SUBAQUEOUS CLOSURE OF TAILINGS, AN ANALOGUE CASE HISTORY[1]

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Abstract: Subaqueous closure is a preferred option for tailings disposal because submergence inhibits oxygen transfer, thereby limiting pyrite oxidation, formation of acidic drainage, and mobilization of metals. However under certain hydrogeologic and geochemical conditions, metals mobilization may still occur even with subaqueous closure.

This paper presents a case history of an analogue site to subaqueous tailings disposal where sediments, in part derived from mine tailings, have accumulated in a 73 hectare (180 acre) reservoir. Intermixed with the small portion of mine tailings are natural detritus (soil and organic material), industrial and agricultural materials.

The presence of the organic material in the sediments has resulted in the formation of geochemical zones within the sediments. Sediments near or at the surface of the reservoir are oxidizing and deeper sediments are reducing. The sediment pore water pH is near neutral; however, limited metals mobilization from the sediments has occurred due to the formation of the geochemical zones. Iron hydroxides and associated arsenic are stable in the oxidized zone but mobile in the reduced zones. As a result, metals have been detected in the ground water in the vicinity of the reservoir. In some instances, the concentration of arsenic has exceeded the Federal Safe Drinking Water Act Maximum Contaminant Limit (MCL).

The area of arsenic MCL exceedance in the ground water is limited and appears to be stabilized because the flux of metals from the sediments is small compared to the flux of ground water through the surrounding alluvial system (i.e. dilution). Also, adsorption and precipitation in the oxidized alluvial system surrounding the tailings may be controlling metals concentrations.

Additional Key Words: Adsorption, dilution, oxidation, reduction

Introduction

Work by U.S. Bureau of Mines has shown the efficacy of subaqueous storage of tailings for inhibiting acid mine drainage formation (Hammack and Watzlaf, 1990; Watzlaf, 1992). Subaqueous storage reduces available oxygen, thereby limiting pyrite oxidation (Watzlaf, 1990) and acid formation.

The occurrence of reducing conditions that can develop in subaqueous tailings storage prevents dissolution of metals associated with sulfide minerals. Sulfide minerals are stable in reducing conditions; however, metals associated with oxides or hydroxides become unstable in a reducing environment and can be mobilized if hydrologic conditions are favorable.

This paper discusses a site where highly mineralized sediments, derived in part from mine tailings, accumulated in a reservoir. During the 80 years of sediment accumulation below water, reducing conditions have developed within part of the sediments and acidic conditions have not occurred. However, combined geochemical and hydrologic mechanisms have caused mobilization of arsenic from the sediments to the surrounding alluvial aquifer. The presence of arsenic in the ground water is limited in extent and stable due

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to dilution by the prolific alluvial aquifer and possibly due to adsorption by ferric oxyhydroxides. Lessons learned from this site may be helpful for refining tailings storage decision-making.

Site Background

The Milltown Reservoir (Figure 1) is located in western Montana, at the confluence of the Clark Fork and Blackfoot Rivers, and covers approximately 73 hectares (180 acres). The Clark Fork River Basin has been the setting for mining activity since 1864. By 1881, Butte, Montana, located about 193 kilometers (120 miles) upstream of the reservoir, was an important mining, milling and smelting center. At least 25 companies were mining copper ore in Butte by 1885, and in 1884, smelters were operating in nearby Anaconda. Some of the wastes generated by these operations, as well as those in adjacent drainages, were added to the normal sediment load of the Clark Fork River. It is likely that wastes included weathered (oxidized) minerals as well as sulfides.

Following completion of the Milltown Dam in 1907, sediment transported by the Clark Fork and Blackfoot Rivers began to deposit in the newly-created reservoir. Data to conclusively document the rate of sediment deposition in the reservoir is unavailable; however, much of the sediment deposited in the reservoir may have arrived during the largest recorded flood in the Clark Fork River above Missoula, which occurred in 1908.

