous alkyl-substituted isomers impact both aerobic and anaerobic environments such as aquifers, freshwater bodies, soils, and sediments. It has been

recently observed that anaerobic biodegradation of aromatic and saturated hydrocarbons is a widespread activity that can occur under nitrate-, iron-, manganese- and sulfate-reducing, and methanogenic conditions.

Using fluorescent in situ hybridization (FISH), Bakermans and Madsen (2002) detected intracellular messenger ribonucleic acid (mRNA) coding for naphthalene dioxygenase, a key enzyme involved in bacterial biodegradation of naphthalene, in coal tar waste-contaminated groundwater. This study suggests the presence of the potential for naphthalene biodegradation in coal contaminated environments.

Summary

Because specific documentation about potential or reported health effects resulting specifically from underground coal slurry injection is scarce, information about coal-related products and activities, coal mining, and other mining activities have been included in the review. Extension of environmental and health effects reported below about coal and/or mining activities to the specific cases of underground coal slurry injection must be pursued with caution since potential leaching mechanisms and environmental and human exposure routes may be different.

Toxic Components of Coal, Coal Refuse, and Coal Combustion Products

Coal slurry typically consists primarily of coal fines, containing elemental carbon, hydrocarbons, complex organic compounds, sulfur, silica, iron oxide, calcium oxide, sodium, and traces of metals (Landsberger et al., 1995; Hower et al., 1996). Toxicities of coal slurry potentially arise from coal components, such as PAHs and salts of heavy metals (Griest et al., 1982; Liu et al., 2000; Manerikar et al., 2008), and from coal

processing chemicals, such as acrylamide which was used as a monomer historically in coal processing. This process has changed. Today, acrylamide can be present in trace amounts from mining activities and also from traces of acrylamide monomer present in the quantities of partially polymerized polyacrylamides now used in coal cleaning (ATSDR, 2006).

Available literature strongly suggests that the likeliest environmental and health concerns of coal slurry injection will be related to heavy metals that have the potential to migrate into nearby aquifers and potentially contaminate water supplies and private wells. According to the National Research Council, the elements of greatest concern in coal are arsenic, boron, cadmium, mercury, molybdenum, lead, and selenium as (NRC, 1980).

Toxicity and Environmental Impact of Coal and Coal-Related Compounds

It is widely recognized that the intensive coal mining in the Appalachian region for more than 200 years has led to extensive surface and groundwater contamination (USGS, 2006). This background of contamination makes it very difficult to isolate the specific impact of underground coal slurry injection on the environment and human health. For instance, coal mining activities are known to generate AMD, an acidic water containing high levels of sulfate and metals that contaminates many streams in West Virginia and Pennsylvania (USGS, 2000). Analysis of VOCs in the northern Appalachian coal region show that toxic chemicals, such as benzene, toluene, ethylbenzene, and xylene (BTEX), halogenated compounds, and tetrahydrofuran, were detected in mined

areas. However, there is no evidence that these observations are specifically related to underground coal slurry injection.

Analyses of hot water tank water from homes in an area contaminated by coal slurry following impoundment failure (Martin County, Kentucky, 2000) showed that water samples taken from both impacted and reference areas often exceeded USEPA drinking water guidelines for several metals, including arsenic, cadmium, chromium, copper, iron, manganese, and lead. Analysis of well water quality in the vicinity of the Sprouse Creek Slurry Impoundment showed that primary drinking water standards were exceeded for lead, arsenic, barium, beryllium, and selenium and secondary drinking water standards were exceeded for iron, manganese, aluminum, and zinc (Stout and Papillo, 2004).

Many reports focus on the environmental impact of coal combustion residues. Although they are not coal slurry *per se*, coal combustion residues potentially contain chemicals that are found in coal slurries (Elmogazi et al., 1988). Generally speaking, release of combustion residues of coal into the aquatic environment has resulted in deleterious effects, such as the accumulation of toxic metals in aquatic organisms (Rowe et al., 2002; Gupta et al., 2002; Reijnders, 2005).

A previously mentioned USEPA report included data on Class V underground injection wells. It intended to evaluate the risk posed to underground sources of drinking water (USEPA, 1999) and is of special interest to this study. A distinct section specifically dedicated to the injection of “coal-cleaning waste” is particularly relevant. The report cites the example of two mines injected with coal slurry: New Elk Mine (Colorado) with coal slurry exceeding drinking water standards for arsenic and total

suspended solids (TDS), and Kindall mine (Indiana) with coal slurry and slurry leachate exceeding drinking water standards for arsenic, cadmium, lead, TDS, sulfate, and manganese. However, the report indicates that no incidents of contamination of a drinking water supply have been documented that are directly attributable to injection into mine backfill wells.

Transport and Mobility of Coal-Associated Contaminants

Evidence of toxic metal leaching has been obtained from the study of impoundments used for coal fly ash storage. For instance, it was estimated that at pH 7.0, a significant fraction of toxic elements, such as chromium, mercury, and arsenic, are leachable and may contaminate groundwater (Wasay, 1992). A previously mentioned USEPA study conducted at an abandoned sand pit used for coal mine refuse disposal (in Poland) concluded that contaminants susceptible to be leached may be divided into three groups: most easily leached (e.g., sulfate, sodium), medium leachability (e.g., copper, zinc, mercury, cadmium, manganese), and slowest leaching (e.g., aluminum, chromium, arsenic, lead). It is uncertain to what degree these data are reliably useful in practice, as there were insufficient measures to provide proof of principle.

Analysis of Phase I Data

Introduction

In order to assess the potential impact of underground coal slurry injection on the environment and human health, Phase I of this investigation conducted quantitative analyses of chemicals present in coal slurries collected at six different locations. The

selection of the sampling sites was made by consensus of the SCR-15 study team with input from citizens and environmental groups concerned about the coal slurry issue.

Southern Minerals

Southern Minerals, located in McDowell County, is the oldest active injection site in the state of West Virginia. There are two large public water supplies near the site that could be potentially affected by the coal slurry injection points.

Loadout

Loadout, LLC in Boone County was selected because it is the only site in the State where no other mining activity occurred in the watershed prior to slurry injection. That means a major part of the watershed was unaffected by mining and, therefore, this site provides potentially useful data to infer a baseline comparison.

Panther

Panther, LLC located in Kanawha County, was chosen regarding the water quality concerns brought by environmental groups and residents of the area.

Power Mountain

Power Mountain, located in Nicholas County, was chosen because, after Southern Minerals, it is the oldest slurry injection point, being the most disturbed by mining activity. In addition, water quality problems in wells located near this injection point have been reported.

Two additional slurry sites were selected in order to have a broader set of locations that allow evaluating the variability of slurry composition only.

Coresco

Coresco, Inc., located in Monongalia County, was selected to assess the variability of slurry in the State. However, Coresco is the only plant in the State of West Virginia that does not use chemicals in coal processing. It is unique.

Marfork

Another slurry composition-only site, Marfork, is located in Raleigh County, and does actually not use slurry injection.

Determining the public health and environmental impacts of coal slurry requires information about the constituents in coal slurry which can potentially be released into the environment. Analysis of the liquid phase of the slurry and leachate was performed in order to provide information about the chemical composition of coal slurry.

Samples of coal slurry and run-of-mine coal were collected at sites where injection activities occurred and were analyzed for a suite of organic and inorganic constituents. The liquid phase of the sample was separated at the lab through settling the solids and decanting the liquid. The solid and liquid portions (phases) of the slurry were then analyzed separately. To further understand the composition of the slurry, a solid coal and simulated coal leachate were also analyzed.

A total of 177 different parameters were analyzed for each sample (see Table 3). These parameters were grouped into five different categories including *metals* (e.g., aluminum, arsenic, chromium, selenium), *general chemistry* (e.g., nitrogen, fluoride, alkalinity, pH), *volatile organic compounds* (e.g., acetone, benzene, xylene), *semi-volatile organic compounds* (e.g., naphthalene, phenol), and *miscellaneous* (e.g.,

acrylamide, cyanide, bacteria). Complete results of the analysis performed during Phase I of this investigation are presented in Appendix-O of the Phase I report (WVDHHR, 2009).

Relationship of Well Water, Surface Water, and Supply Water Chemicals to Groundwater Content

Reasonable estimation of the extent to which groundwater, surface water, and supply water are impacted by nearby leaching wastes is limited by many factors. These include migration potential of contaminants, hydrogeology of the site, and reactivity or biodegradation of contaminants. In addition, this situation is further complicated by the fact that it is virtually impossible to isolate contaminants leaching from underground coal slurry from specific indigenous soil, background, and other contaminants coming from other sources in areas heavily impacted by coal mining activities.

In this investigation, we chose to adopt the most conservative approach with respect to health protection. Contaminants of concern (substances selected for consideration) were selected based on the hypothesis that concentrations measured in the liquid phase of coal slurry samples of the different sites under study could potentially result in equal, but not higher, concentrations in soil, stream water, and drinking water, through the contamination of private wells and water supplies.

Selection of Chemicals to be Reviewed

The first step in the assessment of human health risk is the selection of chemicals to be reviewed. This process compares data from the sites under study to relevant media-specific environmental guideline comparison values (CVs). CVs have

been established on the basis of an evaluation of toxicology literature for a given substance and they are used as screening tools. The comparison values used for this investigation were obtained from the USEPA and the ATSDR.

Exposure to a chemical below its corresponding CV indicates that adverse health effects are unlikely based on current knowledge (historic trends suggest we may raise or far more often lower safe thresholds as mechanisms of toxicity are newly understood). Many safety factors are included in the derivation of these values; they are designed to be conservative (i.e., protective of public health), although the historic trend toward lower thresholds provides a perspective on the limits of our understanding at any time. Chemicals found at a concentration above a CV are considered chemicals to be reviewed. However, exposure to chemicals above a CV *does not necessarily mean* that an adverse health effect will result. Exposure above a CV simply indicates *a need for further evaluation* to determine if the exposure *could have caused* adverse health effects at this site (ATSDR, 2009a). Furthermore, in the absence of historical data, Phase II researchers are discussing the potential for an exposure above a threshold. It is unknown with certainty that such exposure has occurred. Under working assumptions, modeling indicates that it can.

When more than one CV was available for one chemical, it was considered as contaminant of concern if its concentration exceeded at least one of the CVs. Some chemicals have both carcinogenic and non-carcinogenic CVs. For chemicals with both carcinogenic and non-carcinogenic CVs, the most conservative CV (i.e., the lowest) is selected.

Concentrations of different contaminants in samples collected at coal and coal slurry-contaminated sites during Phase I of this investigation were compared to different CVs. Results are presented in Table 4. For all contaminants analyzed in the liquid phase of coal slurry in Phase I of this investigation, Table 4 presents the concentrations determined in each sample (if detected), the corresponding environmental and health guidelines developed by ATSDR and/or USEPA, and whether the contaminant belongs to the 2007 Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) priority list of hazardous substances (<http://www.atsdr.cdc.gov/cercla/07list.html>). Chemicals found at concentrations above a CV (i.e., chemical of concern) are highlighted in bold italics.

According to the comparison presented in Table 4, the metals that are of environmental concern for the different sites include: aluminum, antimony, arsenic, iron, lead, and manganese. Note that all of these except manganese were predicted from the literature review concerning coal waste more generally. However, that list also predicted metals such as cadmium and strontium, which do not appear here. In the category of general chemistry, it was found that nitrogen (nitrite), chloride, fluoride, sulfate, TDS, and pH are of environmental concern. These were all predicted in the literature search. Although most volatile or semi-volatile organic compounds were not detected during Phase I analyses, concentrations determined for a few of them were found to be below the environmental guideline values. The following VOCs were detected: 2-butanone, acetone, acrolein, benzene, *m,p*-xylene, methylene chloride, *o*-xylene, and toluene. The following semi-volatile compounds were detected: *bis*(2-ethylhexyl)phthalate, naphthalene, and phenanthrene. All organics detected are listed as CERCLA list of

priority pollutants. However, their detected concentrations are below the environmental and health guidelines so they are not considered in this study as contaminants of concern.

Environmental guideline CVs used in this screening are the following (USEPA, 2006; USEPA, 2009):

- ***Drinking Water Equivalent Level (DWEL)***: A lifetime exposure concentration protective of adverse, non-cancer health effects that assumes that all of the exposure to a contaminant is from drinking water.
- ***Health Advisory (HA)***: An estimate of acceptable drinking water levels for a chemical substance based on health effects information; a Health Advisory is not a legally enforceable Federal standard, but serves as technical guidance to assist Federal, State, and local officials.
 - ***One-Day HA***: The concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for up to one day of exposure. The One-Day HA is normally designed to protect a 10-kg child consuming 1 liter of water per day.
 - ***Ten-day HA***: The concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for up to ten days of exposure. The Ten-Day HA is also normally designed to protect a 10-kg child consuming 1 liter of water per day.
 - ***Lifetime HA***: The concentration of a chemical in drinking water that is not expected to cause any adverse non-carcinogenic effects for a lifetime of exposure. The Lifetime HA is based on exposure of a 70-kg adult consuming

2 liters of water per day. The Lifetime HA for Group C carcinogens includes an adjustment for possible carcinogenicity.

- ***10⁻⁴ Cancer Risk:*** The concentration of a chemical in drinking water corresponding to an excess estimated lifetime cancer risk of 1 in 10,000.
- ***Maximum Concentration Limits (MCLs):*** The highest level of a contaminant that is allowed in drinking water. MCLs are set as close to the MCLG (Maximum Concentration Limits Goal) as feasible using the best available analytical and treatment technologies and taking cost into consideration. MCLs are enforceable standards.
- ***Secondary Drinking Water Regulations (SDWR):*** Non-enforceable Federal (USEPA) guidelines regarding corrosion control and cosmetic effects (such as tooth discoloration) or aesthetic effects (such as taste, odor, or color) of drinking water. While the regulatory intent of SDWR is non-health and non-enforceable, it should be noted that measures of potential health concern are covered, including manganese, sulfate, and TDS.

Exposure Pathway Analysis in Human Risk Assessment

An exposure pathway consists of five parts:

1. A source of contamination (in the context of a coal slurry risk assessment, this includes the potential toxins in the coal slurry).
2. The “medium” of exposure, including the movement of the contaminant(s) into and through the environment (in soil, air, groundwater or surface water, and onto land) to bring it into contact with people.

3. A point of exposure, or a place where humans could be exposed to the contaminant(s).
4. A way for humans to be exposed to the contaminant(s) (such as by drinking contaminated water or breathing contaminated air).
5. A receptor population or one or more people who may have been or may be in contact with the contaminant(s).

Exposure pathways are considered complete when all five of these elements existed, in series, at some point in the past, exist in the present, or are predictably *likely* to occur in the future. Exposure pathways are considered potential when one or more of the elements is missing or uncertain but could have existed in the past, could be occurring now, or could exist in the future. Pathways are considered eliminated when one or more of these five items does not exist or where conditions make exposures highly unlikely. A completed pathway means that people have been exposed to chemicals. However, the existence of a completed pathway *does not necessarily mean that a public health hazard existed* in the past, exists currently, or is likely to exist in the future. Chemicals found in the completed pathways are evaluated to determine whether adverse health effects could have occurred in the past, are occurring in the present, or could occur in the future (ATSDR, 2009b).

A limitation with this kind of analysis is that it is done once, and designed to evaluate future risk in terms of probabilities. Scientists want and citizens deserve long-term assurances; risk assessments address recent historic measurements and attempt to make reasonable projections based on these. Experts are required to make reasonable projections and, therefore, reject unlikely possibilities. Yet, over long time

periods, some unlikely events will also happen, although it is nearly impossible to predict which unlikely events will occur. Changes in environmental conditions and population activities are also partly unpredictable over long time periods (ATSDR, 2009b).

Chemicals can enter the body in three ways:

- The chemicals can be ingested, either in food or drinking water, and using the water for cooking. Small amounts of contaminants encountered through normal hand-to-mouth activities are known as incidental ingestion.
- The chemicals can enter the body through the skin. This is called dermal exposure. The skin presents an important barrier to metals in most (but not all) of their forms.
- The chemicals can enter the body by breathing air containing chemicals or particles that are small enough to get into the part of the lung where they can be absorbed. This is called inhalation.

Identification of Completed Pathways

Ingestion of and Dermal Exposure to Chemicals in Water – Completed Pathways for the Past, Present, and Future

Metals and elements found in groundwater, well water, supply water, and surface water at the vicinity of slurry injection sites may be naturally occurring or may be related to past coal mining activities. Metals and elements in home supply water may also result from the corrosion of metal objects, such as the metal well casing, water pumps, hot water tanks and their anodes, fittings, and valves, and water pipes in contact with the water. These metals and elements may be either dissolved in the water, found as small

particles in the water, or may be attached to small particles in the water such as clay or sand (silica). People who use this water can come in contact with these chemicals when the water is ingested, when food is eaten that has absorbed chemicals from this water, or by incidental ingestion. The drinking water pathway is considered for the well water and water supply only. Although the chemicals reported in the Phase I report do not readily pass through the skin into the body, the dermal pathway is also evaluated for chemicals that can pass through the skin barrier or cause skin disease by direct contact (ATSDR, 2005; ATSDR, 2006).

Chemicals from the sampling sites could move into the groundwater and soil through leaching or through vaporization. Contaminants could be ingested if present in the drinking water or, from small amounts of ingestion of locally contaminated soil. Contaminants could be inhaled if the chemicals vaporize, i.e., easily move into the air from contaminated water or soil or are aerosolized in the home (showering activity). Contaminants on the skin (dermal contact) could occur by contact with contaminated water or soil.

For the present investigation, the different elements of exposure are identified as follows:

- **Source of contamination:** The sources of the contamination are the potential toxins identified in coal slurry injected underground, including coal products (metals and hydrocarbons), overburden materials in the slurry, and coal cleaning agents.
- **Release mechanism into water, soil, air, food chain (biota) or transfer between media:** Release mechanisms involve leakage from the site of storage,

including the mine pool and anywhere else injected slurry may travel, into groundwater, into surface water, and soil contamination. Transfer mechanics involve migration in the ground with groundwater flow, possibly contacting drinking water and surface water.

- **Exposure points or areas:** Exposure points involve drinking water wells, residential yards, recreational waters, streams, and privately or publicly owned community water supplies.
- **Exposure route:** Exposure routes include ingestion through drinking water, consuming foods from private yards or affected farms, as well as incidental ingestion of a diverse nature (e.g., children playing and gardening at any age), dermal contact with drinking water, stream water, and the soil, and the potential for inhalation in homes (for example, during showering/bathing).
- **Potentially exposed population:** The exposed population involves local residents and those employed at local businesses or attending local schools, the population served by a potentially contaminated water supply, as well as the population in contact with stream and surface water downstream points of contamination.

Summary

During Phase I of this investigation, chemical analyses were conducted on samples collected at six different sites in West Virginia where coal slurry has been injected underground. Samples of coal slurry and run-of-mine coal were collected and analyzed for a suite of organic and inorganic constituents (177 different parameters).

The phase I investigation did not measure and was not designed to measure the entrance of coal slurry into drinking water. At 4 sites, over a limited time period, it did not show a likely direct hazard.

Relationship of Well Water, Surface Water, and Supply Water Chemicals to Groundwater Content

A reasonable estimation of the extent to which groundwater, surface water, and supply water could be impacted by nearby underground injection of coal slurry is determined by numerous physical, chemical, hydrological, geological, and climatic factors. In this investigation, we adopted a conservative approach with respect to health protection: contaminants of concern were selected based on the hypothesis that concentrations measured in the liquid phase of coal slurry from the different sites under study could potentially result in equal, but not higher, concentrations in soil, stream water, and drinking water.

Selection of Chemicals to be Reviewed

The selection of chemicals to be reviewed was based on the comparison of the concentrations detected in the coal and coal slurry samples in Phase I of this investigation with relevant media-specific environmental guideline CVs defined by the USEPA (e.g., MCLs and HAs). Chemicals found at a concentration above one or more CVs were considered as chemicals to be reviewed (ATSDR, 2009a). Based on this analysis, five metals, aluminum, antimony, arsenic, iron, lead, and manganese are considered as contaminants of concern. In the category of general chemistry, nitrogen (nitrite), chloride, fluoride, and sulfate were identified as chemicals to be reviewed. Also,

TDS and pH were detected at levels higher than the CVs. The following volatile and semi-volatile organic compounds were detected: 2-butanone, acetone, acrolein, benzene, *m,p*-xylene, methylene chloride, *o*-xylene, toluene, *bis*(2-ethylhexyl)phthalate, naphthalene, and phenanthrene. Although these organics are listed as CERCLA list of priority pollutants, their concentrations were significantly below the CVs, so they are not considered in this study as contaminants of concern.

