

# **EXHIBIT F**

## **ENVIRONMENTAL IMPROVEMENT PROJECT NOTICE OF INTENT**

# **ALCOA INC. – BAUXITE ENVIRONMENTAL IMPROVEMENT PROJECT NOTICE OF INTENT**

**AUGUST 9, 2010**

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ENVIRONMENTAL IMPROVEMENT PROJECT  
NOTICE OF INTENT

Prepared for

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## **EXECUTIVE SUMMARY**

Alcoa Inc. (Alcoa) hereby submits a Notice of Intent (NOI) of an Environmental Improvement Project (EIP) wherein Alcoa will request a temporary modification of the water quality criteria for selenium in Holly Creek. The EIP process was established by statute and adopted by the Arkansas Pollution Control and Ecology Commission (APCEC). The two-step procedure requires 1) approval of a remediation plan by APCEC, and 2) a third-party rulemaking process to obtain a temporary modification of the water quality criteria for the affected stream while the remediation plan is being conducted.

The final water quality criteria at the end of this project cannot be reliably defined at this time due to 1) the uncertainty of regulatory agreement on the selenium criteria, 2) the lack of proven treatment technology, and 3) the complexity of the effort (e.g., recycle/reuse of 100 million cubic yards of residue, inability to eliminate leachate generation, removing low levels of selenium, treating 4 billion gallons of water annually, etc.). However, the overarching goals of this EIP are to a) protect water quality in the streams receiving Alcoa's discharge, and b) ensure that Alcoa's discharge will be in compliance with local, state, and federal statutes, rules, and regulations. Because of the uncertainty, complexity, and the goals of the project, the project will necessarily be fluid in nature. As new information concerning selenium, its treatment, and finalized standards is developed, the project documentation and National Pollutant Discharge Elimination System (NPDES) permit limits will be revised accordingly.

The proposed Remediation Plan is to develop and implement economically and technically feasible water treatment technology or technologies that will reduce the selenium concentrations in Alcoa's discharge to values that are lower than the water quality criteria. However, as stated in Sections 13 and 15 of the Fact Sheet accompanying Alcoa's NPDES permit, "there is not a currently-available, large-scale, economical treatment system for selenium." Therefore developing and implementing water treatment technologies is the logical approach to reducing the selenium concentration in the discharge. Through this EIP, Alcoa proposes to develop one or more approaches to reduce selenium levels in the effluent.



Following approval of the Remediation Plan by APCEC, Alcoa proposes that a temporary chronic criterion for selenium of 17 µg/L be adopted in Holly Creek. The proposed modification will not alter the current conditions in Holly Creek or the Saline River, into which Holly Creek empties. Biological monitoring in the Saline River and the watershed of Holly Creek will be conducted according to a request from the United States Fish and Wildlife Service (Conway, AR office). Based upon the current state of selenium treatment options, this temporary modification may be in effect for 15 to 20 years, or more, as Alcoa implements the Remediation Plan. As selenium concentrations in the discharge decrease over time Alcoa will seek to have the chronic criterion for selenium appropriately reduced.

## OVERVIEW

Combined, Alcoa and its wholly owned subsidiary, Reynolds Metals Company (Reynolds<sup>1</sup>), own approximately 12,000 acres in central Arkansas, on which they previously conducted bauxite mining and refining activities. These activities ceased completely by 2004. Since that time, Alcoa's primary function has been to manage this vast acreage, including collecting, storing, treating, and discharging stormwater and wastewater from the property under the authority of NPDES Permit No. AR0000582. The annual volume of water treated and discharged from the property averages 2.5 billion gallons. The actual volume of water discharged is a function of rainfall and ranges from 1.5 billion to 4.5 billion gallons annually. The majority of this treated wastewater is discharged into Holly Creek from NPDES Outfall 009. Holly Creek is a small, intermittent stream whose flow consists of a significant amount of the Alcoa discharge throughout much of the year.

Selenium, a naturally occurring element, is found in bauxite ore. Upon refining of the bauxite, the selenium was concentrated in the bauxite residue. The residue is alkaline and produces an alkaline leachate. Certain forms of selenium are more soluble in alkaline environments. The bauxite residue from Alcoa's former refining operations is located in bauxite residue disposal areas (BRDAs) that have been closed under prior agreements with ADEQ.

Selenium was discovered to be an issue in the wastewater discharge in 2000 when Alcoa began preparation for its NPDES permit renewal. Prior to that time, 1) selenium was not known to be an issue in Alcoa's discharge, 2) the analytical capabilities were insufficient to detect selenium at the concentrations found in the Alcoa discharge, and 3) water quality criteria for selenium had not been formally established. Upon further examination, it was discovered that selenium concentrations in Alcoa's discharge and in Holly Creek are in excess of the instream water quality criteria for selenium. The primary source of selenium to Holly Creek via NPDES Outfall 009 is believed to be leachate from the closed BRDAs.

To address the selenium issue at Outfall 009, Alcoa entered into discussions with ADEQ and the US Environmental Protection Agency (EPA) in 2000. These continuing discussions

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<sup>1</sup> Hereafter in this NOI, Alcoa shall mean Alcoa and Reynolds combined, except where otherwise noted.

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resulted in the inclusion of a selenium limit of 17 µg/L in Alcoa's NPDES permit that was renewed in 2008 and a requirement (at Part I, Section B) that Alcoa perform an EIP as set forth in APCEC Regulation No. 2, Appendix B.

The current cost of treating and discharging water from the site is between \$3 and \$4 million annually. Based upon current information and the available treatment technologies, the only known economically and technically feasible means to reduce selenium concentrations to levels at or below the water quality criteria for selenium in Holly Creek would be to construct a pipeline from Outfall 009 directly to the Saline River, with no discharge into Holly Creek. A pipeline consisting of two 30-inch pipes that are capable of carrying 20 million gallons per day for a distance of approximately 3 miles would cost approximately \$6 million. ADEQ indicated to Alcoa that prior to constructing a pipeline directly from Outfall 009 to the Saline River, other options should be explored. The costs of other options such as those associated with removing/reusing the bauxite residue, enhancing the covering of the residue, improving runoff/evapotranspiration, or advanced water treatment options such as reverse osmosis were estimated to range from \$10 million to \$1 billion and do not include the significant operation and maintenance costs that would increase over time.