An analysis of aerial photographs dating back to 1940 suggests that the Clark Fork channel through the reservoir and the adjacent sediment deposits have been relatively stable, and there has been little net deposition or erosion. The reservoir is estimated to contain approximately 5.05 million cubic meters (180 million cubic feet) of sediment grading from fine sand to silt.

In November 1981, the Missoula City/County Health Department found levels of arsenic in four private drinking water wells in Milltown that exceeded the Federal Safe Drinking Water Standard of 0.05 mg/l. A reconnaissance investigation conducted in 1982 found that the presence of arsenic in the ground water was linked to the sediments in the Milltown Reservoir. This initial investigation led to EPA's listing of the site as a Superfund site.

Between 1982 and 1989, eight investigations were conducted in the Milltown area to identify the source and extent of arsenic. From 1990 to 1991, a remedial investigation was conducted to better characterize the geochemistry of the lower portions of the reservoir sediments and to collect additional information regarding sediment mineralogy and chemical interactions within the sediments. The information in this paper is derived from the remedial investigation report (ARCO, 1995).

Hydrogeological Conditions

Figure 2 illustrates the hydrogeological components of the site: the reservoir sediments; the two portions of the alluvial aquifer, one beneath the sediments and the other beneath Milltown; and the bedrock. The hydrogeologic conditions have resulted in arsenic mobilization from the sediments and in containment of arsenic in a small area near the reservoir.

Reservoir Sediments

The reservoir sediments consist of natural detritus (soils and organic material), industrial and agricultural materials, and mine-related waste. The sediments contain fine-grained sands, silts and clays. The bulk of the sediments consist of quartz, micas and feldspars, with smaller quantities of calcite and clay minerals and a small percent of sulfides (Woessner et al., 1984).
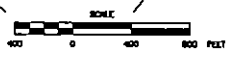
Metal concentrations within the reservoir sediments are highly variable with location and depth. As shown in Table 1, total metals concentrations in sediment solids increase as sediment grain size decreases.
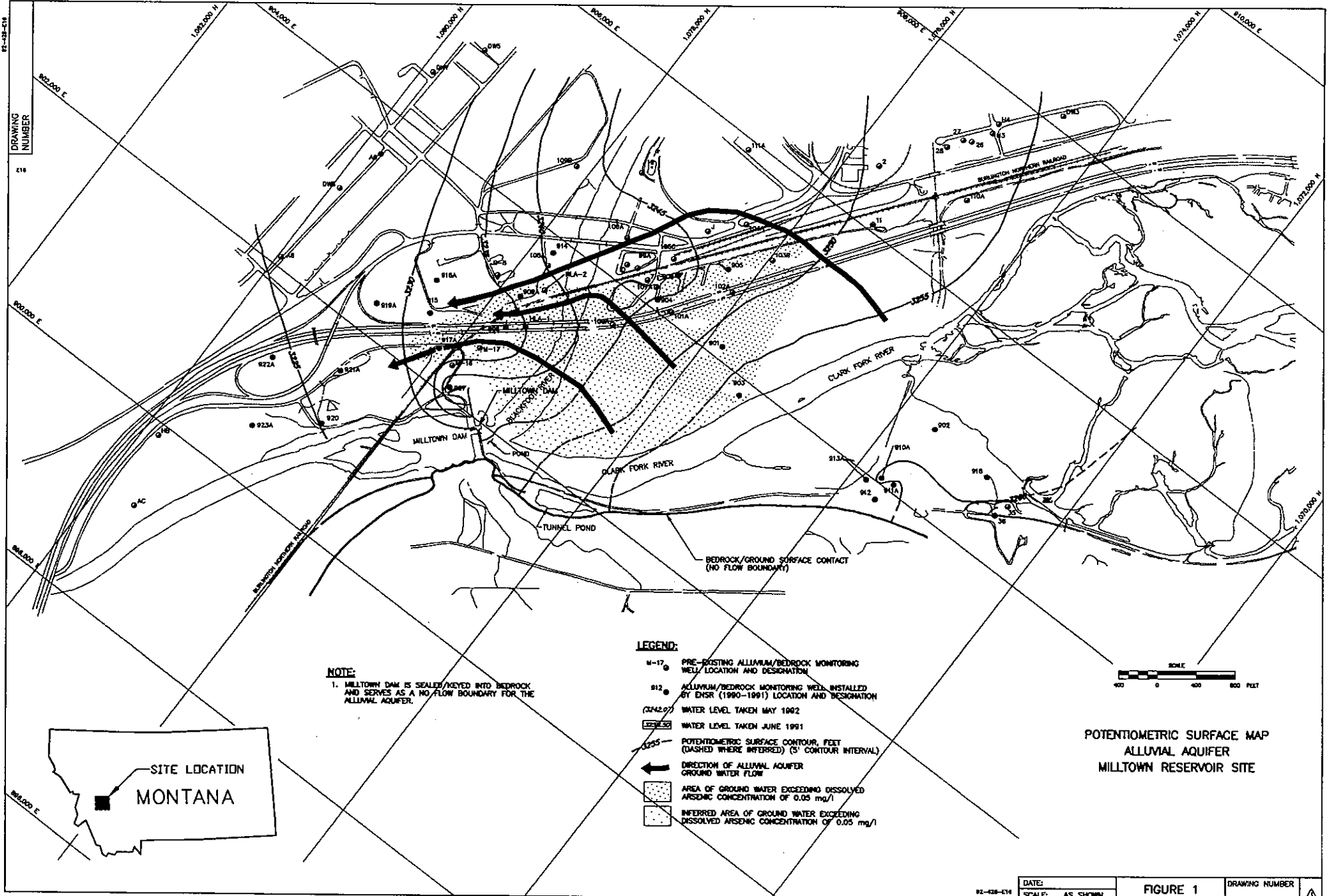
NOTE:
1. MILLTOWN DAM IS SEALED/KEYED INTO BEDROCK AND SERVES AS A NO FLOW BOUNDARY FOR THE ALLUVIAL AQUIFER.