Summary of Exposure Pathway Analysis in Human Risk Assessment

A complete exposure pathway requires the five following elements to be present: A source of contamination, a medium of exposure, a point of exposure, a way for humans to be exposed, and a receptor population. Exposure pathways are considered complete when all five of these elements existed, in series, at some point in the past, exist in the present, or are predictably likely to occur in the future. After review of the different elements potentially involved in the pathway of exposure to contaminants in underground coal slurry, the authors of the present investigation conclude that it is reasonable to believe that a complete exposure pathway(s) can/could have existed in theory and may in the future, although measurements did not detect such events in the Phase I report. The reasons why we make this conservative assumption begin below.

Human Exposure Analysis: Chemicals to be Reviewed

Exposure doses are estimates of how much of a chemical may get into a person's body based on the person's actions and habits. Selection of the chemicals in coal slurry to be reviewed for non-carcinogenic effects were based on the comparison to the estimated dose of exposure with health-based CVs, such as ATSDR minimum risk

levels (MRLs) and USEPA reference doses (RfDs). Chemicals for which the estimated exposure doses were below health-based CVs were eliminated from further review. This means that exposures to these chemicals at these levels are not expected to result in adverse health effects. In the present study, the exposure doses were calculated based on the concentrations of contaminants in the samples analyzed in Phase I of the investigation and reasonable hypotheses regarding body weight and ingestion of drinking water in worst case scenarios as previously described. The selection of a chemical of concern in this type of conservative approach does not mean that we know it to be a health hazard from coal slurry injection. Instead, it means that we thought it prudent to make worst case assumptions in the absence of data, and we included chemicals which might exceed a threshold in the worst case. The following chemicals were found to have exposure doses equal to or exceeding health guidelines CVs for children: antimony, arsenic, cadmium, chromium, molybdenum, silicon, sodium, strontium, nitrite, and fluoride. The following chemicals were found to have exposure doses equal to or exceeding health guidelines CVs for adults: antimony, arsenic, molybdenum, silicon, sodium, strontium, and fluoride.

Estimating Exposure doses

Exposure doses are estimates of how much of a chemical may get into a person's body based on one's actions and habits. The calculations rely on assumptions that identify how much, how often, and how long a person may be exposed to chemicals in the water, as well as environmental sample data that accurately reflect the chemical composition of the water. The review of the possible health consequences from

chemical exposures examined estimated exposure doses from both ingestion and dermal exposures.

Selection of Chemicals to be Reviewed for Non-Carcinogenic Effects

Health-based CVs, such as ATSDR MRLs and USEPA RfDs, are calculated concentrations of a toxin, in specific media (such as water), designed to be protective of public health. Where estimated exposure doses are below these health-based CVs, the chemical of concern is eliminated from further review in risk assessment (ATSDR, 2004). This means that exposures to these chemicals at these levels are not expected to result in adverse health effects. Chemicals to be reviewed for which estimated exposure doses are over the health-based CVs, or for which no health-based CV had been established, are selected for further review.

The review for possible adverse health effects is accomplished by comparing the estimated exposure doses for these chemicals to research such as that outlined in the ATSDR toxicological profiles (<http://www.atsdr.cdc.gov/toxpro2.html>). An exposure dose where no effects are observed is known as the no-observed-adverse effect level (NOAEL). The lowest exposure dose where an adverse health effect is observed is called the lowest-observed-adverse effect level (LOAEL).

Selection of Chemicals to be Reviewed for Carcinogenic Effects

Theoretical cancer risks are calculated on the basis of current environmental data. Cancers can develop over many years. Exposures for each age group are averaged over a 70-year lifetime. The estimates obtained for each age group are added together. This gives a theoretical excess cancer risk for a person who is exposed to the

chemical over the total exposure time noted in the exposure frequency assumptions. This number is multiplied by the cancer slope factor (CSF). The theoretical excess cancer risks obtained using this method are only estimates of risk because of the uncertainties and conservative assumptions made in calculating the CSFs. The actual risk of cancer is probably lower than the calculated number. The true risk is unknown and could be as low as zero. However, the method assumes no safe level for exposure to a carcinogen. Lastly, the method computes the 95% upper bound for the risk, rather than the average risk. Therefore, the risk of cancer is likely actually lower than the conservative computation, perhaps by several orders of magnitude. One order of magnitude is 10 times greater or lower than the original number, two orders of magnitude are 100 times, and three orders are 1,000 times. In the Phase I report, West Virginia Department of Health and Human Resources (WVDHHR) ranked the theoretical excess cancer risks using the following criteria. Theoretical cancer risks less than 1 in 10,000 were considered very low risk and are not discussed in the text. Theoretical cancer risks between 1 and 9.9 in 10,000 were classified as a low risk, 10 and 99 as a moderate risk, and greater than 99 in 10,000 as a significant risk (ATSDR, 2006). A weakness of this approach is the tendency to have better data for well-recorded outcomes such as cancer that permit a robust assessment. Developmental, neurotoxic, and immunologic outcomes provide examples of chronic conditions whose severity is less likely to be based on yes/no considerations of cancer histopathology (“less binary”) and whose recording and the related geographic context are far less robust for risk-assessment purposes. These health outcomes can be equally as important as cancer.

They can pertain to some of the chemicals to be reviewed listed above. However, the methodology for consideration is less well developed.

In the present study, the exposure doses were calculated based on the concentrations of contaminants in the samples analyzed in Phase I of the investigation. Results are presented in Tables 4 and 5. For all contaminants in the samples analyzed in Phase I of this investigation (if detected), Tables 4 and 5 present the calculated exposure doses, the corresponding health guideline CVs developed by ATSDR. Chemicals for which calculated exposure doses equal or exceed at least one health guideline CV are highlighted in bold italics. Table 5 shows the estimates of the exposure doses calculated for a child. The following chemicals were found to have exposure doses equal to or exceeding health guidelines CVs for children: Antimony, arsenic, cadmium, chromium, molybdenum, silicon, sodium, strontium, nitrite, and fluoride. It should be noted that, with the exception of chromium and sodium, these appeared as possibilities based upon the literature review of coal and coal-related waste. Some predicted chemicals, such as lead, also appeared in the literature review but not in Phase I CVs above thresholds. Table 6 shows the estimates of the exposure doses calculated for an adult. The following chemicals were found to have exposure doses equal to or exceeding health guidelines CVs for adults: Antimony, arsenic, molybdenum, silicon, sodium, strontium, and fluoride.

The calculation of estimated exposure doses noted in Tables 4 and 5 and in the section below assumes that a child weighs 10 kilograms (kg) (about 22 lb) and drinks 1 liter of water a day (about 1 quart). The calculation assumes that an adult weighs 70 kg (about 154 lb) and drinks 2 liters of water a day (about 2 quarts). The calculation

assumed that exposure to the chemical occurred every day (meaning that the exposure factor was 1). The estimated exposure dose, in milligrams per kilogram per day (mg/kg/day), is calculated by multiplying the maximum concentration of the contaminant detected (in milligrams per liter) by the amount of water ingested in a day (in liters) divided by the body weight (in kilograms).

In the present investigation, the estimated exposure doses were compared to the following health guidelines (ATSDR and USEPA):

- **Minimal Risk Levels (MRLs):** MRLs are an estimate of the daily human exposure to a substance that is likely to be without appreciable risk of adverse health effects during a specified duration of exposure.
- **Chronic Reference Dose (RfD):** An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily oral exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime.

The Precautionary Principle in the Context of Underground Injection of Coal Slurry

When environmental exposure and health outcome concerns arise that are difficult to interpret because of uncertainty about either the exposures or the health outcomes, one frequently refers to the *precautionary principle*. Two questions that risk assessment raises in general and this report raises in relationship to coal slurry injection are: (1) Does the precautionary principle apply in the context of underground injection of coal slurry; and (2) If so, what does this principle imply in terms of environmental risk assessment, public policy, and, ultimately, coal slurry disposal practice? It should be

noted that the precautionary principle is a human response to absence of data or to theoretical reasons for concern. It is based on absence of knowledge about safety, rather than on presence of certain knowledge about hazard.

First, what is the precautionary principle? In 2005, the United Nations Educational, Scientific and Cultural Organization (UNESCO) and the World Commission on the Ethics of Scientific Knowledge and Technology (COMEST) brought together an expert group that developed a working definition of the precautionary principle (Dolan and Rowley, 2009): *When human activities may lead to morally unacceptable harm that is scientifically plausible but uncertain, actions shall be taken to avoid or diminish that harm.* This definition also clarifies the elements of harm, uncertainty, and proportionate responses. The COMEST concludes that "the grounds for concern that can trigger the precautionary principle need to be plausible or tenable and that the scientific uncertainty should be considerable." Finally, the COMEST also states that the precautionary principle is not based on *zero risks* but aims to achieve lower or more acceptable risks or hazards.

In the context of coal slurry, this implies that scientific evidence must be provided that potential, although uncertain, environmental and/or health hazard *may* occur following underground injection of coal slurry. The evidence collected through Phase I of this investigation, as well as data from extensive literature review, leads to the following published-literature and data summary:

- 1) Coal and coal waste, including coal slurry, contains significant levels of toxic chemicals, notably heavy metals and also aromatic hydrocarbons.

- 2) These contaminants have the potential to leach and contaminate groundwater to various extents that depend on the nature of the contaminant and the site conditions. One Federal reference to such historic leaching does exist, specifically related to coal slurry injection.
- 3) Contaminated groundwater can impact surface water and reach private wells and water supplies, thereby threatening the environment and human health, even though the complexity of groundwater hydrogeology often makes such predictions very difficult.
- 4) There is no reported peer-review-level evidence that underground injection of coal slurry has resulted directly in adverse effect on human health, although a large degree of uncertainty exists.

In addition, several publications from USEPA and the U.S. Geological Survey (USGS) report the negative impact of coal mining and coal waste disposal on wildlife and the quality of surface and groundwater. Although there is limited to no information currently available about the actual harmful effects of underground injection of coal slurry on the environment and human health, there is certainly the *potential* for such effects to occur. Considering the clear existence of a gap in available data and the complexity of the problem, the authors of the present report consider that a large uncertainty exists about the impact of underground injection of coal slurry on the environment and human health.

In this setting, in which data gaps are known to be more prominent than available data, risk assessments generally lead to the following types of recommendations:

- 1) Further environmental and health risk assessment investigations should be conducted. In the specific setting of coal slurry injection, this includes hydrogeological site studies with further routine monitoring so that proof of principle, that coal slurry injection does not harm surface or drinking water, is established over time by actual measurements rather than by a single limited study.
- 2) For coal slurry in general, it also applies further chemical characterization and toxicology testing as a complex mixture with high potential to affect populations.
- 3) Awaiting further scientific evidence about the potential effects of underground injection of coal slurry on the environment and human health, regulatory and technical means should be used in order to characterize, and minimize any effects on the environment, as well as establish proof of principle that the practice works as well over time as individual measurements in limited circumstances may indicate.

Coal Slurry Chemical Risk Assessment

Introduction

The purpose of reviewing is to consider the toxicity of elements, chemicals, or mixtures which are reasonable to consider as chemicals to be reviewed following coal slurry injection. Some assumptions are inevitable when this kind of work is done. One assumption made is about the route of exposure, especially for elements and their salts. For example, coal slurry may contain significant quantities of selenium. In turn, that selenium can exist in many forms, but only some of those forms are relevant. For

example, very extreme heating of a concentrated specimen could, in theory, create selenium dioxide, a potent respiratory irritant. However, unless there is a likely episode of extreme heating leading to a specific selenium species which would then have an important toxicity following a likely respiratory route of exposure, then the authors have generally not included respiratory toxicity for an element species such as selenium. That is because the significant route of exposure, outside of certain workplaces, is oral. The respiratory hazards are highly unlikely to arise from current or foreseeable coal slurry injection practices. The consideration of selenium exposures is limited to forms and routes of exposure that may come from coal slurry, such as contamination of potable water, or crops affected by contaminated water. (Contaminated potable water may create routes of inhalation from showering; that would not be an important consideration for selenium whereas it might be for a volatile organic solvent. The difference is the degree of heating required. Furthermore, the available data implicate metals rather than solvents as chemicals to be reviewed. If solvents were chemicals to be reviewed in this analysis, then consideration of inhalation through hot water and showering/bathing would be more important.) The strengths and weaknesses of assumptions that underlie the risk assessment process are recapitulated with each substance examined.

Metals and Non-Metallic Elements Adjacent to Coal Soils: A Problem of Tracking Sources

Metals adjacent to coal soils have already been discussed. Mining, and especially abandoned mines, present the opportunity for long-term exposure of surface and groundwater to oxidizing surfaces; metal oxides available to enter human drinking water supplies may increase dramatically when mines are abandoned. Also discussed

is that the burden of pollution from soils, or from abandoned mines, cannot be easily distinguished from the same types of burden that come from coal slurry once injected into an abandoned mine. It is possible to instrument sites scientifically, and to record the mining practices and measure the pollutants in adjacent surface and groundwaters over time. Even then, conclusions about original sources of pollution may still be inferences, in part, because mine pool water is in contact with multiple sources.

There are no existing designed studies which specifically address human health in the context of coal slurry or coal slurry injection.

Based on measures and models, chemicals to be reviewed are reviewed with reference to potential health effects. It is important to understand the meaning and limitations of this exercise.

1. The designation of a chemical of concern does not mean that the existing data show with certainty that a health hazard exists. Instead, the modeled data indicate the potential for a hazard.
2. The brief reviews here are, in many cases, of the substances with the lowest tolerances and, therefore, most likely to be considered in a public health context if an additional burden is created.
3. If a chemical which can be in coal slurry is not designated as a chemical of concern, this does not rule out some unpredictable occurrence of a health hazard. It means that such occurrence is not likely or predicted.
4. The chemicals to be reviewed are briefly reviewed for reader convenience. These reviews are not meant to be complete. ATSDR complete reviews of individual chemicals are book-length efforts and are available online. The

extensive literature on these substances is continuously updated. Those needing the latest data are referred to ATSDR reviews and the subsequent, extensive literature which is available in abstract form with links at National Library of Medicine.

Contaminants to be considered are aluminum, antimony, arsenic, cadmium, chloride, chromium, fluoride, lead, manganese, molybdenum, nitrite, selenium, sulfate, silicon, sodium as sodium chloride, and strontium, listed alphabetically. An indicator of water quality, total dissolved solids (TDS), while not a contaminant of concern, is also a topic for consideration. Among the contaminants of concern, aluminum, arsenic, iron, lead, manganese, selenium, and sulfate are most likely to occur in slurry water. Arsenic, cadmium, lead, and mercury, are considerably more toxic than others considered, and the toxicologic knowledge involving ingested manganese is the least understood and most uncertain.

Aluminum

To be completed

Antimony

Antimony is a metal used in some specialty metal alloys. It can be found in trace quantities associated with coal or coal overburden. (For this reason, coal-fired power plants are a source of antimony in the air and soil.) Most surface waters contain less than 5 ppb antimony. Foods also contain only trace amounts of antimony. Outside of workplace exposures, or medical uses, antimony toxicity is rare.

Because workplace exposures have been most relevant, the human toxicology literature concerning environmental (nonmedical) antimony is documented by inhalation studies, particularly early studies of pneumoconiosis and reproductive loss in women exposed by inhalation at work. The acute effects of an unusual toxin group, stibenes, are not relevant to risk assessments of water or soil pollution.

Antimony is not known to be essential for human nutrition, but antimony compounds have been used in health care, notably and at present for the treatment of schistosomiasis and leishmaniasis.

Health Effects

Oral exposure to antimony is most commonly to antimony oxides (such as antimony trioxide) or to organic antimony. Based on animal studies, less than 10% of an oral dose is believed to be absorbed. Animal studies indicate that antimony is then taken up in red blood cells and distributed to a number of tissues, including liver, kidney, bone, lung, and skin. Antimony is excreted in urine and feces. In acute overdoses, such as accidental or intentional mixture to drinks containing 0.5 mg/Kg, adult males vomited. This reaction is consistent with animal toxicology studies. (ATSDR, 1992). Studies of chronic effects of exposure to compounds which may appear in water have been conducted in water-contamination episodes. Important outcomes are not reported.

Health effects are found at higher exposures, characteristic of medical treatments, including changes in cardiac conduction, myocardial damage, anemia, vomiting, diarrhea, and muscle pain.

Exposure Limits

Possibly because toxicity is rare at environmental doses, MRLs have not been developed for antimony. Scant information is available about the use of antimony in urine as a biomarker following oral exposures.

Arsenic

Arsenic is a “metalloid” element (it has some properties of metals) which is most commonly found in the environment as an oxide, chloride, or sulfur-containing compound (inorganic arsenic). Arsenic compounds occur naturally in rocks and may be found in coal overburden. Many arsenic compounds are soluble in water. Thus arsenic may move through the water table or surface water into drinking water and croplands.

The fate of arsenic in either surface or groundwater is complex. High or low pH, sulfide, iron, and salt content affect the fate of arsenic, and easy predictions are not available for West Virginia’s waters, which may reflect these conditions. Depending on the amount of arsenic in surrounding soils, undisturbed surface water and groundwater generally contain approximately 1 ppb arsenic (>80% of drinking water supplies in the U.S. contain <2 ppb), but can in rare circumstances contain much more. Food is the largest source of arsenic in the normal human diet, especially seafood, and crustaceans such as lobster in particular. In contrast to organic lead or organic mercury, naturally occurring organic arsenics are generally much less harmful to humans than inorganic arsenic compounds. In the food chain, and especially in seafood, arsenic compounds may be combined with carbon atoms (organic arsenic). Most of these compounds are of low toxicity.

Recently developed models suggest that, under “general population” conditions, U.S. citizens ingest about 14 times more total arsenic from food sources than from drinking water, and about twice as much inorganic arsenic from food (Xue et al., 2010). From a human health perspective, the inorganic arsenic comparison is more important, and it does suggest that both contribute, especially where water systems may be contaminated. For most of us, food contributes about twice the biological burden of hazardous species of arsenic than water. For populations at high risk, however, this relationship reverses. Arsenic-poisoned populations, other than workplace populations, are generally poisoned by their water.

Arsenic Health Effects

Arsenic is among the oldest of known poisons. It has also been used as a medicine, yet this use is limited by toxicity. Intentional high dose arsenic poisoning is characterized by vascular collapse followed by death. This presentation is not representative of chronic arsenic exposure, which occurs almost exclusively by ingestion under non-industrial conditions.

Arsenic is not known to be an essential element; it is not required for human existence. Arsenic causes deleterious effects for most human organs. Early clinical effects of chronic ingestion involve hyperkeratinization and hyperpigmentation of the skin. These may appear at chronic exposure levels of 0.002 mg arsenic/Kg/d (presented in relationship to kilograms of human body weight). Such lesions typically appear first on palms and soles, and can resemble corns or warts. Chronic arsenic poisoning from naturally contaminated areas in the Bengal region (northeast India, and especially

Bangladesh) provide substantial data about these manifestations. Graphic pictures of arsenic-related skin changes from inhabitants of contaminated areas can be viewed at PathologyOutlines.com.

Arsenic also affects the vasculature. Like lead, it is a cause of hypertension and alterations in cardiac rhythm. Unlike lead, and at slightly higher exposure levels, it also contributes to peripheral vascular disease. A severe form seen in Taiwan, “black foot disease,” presents with distal limb cyanosis and eventually gangrene. It has been attributed to a combination of arsenic and humic acids in drinking water. Arsenic in drinking water also affects lung function.

Findings of excess diabetes with U.S. population-level increases in arsenic exposure (see, for example, Navas-Acien et al., 2008) have been challenged by reanalysis of the same data, using different assumptions about the significance of organic mercury in urine (Steinmaus et al., 2009; Note; part of the discussion is about which toxin, not about the outcome of toxicity.) Reanalysis by the original authors, over a long time period, controlling for seafood intake, again indicated that population drinking water levels of arsenic are associated with diabetes (Navas-Acien et al., 2009a). The authors pointed out that there was other literature also noting similar associations. An accompanying editorial and the general need for prudence in risk assessment both support the need to consider that arsenic exposures below current regulatory tolerances in drinking water may be associated with small increased risks for diabetes in populations. If the associations are proven to be real and causal, substantial numbers of people are affected.

Arsenic-contaminated drinking water causes symptoms very similar to lead exposures such as gastrointestinal distress, including nausea, vomiting, diarrhea, and abdominal pain. And, also similar to lead, arsenic is an important reproductive toxin causing fetal loss and low birth weight, as well as neurobehavioral decrements in children who were exposed in utero. Also, in common with lead, chronic arsenic exposure can lead to distal symmetrical peripheral neuropathy, and anemia/leukopenia.

A consistent population concern is the carcinogenicity of arsenic. Arsenic contamination of drinking water increases the incidence of cancers of the skin, bladder, liver, kidney and, to a lesser extent, lung. (Lung cancer is also noted in workers exposed by inhalation.) Most of the environmental cancer data comes from population studies in areas of the world where arsenic poisoning is substantial, such as Bangladesh.