Performing the necessary research, development, and implementation of economically and technically feasible water treatment technologies is the logical approach to reducing the selenium concentration in the discharge while maintaining the limited existing fishery in Holly Creek. Through this EIP, Alcoa proposes to develop one or more approaches to reduce selenium levels in the effluent being discharged to Outfall 009. Currently no technical approach is known that can effectively and sufficiently reduce the selenium concentrations at a reasonable cost. As discussed later in this NOI, other approaches are not only significantly more expensive, but also require more time and fail to offer predictable results.

The final water quality criteria at the end of this project cannot be reliably defined at this time due to 1) the uncertainty of regulatory agreement on the selenium criteria, 2) the lack of proven treatment technology, and 3) the complexity of the effort (e.g., recycle/reuse of 100 million cubic yards of residue, inability to eliminate leachate generation, removing low levels of selenium, treating 4 billion gallons of water annually, etc.). However, the overarching

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goals of this EIP are to a) protect water quality in the streams receiving Alcoa's discharge, and b) ensure that Alcoa's discharge is in compliance with local, state, and federal statutes, rules, and regulations. Biological monitoring in the Saline River and the watershed of Holly Creek will be conducted according to a request from the United States Fish and Wildlife Service (Conway, AR office) (see Appendix E). Because of the uncertainty, complexity, and the goals of the project, the EIP will necessarily be fluid in nature. As new information is developed, the project documentation and NPDES permit and permit limits will be revised accordingly.

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## **1.0 INTRODUCTION**

### **1.1 Statutory and Regulatory Authority**

In 1997 the Arkansas Legislature passed Act 401 to provide relief from a rigid application of state water quality standards during a long-term remediation project. The title of the Act is “An Act To Encourage Long-Term Environmental Projects; and For Other Purposes.” As stated in Act 401, “the purpose of this act is to preserve the state’s approach to establishing water quality standards, while also encouraging private enterprises to make significant improvements to closed or abandoned sites that are of such magnitude that more than three (3) years will be required to complete the project.” During the triennial review following passage of Act 401, the Arkansas Pollution Control and Ecology Commission (APCEC) incorporated the Act into Regulation No. 2 as Appendix B.

Alcoa’s National Pollutant Discharge Elimination System (NPDES) Permit No. AR0000582, Part I, Section B requires Alcoa to perform an Environmental Improvement Project (EIP), which is detailed later in this document. The Alcoa project described herein meets the Regulation No. 2, Appendix B requirements for an EIP.

### **1.2 Background**

#### **1.2.1 Alcoa Operations**

Alcoa conducted a bauxite mining operation in Saline County, Arkansas, from 1897 to 1990. As part of this continuous operation, Alcoa also operated a bauxite refining/chemicals operation from 1942 until the refinery was sold to Almatris in 2004.

From 1945 until 1984, Reynolds Metals Company (Reynolds) also operated a bauxite mining and refining operation contiguous to the Alcoa operation. Reynolds was purchased by Alcoa in 2000.

Both Alcoa and Reynolds used bauxite residue disposal areas (BRDAs) to contain mineral processing residuals associated with their respective bauxite mining and refining operations. The process by which these residuals were formed began with the bauxite being stripped, mined, hauled to the processing facility, and crushed. The crushed bauxite was then

mixed with a strong (250 grams per liter) solution of sodium hydroxide (caustic) in which the aluminum oxide ( $\text{Al}_2\text{O}_3$ ), also known as alumina, was dissolved. The alumina-laden solution was filtered, and the alkaline residue remaining on the filter was then washed to recover caustic, thickened, and deposited in the BRDAs. Virtually all of the non-alumina constituents (such as selenium) of the bauxite ore were concentrated in the alkaline residue. When rainfall contacts the residue, an alkaline leachate is generated.

The water treatment operations for Reynolds and Alcoa were consolidated in 2002 in order to improve efficiencies. The consolidated treatment system treats both acid mine drainage and leachate from the BRDAs. Although a portion of the water from the treatment plant is discharged into Hurricane Creek via NPDES-permitted Outfall 028 on the former Reynolds site, the majority of the water is discharged via NPDES-permitted Outfall 009 into Holly Creek.

The discharge at Outfall 009 contains, among other constituents, elevated concentrations of selenium. Selenium is the focus of this EIP.

### **1.2.2 Historical NPDES Permit Compliance**

Alcoa has a long history of compliance with its NPDES permit conditions. Four separate streams have historically received discharges from the Alcoa property. These streams include Holly Creek, Hurricane Creek, Dry Lost Creek, and Briar Lick Creek. Currently, only Hurricane Creek and Holly Creek receive discharges from Alcoa.

Discharge monitoring report (DMR) data show few to no issues with permit compliance (e.g., there have been no exceedances during the last two permit periods). Hurricane Creek and Holly Creek meet their designated fishery use as established by their respective use attainability analyses (UAAs) that were approved by the Arkansas Department of Environmental Quality (ADEQ) and the United States Environmental Protection Agency (EPA) in 1995. Both Hurricane Creek and Holly Creek ultimately discharge into the Saline River. The Saline River is highly protected and is designated as an Extraordinary Resource Waterbody, an Ecologically Sensitive Waterbody, and a Natural and Scenic Waterbody.

### 1.2.3 Selenium Discussion

Selenium plays an important role in human nutrition, although its function is not clearly understood. The difference in nutritional and potentially toxic concentrations of selenium has been estimated to be only 20-fold. This is not a particularly wide margin of safety. Selenium's role in aquatic systems is not as well understood, but it is known to bioaccumulate.

Selenium is a naturally occurring element, and according to *Chemical Analysis of Soils and Other Surficial Materials of the Conterminous United States* (Boerngen and Shacklette 1981), selenium concentrations in Arkansas soils range from < 0.1 to 2.5 mg/kg with a mean value of 0.70 mg/kg. Selenium is one of a few of the nonmetals to exhibit variable valence states within the redox range of biological systems. As such, the oxidation states are +6, +4, 0, and -2. All four oxidation states of selenium are prevalent in soils.