SITE LOCATION
MONTANA

LEGEND:

M-17 PRE-EXISTING ALLUVIUM/BEDROCK MONITORING WELL LOCATION AND DESIGNATION

912 ALLUVIUM/BEDROCK MONITORING WELL INSTALLED BY ENSR (1990-1991) LOCATION AND DESIGNATION

(3242.07) WATER LEVEL TAKEN MAY 1992

3235.50 WATER LEVEL TAKEN JUNE 1991

3255 POTENTIOMETRIC SURFACE CONTOUR, FEET (DASHED WHERE INFERRED) (5' CONTOUR INTERVAL)

← DIRECTION OF ALLUVIAL AQUIFER GROUND WATER FLOW

AREA OF GROUND WATER EXCEEDING DISSOLVED ARSENIC CONCENTRATION OF 0.05 mg/l

INFERRED AREA OF GROUND WATER EXCEEDING DISSOLVED ARSENIC CONCENTRATION OF 0.05 mg/l

BEDROCK/GROUND SURFACE CONTACT (NO FLOW BOUNDARY)

POTENTIOMETRIC SURFACE MAP
ALLUVIAL AQUIFER
MILLTOWN RESERVOIR SITE

SCALE
400   0   400   800 FEET
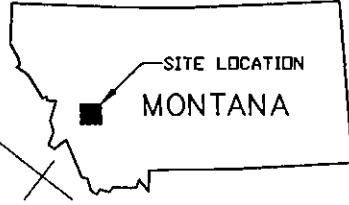
DATE:
SCALE: AS SHOWN
FIGURE 1
DRAWING NUMBER

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Table 1
Summary of Subsurface Metal Concentrations According to Sediment Type