An often overlooked aspect of arsenic toxicity is the effect upon the immune system. Possibly, the reason it is not discussed for purposes of standard setting is that the most direct among potential outcomes, frequency and severity of routine infectious diseases, is seldom captured in population studies of chronic diseases. Consistent evidence suggests alterations of in vitro cellular immune function, even at exposure levels consistent with or below the current USEPA standard of 10 ppb. The question arises whether this finding has meaning for whole organisms. Mice, fed a diet which included 100 ppb arsenic in drinking water, experienced much more influenza morbidity than did influenza-infected control mice. Undesirable outcomes included an initially delayed and subdued immune response, followed by a late and destructive chronic

inflammation (Kozul et al., 2009). This represents a small safety factor between health effects in animals and regulation in water.

Arsenic Exposures and Biomonitoring

Except in workforces exposed to arsenic, population exposures are from food and water. Skin contact is irritating, but does not cause absorption. Inhalation occurs in industry and, in rare community events such as when wood treated with chromate copper arsenate (CCA) is burned indoors for heating. The mean population daily exposures, which come almost exclusively from ingestion, are shown in Table 7.

Of the total sources of oral arsenic intake, an estimated 1-20 µg/d is inorganic (inorganic forms of arsenic are more capable of producing harm). Cereals and grain are important natural contributors to the total load of dietary inorganic arsenic.

Typical groundwater contains <2 µg/L in the U.S. Higher natural levels are commonly encountered in some U.S. regions, including western states where 12% of groundwater supplies exceed 20 µg/L. It is unusual for U.S. surface water to contain more than 10 µg/L arsenic, the drinking water standard (DWS). Parts of Taiwan, Chile, and especially West Bengal (India) and Bangladesh may have much higher exposures, with drinking water concentrations exceeding 100 µg/L.

The U.S. DWS is heavily influenced by arsenic's carcinogenicity. The USEPA has calculated a drinking water "unit risk" of $5 \times 10^{-5} (\mu\text{g/L})^{-1}$ based primarily on cancer outcomes. A definition of unit risk is the upper-bound excess lifetime cancer risk of a continuous exposure of 1 µg/L in drinking water (or, for other exposures in which air is the medium exposure, in air). A question for policy makers is whether associations with

vascular response, immune response, and diabetes deserve additional policy considerations.

Acute arsenic toxicity is usually diagnosed in biomonitoring specimens by urine collection, with 50 µg/L in a spot sample or 100 µg in a 24-hour urine sample as common thresholds. For any biomonitoring, avoidance of seafood in the 48 hours before testing is important, or else speciation of arsenic types (with attendant costs and numerous scientific uncertainties) into specific organic and inorganic forms is required.

The most common source of arsenic exposure is seafood. However, this organic arsenic form is relatively harmless and excreted quickly, largely without entering cells or causing cell damage. (This is a contrast to the organic mercury in seafood, which is hazardous.)

For skin pigmentation/keratosis outcomes, the generally cited exposure level is >0.02 mg arsenic/Kg/d. However, associations at lower levels of exposure have been reported, as low as 0.0043 mg arsenic/Kg/d. This lowest-recorded exposure level associated with non-cancer human health effects corresponded to a peak water concentration of 0.115 µg/L.

Absorbed arsenic is rapidly cleared from blood and either excreted via the kidneys or widely distributed to tissues. Biomonitoring of arsenic is an imprecise measure of either current or historic exposure. It can be done, and it does serve limited purposes with measurements of arsenic in nails, hair, urine, or serum/whole blood. Biomonitoring for environmental exposures is best done in population context and very hard to apply to individuals. This limitation does not apply to episodes of intentional poisoning. They are easy to detect at the individual level, provided the test selection is

appropriate and timed to the exposure. Recent seafood meals greatly influence urinary and serum arsenic but the organo-arsenics detected are not generally regarded as very toxic, so arsenic bio-monitoring is more easily performed in populations which do not eat seafood (NRC, 1999).

For non-seafood-eating populations, or those who have recently abstained from eating seafood, blood levels of arsenic range from 0.1 to 0.4 $\mu\text{g}/\text{mL}$; levels in populations exposed to arsenic in water can be an order of magnitude higher (Lauwerys and Hoet, 2001). Arsenic in urine mostly reflects the previous 48 hours of exposure. In U.S. adults who do not consume seafood and who are not selected for occupational exposure, mean urine arsenic excretion is 3 to 4 $\mu\text{g}/\text{L}$ (NRC, 1999). A threshold value of 35 $\mu\text{g}/\text{g}$ creatinine has been used to monitor for excess urinary excretion, signifying excess exposure, in industrial populations at the end of a work week (ACGIH, 2006). A minority of ingested inorganic arsenic is excreted as inorganic arsenic; humans metabolize most inorganic arsenic to organic forms readily but variably from person to person. Thus, population studies may measure inorganic arsenic (arsenite and arsenate), methyl arsenate, dimethyl arsenate, and arsenobetaine (which was principally but not exclusively from seafood) in order to provide a biomarker of arsenic exposure (Navas-Acien et al., 2009c).

Sulfhydryl groups are an important constituent of keratin, which comprises hair and nails. And, sulfhydryl groups bind trivalent inorganic arsenic (and they bind organic arsenic from seafood much less well). Therefore, hair and nails have theoretical advantages for measuring chronic arsenic exposure including the longer growth life of hair and nails, which may permit detection of past exposures and estimation of chronic

doses. However, the technical difficulties of this approach are easy to underestimate, and insufficient skepticism is given to the probable lack of validity and reproducibility of inexpensive tests commonly available from alternative health care providers who routinely measure a variety of metals in hair and nails as part of a “nutritional screen.” In particular, hair measurements will be uninterpretable in parts of the world where coal is burned or metal smelting occurs (Lauwerys and Hoet, 2001).

Researchers looking for a detailed summary of arsenic health effects and risk levels can find them in the ATSDR Toxicological Profile for Arsenic (ATSDR, 2007). Arsenic oral intake guidelines can be found in Table 8.

Barium

Barium is a nonessential (i.e., the human body does not need it) alkaline earth metal element that can be present in coal and in coal overburden. It is a common element in coal slurry in mineral form. The two common subsurface forms of barium, barium sulfate and barium carbonate, do not mix well with water. Therefore, barium typically does not travel as far in contaminated water as do some other elemental pollutants. For the same reason, barium compounds, once present, may persist for a long time in a polluted area. Barium pollution from mining activities can also be present in less common, more soluble forms, such as barium hydroxide or barium sulfide. Thus, sites such as coal slurry impoundments or underground slurry injections can become a source of primarily local barium contamination, especially in immediately adjacent well water.

Coal mining is not the only local source of barium contamination in Appalachian coal bearing regions. Barium compounds are used in the drilling “muds” of oil and natural gas exploration. Barium can enter surface and subsurface water from drilling operations as well.

Barium Exposure

Most uncontaminated surface and public water supplies in the U.S. contain <0.04 ppm barium (average 30 µg/L). While human barium exposures can occur via oral, inhalation, or skin absorption, the predominant route of human population exposure is considered to be oral, and water is the commonly implicated non-medical source. The USEPA drinking water standard is 2 ppm (2.0 mg/L), far above the level of the average water supply, implying a large margin of regulatory safety for most water supplies. Some seafoods and nuts (such as Brazil nuts) are potential dietary sources of barium. However, dietary barium is not generally considered hazardous.

Barium in its most common forms, such as barium sulfate, is generally regarded as low toxicity. In fact, it is sufficiently non-toxic that it can be used in medical diagnostics because it is radio-dense (shows up on x-ray) and poorly absorbed by the gut. While barium sulfate is relatively poorly absorbed and regarded as minimally toxic, the more soluble forms of barium (barium acetate, barium chloride, barium hydroxide, barium nitrate, barium sulfide) are better absorbed and, therefore, more toxic. Barium carbonate, while not very water soluble, is nevertheless soluble in the human gastrointestinal tract and therefore also toxic. The absorbable barium salts can cause gastrointestinal, cardiac, and CNS toxicity, and even death. These health effects are generally associated with very substantial exposures compared to common environmental levels. The lethal oral dose for adults is 2-4 grams (CDC, 2003).

Barium Toxicity

Large quantities of ingested barium can cause hypokalemia (low serum and cellular potassium) and thereby alter nerve conduction, causing acute and potentially fatal cardiac arrhythmias in humans. Large quantities of barium can also cause severe gastrointestinal hemorrhage. Other acute or sub-acute symptoms, at lower but still substantial doses, include abdominal cramping, watery diarrhea, nausea/vomiting, hypotension, numbness (notably, facial numbness), and muscle weakness (ATSDR, 2007). Barium is not classified as a human carcinogen.

There are no study data to confirm or deny the presence of susceptible populations, but it is reasonable to be concerned about cardiac rhythm in those with pre-existing rhythm disturbances, in those already taking drugs which can independently cause hypokalemia, and it is reasonable to think about greater susceptibility to diarrhea in the very young or elderly. And, a likely susceptible population will be those with inflammatory bowel disease, cancer, or other causes of a non-intact gastrointestinal tract. Any source of gut mucosal compromise may increase absorption. Individuals who are already hypokalemic (for example, from diuretic medications) may be more susceptible to arrhythmias following exposure because the drug and the barium may have additive effects.

Animal studies in rodent species also suggest a need to be respectful of possible chronic kidney damage at repeated high-intake doses, as well as other organ changes, including decreased pup birth weight (Dietz et al., 1992) following maternal exposure. There are also some human anecdotal case reports suggesting this possibility of a reproductive hazard (NTP, 1994) from high environmental barium exposures.

An ecologic study of a population consuming barium-contaminated drinking water associate excess cardiovascular disease within a modeled exposure of 0.06-0.3 mg barium/Kg/day (Brenniman and Levy, 1985) among the elderly (\geq age 65). A limitation of ecologic data is that they are generally considered appropriate for creating but not for testing hypotheses about etiology (causation). A human exposure study involving adult males exposed to barium chloride for four weeks did not detect changes in electrocardiogram or in blood pressure (Wones et al., 1990).

Permissible Exposures to Barium

Based on the information that can be gleaned from human case reports, and based on wide variations in the demonstration of end-organ (mostly kidney) damage in laboratory rodents, the assigned MRL is 0.9 mg barium/Kg/day for intermediate-length exposures (15-364 days).

Barium Biomarkers

Barium is present in human blood and excreted in both feces and urine. In parallel with many elements featuring a +2 valence, it is sequestered in bone and teeth. A geometric mean urine value of 1.5 $\mu\text{g/L}$ has been cited (CDC, 2005). Because of its complicated compartment metabolism, biomonitoring, to the degree useful is most useful during or shortly (days to weeks) after exposure.

Cadmium

Cadmium Exposure and Susceptible Exposure Populations

Cadmium is a blue-white corrosion-resistant metal present in soils, including soils adjacent to coal mining activity. Its most prominent current industrial use is in batteries. Cadmium is not an essential element for human nutrition (i.e., cadmium is not known to be needed for human biological activity). In common with arsenic and lead, it is a pure toxin without a known physiologic benefit for humans. When cadmium infiltrates local soil from any source of pollution, a concern is the very efficient rate of soil-to-plant transfer (Franz et al., 2008). In particular, cadmium bioaccumulates in tobacco, the most common source of major exposures in the U.S. It can also accumulate in other crops when there is a soil source. Because a common exposure source is tobacco, a common route of exposure is voluntary inhalation of burning vegetable matter and involuntary exposures of bystanders. Uptake is very efficient via the lungs.

The Provisional Tolerable Weekly Intake (PTWI) established by the World Health Organization (WHO) was set at 400-500 $\mu\text{g}/\text{person}/\text{week}$ two decades ago (WHO, 1989), or about 7 $\mu\text{g}/\text{Kg}/\text{week}$ for a 70Kg adult, yet more for a child! Because children may be more likely than adults to absorb cadmium, some investigators have suggested lower thresholds for children (Horiguchi et al., 2004), a suggestion common to many toxins. Several studies have identified more cadmium in the tissues of women than in those of men (Satarug et al., 2010). Thus, children and women are potentially sensitive subgroups based on exposure characteristics.

Current thresholds have been criticized as insufficiently protective. A review of the literature shows that exposure levels of 25-30 $\mu\text{g}/\text{d}$ were modeled to produce kidney disease in as much as 1% of the population (Satarug et al., 2010). If this model is

instructive, then the WHO PTWI is more than an order of magnitude above the modeled health effect.

The PTWI often accounts one of two thresholds in sensitive species, either the LOAEL, or the Benchmark Dose (BMD). Using a BMD model, European food safety recommendations have been lowered to 2.5 µg/Kg body weight (ESFA, 2009). Recent reviews demonstrate that it is unclear whether this is low enough (Satarug et al., 2010).

Cadmium Disease

Cadmium's classic target organs are kidney and bone. In addition, cadmium has been associated with diabetes, diabetic nephropathy, hypertension, peripheral arterial disease, myocardial infarction, periodontal disease, and age-related macular degeneration (a cause of blindness). Cadmium is also a carcinogen, primarily identified as a lung carcinogen, but probably also operating in other body systems (Satarug et al., 2010).

Chronic kidney disease can be caused by cadmium. The best-designed U.S. population study, based on NHANES (1999-2006) data, recorded sociodemographic risk factors, chronic kidney disease risk factors, and obtained sufficient data to compute standard measures of kidney function (Navas-Acien et al., 2009b). The commonly used markers of kidney function are the serum creatinine, the calculated glomerular filtration rate (GFR), and albumin (a protein) in urine. In the NHANES study, standard techniques were used to adjust for risk factors other than cadmium and lead in the serum (blood) of participants. Those in the highest quartile of serum cadmium had more proteinuria (albumin in their urine, odds ratio [OR] 1.92, 95% confidence interval [CI] 1.52, 2.43),

and GFR low enough to be considered clinically reduced (OR 1.32, 95% CI 1.04, 1.68), and both of these indicators of chronic kidney disease together (albuminuria and low GFR, together) (OR 2.91, 95% CI 1.76, 4.81) when compared to those in the lowest quartile (Navas-Acien et al., 2009b). Because the cadmium serum values in the NHANES study are broadly representative of the entire U.S. population, and consistent with the well established deleterious effect of cadmium on kidney function, it is uncertain whether or where there are safe thresholds for cadmium exposure. The data also are preliminary, and the association could be interpreted with a plausible possibility of “reverse causation,” a scenario in which those with existing kidney disease accumulate more cadmium. However, for a variety of technical and toxicologic reasons, causation is more plausible and cannot be dismissed. The implication is that each substantive addition of cadmium to the water supply could result in additional chronic kidney disease in the exposure population.

Chromium

Chromium is a blue-white metallic element which occurs naturally in rocks and soil and which is present adjacent to coal and in coal overburden. It has many uses in industry, and it can also be encountered from metal alloy foundries, parts cleaning, paints, wheel bearings, aircraft engine parts, and operating or abandoned tanneries. Older pressure-treated wood from decks and playgrounds can be a source of chromium. Chromium is typically present in US drinking water within a 0.4-8.0 µg/L range, and soils often contain around 400 ppm (Pellegrin and Booker, 2000). Humans can be exposed to chromium in drinking water, many foods, and by inhalation. Adults

absorb less than 10% of ingested chromium. Workers in chromium industries, who are exposed primarily by inhalation, tend to have far higher exposures than the general population. A medical source of substantial exposures can be from chromium-alloy joint prostheses. Chromate compounds may also be absorbed through skin.

Natural chromium exists in several valence states, of which chromium III and chromium VI are of practical importance. Most chromium VI is from anthropogenic (industrial) sources.

Chromium III is possibly an essential element. Human health may suffer in the absence of sufficient chromium, and most adults ingest 20-45 μg chromium (III)/d. Myocardial infarction may be causally associated with low chromium intake (Guallar et al., 2005). Some individuals take chromium III compounds as nutritional supplements in the expectation that chromium will improve glucose metabolism, energy levels, aid in weight loss, and prevent diabetes. Actual clinical trials of chromium compounds yield contradictory and uncertain results about these hypothesized benefits. And, chromium III may have some health risks, in parallel with chromium VI. In contrast, chromium VI is not an essential element, and it is a known cause of gastrointestinal (oral exposure) cancer, lung cancer, and nasal septum perforation in exposed workers (inhalation exposure). For reasons that are not yet clear, the carcinogenicity of chromium VI appears to be potentiated by ascorbic acid (vitamin C). Chromium VI is also a source of allergic skin-contact dermatitis as well as skin ulceration, and respiratory contact can cause asthma. Some ingested chromium VI will be reduced to the presumably less toxic chromium III before it is absorbed. Absorbed chromium VI is distributed to red blood cells, where it is partially detoxified to chromium III, and eventually to kidney, bone,

teeth, hair, and nails. Chromium can be excreted in urine, and can also be transferred from mother to fetus (placental transfer) or mother to baby in breast milk.

Biological Monitoring

Biomonitoring of chromium can be done with blood, urine, hair, or nails. Particular care about use of hair must be taken in areas with coal-fired power plants, or foundries, or other industrial sources of atmospheric chromium, as all of these can deposit chromium onto the surface of hair. Urine is most commonly used. Chromium from environmental sources such as soil is generally insufficient to alter urine levels, and biomonitoring does not accurately distinguish chromium III from chromium VI sources. Even 200 µg/d for three days does not alter detectable levels in urine (Lauwerys and Hoet, 2001). The reference value is 0.5 µg/g creatinine. Higher and different biological exposure indices are noted for exposed workers.

Health Effects of Oral Exposures

The majority of human chromium toxicity literature describes inhalation or dermal exposures, often in industrial settings. A 1965 case report describes a Chinese village whose well water was poisoned by a nearby alloy foundry at 20 mg chromium (VI)/L (ATSDR, 2000). The 156 inhabitants were said to experience oral ulcers, diarrhea, and other gastrointestinal symptoms. Rodents fed water at a calculated dose of as low as 0.77 mg chromium VI/Kg/d were found to have cellular changes in the duodenum (ATSDR, 2000), as well as changes in red blood cell indices. (Reproductive and developmental effects occur in rodents at a much higher dose.) A small population

residing on the site of a former chromium slag landfill did not experience detectable kidney damage (Wedeen et al., 1996).

Sensitive populations do exist. Skin and respiratory allergy are thought to affect about 0.5-1% of the nonworker population. These routes of exposure may be dismissed as irrelevant to waterborne exposures; however, asthmatic patients are more often treated by nebulization. For the sensitized patient, this can provoke a new attack, or worsen an existing bout of asthma.

The most feared outcome of chromium VI exposure is cancer. In humans, this has been amply demonstrated by industrial populations exposed by inhalation. In rodents, increased gastrointestinal cancers may appear after doses around 2.4 mg chromium (VI)/mg/Kg/d.

While chromium carcinogenicity is its most feared effect, allergic sensitivity is actually common and can be associated with inexpensive jewelry, or with residual tanning products found in leather goods (such as shoes). Threshold doses are not established (or establishable) for humans. Rodents can be sensitized with intradermal injection series as low as 0.004 mg chromium (III) Kg. Whether intradermal injection is a realistic model is questionable.

Established Oral MRLs

The oral chronic (\geq /year) MRL is .001 mg chromium (VI)/Kg/d. This is based on gastrointestinal dose-response as measured by histologic reactions in animal studies. However, there are suggestions that stomach cancer rates may be higher in areas of

China with higher chromium in well water (Beaumont et al., 2008). This kind of general observation adds weight to MRL, but does not assist with establishing the actual level.

For chromium III, MRLs are not established, and it is thought that humans should have some minimum intake.

Diesel

Diesel is a refined mixture of petrochemicals and specific additives used in vehicular transportation. It is not fully characterizable, as it is a mixture with general characteristics, which vary with geography and with intended uses. That is, significant variations depend on the geographical source of the crude oil, or the type of engine application. Transportation, agricultural, and mining equipment may each use different formulations. Furthermore, diesel formulations have changed over time to accommodate evolving engine designs. Definitions of diesel generally mention a mixture of C8-C21 aliphatic hydrocarbons with a boiling range of 160-360 degrees C, accompanied by less than 25% aromatic compounds. This may vary. And, additives in small quantities such as biocides may have their own toxicity, and also vary by application. While it is often assumed that diesel in coal slurry comes from equipment leaks, the possibility of convenience-process or disposal uses cannot be ruled out.

Health Effects

There is obviously no nutritional requirement for this manmade mixture. Exposure is most commonly by the respiratory route to diesel exhaust as a complex combustion product. This important and vast literature concerning diesel exhaust is not directly relevant to the consideration of diesel in water.

Acute ingestion of concentrated diesel product is most dangerous because of the potential for unintended aspiration into the lungs, particularly aspiration that may follow from the nausea and vomiting that can follow acute ingestion of fuels. The danger is chemical pneumonitis, which is potentially fatal. It should be clearly understood that this danger relates to the concentrated product, not the concentrations normally characteristic of pollution. In addition, gastrointestinal irritation with nausea and vomiting are possible in oral poisoning episodes (Health Protection Agency, 2007). A limitation of the available literature concerning the oral route of exposure is that inferences concerning diesel are frequently made based upon the much richer literature concerning kerosene (ATSDR, 1995). However, kerosene is more volatile, likely more acutely dangerous following ingestion, and may not contain the same additives.