Bauxite, the ore of aluminum, is a highly weathered clay soil which contains selenium along with virtually all the elements commonly found in earthen materials. Selenium contained in the bauxite is concentrated during the refining process where ostensibly 50% of the ore becomes bauxite residue. Since the selenium remains with the residue, the selenium concentration in the residue is increased by a factor of approximately two. Historically, following extraction of the alumina from the bauxite, the alkaline residue was deposited in the BRDAs. Under the alkaline conditions of the residue, the selenium is more soluble and becomes associated with the leachate that is then captured, treated, and discharged.

Alcoa currently manages two BRDAs that are not contiguously located but which cover approximately 1,000 total surface acres. The BRDAs were closed under agreements with ADEQ; one in the late 1980s (agreement between ADEQ and Reynolds) and one in the late 1990s (agreement between ADEQ and Alcoa). The closure processes included: 1) investigations; 2) feasibility studies; 3) cooperative efforts with ADEQ through review and approval; and 4) closure according to the agreed-upon requirements.

Although the BRDAs are closed, a portion of the rain that falls on them percolates through the soil covers, contacts the alkaline residue, and produces an alkaline leachate. Selenate salt is a form of selenium that becomes more soluble in alkaline environments. Alcoa collects the alkaline leachate containing the selenium in former mining pits, treats it in earthen basins using

neutralization/precipitation methodology, and then discharges it under the terms of the NPDES permit.

During the 2000 NPDES permit renewal process Alcoa discovered selenium in its discharge. At the time of the permit renewal process, selenium criteria had been only recently (1998) adopted by APCEC. Prior to this time the analytical technology was not available to measure the concentration of selenium that was found in Alcoa's discharge. In a method detection limit/practical quantitation limit study and a matrix spike study conducted by Alcoa, the accuracy of analytical data for selenium, particularly at low concentrations, was low. The studies are included in Attachment 4 of Appendix A.

Upon discovery of the selenium issue, Alcoa immediately contacted ADEQ and conducted a site-wide evaluation to determine the source of the selenium. This evaluation revealed that the leachate from the BRDAs was the primary source of the selenium. Although the leachate is treated prior to being discharged by Alcoa, the selenium concentrations remain above the criterion allowed by Arkansas water quality standards, as described more fully in Section 2.0.

#### 1.2.4 Water Treatment

Since its acquisition of Reynolds in 2000, Alcoa has, on average, collected, treated, and discharged approximately 150 million gallons of leachate annually along with 2.35 billion gallons of acid mine runoff under the authority of NPDES Permit No. AR0000582. The annual volume of discharge typically ranges from 1.5 to 4.5 billion gallons with an average of 2.5 billion gallons.

Table 1.1. Discharge volumes.

Type	Minimum Annual Volume (billion gallons)	Maximum Annual Volume (billion gallons)	Average Annual Volume (billion gallons)
Acid Mine Drainage	1.4	4.3	2.35
Alkaline Leachate	0.1	0.2	0.15
<b>TOTAL</b>	<b>1.5</b>	<b>4.5</b>	<b>2.5</b>

The treatment of the alkaline leachate includes: 1) mixing with acid mine drainage; 2) further pH adjustment with sulfuric acid; 3) the addition of polymers for metals and solids removal; and 4) settling in a large (60-acre) pond system composed of four ponds in series before the treated water is discharged to either Holly Creek or Hurricane Creek. Approximately 75% of the effluent is discharged into Holly Creek via Outfall 009 and the other approximately 25% of the effluent is discharged to Hurricane Creek via Outfall 028.

The treatment historically has consisted of pH adjustment and sufficient settling capacity to allow iron, aluminum, and total suspended solids (TSS) concentrations to be reduced such that permit limits were met. The permit limits were established by ADEQ to ensure that water quality standards in the receiving streams were being met.

Upon discovering that the selenium concentrations in the discharge were above the state's water quality criteria, Alcoa began to seek ways to modify the treatment system to reduce selenium concentrations to levels equal to or below the water quality criteria. This effort is ongoing but has not been completely successful due to the fact that selenium at the lower levels and in the form found in the leachate is difficult to remove. Consequently, Alcoa began to seek alternative treatment technologies (see Section 5) that would be capable of reducing the selenium concentrations in the discharge. Because of the volume of water to be treated, the relatively low concentrations of selenium in the water, and the form of selenium in the discharge, there are no currently known biological or chemical treatments capable of reducing the selenium concentrations to levels that meet the selenium water quality criteria and/or permit limits.

## **2.0 DESCRIPTION OF THE AFFECTED STREAM SEGMENT**

The waterbody affected by this EIP is Holly Creek. The entire creek channel is contained on Alcoa property in Saline County, Arkansas. Holly Creek has an existing, but habitat-limited, fishery use and its flow consists almost entirely of the Alcoa discharge throughout much of the year.

### **2.1 Physical Characteristics of Holly Creek**

Holly Creek has a watershed of 10.6 square miles at its mouth and is located entirely in the Gulf Coastal ecoregion of Arkansas. The creek is an intermittent stream that begins at Alcoa's Outfall 009 and continues for approximately 3.4 miles on Alcoa property before emptying into the Saline River. Holly Creek has earthen sides and an earthen bottom. The flow in the creek can range from 0 gallons per minute (gpm) to over 30,000 gpm in just a few minutes and is dependent upon rainfall and/or the Alcoa discharge. Without Alcoa's discharge, the creek would consist only of small pools during the dry portions of the year. Further, Holly Creek has an existing fishery use which is habitat-limited as documented in the 1995 UAA approved by ADEQ (see Section 2.3).

### **2.2 Chemical Characteristics of Holly Creek**

Selenium concentrations in Outfall 009 (and hence Holly Creek) range from less than 5 µg/L to 23 µg/L per the DMR data from October 2005 through December 2008. The selenium concentration in the discharge is typically less than the APCEC acute water quality criterion for selenium (20 µg/L), but typically exceeds the APCEC chronic water quality criterion for selenium (5 µg/L). All other water quality criteria for the constituents historically monitored pursuant to Alcoa's NPDES permit (i.e., pH, iron, aluminum, TSS, total dissolved solids (TDS), sulfate, and flow) are consistently met.