Metal	Statistical Characteristic	Metal Concentration (mg/kg)		
		Sand	Silty Sand	Silt/Clay
Arsenic	Geometric Mean	14.80	113.00	531.00
	Average	16.80	189.40	707.00
	Maximum	27.90	658.00	1,540.00
Cadmium	Geometric Mean	1.10	3.70	16.40
	Average	1.20	6.10	18.90
	Maximum	1.60	20.90	30.50
Copper	Geometric Mean	43.90	512.00	4,243.00
	Average	83.10	1,629.10	5,019.00
	Maximum	209.00	6,620.00	10,600.00
Iron	Geometric Mean	5,982.00	14,908.00	23,592.00
	Average	6,023.00	15,473.00	24,250.00
	Maximum	7,040.00	22,400.00	30,100.00
Lead	Geometric Mean	13.30	82.60	374.00
	Average	15.60	161.20	424.00
	Maximum	27.70	551.00	794.00
Manganese	Geometric Mean	138.20	595.00	1,151.00
	Average	153.00	714.00	1,277.00
	Maximum	255.00	2,060.00	2,090.00
Zinc	Geometric Mean	82.20	558.40	4,381.00
	Average	345.00	1,414.20	5,277.00
	Maximum	987.00	4,610.00	9,520.00

The average thickness of the sediments is approximately 3 meters (10 feet), with the thickest sediment deposits [8.8 meters (29 feet)] located near Milltown Dam and the Blackfoot River, and the thinnest deposits [(2 feet) or less] located at the upstream end of the reservoir. Arsenic concentrations in the sediment pore water increase as sediment thickness increases and sediment grain size decreases.

The hydraulic properties of the reservoir sediments indicate that the sediments have low permeability and do not transmit water easily, especially when compared to the alluvial aquifer. The flow that does occur in the sediments is predominantly downward to the underlying alluvium. In the upstream part of the reservoir, sediments are not fully covered by water and support wetlands-type vegetation. Near the dam, sediments are covered by approximately thirteen feet or more of water. The variation of water depth and the organic content in the sediments has resulted in geochemical zonation. Figure 3 is a simplified illustration of the geochemical zonation within the reservoir sediments, which varies from oxidized to reduced.

Alluvial Aquifer

The alluvial aquifer consists of coarse-grained alluvial valley fill ranging in size from silt to boulders. As illustrated on Figure 2, the alluvial aquifer beneath the reservoir sediments is thin and ranges from approximately 0.6 to 6 meters (2 to 20 feet) thick, and the alluvial aquifer beneath Milltown ranges from 9 to 37 meters (30 to 120 feet) thick.