Direct skin exposure to diesel can cause dermatitis. Diesel fuel is partially absorbable via skin exposure, and that may include exposure to vaporized diesel (ATSDR, 1995). There are rare case reports of acute renal failure after diesel was used to wash hair or hands (Barrientos et al., 1977; Crisp et al., 1979).

There are no useful data concerning chronic human oral exposure to diesel. Rabbits fed 4 to 8 m/Kg/d for 10 of 14 days developed dose-dependent dermal irritation and anorexia, with cachexia and death in the higher-dose group (Health Protection Agency, 2007).

There is no human information about susceptible populations, but it is possible that children are at higher risk. In animal studies, young rats are more susceptible to kerosene toxicity than older rats (ATSDR, 1995).

Other Considerations

Because diesel is rapidly photo-oxidized in sunlight, the formation of peroxy radicals and hyperperoxides is possible in aqueous solutions or suspensions. However, the degree to which this occurs or the potential importance is not known.

A review of EPA, CDC, and National Library of Medicine sites, including the toxicology sites, finds that exposure to diesel in drinking water is sometimes mentioned, and potential acute poisoning hazards acknowledged, but chronic clinical exposures and disease are addressed only in context of respiratory exposures. The reason for this hole in the literature is absence of relevant data. As a result, meaningful thresholds for humans are not established, and biomonitoring is unexplored.

Comment: When a significant common exposure is not well addressed, the plausible reason is absence of significant examples of toxicity in practical settings.

Fluoride

Needs completed

Iron

Iron is an abundant element, but pure iron is rarely seen on the earth's surface because of oxidation. Mined iron has many uses, notably in the manufacture of steel. Iron is an essential element for human metabolism, and iron deficiency is a serious problem in malnourished populations.

Coal related activities can increase iron content in surface water and in the water table. The outcome is not specific to coal slurry. Iron is a common element around coal mining. Once a mine void has been established, water which moves through the mine

environment can transfer iron to surface and groundwater in several forms. This occurs commonly in West Virginia.

Iron in surface water or in groundwater can affect water quality in many ways. Iron oxides are corrosive and can affect water pipes. In addition to creating a rust environment, this corrosion can harbor bacteria, archaea, and viruses or fungi. Bio-films are complex and mutually supportive colonies of different types of microorganisms which are organized with a mucous protective layer. The formation of bio-films makes it extremely difficult to extirpate the undesired growth.

In addition, the metabolites of iron-loving microorganisms can generate sulfate-reducing bacteria which can lead to the production of sulfide compounds. This in turn produces a characteristic “rotten egg” smell that is undesirable in drinking water as is the characteristic dark (red, brown, or black) particulate staining from pipe corrosion. Associated health conditions such as diarrhea or loose stools are not necessarily directly related to iron. They stem from microorganisms and their chemical by-products.

The average adult has about 4 g of iron; men generally have more than women because menstruation and breastfeeding transfer iron from the body. About 70% of body iron is in blood. Iron is essential to the operation of hemoglobin and myoglobin.

The USEPA considers that iron-related health outcomes are not directly toxicologic. Instead, they are either aesthetic (such as staining of fixtures or laundry and metallic taste of water) or physical, related to iron build-up, microbial overgrowth, and corrosivity. For this reason, iron is regulated as a secondary contaminant at 0.3 mg/L National Secondary Drinking Water Regulations (NSDWR). From a health perspective, most humans can tolerate considerably more than this concentration in drinking water

because our bodies handle iron efficiently. However, there is a sensitive population for whom that may not be the case.

Sensitive or Susceptible Populations

Primary hemochromatosis, a genetically inherited disease arises from a “founder” gene mutation that appears to have originated in the Celtic population. Hemochromatosis is by far the most common hereditary condition of Caucasians (with lower rates in Hispanics and African-Americans, and virtually no appearance in West Asians). Individuals who carry both copies of the abnormal gene (genetic recessive condition) can, but do not always, suffer from the effects of iron overload in the liver because they lack the ability to excrete iron. (There is actually a common and a less common abnormal gene variant, and double heterozygote carriers may also manifest the disease.) Most texts indicate that the recessive condition is present in about 1 in 200 Caucasians. Although men and women have the genetic condition with equal frequency, men are affected at younger age and more often because women of child-bearing age are protected, to some degree, by iron loss through menstruation. Many people who have the genetic recessive susceptibility never get the clinical condition, so genetic testing is not (yet) recommended. Patients are detected by routine screening of iron status, or else because of presenting symptoms. Presenting symptoms can include arthritis, diabetes, fatigue, heart problems, darkened skin, testicular atrophy, and cirrhosis of the liver.

Individuals with clinically significant hemochromatosis are treated by periodic phlebotomy (bloodletting), one of the few known indications for this ancient treatment.

Phlebotomy is surprisingly effective for mitigating and even reversing the progression of clinical hemochromatosis. The arthritis tends to remain after treatment.

Iron exposure from water in the setting of hemochromatosis

Most humans get the majority of their iron from food. Iron supplementation is also increasingly common, especially in developed countries; iron is a frequent addition to multivitamins. Special diets and avoidance of vitamin supplementation are part of the medical regimen for hemochromatosis. Whether water is a significant source of iron compared to food is not really known, but at least one reputable website (Medicine.net) has made the point that patients with hemochromatosis should avoid water that is high in iron. The possibility that inputs to iron content of drinking water can affect susceptible people is a risk consideration. However, consensus threshold recommendations for iron in water have not been established for this sensitive population.

Lead

Sources of Lead

Lead is an extremely heavy, dull, gray-black metal usually found as an oxide, or salt, or sulfide in the earth's crust, generally in a 2+ oxidation state. It has numerous uses in industry, and historic human exposures in the U.S. have usually been from leaded gasoline, from lead-based paint or glaze, and from lead pipes in older water systems. Household plumbing fixtures were required to greatly reduce lead content in solders and fittings following a 1998 revision to the Safe Drinking Water Act (SDWA). (Well pumps may contain up to 8% lead, however.) The potential sources of human exposure in the household and on the job are quite diverse. Modern humans have been

exposed to far more lead than their pre-industrial ancestors. We can infer this from the amount of lead deposited into ice cores through the centuries and test it definitively by measuring the concentrations of lead in ancient and modern bones.

Lead, present in coal in very small quantities, and in coal overburden, is a chemical of concern because it is so extraordinarily toxic, even at low doses, without a known threshold for safe exposure, and not because it is a major contaminant of coal or coal slurry. Health studies show that even small inputs are problematic. Lead adheres to sediment and soil particles very well, and lead in soil that can be transported on shoes or vehicles and tracked back into the home is a potentially important source of exposure that will not be emphasized in this section. Lead in soil was not determined to be a long-lasting problem in the Martin County event. Acid rain, characteristic of the Appalachian environmental conditions in coal-burning regions, may also leach lead from soil and sediment into nearby surface water. Most surface and groundwater contains only small concentrations of lead, typically less than 0.005 ppm (ATSDRc, 2007). Fewer than 1% of U.S. public water systems have lead levels over 5 µg/L. Acid water supplies can leach lead from plumbing fixtures, however, so the concentration of lead from tap water can exceed the concentration from source water in some water systems and in individual homes.

Human Exposure and Uptake: Exposure Susceptibility

Adult volunteers absorb a mean of 6% ingested lead, but this may increase to 60-80% if the gut encounters lead after a greater-than-24-hours fast. And, the gastrointestinal tract of children absorbs calcium and lead much more easily than that of

adults, with an absorption rate of approximately 50% in small children. The gastrointestinal apparatus of young children normally absorbs calcium and other elements with “plus two valence” far better than the same process in adults. This creates an obviously greater susceptibility for children based on relative exposures. Furthermore, iron deficiency (more common in women and in breast-fed infants) may increase the efficiency of absorption of plus two valence compounds such as lead. Women of childbearing age and especially children are sensitive populations for greater exposure than the same concentration presented to the gut of adult males.

Once in the body, lead tends to first enter the bloodstream. The half-life for residence in the bloodstream is approximately equal to the half-life of the red blood cell, which is slightly longer in adults than in children. While in the bloodstream, lead is also presented to soft tissues, such as the brain, peripheral nerves, and kidneys. From the bloodstream, lead is concentrated in bones and teeth, where it may reside for a half-life of a decade or more. However, there are health conditions which can mobilize lead from bone back to bloodstream, including degenerative bone disease, such as osteoporosis and Paget’s disease, as well as normal conditions such as bone healing and pregnancy.

Health Effects of Lead, Including Susceptible Populations (Children)

Lead is an impressive toxin, with a protean list of health effects; a more dramatic effect on susceptible populations (infants and children), and lifelong negative outcomes at low doses. Virtually all human organ systems can be affected by lead exposure. The following paragraphs list only the most important of many known outcomes of lead

exposure, which center primarily on neurologic, cardiovascular, and renal decrements to health.

By far the most important outcomes of human lead exposure relate to documented central nervous system capacity. While this definitively occurs in both children and adults, substantial human population data from multiple races, cultures, and nations indicate that infants and children are more susceptible to permanent damage, and at lower doses. Children who have been lead poisoned consistently perform worse than other children in measures of intellectual and social achievement, and are more likely to suffer from poor social attainment in numerous ways (ATSDRc, 2007). For example, IQ (Chen et al., 2005; Canfield et al., 2003), math/reading skills (Lanphear et al., 2000), and social behavior (Chiodo et al., 2004) are all negatively associated with blood lead. Infant development is negatively associated with first-trimester maternal plasma lead (Hu et al., 2006). These findings are robust to adjustment for race, parental education, and markers of family socioeconomic status. Reverse causation has been ruled out by well designed studies; the associations are causal. Put simply, lead poisoning of children robs them and society of potential achievements. In a population context, when lead poisoning affects many children, the societal burden is inferred to be substantial.

Low-Level Lead: Dose-Response Studies of Human Performance

Target blood lead levels (BLL) have been revised and revisited since the 1960s. The latest target recommendation of acceptable BLL levels has been <10 micrograms/deciliter ($\mu\text{g}/\text{dl}$) since 1991. Since then various studies have established the

persistence of population health risks even below the acceptable limit of $<10 \mu\text{g}/\text{dl}$. It is unclear whether there is an established safe threshold. Recommendations for still lower levels in biomonitored blood are surfacing.

Canfield and others (2003) measured blood lead concentrations in 172 children at 6, 12, 18, 24, 36, 48, and 60 months of age and administered the Stanford-Binet Intelligence Scale at the ages of 3 and 5 years. The results showed that the blood lead concentration was significantly and inversely associated with IQ. It was statistically derived that IQ declined by 7.4 points as lifetime average blood lead concentrations increased from 1 to $10 \mu\text{g}/\text{dl}$. The lifetime average BLL was measured to be $7.7 \mu\text{g}/\text{dl}$ at 3 years and $7.4 \mu\text{g}/\text{dl}$ at 5 years. This model of persistent adverse health effects even below the acceptable levels of $10 \mu\text{g}/\text{dl}$ is consistent with other studies. The degree of performance decrement may vary among studies (this example is higher than many); the presence of deleterious effects does not. Virtually all studies document diminished neurocognitive performance in relationship to blood lead.

Min and others (2009) evaluated the impact of early postnatal lead exposure measured at age 4 on children's IQ and academic achievement up to 11 years of age. Their analyses of subgroups of children with blood lead levels $<10 \mu\text{g}/\text{dl}$ showed detrimental lead effects even at the $5 \mu\text{g}/\text{dl}$ level, adding evidence to the detrimental effects of low-level exposure to lead.

Jedrychowski and colleagues (2008) assessed the neurocognitive status of 6-month-old infants whose mothers were exposed to low but varying amounts of lead during pregnancy. Their results led to a recommended cutoff for cord blood lead levels at $\leq 1.67 \mu\text{g}/\text{dl}$. The basis for this recommendation stems from finding that the infants

scored lower by 1.5 points, as measured by instruments of intelligence testing appropriate for age, for every increase by one unit (1 µg/dl) of lead concentration in cord blood. Further, the risk of the presence of a diagnosis of developmental delay was twofold greater among those children with higher cord blood levels.

Blood Pressure, Kidney, and Vascular

In adults, higher blood and bone lead levels (as measured by KXRF in human tibias) correlate with elevated blood pressure (Hu et al., 1996; Nash et al., 2003). While most studies of blood pressure have been done on adult populations, it is also the case that lead poisoning in childhood is associated with an excess incidence of hypertension in adulthood. And, higher prenatal lead in mothers is associated with higher resting blood pressure in childhood, even at background population levels (Gump et al., 2005).

Similarly, when age and other covariables are accounted, decreased kidney function as measured by calculated GFR is associated with lead exposure as measured in blood or bone, even biomonitored exposures as low as 10 µg/dl or lower (Payton et al., 1994; Kim et al., 1996; Tsaih et al., 2004).

Studies on other organ systems have noted similar detrimental effect of chronic and cumulative low levels of lead exposure. Menke and others (2006) measured blood lead levels in a nationally representative sample of 13,946 adult participants of the third NHANES, who were recruited in 1988 to 1994 and followed for up to 12 years for all-cause and cause-specific mortality. The lower quartile of BLL was <1.94 µg/dl, and the upper quartile was >3.62 µg/dl, which fell well within the acceptable standards. However, when analyzed for all-cause mortality among the subjects, the hazard ratio

was 1.25 for the upper quartile as compared to the lower quartile, the difference was statistically significant. For cardiovascular mortality, the hazard ratio was 1.55, and blood lead level was significantly associated with both myocardial infarction and stroke mortality at blood levels $>2 \mu\text{g/dl}$). No association was found between blood lead levels and cancer in this study, although lead is potentially a weak carcinogen.

In the cardiovascular system, it has been found that blood lead levels were strongly associated with the elevation of both systolic and diastolic blood pressure, at a level below the current U.S. occupational exposure limit guidelines (Nash et al., 2003). In this study, women aged 40 to 59 years were the age group most vulnerable to developing low-level lead-related hypertension.

Munter and others (2003) concluded that even low levels of exposure to lead in individuals suffering from hypertension can lead to chronic kidney disease (CKD). Among persons with and without hypertension, mean blood lead was 4.21 and 3.30 $\mu\text{g/dL}$ respectively, and the prevalence of CKD was 10% and 1%, respectively. Reverse causation is a consideration in this study design, but this study does not stand alone. Additional evidence of low-level lead as a major factor in the development of CKD exists in multiple studies (Ekong et al., 2006).

Reproduction and Endocrine

Fertility is affected by low-level blood lead exposure. Chang and colleagues (2006) investigated the risk for infertility in women after low-level lead exposure. After controlling for age, body mass index, smoking, Chinese herbal medicine use, and irregular menstruation, it was concluded that the risk of infertility among women with

BLL >2.5 µg/dl was three times greater than in women with BLL ≤2.5 µg/dl. Dunder and others (2006) also described the effect of low-level lead exposure on thyroid hormones, specifically FT4.

Uric Acid and Saturnine Gout

Shadick and others (2000) confirmed that the long term accumulation of lead is associated with an increased uric acid level in middle-aged and elderly men. The association of lead with gout has been recognized for centuries, but the recognition of stepwise associations of increasing uric acid, the major risk factor for one kind of gout, with increasing biomonitored dose, is a new finding.

Cellular Effects

Lead also has increased toxicological and population effects on hemoglobin synthesis and human red blood cell function (Schwartz et al., 1990). Hemoglobin is the molecule that allows red blood cells to capture oxygen from the lungs and to then deliver oxygen to points of use in the body—essentially all organs and tissues. By interfering with the formation of hemoglobin, lead poisoning can lead to ineffective blood cell formation, enhanced speed of cycling red blood cells, and anemia. Lead poisoning is characterized as both a cause and an outcome of anemia. Young children exposed to lead produce more of the hormone erythropoietin, which in turn stimulates a compensatory production of new red blood cells, and their guts absorb more lead.

The possibility that lead, at general population levels of exposure, may increase periodontal bone loss (Dye et al., 2002) is an important consideration for Appalachian mining regions, with their historic pattern of poor oral health.

There is increasing evidence that oxidative mechanisms play an important role in the development of many diseases. There is also evidence that low-level lead exposure can induce oxidative stress. Ahamed and others (2006) have found that such exposure induces oxidative stress by alteration of glutathione in blood and catalase in red blood cells (RBCs). The levels of these enzymes also correlate with delta-aminolevulinic acid dehydratase (delta-ALAD) inhibition. Similar effects were noted by Oktem and others (2004), who noted that lead-induced oxidative stress might have a detrimental effect on renal function as well.

Cancer

Although cancer is among the less impressive toxicological attributes of human lead exposure, lead is considered a human carcinogen by the International Agency for Research on Cancer (IARC).

Manganese

To be completed

Molybdenum

To be completed

Nitrate

To be completed

Selenium

Selenium is a non-metallic element naturally present in the overburden materials associated with coal mining operations, and small amounts of selenium are directly associated with coal. Also, many forms of selenium are not readily soluble in water.

Once dissolved in water, however, selenium compounds can be highly mobile. Humans can be exposed to selenium that originates in coal slurry through drinking water or from uptake by plants or animals that are food sources.

Selenium Health Effects

Selenium is an essential trace element; humans need small amounts for thyroid metabolism and for the operation of cellular anti-oxidation defense mechanisms. Geographies (such as parts of China) with selenium deficient soils and food experience health problems, which are probably due to the selenium deficiency. The best known medical condition associated with selenium deficiency is Kashin-Beck disease, a combination of severe, deforming osteoarthropathy and cardiomyopathy, appearing in young children in selenium deficient regions of China and Tibet (Stone, 2009). The disease and its dramatic effects are partly reversible with selenium supplementation. Selenium deficiency is an underlying cause, but mycotoxins from grain and other sources of oxidative stress are considered to play a role.

Because selenium is an essential trace element with antioxidant properties, it may theoretically be useful in greater than minimum amounts for the prevention of cancer or other chronic disease. Cancer prevention has been evaluated in a number of studies of selenium supplementation. Some data support a cancer prevention role for selenium, whereas others do not. In practice, such benefits have not been definitively established, and recent epidemiologic evidence suggests there is actually a potential risk in supplementation. A very well done study from national databases shows that serum selenium concentrations are positively associated with adult-onset diabetes

(Laclaustra et al., 2009). The highest population quartile of serum selenium ($> 146 \mu\text{g/L}$) had more risk (OR 7.64; CI 3.34-17.46) than the lowest quartile ($<124 \mu\text{g/L}$). While the direction of association is not clear from this study alone, oral supplementation trials are associated with increased risk in populations (Stranges et al., 2007). Also, the available studies about bio-available selenium and peripheral arterial disease suggest (but do not prove) a “U-shaped” association with possible benefits up to normal physiologic levels and then vascular disease risks at higher levels (Bleys et al., 2009). Selenium supplementation may also increase the risk of non-melanoma skin cancer (Duffield-Lillico et al., 2003).

Acute selenium toxicity is rare outside of poorly controlled selenium workplaces. Very high acute doses have been reported to cause diarrhea and tachycardia. Long-term intake of exposures 10-20 times the recommended daily allowance (RDA) causes brittle, abnormal appearing nails, hair loss, tooth discoloration and decay, and a neurologic syndrome characterized by unsteady gait which may progress to paralysis. The oral exposures required to cause selenosis, including nail deformation, in Chinese adults was an estimated daily intake of 0.91 mg/d (Yang et al., 1989a).

Small exposures to selenium compounds have been demonstrated to be necessary for thyroid metabolism, whereas larger exposures (several times the RDA or more) can be shown to reduce serum T_3 hormone. However, hypothyroidism as a result of selenium exposure has not been documented.

Epidemiologic studies show associations between selenium and dental caries (Hadjimarkos, 1969) as well as mottled teeth (Yang et al., 1989b), loss of hair, and nail deformities. Interactions between selenium and fluoride have been proposed as a

mechanism. Very high intakes of selenium (in China) have been associated with peripheral neuropathy and arthralgia (Yang et al., 1983). High-concentration skin exposures can be irritating.

One form of selenium, selenium sulfide, causes cancer in laboratory rodents when they are fed this compound in daily doses at very high levels. This particular form of selenium is regarded as unusual in most environments because it does not readily dissolve in water; the presence of sulfides in coal slurry and in mine drainage may be a consideration. Selenium element also disrupts normal sperm formation and reproductive cycles in laboratory rodents. The significance of these findings for humans is not known; no reproductive problems associated with selenium exposure are documented so far for humans. Selenium does cross the placenta to enter the fetal circulation. However, no reliable studies to date show selenium exposure to be associated with birth defects in humans. Volunteers fed high selenium diets did experience small decreases in sperm motility, but these decreases were inconsistent over time (Hawkes and Turek, 2001).