Selenium concentrations in Holly Creek were only recently discovered to be in excess of the current chronic criterion. However, these selenium concentrations are believed to represent historical conditions and not a recent change in stream conditions. Although selenium

concentrations may have a limiting effect on the fishery in Holly Creek, the lack of sufficient habitat in Holly Creek also limits the fishery. If the selenium concentrations were reduced to levels below the water quality criteria, the fishery in Holly Creek would continue to be limited (1995 UAA) by the lack of sufficient and appropriate habitat. Both EPA and ADEQ supported the conclusions of the 1995 UAA , which demonstrated that habitat is limited in Holly Creek and that without Alcoa's discharge, flow characteristics of the creek would change such that the creek would become a series of pools during dry weather and thus further limit the habitat.

### **2.3 Biological Characteristics of Holly Creek**

The fishery use assigned to Holly Creek is a habitat-limited fishery. The 1995 UAA documented that Holly Creek's designated fishery use is an existing use, and has historically been met, but that the habitat available for fish reproduction is limited. The creek does support aquatic biota comprised primarily of spotted bass, bluegill sunfish, longear sunfish, and mosquito fish. Many of the aquatic life uses that exist in Holly Creek are due to the fact that Alcoa's discharge from Outfall 009 supplies sufficient water to the creek for much of the year to sustain the aquatic life. Thus, without the discharges from Alcoa, the fishery in Holly Creek would be further limited by the lack of available water during the dry season.

In addition to habitat limitations, selenium concentrations found in the water column of Holly Creek bioaccumulate in the fish in the creek, resulting in elevated selenium concentrations in the fish tissue. Selenium concentrations in fish taken from Holly Creek (see Table 2.1) are typically above those concentrations that the literature (Lemly 2002, EPA 2004) suggests will likely cause reproductive effects. However, observations support that a reproducing bluegill fishery exists in Alcoa's No. 3 treatment pond and in Holly Creek's headwaters below Outfall 009. See Appendix A for additional selenium data and information related to selenium treatment technologies.

Table 2.1. Summary of whole-body selenium concentrations in fish collected from the Saline River and Holly Creek.

Location	Species	Total Selenium (mg/Kg dry weight)	
		9/17-18/03	7/20-22/04
Saline River (upstream)	LMB	1.52	2.19
		1.40	1.11
	SB	1.44	2.29
		1.49	1.19
	LESF	1.60	1.92
		1.11	1.50
			1.62
			1.83
	CC	0.91	1.38
		1.07	
Saline River (downstream)	LMB	1.89	1.91
		1.89	
		1.89	
	SB	1.68	1.80
			1.65
			2.62
	LESF	1.40	2.26
		0.93	1.84
			1.54
	CC	0.75	
Holly Creek	SB	9.21	
	LESF	22.1	27.2
			25.4
			26.9
	BGSF	26.4	34.8
		23.3	13.1
			25.1
			24.0
			22.2

Notes:

LMB = largemouth bass (*M. salmoides*);SB = spotted bass (*Micropterus punctulatus*);LESF = longear sunfish (*Lepomis megalotis*);CC = channel catfish (*Ictalurus punctatus*);BGSF = bluegill sunfish (*L. macrochirus*).



## 2.4 Summary

Alcoa's discharge comprises the bulk of the flow in Holly Creek for much of the year. The discharge contains selenium concentrations that range from less than 5 µg/L to 23 µg/L. As documented by the 1995 UAA, a limited fishery use exists in Holly Creek due to the habitat limitations. Both ADEQ and EPA agreed with and approved the UAA study results. Appendix A provides details relative to selenium treatment technologies to address selenium issues in Holly Creek.

The literature (Lemly 2002, EPA 2004) suggests that selenium concentrations in the fish captured from Holly Creek are sufficient to limit reproduction. However, if selenium could be totally removed from the effluent, the fishery use in Holly Creek would still be limited due to habitat limitations. Without Alcoa's discharge, the fishery in Holly Creek would be even more limited because the flow in Holly Creek consists largely of Alcoa's discharge for a portion of the year.

Maintaining the current discharge conditions and concentrations is expected to protect both existing and designated uses in Holly Creek as well as in the Saline River. ADEQ ambient water quality data as well as biological data collected by Alcoa demonstrate that the Saline River is meeting its designated uses.

Although Holly Creek discharges into the Saline River, results of the monitoring conducted in the Saline River for the 1995 UAA as well as subsequent monitoring by Alcoa and ADEQ (Ambient Water Quality Monitoring Network) demonstrate that it supports a healthy fishery both upstream and downstream of its confluence with Holly Creek. Additional monitoring conducted upon discovery of the selenium issue demonstrated that designated uses (i.e., drinking water, fishery, primary contact, Extraordinary Resource Water, Ecologically Sensitive Waterbody, and Natural and Scenic Waterway, etc.) and existing uses (i.e., drinking water, fishery, primary contact, Extraordinary Resource Water, Ecologically Sensitive Waterbody, and Natural and Scenic Waterway, etc.) are being met. Selenium concentrations in the water column and in tissue of fish taken from the Saline River were near background levels. In addition, a mussel survey conducted by Davidson in 1997 and Davidson and Gosse in 2001 in the Saline River below its confluence with Holly Creek revealed a healthy mussel population.

Waters impacted by mining and refining have been discharged into Holly Creek and the Saline River throughout Alcoa's long history in Saline County. The selenium concentrations and habitat limitations in Holly Creek result in a limited fishery; however, without Alcoa's discharge, the fishery in Holly Creek would be further limited. ADEQ ambient water quality data as well as biological data collected by Alcoa demonstrate that the Saline River is meeting its designated uses. The Saline River remains a highly regarded fishery with excellent water quality.

### **3.0 AMBIENT WATER QUALITY FOR SELENIUM**

#### **3.1 Water Quality Criteria for Selenium**

Water quality criteria for selenium were adopted by APCEC in the late 1990s. This included a chronic criterion of 5 µg/L and an acute criterion of 20 µg/L. The criteria were based on freshwater aquatic criteria developed by EPA. Currently EPA's criteria for selenium are under review and are expected to change during the course of this EIP.