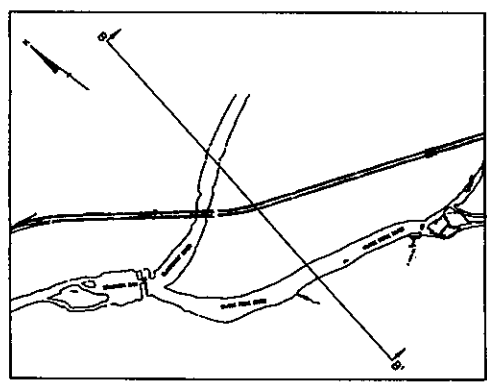Figure 1 shows the potentiometric surface map and ground water flow directions at the site based
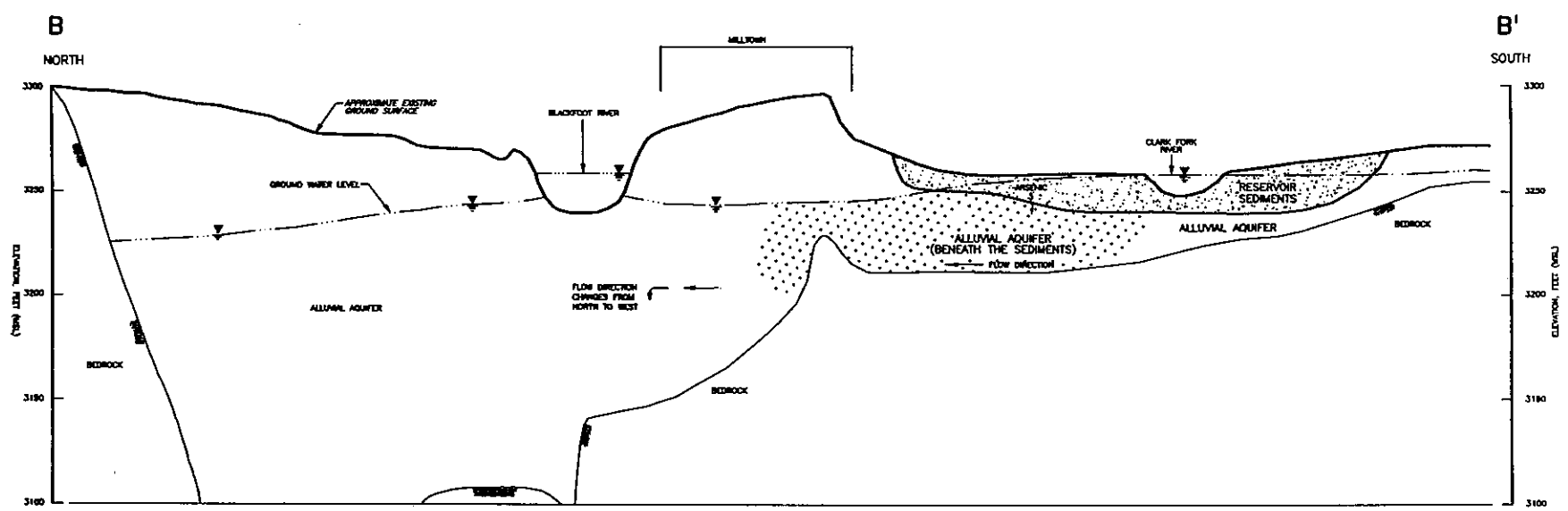
CROSS SECTION B-B'
LOOKING EAST

LEGEND

- RESERVOIR SEDIMENTS
- GROUND WATER EXCEEDING DISSOLVED ARSENIC CONCENTRATION OF 0.05 mg/l

NOTES:

1. THIS DRAWING IS EXAGGERATED APPROXIMATELY 20X VERTICALLY AND IS NOT TO SCALE.

CROSS SECTION LOCATION
(NOT TO SCALE)

CONCEPTUAL HYDROGEOLOGIC MODEL
MILLTOWN RESERVOIR SITE

DATE:		
SCALE:	FIGURE 2	DRAWING NUMBER

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on 1991 and 1992 water level measurements. The direction of ground water flow in the alluvium beneath the reservoir sediments is the result of "no flow" boundaries. A "no flow" boundary is located on the south and southeast sides where the alluvial aquifer abuts against the bedrock that forms the flanks of the valley.

The Milltown Dam also represents a "no flow" boundary because the sediments in this area were removed during dam construction and the foundation of the dam was keyed into the underlying bedrock. As a result, ground water flow is to the north away from the "no flow" boundaries and around the north side of the dam into the laterally extensive and highly transmissive aquifer beneath Milltown contained within a bedrock trough.

Beneath Milltown, alluvial ground water flow trends towards the north until beyond the Milltown dam, where the flow components trend toward the northwest and down the Clark Fork Canyon. The saturated thickness of the alluvial aquifer beneath Milltown is highly variable, ranging from 9 meters (30 feet) to over 37 meters (120 feet), reflecting the uneven underlying bedrock surface. The greater thickness corresponds to higher transmissivities and flux for this portion of the alluvial aquifer.