By far the most complete discussion of selenium toxicity is the ATSDR Toxicological Profile (2003), which is available online from the CDC. However, important data about diabetes associations was developed after publication. And, no population studies address the recently raised question of relevant concentrations of selenium in water and diabetes.

Selenium Exposure and Biomonitoring

Blood selenium in humans does correspond to recent selenium exposures, but there is no good bio-monitoring test for chronic burden from past exposures. Individual

tests for selenium as a biomarker of health or toxicity are probably not generally useful unless poisoning is suspected, or in the context of wider, thoroughly designed population studies. Population studies can use blood, urine, or nails. (There is a significant potential problem with using an external biomarker such as hair, with its large surface area, in a coal-burning region. Selenium is emitted to the atmosphere when coal is burned, and coal measured on hair or nails can be in or on the sample. Because of the larger relative surface area and greater surface adherence, this is likely a more significant problem for hair than for toenails.)

Selenium Exposures: Recommendations and Tolerances

In general, most human exposure to selenium comes from food sources, and water sources become most important when they affect locally grown crops. Because many health-conscious individuals voluntarily take selenium supplements in hopes of obtaining an antioxidant benefit, there are also substantial supplementation exposures from non-food sources. The likely forms of selenium encountered in food (and in food supplements) are selenate, and selenium element. In specific areas where there is substantial water pollution, drinking water is also an important source. Selenate and selenite are the typical forms in water runoff from polluted areas. Selenium in selenite is in the +4 oxidation state and occurs as the oxyanion SeO_3^{2-} . This form is considered more biologically active (and more toxic). It sorbs readily to sediments such as ferrihydrate. It also undergoes oxidation to selenate. For these reasons, selenite is predicted to travel less far in groundwater than selenate. However, an ATSDR review (2003) suggests that selenite and selenate are equally common in surface waters.

Selenium in selenate occurs as the oxyanion SeO_4^{2-} and is in the +6 oxidation state. Sodium selenate is a particularly mobile selenate compound. In contrast, selenium element has low solubility, and may not travel far in water.

Common sources of dietary selenium are cereals, breads, pasta, nuts, eggs, and meat. The estimated U.S. population daily intake is 0.071-0.152 $\mu\text{g}/\text{d}$, with an estimated mean of 0.114 $\mu\text{g}/\text{d}$ for all ages and sexes (ATSDR, 2003; USDHHS, 2002). Lower levels of selenium are found in milk and in breast milk. Childhood blood levels of selenium do appear to vary with the amount of selenium in soil (Yang et al., 1989b), at least under high-exposure conditions. Selenium supplementation products can contain 200 $\mu\text{g}/\text{tablet}$; this is a higher supplemental dose than is generally considered prudent. Home use of selenium supplements is thought to pertain to adults much more than to children. Home products such as selenium shampoos are not considered to be a skin-absorption hazard.

For adults, the RDA of selenium is 55 $\mu\text{g}/\text{d}$ or 0.8 $\mu\text{g}/\text{Kg}/\text{d}$. The U.S. National Academy of Sciences (NAS) has recommended a Tolerable Upper Intake Level (UL) of 400 $\mu\text{g}/\text{d}$ for adults. (Recent data concerning diabetes may prompt re-evaluation and exert downward pressure on recommended tolerable limits; however, readers should recognize this thought as speculative because it precedes the activities of future review groups.) Based primarily on the Chinese population, a LOAEL of 0.023 mg/selenium/Kg/d, a NOAEL of 0.015 mg selenium/Kg/d, and an MRL of 0.005 mg selenium/Kg/d have been proposed (ATSDR, 2003).

There are also recommended guidelines for drinking water intake, 0.9 µg/Kg body weight in adults (WHO, 2001), as well as USEPA guidelines. The USEPA guidelines for selenium uptake are provided in Tables 9 and 10.

Silicon

To be completed

Sodium

To be completed

Strontium

Strontium is an element which is found in a number of minerals in nature. Although we are used to reading about strontium in association with radiation physics, the strontium in nature that can be associated with coal and coal overburden is mostly non-radioactive. Strontium enters the environment when coal is burned or cleaned, or when water runs through minerals bearing strontium. Most but not all strontium minerals can be dissolved or suspended in water. Strontium in small quantities is also naturally present in food, especially grains, leafy vegetables, and milk.

Most drinking water in the U.S. has less than 1 ppm strontium. The radiation from strontium in water is generally very small, less than 0.1 pCi/L (or .004 Bq/L). (Picocuries [pCi] and becquerels [Bq] are standard measures of ionizing radiation, named for scientists.)

Strontium Exposure and Metabolism

Most public health considerations of strontium involve inhalation, because strontium is easily inhaled in dust and easily absorbed via the lungs. In

contrast, strontium is not well absorbed via the gut. However, and in common with lead, infants and small children may be a susceptible population for greater exposure as there is some evidence that they are more exposed from dairy products such as milk, and they absorb strontium better because their guts absorb calcium better than adults. Strontium is also slightly permeable through skin; however, this is not considered an important route of exposure in most circumstances.

Because the human body handles strontium in ways similar to calcium, strontium is rapidly distributed in the blood once absorbed and then the blood effectively distributes the strontium to other parts of the body. Over time, much of the absorbed strontium will be deposited on the surface of bones or teeth. And, like calcium, the strontium in bone is reabsorbed and in equilibrium with strontium in the blood. Thus, strontium is also gradually excreted over time. This description of strontium metabolism resembles the description of what happens when humans ingest lead.

Strontium and Health

Strontium is not considered an essential element; it is thought that humans can survive without it. On the other hand, there are some potential health benefits of strontium. Calcium absorption may be slightly better in the presence of strontium. Strontium has been used in successful clinical trials to improve the bone density of patients suffering from osteoporosis.

Despite its fearsome reputation, strontium is not a known toxin in its common, non-radioactive form in the local coal environment. Because most strontium is in the coal-processing waste stream, there is no reason to consider strontium as a

significant hazard in most circumstances. A possible exception to this statement is that one form of strontium mineral, strontium chromate, can be toxic. However, the toxicity is inherently from the chromate compound, not the strontium. There is a separate consideration for chromium toxicity. In calcium-deficient children, too much strontium can contribute to brittle bones. The USEPA drinking water designation of 4 mg/L accounts for this risk. Details about strontium toxicity in the context of risk assessment can be seen at <http://www.atsdr.cdc.gov/toxprofiles/phs159.html>

Total Dissolved Solids

To be completed

Summary of Health Effects

Existing data, while sparse, suggest that arsenic, cadmium, and lead are potential chemicals of concern and candidates for ongoing monitoring, in the context of possible contamination by coal slurry. Because of their known toxicity, these have low (lead and arsenic), and potentially low (cadmium) thresholds for inducing unfavorable changes in human health. Exposures to these elements can result in several kinds of detrimental changes in human population health if introduced into drinking water. Furthermore, small changes in water quality are theoretically capable of causing human health effects when enough people are exposed. That judgment is based on health literature. Small increments to oral exposures are reported to have caused population health effects, in well-designed studies, in some part of the world. In no case is that circumstance known to be from coal slurry, however.

A fourth element, iron, also presents a potential health risk limited to a susceptible population. The susceptible population comprises people who have inherited two genes for a condition known as hemochromatosis. They are homozygous or double heterozygous for either of the two recessive genes that diminish the normally excellent human capability to safely handle and excrete environmental iron. Those susceptible may suffer from liver disease if exposed to sufficient iron; they benefit from reductions in exposure to iron. The population at risk is descended from northern Europeans (such as Scots-Irish), and the gene frequency is high enough so that the disease, hemochromatosis, is actually seen. Thus iron contamination of water is a potential contributor to a public health concern in West Virginia.

The Wheeling Jesuit University data suggest that arsenic, barium, cadmium, iron, lead, and selenium may enter southern West Virginia water in excess of drinking water standards. Slurry liquid is a potential source, based on concentrations documented in the Phase I, SCR-15 report. We do not have concrete evidence that slurry injection alone has substantially contributed to or caused the exposures of greatest concern within data sets reviewed. In fact, the Phase I data provide reason for optimism that the sites monitored are not important recent sources of such exposures, but important data gaps must be acknowledged. The Wheeling Jesuit University report is evidence that such exposures do occur, regardless of sources. Although slurry water is demonstrably a potential source, the specific sources of contamination are unclear. (We do not have sufficient measures to reliably identify, separate, implicate, or absolve sources; this is a data gap.)

Of the chemicals reviewed, arsenic, cadmium, and lead are universally hazardous. Iron is hazardous to a population subset, and all are found in drinking water. Table 18, a review of drinking-water regulations, illustrates the nature of water-consumer protection, including the absolute vulnerability of those who rely on wells, and the relative vulnerability of small and even medium-sized municipal systems.

Comparison of Drinking-Water Sampling Frequencies to Potential Health Hazards

The Federal plan for protecting consumers of drinking water (summarized in Table 18) does not invariably protect the public from intermittent, unintentional introduction of hazards such as arsenic, cadmium, or lead.

Private wells are simply not regulated. Water systems that serve small populations may be checked by infrequent sampling (every three years) in the case of lead, or no sampling for other potentially important intermittent pollutants.

Intermittent exposures to elements of health importance, when they do occur, are not necessarily accompanied by odor, visual, or taste warning properties. When sampling is seldom, or never, reliance on drinking-water monitoring is incompletely protective in the setting of potential intermittent introductions of the most important chemicals under consideration. These are the chemicals of concern: arsenic, cadmium, and lead, as well as iron because of the potential harm to a susceptible population. When a new or intermittent hazard is introduced to seldom- or never-sampled water supplies, other means to secure drinking-water security should be a consideration.

Coal Slurry Underground Injection Control Data Evaluation

Coal Slurry Production

Coal Processing

When coal is initially removed from the mine, it is called raw or run-of-mine (ROM) coal. It contains coal and associated shales removed by the excavation equipment. Depending on the customer's requirements, it may be cleaned by crushing, sieving and washing to remove impurities such as shale and pyrites. Coal cleaning is accomplished in a wash, or preparation plant, and results in clean coal for shipment to the customer and rejected rock, known as refuse or tailings.

The first step in the preparation process is characterization of the ROM coal. In this step, wash-ability studies are performed in order to determine how much coal can be produced at a certain size and specific gravity. Step two, the liberation process, occurs through the size reduction of the ROM coal. Grinding the coal to a finer size allows removal of increasing proportions of impurities. Coal from various seams may be cleaned and blended at the preparation plant resulting in a more homogeneous mixture of coal. Step three is the separation of the liberated particles. The ROM coal is made into slurry by adding water and additives and using various machinery (such as jigs and cyclones) to achieve the separation of the coal from its associated impurities. The fourth and final step in coal processing involves transporting the clean coal to market and disposing of refuse. Refuse disposal is governed by environmental rules and regulations (NAS, 2007). In general, the refuse consists of about 1/3 fines and 2/3 coarse refuse. Coarse refuse is generally sized between coarse sand (2 mm) and 3

inches in diameter. Coarse refuse is transported in rock trucks or conveyors to the disposal facility. Fine refuse (smaller than sand size) is then transported hydraulically to a surface impoundment or an underground disposal site. This discussion focuses on the refuse fines or slurry fraction of coal tailings that have been placed in the open void space left after underground coal mining.

Coal slurry consists of both solid and liquid fractions. The rocks, minerals, and soil removed from the coal, as well as the water used to wash the coal, are the major constituents of coal slurry (Nicol, 1997). In addition to the minerals in coal slurry that were exposed by coal preparation, other chemicals may be present that were used to facilitate the washing and other preparation processes used in the coal preparation plant. To permit dewatering of the slurry under controlled conditions, it is placed either in surface impoundments or in underground coal mine voids. Each approach has its advantages and disadvantages.

Limited data permit a range of interpretations regarding the pollution potential of coal slurry. Testing of water in four underground slurry injection sites in southern West Virginia determined that two of the four sites were influenced by the injected material. Although some slurry constituents were found to have migrated from the slurry to the mine pool, there was no evidence that any of these pollutants had migrated into the surrounding surface water (WVDEP, 2009).

There are also some useful historic data. Libicki et al. (1983) found that pollutants from coal refuse stored in abandoned mining pits had migrated into the surrounding groundwater. The migration of such pollutants is predicted by column studies. Pollutants could be divided into three-column study categories: most leachable

(chlorine, sulfate, sodium, and potassium), medium leachability (copper, zinc, mercury, strontium, cadmium, boron, manganese, molybdenum, and cyanide), and least leachable (magnesium, aluminum, chromium, arsenic, lead, ammonia, and calcium). The level of groundwater contamination was found to be due to two main factors: the leachability of the waste and the sealing of the bottom of the pit by clay particles washed from the top of the waste pile. Self-sealing by clay particles was observed in the column studies, but could not be proven in the field because the bottom of the pit was not sampled and water levels were unknown.

Seven sites were researched by Smith (1987) to determine if injection of coal slurry had any impact on nearby groundwater. She found that the concentrations of various parameters in the mine pool groundwater were influenced by the initial pH of the mine pool. Injection of coal slurry into alkaline mine pools generally decreased metal concentrations and increased sulfate concentrations.

The migration of aqueous slurry can also be influenced by the depth and structure of the target mine voids. If a mine is below drainage (below the local water table), then it will eventually flood when mining ceases. Upon flooding, the mine pool will achieve pressure equilibrium with water in the unmined strata thus slowing the migration of slurry that was injected into the mine (WVDEP, 2009).

Surface impoundments are the most common form of slurry disposal. Coal slurry injection into underground voids is the alternative to surface impoundments. Surface impoundments usually occupy the heads of stream valleys. Surface impoundments disrupt habitat and may be long-term sources of AMD. They may also pose a long-term

geotechnical risk and may require indefinite maintenance, or at least monitoring, to ensure that the integrity of the containment structure is maintained.

Underground slurry injection has the advantage, in comparison to surface impoundments, of placing the most geo-technically unstable fraction of the tailings underground where, if the site is chosen carefully and the injection works as planned, it will not exit to the surface. Depending on the degree of flooding, underground coal mines may become anoxic and thus constrain further oxidation of pyrite. This constraint on iron oxidation, in turn, limits production of acidity and metal leachates. These are advantageous attributes. The disadvantage of underground slurry injection is that its flow path within the mine voids and its effect on mine and surrounding groundwater chemistry are poorly understood and potentially difficult to measure, especially without substantial advance planning. In West Virginia, 10-15% of coal slurry is injected underground (WVDEP, 2009).

Factors That Affect Slurry Chemistry

Since coal slurry consists of a solid and an aqueous phase, it is important to distinguish their properties and chemistries. Due to the nature of their different chemical environments, compounds found in the solid refuse particles may not be found in the aqueous phase, and vice versa.

With the exception of the chemicals added during coal processing, the chemistry of coal slurry is very similar to coal itself. The specific chemistry of coal slurry is determined by the characteristics of the coal, the associated rock, and the quality of the water used in the coal cleaning process. In addition to the fine coal refuse and water

found in slurry, a heterogeneous mixture of many other chemicals may be found as well. Unfortunately, many of these chemicals are proprietary and the manufacturers are often unwilling to disclose exactly what is in the chemical. This trade secrecy constrains the completeness of risk assessment efforts for any means of slurry disposal.

The State of West Virginia has a list of 237 chemicals that are allowed in coal slurry when it is injected underground. These chemicals are permitted for injection because they do not meet the definition of a hazardous material under the Resource Conservation and Recovery Act (RCRA). Only those constituents listed in the Underground Injection Control (UIC) permit may be part of the injectate (WVDEP, 2009).

Aqueous Phase

The aqueous (liquid) phase consists of water, additives, and elements that dissolve out of the solid phase. Many of the compounds added during coal cleaning are organic. They are often difficult to analyze accurately and analytical results may be confounded by the fact that additives used may bind to coal and that coal itself releases a number of similar organic compounds.

In an aqueous environment, chemical reactions are influenced by the dipolar nature of the water molecule. Because a water molecule has both positive and negative sites, it can associate with both anions and cations. Depending upon solubility and the hydrophobic/hydrophilic nature of the substance, water may totally or partially dissolve the substance. In addition to soluble compounds, the aqueous phase includes colloids. Colloids typically consist of suspended particles which can pass through the typical

laboratory filtration. Colloids are mixtures in which one substance is evenly dispersed in another. They contain particles in the size range between 10^{-9} m and 10^{-6} m (Hiemenz and Rajagopalan, 1997), typically less than 0.45 microns. Since these particles will pass through the typical laboratory filtration process, they are accounted for in the dissolved analyses. The total analysis, on the other hand, will account for precipitated, suspended solids as well as dissolved and colloidal fractions. For this reason, water samples are analyzed for both dissolved and total concentrations.

In the case of coal slurry, the aqueous phase consists of fine coal, minerals, and additive chemicals from the coal preparation process in a solution of water. As a result, the extent to which these additives pass into the aqueous phase of coal slurry can only be estimated by analyzing the resulting aqueous phase chemistry.

The aqueous phase of slurry is much more mobile than the solid phase particles and much more likely to migrate from its original location since it will be transported as a dissolved or suspended constituent of water. Because of this, there is concern that groundwater supplies may become contaminated by coal slurry. In the Phase I study, testing of water in four underground slurry injection sites in southern West Virginia determined that two of the four mine pool sites were influenced by the injected material. Although some slurry constituents were found to have migrated from the slurry to the mine pool, there is no irrefutable evidence that these pollutants had migrated into the surrounding surface water (WVDEP, 2009). Table 11 summarizes the aqueous phase of five coal slurries studied in SCR-15 Phase 1.

Solid Phase

To determine the composition of solid phase coal slurry, the material is filtered, dried, crushed and digested to release elements trapped inside the coal/rock matrix. The digestion process uses chemicals that dissolve the coal and rock matrix. Those elements that remain in the solid phase after going through the coal cleaning process are resistant to weathering. Results of the digestion and analysis are dimensioned as mg/kg. Buttermore et al. (1978) explained that the typical size of the solid phase of coal refuse is greater than 1/16." These larger materials have a relatively low surface area and do not weather quickly. Solid phase coal chemistry consists of many elements that do not leach into the aqueous phase because they are bound in stable minerals such as long, organic chain and ring compounds. When evaluating the solid phase of a substance, mobility and availability of the constituents in the environment are not taken into account.

In its Phase I report, the WVDEP (2009) analyzed the solid phase of coal slurry from 6 different sites for over 175 different parameters. In order to further understand the slurry composition, they also analyzed the raw coal and a simulated coal slurry leachate for the same analytes. The coal slurry leachate was made by crushing the raw coal, adding de-ionized water, and tumbling the solution for 24 hours. Most of the organic compounds found in the solid slurry were in the PAH group. Eight chemicals were found in the slurry that were not found in the corresponding coal sample. However, only one sample was taken, which does not provide a large enough sample set to determine the exact source of these compounds. Table 12 summarizes the organic coal and slurry composition.

The inorganic chemistry analysis of five of these Phase I report samples (Tables 11 and 12), compared to threshold values, found that iron was an important metal in the slurry, while aluminum, antimony, arsenic, cadmium, iron, lead, and manganese reached thresholds as contaminants of concern. Sulfates were a prominent finding, highest at the Coresco site and lowest at the Southern Minerals site, which may be due to the initial sulfur content of the coal. Fluoride, nitrogen, and total dissolved solids were also contaminants of concern based on slurry data.

Historic research on the solid phase of coal slurry has shown that various factors may influence its chemistry. Wewerka et al. (1976) determined that Al, Si, Fe, Ca, and Mg dominate the coal-associated minerals. Table 13 details the trace elements found in coal refuse alone. Some of the minerals that were found associated with these trace elements included: quartz, chlorite, illite, calcite, pyrite, and muscovite, among others.

Concentrations of trace elements in slurry can be affected by the coal preparation process; waste rock handling affects slurry chemistry. Wewerka et al. (1976) showed that drainage from coarse coal refuse piles was much more concentrated with respect to boron, barium, chromium, manganese, and strontium, than was drainage from underground mining because the exposed waste being much more susceptible to leaching and oxidation. Another factor that may influence slurry chemistry is whether the slurry is exposed to an alkaline or acidic environment. Many of the metals associated with the coal waste have low solubility at higher pH values, meaning that they are less mobile in the alkaline environment (Cobb et al, 1999).

Slurry Physical Characteristics

The physical characteristics of coal slurry are determined by the coal preparation process and the mineralogy of the coal. These characteristics may be quite variable. By its nature, coal slurry is a mixture of many different substances. The three major product streams from a coal preparation plant are coal, waste, and middlings, or coal with too many impurities to be burned in a power plant (Osborne, 1988). These materials are often separated from one another in a flotation tank. The middlings and the waste settle to the bottom of the tank while the coal, which is hydrophobic, associates with bubbles in the tank, causing it to float to the surface. Often, both the middlings and the waste rock are disposed of as coal slurry. Because of this, particle size, specific gravity, porosity, viscosity, etc. can be very different among different coal wastes. A comparison of coal, fresh coal waste, and weathered coal waste can be found in Table 14.