#### **3.2 Existing Water Quality**

Water quality criteria in Holly Creek are being met, with the exception of selenium. It is now known that the selenium concentration in Alcoa's treated effluent and in Holly Creek typically exceeds the chronic criterion of 5 µg/L. The selenium concentration in Alcoa's discharge typically ranges from less than 5 µg/L to 23 µg/L. Because Alcoa's discharge into Holly Creek is at the headwater of Holly Creek, there is little or no dilution available.

#### **3.3 WQS Post EIP**

The final water quality criteria at the end of this project cannot be reliably defined at this time due to 1) the uncertainty of regulatory agreement on the selenium criteria, 2) the lack of proven treatment technology, and 3) the complexity of the effort (e.g., recycle/reuse of 100 million cubic yards of residue, inability to eliminate leachate generation, removing low levels of selenium, treating 4 billion gallons of water annually, etc.). Upon completion of the EIP, the end goals are to a) protect water quality in the streams receiving Alcoa's discharge, and b) ensure that Alcoa's discharge is in compliance with local, state, and federal statutes, rules, and regulations.

However, since EPA's criteria for selenium are under review and are expected to change during the course of this EIP, one cannot accurately predict what the water quality criteria for selenium will become. Furthermore the treatment of selenium has and will continue to evolve over time. The purpose of the EIP is to provide sufficient time for Alcoa to develop and implement treatment technologies such that the water quality criteria for selenium are met.

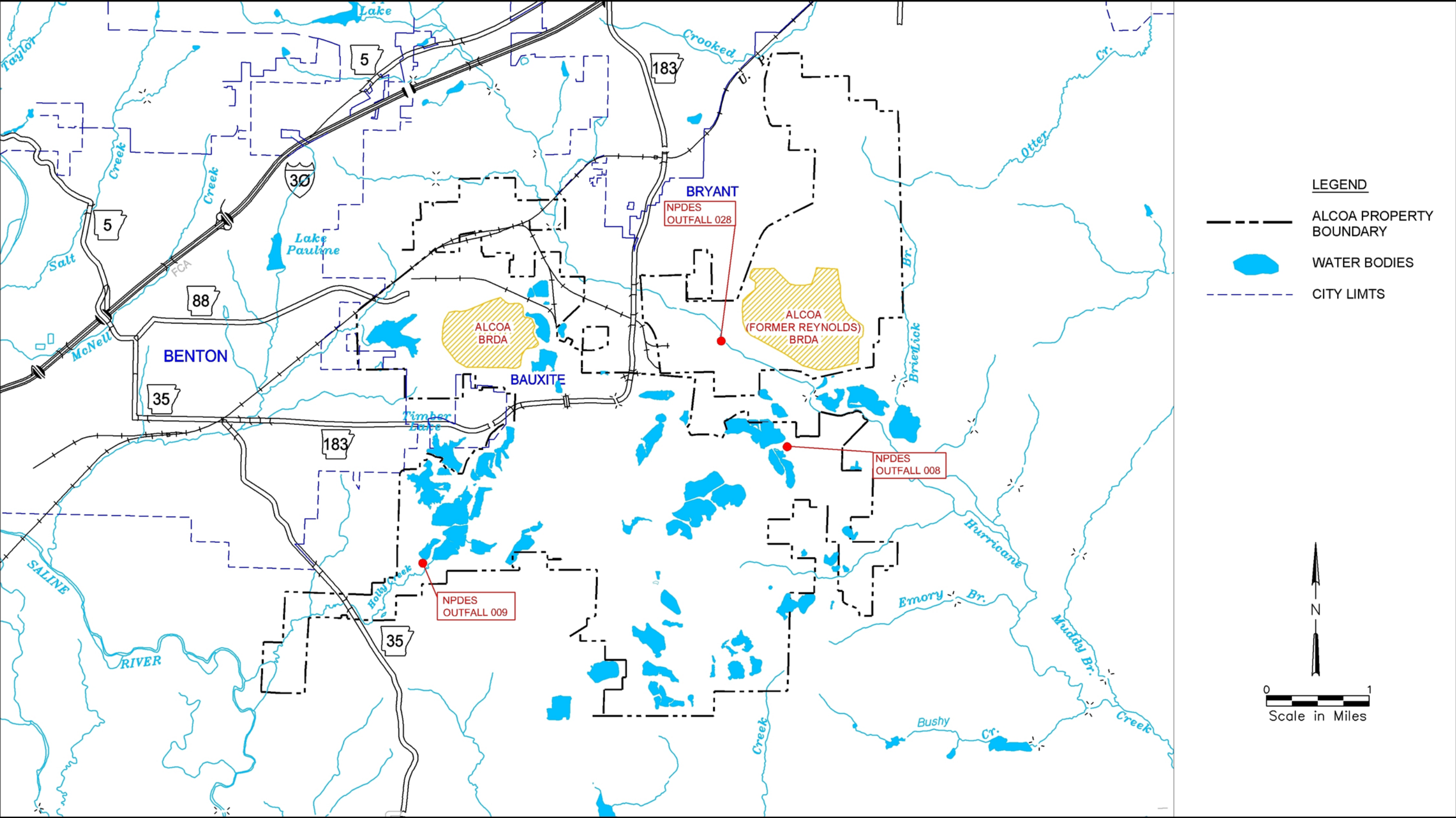


Figure 3.1. Site map.

## **4.0 AFFECTED WATER QUALITY**

As stated in Section 3.0, Holly Creek does not meet the chronic water quality criterion established in APCEC Regulation No. 2 for selenium. The selenium concentration in Alcoa's treated effluent (measured at Outfall 009) typically ranges from less than 5 µg/L to 23 µg/L. It is anticipated that unless an economically and technically feasible treatment technology can be developed and implemented or a pipeline from Outfall 009 directly to the Saline River is constructed, the Outfall 009 discharges will exceed future permit limitations for selenium derived from the chronic criterion. As previously stated, the selenium criteria are currently under review by EPA and it is likely that the criteria will change during the course of this EIP.