Bedrock

The bedrock has two important features which control hydrogeological conditions at the site. First, its permeability is orders of magnitude less than the alluvium; therefore the bedrock is considered the lower physical boundary of the alluvial aquifer. Second, the shape of the bedrock surface controls the thickness of the alluvium.

Geochemical Conditions

The presence of arsenic in the alluvial aquifer, illustrated on Figures 1 and 2, originated from the downward migration of arsenic contained in the reservoir sediments in a two-stage process. First, due to geochemical conditions in the sediments, arsenic that had previously been bound in the sediments was mobilized into the sediment pore water. Second, the arsenic-bearing pore water percolated downward through the sediments and into the underlying alluvial aquifer.

The geochemical conditions that permit mobilization of arsenic were evaluated during the reservoir sediment investigation, which included sediment core sampling and analysis, a cone penetrometer survey, mineralogical analyses, sequential extraction, and pore water sampling and analysis.

Reservoir Sediment Chemistry

The correlation of metals concentrations and sediment grain size was used to determine average sediment arsenic concentrations. The average concentration of total arsenic in the reservoir area is approximately 500 mg/kg close to the dam and approximately 200 mg/kg in the upstream part of the reservoir. Results of sequential extractions indicated that the largest percentage of arsenic (approximately 64 percent) is bound within residual minerals, primarily sulfides. Mineralogical analysis of sediments indicated that approximately one to three percent of the sediments consist of sulfide minerals. Pyrite (FeS_2), enargite (Cu_3AsS_4), sphalerite (ZnS), and tennantite ($Cu_{12}As_4S_{13}$) were identified. These sulfide minerals are distributed in small amounts throughout the sediments. Based on sequential extractions, approximately 10 percent of the total arsenic in the sediments is exchangeable. Exchangeable arsenic is presumed to be adsorbed to iron oxyhydroxides and is present throughout the sediment profile.

The dissolved fraction of arsenic in the sediments, as represented by sediment pore water, accounts for only 0.3 percent of the total arsenic in the sediments sampled. Where sediment thickness and arsenic concentrations are the largest, arsenic concentrations in pore water averages 2.4 mg/l in the pore water. In other areas, sediments are thinner or composed predominantly of coarse-grained sediments. These sediments have average arsenic concentrations in pore water below 0.05 mg/l, and do not appear to be

contributing to the exceedance of the arsenic drinking water standard.

Dissolved arsenic concentrations in sediments generally increase with depth and are largest at locations where the thickness of fine-grained sediments is greatest. As sediment thickness increases, different geochemical conditions develop because of decreased contact with oxygen-bearing water. These different conditions allow mobilization of arsenic from the sediments.

Conceptual Geochemical Model

Figure 3 is a simplified conceptual model of the geochemical zones that occur in the Milltown Reservoir sediment/alluvial aquifer system, based on mineralogical and pore water data. The conditions in the geochemical zones directly control the mobilization and removal of arsenic, iron and sulfate/sulfide in the system.

Oxygenated surface reservoir water enters the upper part of the sediments. As the water percolates downward through the sediments, the oxygen in the water is consumed by reactions with organic matter and sulfide minerals. Therefore, water has progressively less oxygen as it moves downward through the sediments. This results in a zonation of the sediments into an upper oxygenated (oxidized) zone and a lower oxygen-depleted (reduced) zone. Between these two zones is a transition zone that has oxygen concentrations less than the oxidized zone but not fully depleted. The depth intervals for each zone vary across the reservoir and depend on sediment grain size and surface vegetative cover.

In the oxidized zone, oxide minerals such as iron oxide and hydroxide are stable and do not readily dissolve. Sulfide minerals, such as pyrite and enargite, are unstable in the oxidized zone and gradually dissolve, resulting in iron, sulfate and arsenic entering the pore water. However, iron and arsenic concentrations remain small in the pore water because iron oxidizes and precipitates as iron oxyhydroxides, which adsorb the arsenic.