Although the Phase I report did not describe the physical characteristics of the coal slurry they sampled (WVDEP, 2009), other research has been performed on this topic. Buttermore et al. (1978) divided coal slurry into two different sizes categories:

1. Gob: particles greater than 1/16", mostly rock and waste coal.
2. Fines: particles less than 1/16" diameter, material in slurry solution.

Other researchers place the cutoff between coarse and fine material at 28 mesh (0.02 in.; USEPA, 1980) and 1 mm (NSF, 1975). Particle size of the coal refuse is important because it affects how quickly the refuse settles out of solution. This in turn affects waste-handling procedures at coal preparation plants. Eggert et al. (1980) determined that large pieces of slurry would settle out first because of a reduction in fluid velocity as

the slurry was discharged from a pipe. Remaining coarse tailings were deposited as the slurry flowed across the surface of the storage area. The fluid velocity dropped again when the slurry reached the standing water of the impoundment. At this point, only clay-sized particles still remained in suspension. Eggert et al. (1980) also estimated that roughly half of the particles were in the size range 0.0965-0.1067 mm. Particles this small create material handling problems due to the large amount of moisture they absorb. Faster weathering and mobilization of pollutants would also occur due to the small particle size.

Southern West Virginia Streams

Background Chemistry of Mined Watersheds

The WVDEP performed some in-stream sampling as part of the SCR-15 Phase I report. For this report, data from the in-stream samples were categorized by whether or not the watersheds had a history of mining. In all, two in-stream samples from mined watersheds (Southern Minerals and Panther) were collected from three different sampling locations (WVDEP, 2009). Neither of the two locations were affected by slurry injection activities, as they were either up-gradient of slurry injection or sampled from a different part of the watershed. For the “background chemistry of mined watersheds” section of this report, “background water chemistry” data are defined as those data which are affected by mining activities, but not by slurry injection. These data are important because they enabled the research team to observe the water quality conditions previous to slurry injection.

Southern Minerals

There was one background chemistry sample site (SM-4) in the Southern Minerals sampling area. SM-4 was chosen as representative of the background water chemistry because no slurry injection occurred upgradient of this sample point. This site was located on Elkhorn Creek. The dominant ions that influenced this water were calcium-sodium-bicarbonate. Bicarbonate concentrations at SM-4 contributed to high alkalinity (204 mg/L) and a pH value of 8.0. The geology surrounding SM-4 is largely shale. Sampling showed no contamination by organic compounds, with the exception of a trace amount of Total Petroleum Hydrocarbons. Regarding dissolved metal concentrations for SM-4, most analytes were below quantification limits, but above detection limits. As such, the reported result is an estimate. With the exception of calcium, magnesium, potassium, silicon, sodium, and strontium, concentrations of all ions were less than 0.3 mg/L. General chemistry at SM-4 was typical of mine-impacted water in this region, with sulfate concentrations of 99 mg/L, chloride concentrations of 4.96 mg/L, and Total Dissolved Solids (TDS) of 331 mg/L. No other background chemistry data was available within the delineated Southern Minerals area (WVDEP, 2009).

Panther

One background chemistry sample site was taken in the Panther sampling area (PL-4) as part of the sampling for SCR-15. PL-4 was located upstream of the Wet Branch Refuse area, which also placed it upstream of any slurry injection. Water at PL-4 was found to be a weak magnesium-sulfate (magnesium-sulfate) water type. No

Volatile Organic Compounds (VOCs) or Semi-Volatile Organic Compounds (SVOCs) were detected at PL-4. Dissolved metal concentrations were either undetectable or below 0.1 mg/L, with the exception of calcium, magnesium, potassium, silicon, and sodium. A pH of 6.78 at PL-4 was the lowest of all sample sites in the Panther sampling area. However, the conductivity and TDS were the lowest values among all Panther sampling area sites (WVDEP, 2009).

Some historic data were available for the Wet Branch Watershed (Table 15) Sites 001 and 002 are associated with previously permitted mines and were sampled as part of the permitting process. Site 001 is located in the headwaters of Wet Branch, while Site 002 is at the mouth of Wet Branch. USWB (Up Stream Wet Branch) and DSWB (Down Stream Wet Branch) were also sampled during the permitting process for a previous coal mine in this area. Although the locations of the upstream in-stream site USWB and the downstream site DSWB do not coincide with Sites 001 and 002, they are similar because they detail the historical water quality of Wet Branch before slurry injection. Although the data does not show any specific trend, it illustrates water quality changes between 1981 and 2007 (WVDEP, 2009). Since slurry injection did not occur in this area until 1996, Site 001, Site 002, USWB, and DSWB provide water quality data within the Wet Branch watershed that are unaffected by slurry injection.

Power Mountain

Two in-stream samples were taken at Power Mountain. However, both of these are downstream of slurry injection activities. Because of this, no samples from the SCR-15 report adequately represent “background” water chemistry at this site.

However, historic data within the Twentymile Creek watershed was taken before slurry injection occurred. Two in-stream samples (Sites #9 and #10) were taken downstream and upstream, respectively, of the confluence of Sugarcamp Branch and Twentymile Creek in 1983 while mining was occurring. One other sample (Up Stream Twentymile Creek, or USTC) was taken upstream of the Hutchinson Branch No. 1 mine, which drains into Spruce Run. Although the sample point USTC was sampled after slurry injection began, it was taken upstream of any injection activities. The historic data taken in the Twentymile Creek watershed is described in Table 16.

Loadout LLC

Although there was no sampling performed as part of SCR-15 in the Loadout project area that could represent baseline data, historic data were collected in this area for proposed mining permits and permit amendments. No organic chemistry data was collected at any point prior to the SCR-15 study in the Fork Creek watershed. Aqueous chemical sampling was conducted prior to the O-513-99 permit amendment. All analytes were below detection limits, except selenium which was detected at a concentration of 3.0 µg/L in a sample collected below a coal preparation plant. Other baseline data were collected for mining permits. Mining in the Fork Creek watershed did not begin until 1996, so both pre-mining and post-mining data were available. A general trend of increasing levels of TDS, conductivity, alkalinity, and sulfate was found in this data, particularly below mining activities. This trend appeared to occur as mining progressed over time in the watershed.

Other Baseline Data

Another source of baseline stream chemistry data for the southern part of West Virginia outside of the SCR-15 Phase I report is a report contracted by the WVDEP to Ackenheil Engineers Geologists (AEG). This report was written to determine the feasibility of a water line extension along Prenter Road in Boone County, West Virginia. AEG performed a Phase I preliminary investigation to determine if, and to what extent, mining operations had affected groundwater in the area. The AEG Phase I report determined that mining was associated with significant groundwater impacts. In January of 2008, AEG conducted a Phase II Grant Supporting investigation to provide supporting information to the WVDEP regarding the quality of the local groundwater. Water chemistry samples from wells, streams, and mine openings were obtained to support the generation of the report. Twenty-eight sites were sampled, with six of these being in-stream, baseline samples (ST-1 through ST-6; AEG, 2008).

Five of the six stream samples were determined to be affected by mining activities. Four (ST-1 through ST-4) were all magnesium-calcium-sulfate water types, one (ST-5) was sodium-magnesium-sulfate-chlorine-bicarbonate, and one (ST-6) was magnesium-calcium-sulfate- bicarbonate. Organic chemistry parameters were not sampled as part of this report. All of the samples were alkaline with the exception of ST-6. At this site, a pH of 4.9 and an acidity concentration of 139 mg/L were found. The acidic conditions found at site ST-6 were likely due to differences in the local geology. With the exception of site ST-3, iron, aluminum, and manganese concentrations were low. Conductivity and sulfates were higher at sites ST-3 and ST-5.

This is likely because these two sites were closest to active mining, which has a larger effect on water chemistry than pre-existing mining (AEG, 2008).

Background Chemistry of Unmined Watersheds

In addition to samples collected in mined watershed as part of the SCR-15 Phase I report, one of the samples collected at Loadout is representative of an unmined watershed (site LL-4). No surface mining was conducted in the headwaters of Wilderness Fork until after 1996. Site LL-4 is situated in a tributary of Wilderness Fork that has remained unmined since 1996 (WVDEP, 2009). Site LL-4 was located upstream of the dewatering borehole for the Nellis mine. While the Nellis mine does inject slurry, the injection point is downgradient of site LL-4. Thus, this sample may be used as representative of an unmined watershed and serve as a background sampling point.

Site LL-4 was deemed to be a calcium-magnesium-sodium-sulfate-bicarbonate water type. No organic compounds were detected at this site. Dissolved metal concentrations were either undetectable or below 0.3 mg/L, with the exception of calcium, magnesium, potassium, silicon, sodium, and strontium. General chemistry taken at site LL-4 was indicative of a site that had not been mined. Sulfate (16 mg/L) and TDS (180 mg/L) were both fairly low. Sulfate concentrations below 30 mg/L and TDS concentrations below 120 mg/L are common for unmined watersheds in this region (WVDEP, 2009).

Other Related Studies

A study was initiated by the West Virginia Department of Natural Resources to evaluate the effects of coal slurry injection into underground coal mines in southern West Virginia (Smith and Rauch, 1987). The authors concluded that “the injection of slurry into alkaline mine pools seems to generally improve the water quality within the mine pool by decreasing iron, manganese and total suspended solids and increasing pH and alkalinity. Sulfate, however, increased in concentration from the injected slurry effect.”

During the period 2004-2005 a study was conducted near Williamson, Mingo County, West Virginia by Wheeling Jesuit University (WJU). Data from the 2004 sampling was included in a draft report (WJU, 2004). The 2005 data were not published but were evaluated in this study. Collectively the 2004 and 2005 data prepared by WJU will be referred to as the WJU study. The WJU data are presented in Table 17 and summarized in Table 18. The WJU data make it clear that many of the sampled water sources were affected by sewage. Reduction/oxidation potential was measured at 67 sources and 60% of those were reducing. The average reduction/oxidation potential was -130 mV for those samples in the reducing category. Such strongly reducing conditions require an effective electron donor. Labile organic matter as found in sewage is the likely source. Coal, on the other hand, while organic is highly recalcitrant (otherwise it would not have survived for 220 million years) and is not an effective reducing agent. The WJU study revealed that 90% of the water sources were contaminated with coliforms and 40% of all samples were contaminated with fecal coliforms. In addition, the samples were contaminated to varying degrees with metal

and other ions that exceeded USEPA DWS. Among the primary drinking water standard exceedences, lead was the most common at 15% followed by barium and arsenic at 4% and selenium and cadmium at 2% and 1%, respectively. Not all of the samples in the WJU study were water that came from the tap. A number of samples were supernatant liquids from sludges that accumulated at the bottom of hot water tanks. While those samples accounted for many of the higher secondary contaminant concentrations, they accounted for none of the primary contaminant exceedences and only about 10% of the aluminum, iron and manganese exceedences.

The WJU study identified no cases where the following contaminants exceeded either primary or secondary DWS: chromium, beryllium, thallium, copper, antimony, silver and mercury. Table 19 summarizes the slurry liquid concentrations of contaminants that were detected in the WJU study and the average values of those exceedences. Both dissolved and total slurry liquid analyses are presented. With few exceptions, the average concentrations reported in the WJU study were substantially higher than those found in the undiluted slurry liquids.

The results of the WJU study and the slurry concentrations identified in SCR-15 pointed to a set of contaminants of concern: arsenic, lead, selenium, aluminum, iron and manganese.

Another study was conducted to evaluate drinking water issues related to mining and processing in the same area of Mingo County, West Virginia (ATSDR, 2005). It concluded that, while domestic wells in the study area were polluted with coliforms and metals common in mining (iron, manganese, aluminum), there was no evidence pointing to coal slurry per se as a health risk.

Southern West Virginia Groundwater

Groundwater flow in this region of West Virginia is mainly controlled by three factors: the distribution and type of recharge that infiltrates into the groundwater basin, topography of the recharge area, and the hydraulic conductivity of the material through which the groundwater flows (WVDEP, 2009). These factors may in turn be affected by a host of other elements, including soils, climate, lithology, and geologic structure, among others. Both surface and underground mining can drastically alter these factors in a variety of ways. For example, groundwater recharge rates can be altered depending on the degree of compaction of the surface material, as well as how the site is revegetated. Post-mining topography will impact groundwater recharge as well. Surface topography can be altered from its original contours depending on the final reclamation plan. Hydraulic conductivity of a surface mining site can be greatly affected by the overburden, which must be removed and replaced as mining progresses. Mine spoil may be more conductive than parent material by several orders of magnitude due to larger void spaces between pieces of mine spoil (Hawkins, 1995). In underground mining, hydraulic conductivity also can be significantly altered by collapsed and fractured roof rock (Kendorski, 1993).

The direction of groundwater flow is determined by differences in hydraulic head. Groundwater flows from areas with higher hydraulic head to areas with lower hydraulic head as the water system attempts to reach equilibrium. In an unconfined aquifer, water table elevation can be used to determine the distribution of hydraulic head and indicate the direction of groundwater flow. The local topography, coupled with spring (discharge

area) and possibly well (water level) mapping, are used to estimate the direction of groundwater flow. In an open, flooded mine pool, the groundwater flow system is often radically different than the aforementioned undisturbed strata. The mine water will flow relatively unimpeded down -dip along the floor of the mine until a barrier is encountered. These barriers are usually in the form of a coal barrier or a previously flooded section of the mine. Once flooded, the mine water flow system is then dominated by the significantly lower hydraulic conductivities of the coal and overlying geologic units (WVDEP, 2009).

Aquifers may be categorized by their hydraulic conductivity (permeability). The two types of permeability are primary and secondary. Primary permeability refers to the intergranular spaces of the transmitting medium. It may be more significant in unconsolidated sediment types, but is less important in the consolidated bedrock of the Appalachian Plateau. Secondary permeability is the permeability in a rock strata developed after its deposition, typically from the weathering and fracturing of the rock strata (Williamson and Carter, 2001). Abandoned underground coal mine voids may serve as large secondary permeability pathways. Flow in an underground mine is different from typical intergranular and fracture flow. Due to the scale of the operations, underground mines may impact the hydrology of a given area to a greater extent than a surface mine. Interbasin transfer of groundwater is a common event associated with underground mines. The voids created during mining act as a large sink which draws in groundwater. At the conclusion of mining, the mine void becomes a highly permeable aquifer which can alter the local flow regime both physically and chemically. Due to the interconnected nature of many mine-void aquifers, there is a high possibility of

postmining transfer of the resulting mine-pool water throughout the interconnected mine workings (WVDEP, 2009).

Acidic Mine Pool Water Background Chemistry

The geology in this region is from the Pennsylvanian Age. The majority of the rock is sandstone, with layers of coal, limestone, and shale interspersed among the sandstone. Groundwater in Southern West Virginia is often found in sandstones and carbonates, which impart to groundwater a higher pH and lower metal concentrations (National Research Council Committee on Groundwater Resources in Relation to Coal Mining, 1981). Because of the large amount of alkaline material found in the geology, acidic groundwater is often more difficult to find in southern West Virginia than in the northern part of the State, where the geology is much more likely to be acidic. This applies to mine drainage in southern West Virginia as well. As coal and its associated minerals are exposed to the atmosphere during the mining process, the carbonate minerals located in the nearby geology cause alkaline mine drainage.

Although none of the sample sites in the SCR-15 study were taken from acidic mine pools, other data that are from acidic environments are available for this region of West Virginia. AEG (2008) sampled 18 residential wells and 4 mine drainage sites to determine the viability of a water line extension in eastern Boone County, West Virginia within the Laurel Creek watershed. Of the sampled sites, two acidic mine drainage sites and 4 residential wells were located. Table 20 gives the data for these sample points. The two sites labeled MD-3 and MD-4 are mine drainage sites sampled at a mine portal, while WL-12, 13, 14, and 15 are samples drawn from residential wells.

All six sample sites had a pH below 5.0. Metal concentrations were mostly low, with the exception of aluminum concentrations in MD-3 and MD-4. Sulfates were also fairly low, with the exception of MD-4 and WL-12.

Stiff diagrams were also constructed for each sample site. A Stiff diagram is a graphical comparison of the relative concentrations of specific anions and cations of several different samples (WVDEP, 2009). The direction and length of each corner of the diagram illustrates sample chemistry. Stiff diagrams can help the researcher identify samples that have similar or dissimilar compositions.

The shape of the plots for both MD-3 and MD-4 were similar. However, MD-3 had much smaller peaks, meaning that this site was not dominated as heavily by any specific ion group. MD-3 plotted as a sodium-calcium-magnesium-sulfate-chlorine water type and MD-4 was a calcium-magnesium-sulfate water type. WL-12 and WL-15 also had similar Stiff diagrams, with both waters described as magnesium-bicarbonate-sulfate. The dominating ions in WL-13 and WL-14 were quite different from the other sample sites. WL-13 was a magnesium-calcium-bicarbonate-sulfate water type and WL-14 was a sodium-calcium-chlorine-bicarbonate (AEG, 2008).

Alkaline Mine Pool Water Background Chemistry

All groundwater samples taken as part of SCR-15 were from alkaline sources. There were 18 groundwater samples taken as part of this study. Three sites were sampled in the Southern Minerals sampling area, six in the Loadout area, three in the Panther area, and six in the Power Mountain area (WVDEP, 2009).

Southern Minerals

The three groundwater samples taken in the Southern Minerals sampling area were sites SM-5a/b (also named GW-1), SM-6, and SM-7. The major ions indicate the water type for sample site GW-1 (SM-5a and SM-5b) to be sodium bicarbonate (Figure 1). GW-1 was previously used as a groundwater monitoring well, but for the past several years had also been used as a slurry injection site. The well is an open borehole that is cased to a depth of about twenty feet. Two zones for the well were sampled. SM-5a, which was identified as the deep zone of the well, consisted of the settled solids. SM-5b was identified as the shallow zone and represented the supernatant, or liquid portion found above the slurry sediment (WVDEP, 2009).

GW-1 is likely part of an intermediate zone in which chloride has been removed by flushing with infiltrated surface waters. However, significant concentrations of sodium remain that are likely adsorbed to clays and similar materials in the sediment. This chemistry would lead to the Sodium Bicarbonate water that was found at this site. The elevated sodium is a result of cation exchange, with sodium released from the exchange sites and replaced by calcium and magnesium (WVDEP, 2009).

Only two semi-volatile organic compounds and no volatile organic compounds were detected in these two samples. Both samples also had detectable concentrations of Total Petroleum Hydrocarbons (TPH's). Tables 21 and 22 describe selected organic and inorganic water chemistry results, respectively. Sites SM-6 and SM-7 are artesian discharges. SM-6 surfaces along U.S. Route 52 and SM-7 is a downdip discharge from the adjacent abandoned Pocahontas Capels Mine. The major ions indicate the water type for both sample sites SM-6 and SM-7 as sodium-bicarbonate (Figures 2 and 3).

These two sites represent the hydrologically interconnected discharges from the flooded Pocahontas No.3 and No.4 seam mine voids. Water chemistry for these sites indicates that deep groundwater is mixing with fresh water from the surface within the deeper circulation of the mine pool, which is characterized by the Sodium Bicarbonate water type (WVDEP, 2009).

Chemistry results from the lab detected no semi-volatile or volatile organic compounds for either site. Elevated dissolved iron and alkalinity concentrations were found at SM-6 as well as fairly high sulfate concentrations at both sites. Table 23 details selected general and inorganic chemistry results for SM-6 and SM-7. No other baseline chemistry data was available for this sampling area (WVDEP, 2009).

Loadout

The six groundwater samples taken in the Loadout sampling area were sites LL-1, LL-7, LL-8a, LL-8b, LL-12, LL-13, and LL-14. Samples LL-1, LL-7, LL-8a, LL-8b, and LL-12 all represent groundwater associated with mine pools in the Eagle coal seam. Sample LL-13 is from a deep mine, located in the #2 Gas seam which lies above the Eagle Coal seam. Sample LL-14 was taken from the Nellis mine. Table 24 and Figure 4 give locations and descriptions of the water sampling sites in the Loadout sampling area.

Direction of groundwater movement in the Fork Creek watershed is controlled by fractures near the surface at shallow depths (<200 feet), as well as the dip of the mine voids (Wyrick and Brochers, 1981). The most extensive and deepest of these existing mines is the Eagle Seam mine works. These mine works are shown in Figure 4 as the

yellow outlines. The Eagle Seam mine works underlie much of Fork Creek watershed, causing them to have a large impact on groundwater movement in this watershed. Within these open mine voids, groundwater will flow in a down dip direction.

None of the Loadout groundwater sampling points detected any organic constituents, with the exception of 1,2,4-Trimethylbenzene at point LL-7. This compound was detected at a low concentration of a 0.6 µg/L. A possible source of this chemical is as a fuel material that was used during the mining process.