## 5.0 MODIFICATIONS SOUGHT AND ASSOCIATED JUSTIFICATION

### 5.1 Requested Modification

During the term of this EIP Alcoa will seek a temporarily modified chronic selenium criterion of 17 µg/L for Holly Creek. Currently the instream chronic selenium criterion is 5 µg/L for total recoverable selenium. This request represents no change from the current conditions and is based upon discussions between Alcoa, ADEQ, and EPA that resulted in the requirement for an EIP to be included in Alcoa's NPDES permit. Although selenium concentrations in Holly Creek were only recently discovered to be in excess of the current chronic criterion, these selenium concentrations are believed to represent historical conditions and not a recent change in stream conditions. While selenium concentrations may have a limiting effect on the fishery in Holly Creek, habitat limitations in the stream also limit the fishery such that if the selenium concentrations were reduced to levels below the criteria, the fishery in Holly Creek would continue to be limited by the lack of sufficient and appropriate habitat (1995 UAA).

Based on research and studies conducted by Alcoa since 2003, it is evident that no treatment approaches are currently known that will sufficiently and economically reduce selenium in the effluent to concentrations that will meet anticipated future permit limitations and anticipated water quality criteria. Because 1) Alcoa cannot cease discharging, 2) no treatment is currently available to sufficiently reduce selenium concentrations, 3) several mitigation efforts have already been implemented, and 4) additional mitigation efforts will take years to manifest their effect, the only other potential option available to Alcoa at the present time is to change the point of discharge by constructing a pipeline from Outfall 009 directly to the Saline River. However, the 1995 UAA demonstrated that without Alcoa's discharge, flow characteristics of the creek would change such that the creek would become a series of pools during dry weather, thus further limiting the habitat. Accordingly, ADEQ concluded that prior to constructing the pipeline, other options should be explored.

Under these circumstances, Alcoa is requesting that the modified water quality criteria for selenium be in effect for a period that may be in effect for 15 to 20 years, or more, as Alcoa implements the Remediation Plan and/or other solutions to sufficiently reduce the selenium

concentrations. Reductions in selenium concentrations are occurring with the existing treatment system although the treatment is not sufficient to meet the current instream criteria. Thus, Alcoa's Remediation Plan is to research, develop, and implement economically and/or technically feasible treatment technologies that result in improvements to the treatment system such that the gap between selenium concentrations in the discharge and the instream criteria will close. The length of time the modification will be needed is contingent upon whether, and how quickly, treatment technologies can be developed and implemented. In the event that significant treatment improvements are made, or other options for reducing the selenium in the discharge become available within a shorter timeframe, the length of time the modification will be needed will be reduced accordingly. Although research and studies conducted by Alcoa since 2003 have demonstrated that no treatment approaches are currently known that will sufficiently reduce selenium in the effluent to concentrations that will meet anticipated future permit limitations and anticipated water quality criteria, Alcoa continues to conduct research and studies on technologies to reduce selenium in its discharge.

## **5.2 Support Information for the Modification Request (Temporary Criterion)**

The basis for a temporary site-specific criterion is provided in 40 CFR 131.10(g). The following conditions at 40 CFR 131.10(g) are met at the Alcoa site for the EIP-based temporary modification of the selenium criterion:

- “(3) Human caused conditions or sources of pollution prevent the attainment of the use and cannot be remedied or would cause more environmental damage to correct than to leave in place;”
- “(5) Physical conditions related to the natural features of the water body, such as the lack of a proper substrate, cover, flow, depth, pools, riffles, and the like, unrelated to water quality, preclude attainment of aquatic life protection uses;”
- “(6) Controls more stringent than those required by sections 301(b) and 306 of the Act would result in substantial and widespread economic and social impact.”

Furthermore, 40 CFR 131.11(b)(1)(ii) provides states with the opportunity to adopt water quality criteria that are “modified to reflect site-specific conditions.” Site-specific criteria, as

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with all water quality criteria, must be based on a sound scientific rationale in order to protect the designated use.

### **5.2.1 Feasibility of Treatment**

The neutralization/precipitation treatment system currently used by Alcoa cannot remove selenium to concentrations that are below the APCEC chronic water quality criterion for selenium. Other viable treatment approaches to remove selenium from Alcoa's discharge have not yet been identified largely due to the volume of water to be treated, the form of selenium in the discharge, and the relatively low level of selenium in the discharge. Using reverse osmosis (RO) to treat the leachate at its source is not practical at this time due to the effect of high alkalinity on the membranes and the effect of scaling upon the neutralization of the alkalinity. Additionally, RO produces a contaminated regeneration effluent that requires further treatment for selenium fixation or removal before disposal. Thus, the selenium removal problem still exists but in a more concentrated form. Biological treatment of Alcoa's leachate has shown promise for treating selenium, but results of a biological treatment study indicated that selenium concentrations were not consistently reduced to the required levels. Additional research is needed to determine if the selenium concentrations required to meet the chronic water quality criterion in Holly Creek can be achieved.

### **5.2.2 Treatment Options Evaluated by Alcoa**

Alcoa has considered numerous selenium treatment technologies relative to both the source of the selenium and the effluent. Treatment technologies that have been considered by Alcoa include:



1. Wetlands,
2. Reverse osmosis,
3. Ion exchange,
4. Bioreactors,
5. In-lake treatment,
6. Anaerobic removal,
7. Constructed microbial mats,
8. Hydroxide/sulfide precipitation,
9. Zero valence iron reduction and precipitation,
10. Sulfate co-precipitation,
11. Ferrous hydroxide reduction and co-precipitation,
12. Adsorption with Alcoa F-1 alumina, and
13. Compost filters.

### **5.2.3 Pilot Testing**

Based on the treatment options that have been evaluated, Alcoa has conducted pilot tests on certain modified treatment technologies to determine their potential for application at the site. Pilot studies that involve the use of biological systems to treat selenium in the BRDA leachate have been conducted and will continue. If these tests or other pilot tests show promise, they will be scaled up to further evaluate their effectiveness, applicability, feasibility, and collateral effects, if any.