In the reduced zone, sediments are in contact with oxygen-depleted (reduced) water. Iron oxyhydroxides are unstable and gradually dissolve, allowing iron and the arsenic associated with iron oxyhydroxides to enter the pore water. As long as sufficient sulfate is present in the pore water and the sulfate reduces to sulfide, iron-sulfide precipitates will form and control the concentration of iron in pore water. However, sulfide becomes depleted through precipitation reactions. In the deeper zones of the sediments, pore water lacks sufficient sulfide for further precipitation.

The pore water containing iron and arsenic, but depleted in sulfate/sulfide, continues to percolate downward into the underlying alluvium. Within the alluvium the reducing conditions return to oxidizing conditions as the small volume of reduced pore water mixes with the much larger volume of oxidized water flowing through the alluvium. Oxide minerals are stable in the oxidized alluvium, resulting in the precipitation of iron oxyhydroxides. Arsenic is adsorbed by the newly formed iron oxyhydroxides, resulting in a decrease in arsenic concentrations as alluvial aquifer water moves downgradient of the sediments.

<u>Controls on the Arsenic Concentrations</u>

Figure 1 shows the shape and location of the area in the alluvial aquifer having dissolved arsenic concentrations exceeding 0.050 mg/l. The presence of arsenic at or greater than this concentration is, for the most part, located beneath the reservoir sediments. The arsenic concentrations in the ground water fluctuate slightly between sampling events but do not exhibit a consistent trend towards increasing or decreasing concentrations. Concentrations at the upgradient and downgradient monitoring wells are also stable, with the majority of the concentrations at or slightly above laboratory detection levels.

As shown on Figure 1, the shape and location of the arsenic in the ground water are consistent with

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GEOCHEMICAL ZONE	REMOVED FROM SOLUTION		IN SOLUTION	
	PRECIPITATED	ADSORBED		
OXIDIZED	IRON OXYHYDROXIDE MANGANESE OXIDE	ARSENIC BY IRON OXYHYDROXIDE	SULFATE	SEDIMENT
TRANSITION	–	ARSENIC BY IRON OXYHYDROXIDE	SULFATE IRON, ARSENIC MANGANESE	
REDUCING: SULFUR AVAILABLE	IRON SULFIDE	–	IRON, ARSENIC MANGANESE	
REDUCING: SULFUR DEPLETED	NO NEW MINERALS FORM	–	IRON, ARSENIC MANGANESE	
REDUCING: SULFUR DEPLETED	NO NEW MINERALS FORM	–	IRON, ARSENIC MANGANESE	ALLUVIUM
OXIDIZED	IRON OXYHYDROXIDE MANGANESE OXIDE	ARSENIC BY IRON OXYHYDROXIDE	–	

CONCEPTUAL MODEL OF GEOCHEMISTRY
MILLTOWN RESERVOIR SITE

DATE:		FIGURE 3	DRAWING NUMBER
SCALE: N.T.S.			

ground water flow directions. The arsenic is confined to a limited area within the alluvial aquifer because of geochemical reactions and dilution. Adsorption limits the extent of elevated arsenic concentrations by removing arsenic from solution through geochemical processes. In oxidized portions of the alluvial aquifer, precipitation of iron oxyhydroxides is likely. The iron oxyhydroxides provide a substrate for arsenic adsorption.

Dilution limits the extent of elevated arsenic because a small volume of pore water that has arsenic concentrations in the milligram per liter range mixes with a much larger volume of water flowing in the alluvial aquifer that has nondetectable or part per billion arsenic concentrations. The mechanisms of dilution and adsorption result in stability in the extent of the arsenic in the ground water at the Milltown site. Dilution and adsorption are expected to continue to operate at the Milltown site and to provide control on arsenic migration.