Inorganic and general chemistry showed generally higher concentrations in groundwater than in surface water. This is likely due to the passage of the groundwater through the mineralized environment of the various Eagle Seam deep mines in the Loadout sampling area. High levels of sodium, potassium, carbonate and sulfates were found in the groundwater samples (Tables 25 and 26). Strontium was also found in elevated concentrations in several groundwater samples that were associated with abandoned deep mine works in the Eagle Seam. These Eagle Seam mine works also had elevated iron and manganese concentrations. Aluminum concentrations were also elevated in many samples, most notably at sites LL-1 and LL-12 (Table 25). Sample LL-12 appears to illustrate alkaline mine drainage contamination. It is visibly stained with iron and has elevated levels of iron, manganese, beryllium, aluminum, nickel and sulfate. Sample LL-12 also shows an elevated lead concentration of 0.0106 mg/L (Table 25; WVDEP, 2009).

Baseline sampling data was also taken by the Fork Creek mining company as part of its mining permit. Four samples (BGW-22 through BGW-25) were taken during 1997-1998. All four sites were taken from abandoned mine pools (Table 27). No

testing was performed for either organic compounds or heavy metals at any of these sites. Similar to current water chemistry, this data from the four abandoned mine pool sites showed elevated concentrations of total dissolved solids, sulfates, iron, and aluminum (Tables 28-31).

Panther

Three groundwater points were sampled in the Panther sampling area. These sites were named PL-5, PL-2, and PL-6. Sample site PL-5 was considered both a ground and surface water site. PL-5 represents surface water which began as a seep on top of a refuse pile. The seep then drained through the pile (where it became groundwater) and discharged from the toe of the refuse. It is likely that the water from the seep mixed with other groundwater sources within the pile. PL-5 was characterized as a sodium-sulfate water type (Figures 5 and 6; WVDEP, 2009).

No Volatile Organic Compounds (VOCs) or Semi-Volatile Organic Compounds (SVOCs) were found at PL-5. Selected inorganic and general chemistry is summarized in Table 32. PL-5 shows the highest concentrations of all three sites regarding sodium, chloride, sulfate, and conductivity. This is likely due to the mineralization of the water after it has infiltrated through the refuse pile (WVDEP, 2009).

PL-2 is a mine dewatering borehole for mine UO-391. The water type for this sample was determined to be Sodium Bicarbonate, with weak influences by chloride and sulfate (Figures 5 and 7). No VOCs or SVOCs were found at PL-2 with the exception of TPH compounds. The concentrations of the TPH chemicals were as follows: Diesel Range (0.92 mg/L), Oil Range (4.16 mg/L), and Oil and Grease (2.20

mg/L). PL-2 had the highest concentration of bicarbonate among the three groundwater sites (Table 32; WVDEP, 2009).

PL-6 is the residential well of Owen Stout. The water type for this sample was determined to be Calcium-Bicarbonate (Figures 5 and 8). No VOCs or SVOCs were found at PL-6. PL-6 had the highest concentrations of manganese, iron, silicon, and acidity among the three groundwater sites (Table 32; WVDEP, 2009).

One historic groundwater sample site was available for comparison to the current Panther groundwater data. The Mollie Bailey well was sampled as part of mining permit #O-112-83 (WVDEP, 2009). This well was located within the current Wet Branch Refuse Area. Table 33 shows that the water chemistry of the Mollie Bailey well is significantly different from the three current Panther sample sites taken at sample points PL-2, PL-5, and PL-6. Historical permit data from the Mollie Bailey monitoring well was available, but current data from this well were not available, because the well has been buried (WVDEP, 2009).

Power Mountain

Groundwater was sampled at eight different points in the Power Mountain sampling area. However, PM-1 and PM-2 were excluded as baseline water quality points because they are below coal slurry injection sites. The remaining six baseline sites were named PM-6, PM-9, PM-10, PM-11, PM-13, and PM-14. Table 34 gives descriptions of the sample points and Figure 9 shows their locations (WVDEP, 2009).

PM-6 was a sample taken from a monitoring well in the Flying Eagle mine pool. This sample has a water type of Sodium-Sulfate (Figure 10). The only organic

compounds detected at PM-6 were microgram concentrations of benzene (0.3 ug/L) and toluene (0.3 ug/L). The source of these compounds may be from leachate of the coal seam within the mine or remnants of equipment left in the mine. High concentrations of sulfate, sodium, and strontium, as well as high conductivity and TDS, are indicative of mining-influenced water. Table 35 gives more water chemistry results for PM-6 (WVDEP, 2009).

PM-9 was taken from the Naylor's well. This sample is a magnesium-sulfate water type (Figure 11). No organic compounds were detected at PM-9. Metal concentrations in this sample are also low (Table 36). However, sulfate is elevated compared to historic groundwater data seen in Table 37. It is likely that the observed elevated sulfate concentrations are due to mining impacts (WVDEP, 2009).

PM-10 was taken from the Corbetts' well. This sample is a sodium-bicarbonate water type, which suggests that this water source is not impacted by mining (Figure 12). No organic compounds were detected at PM-10. Although still fairly low, iron, aluminum, and manganese are highest at this site when compared to the other two residential wells (Table 36). Iron and aluminum concentrations are above the Federal secondary drinking water standards at PM-10. However, sulfates were not detected in this sample (WVDEP, 2009).

PM-11 was taken from the Mullins' well. Although PM-9 and PM-11 are near one another, their water quality is vastly different. This sample is a sodium-bicarbonate water type, which suggests that this water source is not impacted by mining (Figure 13). No organic compounds were detected at PM-11. PM-11 had much lower overall metal

concentrations than PM-9. PM-11 did have a high sodium concentration (Table 36). Sulfates were also very low (WVDEP, 2009).

PM-13 was taken from a seep downslope of the Rhonda Eagle mine. This sample is a calcium-sulfate water type (Figure 14). No organic compounds were detected at PM-13. This site is characterized as having elevated metal concentrations, sulfate, and TDS (Table 35), which are consistent with results of groundwater from mining impacted areas in southern West Virginia. This water chemistry may also be influenced by slurry injection that has taken place within the mine (WVDEP, 2009).

Historical mine pool data is also available for other mines near the Rhonda Eagle mine. TDS and sulfate concentrations are lower in these historic data before slurry injection (Table 38). A review of some historical data on mine pool water quality for selected mines prior to slurry injection. The table also shows water data for the mine pool at the Jerry Fork Mine, an adjacent mine on the Eagle coal seam where slurry injection did not occur. Water quality of the Jerry Fork Mine shows lower sulfate and TDS concentrations than those samples from the other mines (Table 38). The sample from the Jerry Fork mine is therefore more representative of baseline groundwater quality in this region (WVDEP, 2009).

PM-14 was sampled from the entry of the Radar Eagle mine. This sample is a weak calcium-sulfate water type (Figure 15). No organic compounds were detected at PM-14. This site is characterized as having low metal concentrations (Table 35). TDS and sulfates are also low. This water quality is indicative of an unmined watershed. This may be because of shallow ground cover, which gives the groundwater a short flow path. The infiltrating groundwater may be short circuiting the mine (WVDEP, 2009).

Another source of baseline groundwater data is the Prenter Waterline Feasibility Study (AEG, 2008). Groundwater sampling consisted of 18 residential wells (WL-1 through WL-18) and 4 mine pool samples (MD-1 through MD-4). Water chemistry results for all sample points are shown in Table 39 and Piper Diagrams showing water types for each sample are described in Figures 16 and 17.

Piper diagrams detail clusters of data points which indicate if a specific water sample has a similar composition to another sample. Piper diagrams are created by plotting the major cations and anions as percentages of milliequivalents in two base triangles. The data in these triangles is projected to a diamond graph which may reveal useful trends and relationships for large sample groups (WVDEP, 2009).

Although all samples were taken in a mined watershed, none of the WL samples showed impacts from mining as evidenced by where they plotted on the Piper Diagram (Figures 16 and 17). This may be due to the wells accessing water that is in a shallow bedrock aquifer and thus do not have a high level of communication with area streams. All wells sampled were also fairly distant from mining. Mining took place at least 1,000 feet upslope from the wells, which gave the groundwater an opportunity to flow through the geologic strata before it was pumped out of the well. The geology in this area is not conducive to poor groundwater quality.

Mass Balance Model

Underground Mine Pools

There are no studies that systematically and temporally evaluate the effect of slurry injection on mine water chemistry in southern West Virginia. That is, there are no

studies that characterize a mine pool prior to, during and after slurry injection while documenting the quality and quantity of injected slurry. However, SCR-15 sampled mine pools up and downgradient of slurry injection. Another study by WJU sampled 97 domestic water sources (mainly private wells) in Mingo County, West Virginia in 2004 and 2005. The intention was to determine whether well chemistry pointed toward coal slurry as a source of contamination. While not conclusive with respect to the source of contamination, the WJU study was useful in that it identified a suite of inorganic contaminants that occurred at levels in excess of USEPA DWS in domestic wells near mining and slurry activities. Those exceeding the primary DWS included: arsenic, barium, cadmium, lead and selenium. Secondary drinking water exceedences included: coliforms, TDS, pH, aluminum, iron, manganese and zinc. These will be taken as the initial contaminants of concern.

Analyses of coal slurry liquids presented in the SCR-15 report indicated that the Southern Minerals, Panther and Coresco slurry liquids exceeded the primary DWS for antimony while the Panther slurry liquid also exceeded the primary DWS for arsenic. Among the secondary drinking water standards, only aluminum, iron and manganese were exceeded. While total analyses were invariably higher than dissolved concentrations there were few differences between the two with respect to whether the drinking water was exceeded (Table 11).

A subset of contaminants identified in the WJU study was subjected to a mass balance analysis to estimate whether enough was injected with slurry to cause the receiving mine pool to exceed drinking water standards. The concentrations of all of these contaminants in coal slurry were evaluated and those that did not originate in coal

slurry or did not occur in the slurry samples at concentrations above DWS were eliminated. In fact, most did not exceed DWS but the following were subject to the mass balance analysis: arsenic, lead, selenium, aluminum, iron, manganese, sulfate and TDS. The WJU study did not include sulfate but it was included in the mass balance analysis since it results from pyrite oxidation and is a common indicator of mine drainage.

Among the organic contaminants that were evaluated in SCR-15 Phase 1 only diesel appeared to be directly traceable to coal slurry and present in a large number of samples. It was, therefore, chosen as the organic marker across the four study mines.

Concentrations of dissolved contaminants in the slurry were used in the mass balance analysis since it was hypothesized that the dissolved fraction best estimates the mobile fraction of the slurry. Chemical analysis of the solid fraction of the coal slurry does not indicate which ions will become mobile or what concentrations they would achieve. It was anticipated that comparison of slurry affected mine pool chemistry to results of the mass balance analysis would provide a test of this hypothesis.

The mass balance analysis was developed to estimate the maximum contaminant concentrations that could develop as a result of slurry injection. The analysis was conducted on the four mines studied in detail in the SCR-15 Phase I report: Southern Minerals, Loadout LLC, Panther, LLC and Power Mountain. The mass balance analysis used site-specific data such as slurry contaminant concentration, injection rate, period of injection and mine area (Table 40). The analysis calculated the volume of water injected as slurry and the mass of the dissolved constituents (the mobile fraction). In an underground mine, the mass of contaminant injected with slurry

will be diluted by the volume of groundwater infiltrating into the mine. The volume of infiltrating groundwater was estimated on the basis of the mine's surface area and an assumed infiltration rate of 0.25 gpm/acre/year. That value is at the low end of the generally assumed infiltration range of 0.2 to 1.0 gpm/acre/year. Thus, a conservative dilution factor was used. All of these mines were small, ranging from 2.0 to 5.12 square miles. Infiltration rates indicated that even if 100% of the mine voids were available to fill with water, then the pools would be replaced in between a shortest time span of 1.3 years for Panther and a longest time span of 3.1 years for Southern Minerals. Planned injection periods would exceed all of those numbers. Since the flooded volumes of the mines were not known and the pool replacement times were short, dilution of the existing mine pool was not considered. There were no data to indicate the degree of mine void flooding or concentrations of contaminants in either the mine pools or the infiltrating water, so the analysis assumed that slurry was the only source of contaminant. Thus, estimated parameter reflected the net effect of slurry addition on mine pool water quality. We do not know the degree of flooding in the mines or the extent to which there is open access of atmospheric gas exchange. Thus, it must be assumed that pyrite oxidation continues and, even though there may be sufficient alkalinity to maintain an alkaline pH, secondary contaminants, sulfate, iron, manganese and aluminum will continue to be produced.

If contaminant ions do not come out of solution in the mine pool by mechanisms such as precipitation or sorption, then their equilibrium concentrations would be dominated by dilution with groundwater infiltrating into the mine. Since the mass balance model only accounts for dilution, the difference between the model estimate

and the observed values should reflect the extent to which either additional ions are liberated from solids in the mine (net gain) or the extent to which ions are removed from solution by the above mechanisms (net loss). If ions are conservative and slurry is the only source, then during the slurry injection period contaminant concentrations will increase to a level where the mine pool chemistry is dominated by dissolved ions in the slurry. After slurry injection ceases, those levels will decline as infiltration water flushes contaminants out of the mine voids. Since injection into all of these mines is expected to extend for at least 10 years, no decay curve was included in the mass balance model. It was also assumed that all study ions are conservative. That means that there was no attempt to identify how much of the contaminant would sorb to solids or react to form insoluble precipitates. In reality, many of the contaminants would tend to precipitate based on pH and redox conditions. For example, most of the aluminum will precipitate as a hydroxide at pH greater than 4.5 while arsenic and selenium (selenite) would sorb to ferrihydrite, the result of iron precipitation in oxidizing conditions. However, estimation of the extent of sorption and the resulting ion solubilities would require sophisticated geochemical sampling and modeling that would be beyond the scope of this study. Thus, the assumptions favor conditions that would yield maximum contaminant concentrations.

The mass balance analysis assumed that the soluble contaminants in the slurry will be diluted by largely uncontaminated water infiltrating through the roof of the mine. The output of the mass balance analysis was compared to the water quality upgradient and downgradient of slurry injection sites identified in SRC-15 (Table 41). The table indicates contaminant concentrations in groundwater samples that are presumed to be

unaffected by (upgradient of) slurry injection and slurry liquids and samples that are presumed to be affected by (or downgradient of) slurry injection. Average values are given for the affected samples and they are compared to the results of the mass balance analysis. The results are discussed below and separately for each of the four study mines.

Surface Water

A mass balance analysis was not undertaken for surface water since no flow data are available. Therefore, discussion of the effects on surface water rely on observed concentrations and comparison with aquatic life standards.

The analyses discussed above are based on SCR-15 data which represents unreplicated samples taken over a several year period. Ideally, multiple samples of surface water, groundwater and slurry would be available so that sampling error and population variance could be calculated. While these limitations should be taken into consideration when assessing the results, they are to some extent, compensated by the fact that four mines were studied, yielding a sort of replication. It should also be remembered that mine flow pathways are not straightforward. Chemical characterization of a mine pool without slurry injection is difficult and can yield very different results in different parts of the mine.

Effects of Coal Slurry Injection

Groundwater

Table 41 summarizes the results of groundwater monitoring upgradient and downgradient of slurry injection. It also includes slurry chemistry and the results of the

mass balance analysis. The results are compared to primary and secondary USEPA DWS. The results are discussed below.

Southern Minerals

The slurry at this site exceeded the secondary DWS for aluminum and iron. However, none of the primary drinking water contaminants: arsenic, lead, selenium exceeded their DWS in either the upgradient, downgradient or slurry liquid samples. The upgradient sample exceeded the secondary DWS for manganese and TDS. Half of the downgradient samples complied with DWS while one of the other two exceeded secondary DWS for iron, manganese and TDS and a fourth sample exceed secondary DWS for iron and manganese. On average the downgradient wells exceeded secondary DWS for iron, manganese and pH. The mass balance analysis correctly predicted no effect on primary contaminants from slurry injection and identified manganese as a secondary contaminant. The model predicted an iron concentration of 0.2586 mg/L, slightly below the secondary DWS of 0.3 mg/L. The higher levels of iron, aluminum and manganese in the downgradient wells suggest ongoing pyrite oxidation in the mine voids. The rate of pyrite oxidation is likely very slow as the model predicted 45 mg/L of sulfate while 53 mg/L were observed. Diesel was not observed in the upgradient well or the slurry but appeared in two of four downgradient samples averaging 0.215 mg/L.

Loadout LLC

Like the Southern Minerals site, no exceedences of primary DWS were observed in upgradient, downgradient or slurry samples. Mass balance model predictions were

consistent with these observations. Upgradient groundwater samples exceeded most of the secondary drinking water parameters including pH. Downgradient of slurry injection, pH increased which probably accounted for lower concentrations of aluminum and iron. On average, the downgradient samples exceeded secondary DWS for iron and manganese. The model incorrectly predicted an exceedence for aluminum and was likely wrong because it did not account for the higher pH in the mine pool which would have precipitated aluminum as a hydroxide. The model yielded reasonable predictions of iron concentrations: observed 0.332 versus 0.264 mg/L and manganese: observed 0.096 versus 0.031 mg/L. Diesel was observed in the slurry in a concentration of 16.6 mg/L. However, it was not detected in any of the downgradient samples.

Panther LLC

While the other three mine sites had multiple groundwater samples, monitoring at this site consisted of one upgradient and one downgradient well. This was the only site where slurry liquids exceeded primary DWS. Arsenic was present in the upgradient well but both arsenic and lead concentrations, were zero in the downgradient sample. The mass balance model predicted concentrations greater than zero, yet below DWS. The lower, observed values may be the result of arsenic sorption to ferrihydrite and precipitation of lead hydroxide at the higher pH in the mine pool. Otherwise, only TDS exceeded the secondary DWS. Iron and manganese concentrations were both higher in the upgradient than in the downgradient well. The mass balance model predicted a TDS of 490 mg/L (the secondary DWS is 500 mg/L) while the observed value was 791

mg/L. While diesel was not detected in the slurry, it was detected in the downgradient well at a concentration of 4.16 mg/L.

Power Mountain

Not arsenic, lead nor selenium exceeded their respective primary DWS in the upgradient, downgradient or slurry samples. However, arsenic increased downgradient of slurry injection (to 13% of the primary DWS) yet it was not detected in the slurry. This was the only case where arsenic was higher in the mine pool water than in the slurry. In fact, other than a slightly higher lead concentration in Southern Mineral's mine pool water than in the slurry liquids (0.0008 mg/L slurry versus 0.0013 mg/L average in the mine pool) this was the only case where mine water concentrations exceeded concentrations found in slurry liquids for arsenic, lead or selenium. This suggests that the liquid fraction is a robust predictor of the mobile fractions of these elements. Levels of both aluminum, iron, manganese, sulfate and TDS all increased downgradient of slurry injection well beyond the concentrations predicted by the mass balance model suggesting ongoing pyrite oxidation in the mine voids. While diesel was observed in the slurry, it was absent in the upgradient and downgradient samples.

Surface Water

Streams were sampled upgradient and downgradient of slurry injection sites in SCR-15. The results are summarized in Table 42. The same parameters were used in this analysis as in the previous section on groundwater effects. Dissolved ion analyses are used throughout this discussion except for slurry where the data indicate the total analysis of the aqueous fraction. The data are compared to West Virginia water quality

criteria for warm water fishery (WWF). Concentrations above WWF are considered exceedences. There are no WWF criteria for sulfate, TDS or diesel.

Southern Minerals

The upstream sample did not exceed any of the WWF criteria. The slurry at this site exceeded the WWF criterion for selenium with a concentration 0.008 mg/L and one downstream sample measured 0.007 mg/L. The WWF criterion for selenium is 0.005 mg/L. The other downstream sample was 0.002 mg/L. No other WWF criteria were exceeded either in the slurry or in the downstream samples.

Loadout LLC

One of the upstream samples at this site exceeded the WWF criterion for selenium and the slurry liquids exceeded the WWF criteria for selenium and aluminum. However, none of the downstream samples exceeded the WWF criteria.

Panther LLC

There were no upstream exceedences of WWF criteria at this site. Slurry exceeded WWF criteria for lead and selenium. The downstream sample did not exceed any of the WWF criteria. The only exceedence occurred downstream of a surface slurry impoundment where the selenium concentration was measured at 0.007 mg/L. Otherwise all WWF criteria were met at this site. Diesel was not detected in either the stream samples or the slurry.

Power Mountain

One of the two upstream samples exceeded WWF criteria for selenium and manganese at this site. The slurry exceeded WWF criteria for selenium and there were no downstream exceedences of WWF criteria. Diesel was detected in the slurry but not in the downstream sample.

In summary, the data show no in-stream exceedences of WWF criteria downgradient of slurry injection in a underground mine. The only exceedence of a WWF criterion was in the discharge from a surface refuse impoundment at Panther.