### **5.2.4 Mitigation Efforts**

Over the past thirty plus years, Alcoa has successfully mitigated much of the effects of the historical mining and refining operations on the environment, including but not limited to the following:

1. Reclaimed over 5,500 acres of mined land to meet or exceed ADEQ reclamation standards;
2. Constructed and operated four water treatment plants capable of treating over 5 billion gallons of water annually with an average of 2.5 billion gallons treated annually since 1977;
3. Closed approximately 1,000 acres of BRDAs per ADEQ guidance;
4. Installed clay cover on the Alcoa BRDA to reduce infiltration;
5. Graded the Alcoa BRDA surface to improve runoff;
6. Installed leachate collection systems;
7. Established a healthy and vibrant vegetative cover on the BRDAs to improve evapotranspiration; and
8. Diverted stormwater to the treatment system.

All of these efforts have resulted in improving the quality and reducing quantity of the water that is discharged from the site. Since some of these efforts were conducted simultaneously, the effect of each effort is difficult to quantify. The effect of these efforts to reduce the selenium concentration in the discharge is unknown since the selenium issue was only identified after many of these efforts were initiated. While the selenium concentrations in the discharge may exceed the chronic criterion for selenium in Holly Creek, these concentrations represent values that one would expect after treatment using conventional technologies.

#### **5.2.4.1 Reclamation**

The over 5,500 acres of Alcoa land disturbed by mining activities that have been reclaimed is an outgrowth of Alcoa's support of regulations related to the reclamation of lands disturbed by mining activities. Prior to the development of federal standards in 1977 for coal mine reclamation, Alcoa worked closely with Arkansas regulators and the Arkansas Legislature to develop the Open Cut Land Reclamation Act of 1971. Over the next 40 plus years, Alcoa sought, improved, developed, and implemented reclamation techniques that best suited the conditions related to the mining of bauxite in central Arkansas. Those reclamation efforts have been successfully used on over 8.5 square miles of land disturbed by mining activities such that the reclaimed areas are now self-sustaining.

#### **5.2.4.2 Water Treatment**

In the early 1970s Alcoa also constructed and operated a pilot water treatment plant to treat acid mine drainage. This gave rise to the construction and operation of larger and additional water treatment plants that allowed Alcoa to collect, treat, and discharge water from the entire area disturbed by mining and refining activities. The water treatment facilities have been continually improved over the years to include treatment of additional waste streams and to meet instream water quality criteria that have become more stringent and/or that have been more recently adopted. Selenium only recently became a constituent of concern in Alcoa's discharge due to improved analytical techniques and the recent adoption of selenium criteria. Consequently, Alcoa is seeking to develop a treatment system such that Alcoa's discharge meets the selenium water quality criteria and permit limits.

#### **5.2.4.3 BRDA Closure**

Approximately 1,000 acres of BRDAs that were associated with the refining operations were closed once the refining operations ceased using closure techniques and processes that were approved by ADEQ. Closure of BRDAs of this magnitude had not been attempted previously either in Arkansas or in other parts of the United States. Thus no precedent for closure of the BRDAs existed at the time these BRDAs were closed. Numerous approaches and techniques for closure of the BRDAs were evaluated and several were attempted. The approach that provided the greatest degree of success involved removing, treating, and discharging one billion gallons of stored alkaline water, topographically shaping the area by moving 2.4 million cubic yards of residue, applying 0.4 million cubic yards of capping material, applying 0.6 million cubic yards of soil cover, and planting cool and warm season vegetation to control erosion and improve evapotranspiration.

#### **5.2.4.4 Reuse of Bauxite Residue as Liming Agent**

Bauxite residue has been used as an alternative liming agent to reclaim the land disturbed by mining activities. This effort reduced the amount of natural resources (agricultural lime) needed to neutralize these acid mine soils. By using over 500,000 cubic yards of bauxite residue

to reclaim mined land, Alcoa beneficially used a significant portion of the residue. This effort neutralized both the acid mine soil and the alkaline residue such that both were improved. As a result, vegetation is now established and is thriving on land that was previously barren. In addition, Alcoa avoided the use of a significant volume of a natural resource in the form of agricultural lime. Using bauxite residue as a liming agent, rather than hauling agricultural lime from over 100 miles away, also avoided significant fuel consumption. Other uses for bauxite residue have been pursued. Some of these include, but are not limited to, cat litter, oil dry, bedding in poultry houses, sorbents, ice melt, reactants, etc. Additional ways to recycle/reuse the residue and/or leachate continue to be evaluated but are not foreseen to have a significant effect on the current inventory of Alcoa's bauxite residue in Arkansas. It is important that any reuse of the bauxite residue is done carefully and in such a manner that it does not present a hazard to the environment, but rather results in an overall improvement to the environment.

### **5.2.5 Mitigation Approaches Not Implemented**

Some of the potential mitigation approaches that Alcoa has evaluated have not been implemented due to impracticability, costs, and/or long-term effectiveness. These include, but are not limited to: 1) further reducing infiltration of rainfall through the soil cover on the BRDAs; 2) recycling/reusing the bauxite residue in certain circumstances; 3) recycling/reusing the leachate from the BRDAs; 4) using products of combustion from the refinery as a neutralizing agent for the leachate, and 5) reverse osmosis.

#### **5.2.5.1 Further Reducing Infiltration of Rainfall**

Determining the degree to which cover improvements will be practical or cost-effective is difficult at best. A number of factors individually and in combination (e.g., site size, color of the leachate, etc.) present a significant challenge to adequately prepare a hydrologic model of the site. However, results from an attempt by MFG, Inc. to model a portion of the BRDA (Reynolds Metals Company Hurricane Creek Brown Mud Lakes Hydrogeological Conceptual Model, 2002) suggest that downward migration occurs at the rate of 2.7 to 3.8 ft per month. This rate of downward migration was estimated at near maximum hydraulic head. One would expect this rate

to decline as the head is reduced. Given this unknown plus the unknown as to the distance of travel before entering the leachate collection system, it is difficult to accurately determine the time required for a molecule of water that enters the soil surface to exit as leachate. In fact, the time required will also be a function of how far from the toe of the BRDA that the molecule entered the soil surface. However, given that the BRDAs are approximately 100 ft in thickness at the peak, it is believed that it will take years for a water drop to become leachate that reaches the treatment system. Thus, any cover improvements made today will not result in a significant reduction of leachate volume for a considerable amount of time.