Summary and Conclusions

Sediments derived in part from mining, milling and smelting activities accumulated in Milltown Reservoir and have been in place for about 80 years. The sediments include arsenic associated with sulfides and arsenic associated with oxyhydroxide minerals. Geochemical zones formed within the sediments due to inclusion of organic material during sediment deposition and fine sediment grain size that inhibits water movement.

Arsenic has mobilized from the sediments as a result of the occurrence of arsenic associated with oxyhydroxides in the reduced geochemical zone within the sediments. The arsenic has entered the underlying and adjacent alluvial aquifer, but the arsenic plume is limited in extent. The limitation is due to dilution of arsenic by the prolific alluvial aquifer and to adsorption of arsenic by ferric oxyhydroxide.

The mobilization of arsenic from sediments at the Milltown Reservoir indicates that:

- Reducing conditions may develop during subaqueous storage; therefore, subaqueous storage of mine waste is best applied to sulfide minerals, and

- Evaluation of site hydrogeology is important when considering use of wet storage.

Acknowledgment

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GEOCHEMICAL CHARACTERIZATION OF MINE DRAINAGE SOURCES IN THE CHALK CREEK DISTRICT, COLORADO[1]

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Abstract: High concentrations of zinc, manganese, cadmium, and other metals have been measured in waters throughout the Chalk Creek district since 1985, when contaminated spring runoff resulted in a substantial loss of trout fingerlings within Chalk Creek and the Chalk Creek hatchery. Chalk Creek is located in Central Colorado within a region of several abandoned mining districts. Initially, the treatment of mine drainage discharged from the Golf Tunnel adit was considered to be the primary remediation action required at the site. The hypothesized bedrock fractures within the floor of the Golf Tunnel as well as contaminated water at several monitoring wells indicate that ground-water flow paths are present within the system and serve to transport metals. These findings hold significant implications for remediation, which may need to be expanded into the treatment of contaminated ground water and tailings seepage. In this study, geochemical modeling was used to attempt to locate subsurface flow paths and characterize the weathering processes generating contamination. It was found that the availability of site chemistry, mineralogy, and hydrology assisted in confirming predictions from the modeling of geochemical processes. Therefore, geochemical modeling data will ultimately assist in appropriate remediation decisions.

Additional Key Words: Zinc, Manganese, Geochemical Modeling.

Introduction

Site Location and Geology

The Chalk Creek mining district is located in the Sawatch Mountains of Colorado at an elevation of approximately 3048 m (10,000 ft.) to 3658 m (12,000 ft.). In 1985, heavy metal contamination to Chalk Creek was attributed to the abandoned mining activities of the Mary Murphy and Iron Chest Mines (Science Applications International Corporation, 1993). The Golf Tunnel adit is located approximately 53 m (175 ft.) upslope from Chalk Creek and serves as the main drainage mechanism for upper mine levels of the Mary Murphy and Iron Chest Mines (see Figure 1). The water discharged from the adit is high in zinc and manganese, but the pH is near-neutral (SAIC, 1993). Discharge from the Golf Tunnel is currently estimated to be from 3.8 L/s to 4.4 L/s (60 gal/min to 70 gal/min) (SAIC, 1993).

Roughly 75% of the ore obtained from the district was from the Mary Murphy mine. The ore consisted of gold, lead, zinc, silver and some copper. Most of the ore was mined from pyritic veins in the Mount Princeton quartz monzonite, which is the dominant intrusive body of the region. The pyritic quartz veins primarily are made up of galena, sphalerite, and some chalcopyrite. Local occurrences of calcite, rhodonite, rhodochrosite, barite, and fluorite have also been observed (Dings and Robinson, 1957).

The remediation of the Chalk Creek site falls under the jurisdiction of the United States Environmental Protection Agency (USEPA) through Section 319 of the Clean Water Act, which deals with nonpoint pollution sources. Chalk Creek was specifically selected for the nonpoint source program, due to its flow into the

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