The above discussion is based on stream samples that were analyzed for dissolved ions except for sulfate and TDS which were total analyses. Slurry ion concentrations were all based on total analyses (Table 42). Table 43 was prepared to evaluate whether using total ion analyses would change the conclusions. While concentrations of several ions were higher than in the dissolved fraction, they did not result in any additional exceedences of WWF criteria.

Comparison of Contaminant Concentrations with Water Quality Standards

Primary Drinking Water Standards (DWS)

Only the Panther slurry liquids exceeded primary DWS. Specifically, arsenic in the Panther liquid fraction was 0.0113 mg/L while the primary DWS is 0.010 mg/L. Lead was 0.0775 mg/L while the primary DWS is 0.015 mg/L. The mass balance model estimated low levels of arsenic and lead below the drinking water limit. However, the water sample from the well downgradient from the Panther slurry injection site was below the detection limit with respect to both arsenic and lead. This may be explained

by sorption and precipitation of lead and arsenic within the mine, reducing concentrations below estimates based solely on dilution with infiltrating groundwater.

The mass balance model predicted that none of the primary DWS for arsenic, lead and selenium would be exceeded in the four mines. Observations confirmed these predictions (Table 41). The mass balance model did not predict any exceedences of the primary DWS for arsenic, lead or selenium. The mass balance model tended to overestimate the concentrations of arsenic, lead and selenium. Seventy five percent of the mass balance predictions exceeded the observations, suggesting either systematic sampling error or precipitation/sorption of contaminants in the mine. In the absence of evidence to suggest that the pH or redox status of the mines would change dramatically, it is expected that this sequestration would be permanent. Only three upgradient groundwater samples were at a pH 6 or below: PM 9, LL 12 and LL 13. PM 9 was from an updip mine that had not received slurry injection while LL 12 was a seep on the updip cropline of an injection mine and LL 13 was a domestic well outside the mine boundaries. All other upgradient and downgradient groundwater samples had a pH greater than 6.5. This suggests that the acid/base balance in the mines is alkaline.

Secondary Drinking Water Standards (DWS)

At least one of the secondary drinking water contaminants exceeded secondary DWS upgradient and downgradient of slurry injection in all of the mines. Manganese exceeded the secondary DWS upgradient of slurry injection in all of the mines while iron, aluminum and TDS exceeded the secondary DWS in half of the mines. Downgradient of slurry injection, TDS, exceeded the secondary DWS in all mines while

iron and manganese exceeded the secondary DWS in 75% of the mines. Aluminum exceeded the standard in half of the mines. In nearly all cases the predicted secondary contaminant levels were lower than the observations. Since most of these were products of pyrite oxidation they are likely produced in the unflooded portions of the mines. However, the low concentrations of sulfate indicate that pyrite concentrations are very low.

Diesel was detected in three groundwater samples representing two mines. In both cases, diesel was not detected in the slurry injected into those mines.

Summary and Conclusions

Groundwater

Two primary sources of data were evaluated in this section: the WJU study and the SCR-15 Phase 1 report. The WJU study was useful in identifying a list of three primary drinking water contaminants for detailed study: arsenic, lead, selenium and six secondary drinking water contaminants: aluminum, iron, manganese, sulfate, TDS, pH. Diesel was also studied though it is not subject to a DWS. The SCR-15 report provided four case studies of slurry injection into mines. In preparing the SCR-15 report the slurry injected into each mine was characterized and surface and groundwater samples were taken upgradient and downgradient of slurry injection. The results did not indicate any exceedences of primary DWS as a result of slurry injection. The elements comprising the secondary DWS are associated with alkaline mine drainage. Thus, while pyrite oxidation was active, acidity was neutralized by alkaline, leaving sulfate, TDS, manganese, iron and aluminum in solution. Secondary DWS were commonly

exceeded both upgradient and downgradient of slurry injection. Downgradient concentrations were generally greater than was predicted by the mass balance model suggesting continuing pyrite oxidation although at a slow rate as indicated by the low sulfate concentrations. Downstream of slurry injection, concentrations of secondary contaminants increased at Power Mountain and did so to a lesser extent at Southern Minerals. On the other hand, secondary contaminants decreased at both Loadout and Panther. The data show no general increase in secondary contaminants as a result of slurry injection.

Diesel was detected in three groundwater samples representing two mines. In both cases, diesel was not detected in the slurry injected into those mines. The SCR-15 report indicated that the analytical similarities between the organic compounds associated with coal and the analytical results for diesel make conclusions difficult if not impossible. That, coupled with the inconsistent appearance of diesel in the sampling results make it impossible to draw any conclusions other than the fact that the appearance of diesel downgradient of slurry injection did not coincide with the detection of diesel in the slurry.

Surface Water

Analysis of the effects of slurry injection on groundwater was based on the four case studies in the SCR-15 report. Consistent with the objective of identifying adverse effects of aquatic life, surface water was assessed in comparison to the WWF standard. It is important to note that the WWF for selenium is 0.005 mg/L versus the 0.050 mg/L primary DWS. Thus selenium appears out of compliance more commonly with regard

to stream samples than in groundwater samples. In fact, all four slurry liquids exceeded WWF for selenium. Selenium exceeded the WWF in two of the upstream samples but both were surface mine discharges that were not associated with coal slurry. The only downstream samples that exceeded the WWF for selenium were discharges from surface slurry storage areas. None of the stream samples were out of compliance with regard to selenium or any other WWF contaminant (Table 42). That conclusion was the same whether total or dissolved ion analysis was used (Table 43).

In summary, the results based contaminants identified in the WJU study and the data generated through SCR-15 and summarized in this section are straightforward. The data do not identify a link between slurry injection in any of the four study mines and exceedences of primary DWS for arsenic, lead or selenium in the mine pool water downgradient of slurry injection. Contaminants associated with alkaline mine drainage: aluminum, iron, manganese, sulfate and TDS, however, often exceeded secondary drinking water standards upgradient, in the slurry liquids and downgradient of slurry injection. Their concentrations were generally much higher than could be accounted for through slurry injection alone suggesting ongoing pyrite oxidation in the mines.

These conclusions reflect data collected at four slurry injection sites: Southern Minerals, Loadout, Panther and Power Mountain. The data represent single sampling events. That prevented statistical testing to determine the confidence interval about the data points. However, the consistency of the results among the four mines suggests that the results may be representative of slurry injection in southern West Virginia underground mines.

Recommendations

The type of monitoring network established in SCR-15 is fundamentally sound. Slurry chemistry was characterized and groundwater sampling stations were established upgradient and downgradient of each mine's slurry injection point. Similarly, surface water was sampled upstream and downstream of the slurry injection points. The study mines were mapped, the general direction of groundwater flow was identified and the sampling stations and injection points were identified.

However, there were shortcomings with the monitoring program that should be rectified in any future studies. For example, a slurry monitoring program should include regular and repeated sampling with respect to chemistry, volume and the proportions of liquid to solid fractions. It should involve thorough characterization of the receiving mine: area, interconnections with other mines, flooded area and pre-injection chemistry.

The mass balance approach used in this study correctly predicted exceedences of the primary contaminants: arsenic, lead and selenium. Mass balance modeling was less successful in estimating secondary contaminant exceedences due to the high background concentrations and the likelihood of ongoing generation of aluminum, iron, manganese, sulfate and TDS. However, it indicates the extent to which slurry injection contributes to the concentrations of these parameters. Also, the mass balance approach should be used to estimate the potential for primary contaminant exceedences in advance of slurry injection.

How the Known or Suspected Hazards of Injection Compare to Other Means of Dealing with Slurry from Coal Operations

Background of Coal Refuse

Coal refuse is noncombustible material that is separated from coal during the mining or cleaning process. Refuse includes waste rock, clays, fine dust size particles, and by-products from coal cleaning including slimes (additives used in dewatering) (Arnold et al., 2007). The source of the refuse begins with the material mined from underground coal seams that is both above and below the coal, including the sediments within the coal seam. Surface coal mining produces refuse from the removal of overburden and rock, excavated material from shafts, and from other working space within the mine. Coal waste is commonly categorized into Coarse Refuse and Fine Refuse. Both of these divisions are discussed below.

Coarse Coal Refuse (CCR)

Beginning at the mining of raw coal, commonly referred to as ROM coal, the coal is divided into separate size fractions for cleaning. The modern course size is graded dimensionally with particle sizes up to 3 inches and has a small percentage of fines (<10%; MSHA, 2007). However, the historical hand-picked coal and slate sizes would fall into dimension ranges larger than those produced by modern automated processes with sizes approaching 6 inches (Arnold et al., 2007). The coarse refuse material is by its nature a reject material. This material is produced after ROM coal is fed to a preparation plant for cleaning and it is the first level of separated, non-combustible, material rejected from the plant cleaning circuit. Coarse refuse is either trucked or belted to an approved refuse site.

Fine Coal Refuse (FCR)

The fine refuse begins as fragments of ROM coal and coarse refuse produced in the preparation plant by the screening, cyclone separation, wet cleaning processes, and other processes. These material sizes range very fine (<1mm, No. 200 sieve) and to ultra fine size ranging less than 1 mm. The accumulation of fines in slurry waters are of such a small size that further separation is extremely difficult. This fine reject is usually capable of being pumped to a disposal site.

The cleaning process may use chemical additives to assist in coal/waste separation. These additives include magnetite slurry, flocculants as thickeners, and coagulants. The magnetite is washed off of the material in the wet cycle operation and the process water is then recycled in the plant. However, coal refuse may leave the plant with surface moisture contents of 8 to 15 percent. (MSHA, 2007)

Existing Methods for Disposal of Coal Waste

The disposal of coal waste consists of two basic types: i) Impounding structures, and ii) Non-impounding structures. Impounding structures by their nature impound water, sediment, or slurry to regulated elevations and volumes. Non-impounding structures include piles and fills, and do not impound water or slurry.

The implementation of the impounding refuse storage facilities depends on several factors. The most important factor is the projected production volume of refuse (fine and coarse) from the mine(s). The production capacity will determine the necessary fill volume and determine the size of the facility. Disposal of coal waste is dependent on the final physical condition of the reject material, volume, and amount of water to

separate from the fine tailings inconsideration of production. The current and historical methods for the final disposition of coal waste include:

- Impoundments (dams and embankments, incised ponds, diked ponds)
- Coal Refuse fills
- Coal Refuse Piles (Coarse, Combined, Segmented)
- Slurry Cells
- Underground Injection

The above listing specifically does not include physical separation methods such as mechanical filter separation for dewatering slurry or dry cleaning method alternatives. These methods also produce fines which must be disposed of as well. The fine coal refuse may be initially dewatered using technologies including the addition of thickener chemicals which transform the slurry into a thickened paste. Mechanical dewatering equipment includes: belt filters, vacuum, press, plate, and frame filters. (MSHA, 2007)

Impounding Facilities

Coal Waste Impoundments

Coal waste impoundments are impounding facilities and hold coarse and fine refuse, slurry, and process water. There is a legacy of reclaimed coal refuse piles and impoundments going back to the 1850's. In West Virginia a WVU study was performed in 2003 (Quaranta et al., 2004) to identify and assess safety aspects of the State's coal waste impoundments. From this initial study approximately twenty percent of the then total permitted impoundments were visited and three distinct categories of impoundments were identified and are presented as follows:

Category I: Impoundments designed, constructed, operated, and reclaimed prior to 1972.

Category II: Impoundments designed, permitted, constructed, and operated prior to 1972 then renovated between 1972 and 1977 for compliance with the Surface Mining Control and Reclamation Act (SMCRA), and which continue to be permitted and remain open, or reclaimed, and

Category III: Impoundments designed, permitted, constructed, and operated / reclaimed post SMCRA.

The Category I sites were the oldest sites and two of these were visited. Each had major remedial repair performed within the past two years. These sites were under the authority of the WVDEP. The Category II sites observed were either significantly renovated during operation by the mine owners for compliance with WVDEP and MSHA regulations; were not permitted for further expansion/use due to non-compliance with underground mining variances; or are permitted but non-active and continue to impound water. The Category III sites visited were in full operation and these sites also exhibited innovative design approaches for the engineering of drainage and water removal systems. The Category III sites appear to be the soundest impoundments within the State.

The coal impoundment facility is actually a storage and water holding system that is designed to separate coarse and fine coal refuse and retain process wash water for reuse.

Coal waste impoundments which incorporate coarse refuse as the embankment fill material routinely use cross-valley construction in West Virginia. Besides cross-valley

impoundments, other configurations can include side-hill impounding embankments, and incised and diked ponds. The cross-valley impounding structures using coarse refuse as the majority of the fill are built as embankment dams with layered fills of coarse refuse. The embankment dam then has fine slurry and water placed behind the structure. This cross-valley configuration is illustrated in Figure 18 after MSHA, 2007.

The cross-valley impoundments may be constructed using one of three distinct method variations: i) Upstream construction, ii) Centerline construction, and iii) Downstream construction. Each variation has unique attributes that offer the owners options on fill volume placement and relative proportions of coarse and fine refuse, and process water use.

Incised Impoundments

An incised impoundment is constructed by excavating into the natural ground surface or into an engineered fill surface. This type of impoundment is completely underground. The facility may be used to dispose of fine coal refuse and to consolidate slurry material.

Non-Impounding Facilities

Non-impounding facilities include configurations of material stored in valley-fills, side hills, ridge-dumped, and heaped.

Coarse Refuse Embankments and Piles

The coarse refuse embankments are designed for separate disposal of the coarse refuse from the fine refuse. Coarse refuse embankments do not include zones for fine refuse disposal. Coarse refuse embankments are designed to generally be constructed of coarse materials having a range of grain size distribution and when all compacted reach an engineered design strength for structural stability.

Combined Refuse Piles

Combined refuse piles and embankments are designed for co-disposal of coarse and fine coal refuse. The refuse may be both combined or blended but may also be zoned or segregated within the pile. Combined piles have many challenges with operation due to the higher moisture contents of the fine refuse. In order to properly handle the combined refuse, large areas are required in order to dry the material prior to final placement. The combined refuse drying is also challenged by seasonal precipitation and cold temperatures which reduce the evaporative cycle and prevent material placement.

Slurry Cells

Slurry cells are classified by MSHA (MSHA, 2007) as small ponds constructed within coarse refuse piles or embankments that may receive fine refuse and slurry. The disposal of the fine refuse and slurry is done on a small scale and usually multiple cells are operated concurrently. The primary function of a slurry cell is to dewater and consolidate the water saturated fine coal refuse. After the fine refuse is dewatered the

cell may be covered with a layer of coarse refuse. Another option is for the slurry to be excavated and blended to a coarse refuse for co-disposal in a larger pile.

Underground Injection

Underground injection is limited to disposal of fine coal refuse into abandoned underground mine workings. The objective of this type of material disposition is to site an injection point where there is unobstructed injection volume and a mine structure that exists where the liquid may be contained. There are two classifications of underground slurry disposal: i) Controlled Flushing and ii) Blind Flushing.

Controlled Flushing

Controlled flushing is a method used when mined refuse materials are backfilled into abandoned underground mines. The mines may be either dry or wet and are open to mine personnel for work. This technique involves hydraulically flushing a slurry of crushed coal fines blended with water and pumped from well head locations into a piping distribution network for placement. The method can distribute a slurry having 30 to 50 percent solids mixed with water. Depending on the settling of the fine refuse fraction the process water may be recovered and reused in the process to minimize makeup water use.

The controlled flushing is operated by miners installing a pipe network within the mine workings in order to distribute the slurry injectate. The mine personnel are able to direct the slurry fill into the desired zones and maintain the pipe network. The technique enables point source deposition and process water recovery is possible. For water recovery the slurry deposition methodology incorporates controlled seepage techniques

through leaky bulkheads and sumps. The leaky bulkheads are constructed at existing openings and consist of wooden timbers arranged to form a wall. This timber wall will retain the pressure of the solid slurry materials and will have gaps or spaces where water can seep. The water may then be collected in sumps.

The collected water may then be pumped to the surface to be re-blended with crushed refuse and re-injected. Using this method it is possible to develop horizontal distribution zones of 600 feet measured from the injection source.

Blind Flushing

Blind flushing is a method of slurry disposition used when access to underground workings is either unsafe or impossible. The disposal approach involves developing a detailed plan identifying a grid of injection borehole wells. The borehole wells are arranged to intersect the abandoned mine openings which were previously used as haul routes, air supply / return routes, or openings from room and pillar mining.

The slurry is pumped from the surface into a borehole well with little control of placement possible. The pumping will continue until no more slurry can be placed.

This type of storage requires larger volumes of water compared with controlled flushing. This is because the higher water volume and injection flow rate would be used to disperse and fan out the distribution of the refuse fines. Widening the distribution zone will minimize the concentrated deposition at the immediate borehole injection area. Studies on borehole injection report that slurry solids are also reduced to ranges of 17 percent as compared to 30 to 50 percent for Controlled Flushing. Figure 20 is a

borehole plan layout for a proposed mine injection project illustrating the location of a borehole and abandoned mine workings.

Exposure Characterization of Existing Coal Waste Systems

This section addresses the potential mechanisms and pathways for the introduction of coal slurry or process water introduction into the environment from coal waste facilities.

The introduction of coal refuse slurry, impounded process water, and surface water impounded from natural precipitation storage into the subsurface depends on many factors including the geology and hydrogeology of the specific site source, and the potential for subsidence of overburden structure into abandoned mine workings. Impounded facilities may be separated into two zones which include the impoundment dam foundation zone and the basin zone. The foundation zone is well characterized by geotechnical engineering studies and field construction. The groundwater seepage and strength aspects of this zone would not be expected to provide a significant source of water into the subsurface and is, therefore, not further considered. The basin zone includes the areas of the impounded facility which store water where the drainage elevation permits water or slurry flow into subsurface voids.

Slurry Seepage from Impounded Facilities into Basin Geology

This section addresses the potential for impounded slurry, process water, and precipitation storage to seep through the natural openings within the basin soil and rock. The NRC (2002) identified that the site geology within the storage basin at an

impounded storage facility located in the Appalachian Plateau is strongly fractured and yet has a low porosity.

The regulatory permit requirements are the driver for the impoundment basin area construction practices. The perimeter of the impoundment basin is stripped of its vegetation, topsoil and loose rock overburden during the progressive construction of the refuse placement lift elevations. Therefore as the impoundment rises in elevation the pool water is placed in direct contact with the exposed rock. The steep topography typical of an impoundment basin would expose the cracks, faults, coal seam outcrops, and other preferential pathways for water and coal slurry seepage.

The NRC (2002) cites references which present geologic conditions under which slurry or impounded water would enter the groundwater system within the exposed rock faces of a basin. The NRC discusses that the exposure of regional joints and fractures on shallow near-surface fracture system produce a myriad of groundwater flow paths. The majority of this seepage water in the coal-bearing rock is transmitted in features including fractures, joints, bedding planes, and coal cleats. These permeable features can extend from bedrock surfaces to depths of 200 feet.

Subsidence

Mine subsidence is the ground movement resulting from collapse of subsurface rock strata into a mine opening. Subsidence occurs in working and abandoned mines and causes weakness in strata and may accompany water flow from overlying layers of high permeability or water storage. Mine subsidence causes vertical cracks in strata and bed separation. In the horizontal plane the subsidence results in rock joint

separation. Both of these subsidence induced effects would provide permeable zones for water and slurry transport into strata layers confining the regional groundwater.

Slurry Infiltration & Mobilization from Impounded Facilities Into Coal Mine Workings

Surface coal slurry impoundment and slurry cell discharges into the subsurface, surface, and underground mine workings are possible. Failure mechanisms have been documented by the OSM based on investigations of mine inundations. The failure mechanisms are caused by active and permitted impoundments having considerable water pool depths or reclaimed impoundments with saturated slurry. The following mechanisms apply to impoundments (OSM, 2001).

Failure of Sealed Underground Mine Openings

This infiltration could be caused by the mine opening seal made of rock and soil or other material which would fail and allow slurry to directly enter abandoned mine workings. Mine openings include punch-outs, portals, horizontal drainage ventilation conduits, and auger holes that connect with underground mines.

- Breakthrough at an unsealed underground mine opening: This source of water and slurry would entail the direct inundation of workings from mine openings which had not been permanently sealed.
- Breakthrough at coal barriers: Barriers include ground contours between underground mines, soil/rock barriers between auger holes and underground mines, and shallow drift mines with underground mines. Hydraulic pressures of

slurry and water stressing small or thin sections of soil/rock barriers allowing slurry to uncontrollably enter a mine.

- Breakthrough at Strata overlying the coal seam: Water and slurry entering a mine or subsurface opening into a mine through natural fractures and joints, and mining-induced fractures from roof falls, sinkholes, and subsidence.

Slurry Distribution from Underground Injection

The distribution of slurry either using controlled or blind flushing results in an increase to the hydraulic head within the flooded portions of the mine. Methods to contain the slurry are limited to bulkhead construction and sustainability between the open mine passages. Another option is to collect the seepage water into sumps and transfer to the surface for subsequent reuse.

Conclusions

- To be completed

Recommendations

- To be completed

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