Reducing infiltration of rainfall through the soil cover on the BRDA was determined to be extremely expensive with little or no assurances of the level to which infiltration will be reduced. Clay caps are typically installed for this purpose. Models are available to predict the amount of water that will infiltrate through the clay cap. However, the level to which infiltration will be reduced cannot be accurately estimated. By definition a low permeability value indicates that water will percolate through the cap. Thus, clay exhibiting a low permeability value (e.g.,  $1 \times 10^{-9}$  cm/sec) will still allow some percolation of water through it.

A clay cap was installed on the Alcoa BRDA and although the volume of infiltration was reduced it was not reduced to a level that eliminated leachate or the selenium issue. In addition, sources and availability of clay sufficient to provide the level of permeability desired for this effort is limited in the area. Appendix C provides details related to the cost associated with installing additional clay cover.

Another method of reducing infiltration is to install a geomembrane liner. These liners are difficult to install on small areas in such a manner that they do not leak at the seams and/or due to punctures. Although installing a geomembrane liner on 1,000 acres is possible, doing so is a formidable task and quite expensive. Further, flexible membrane liners have a finite life and would need to be replaced since they would be needed at the Alcoa site for a protracted period of time. The anticipated lifespan of a flexible membrane liner ranges from 30 to 100 years. Leachate generation from the BRDAs is estimated to occur for multiple life spans of flexible membrane liners. The cost estimate for installing high-density polyethylene (HDPE) or a geosynthetic clay layer ranges from \$58 to \$68 million and is further described in Appendix C.

Improving the degree of slope will aid in the runoff of surface water and thus reduce infiltration. Altering the degrees of slope on the BRDA from the current 1% slope to a 2% slope would require approximately 7.3 million cubic yards of material (Appendix C). The cost would be in excess of \$100 million. Although improving the degree of slope will reduce the volume of water that infiltrates the residue, leachate formation will not be eliminated.

#### **5.2.5.2 Recycling/Reusing the Bauxite Residue**

Although approximately 650,000 cubic yards of the bauxite residue was used as a substitute for agricultural lime and cat litter, approximately 100 million cubic yards remain on site. The residue can be used for other purposes as well including, but not limited to, road base, sorbents, cement, fillers, oil dry, ice melt, and reactants. Transportation of the material limits the practicality of these uses. Moving a truckload 65 miles would cost an average of \$200 per truck load, and with 4,000,000 truckloads existing on the site, it would cost almost \$1 billion to move the material this distance. It is unreasonable to expect that sufficient end-users within a 65-mile radius of the site could be identified within a reasonable timeframe. Therefore, additional costs would result as the transportation distance increased. In addition, the product is unknown to most of the end-users, and as such, significant testing would be required before significant volumes could be utilized.

#### **5.2.5.3 Recycling/Reusing the Leachate**

The leachate has potential to be used in any process where alkalinity is needed. This potentially includes paper mills, tanneries, water treatment, silica gel production, etc. Although the leachate is considered to be strong (10 grams per liter) relative to its impact on the environment, it is relatively weak for most industrial applications. Since the leachate is not concentrated, transportation costs for the end-user are greater. Assuming 3,500 gallons of leachate per truckload, 42,850 truckloads are produced each year. Using similar hauling costs as above, approximately \$7,500,000 per year would be required to truck the material a distance of only 50 miles.

#### **5.2.5.4 Combustion Products**

The bauxite refining process results in the combustion of significant volumes of natural gas. One of the products of combustion is carbon dioxide. Alcoa evaluated the potential of using the products of combustion as a neutralizing agent for the alkaline leachate. This effort did not prove to be economical.

#### **5.2.5.5 Reverse Osmosis**

Water treatment technologies vary in terms of effectiveness and costs. The high concentrations of dissolved minerals in the Alcoa BRDA leachate and the large volume of water to be treated result in RO being prohibitively expensive.

For example, installing an RO system capable of sufficiently reducing the selenium concentrations in Alcoa's discharge to levels below the chronic criterion will require a significant upfront capital outlay. Moreover, the operating costs of an RO system for a waste stream of the concentrations found at Alcoa are estimated to exceed \$0.005 per gallon (Appendix A). For a system that treats over 3 billion gallons per year, the annual treatment cost would be over \$15 million. Furthermore, RO produces a contaminated regeneration effluent that requires further treatment for selenium fixation or removal before disposal. Thus, the selenium removal problem would still exist but in a more concentrated solution. Dewatering this solution would prove to be a difficult task, because the solids still exist as extremely fine particles. It is not feasible at this time to use RO for treating the leachate at its source due to the high alkalinity and the effect of scaling upon the membranes. The cost of pre-treating the leachate to neutralize alkalinity and reduce iron/aluminum is expected to increase the cost of an RO system as described above.

Other than RO, no other treatment technology has been demonstrated to effectively decrease selenium concentrations to values that are less than the current criteria. However, Alcoa will continue to evaluate other water treatment technologies with the goal of finding one that has a demonstrated ability to cost-effectively reduce the selenium concentration in the discharge to acceptable levels.

### **5.2.6 Economic Evaluations**

The environmental benefit of each mitigation effort must be weighed against the economics of the effort to avoid the potential of spending millions and millions of dollars with minimal environmental benefit in return. Due to the scale of the Alcoa Remediation site, no effort to mitigate the source of the selenium has proven more cost-effective and beneficial to the environment than water treatment. Current treatment technologies, though, will not adequately reduce the selenium concentrations in the volume of leachate that is being generated at the site. However, with sufficient time for experimentation and implementation, Alcoa may be able to develop a treatment approach that will remove selenium to levels that are environmentally acceptable. In the event that no such effective water treatment technology can be developed (or site-specific criteria cannot be adopted), another alternative may be to construct a pipeline directly from Outfall 009 to the Saline River.



## **6.0 PROPOSED REMEDIATION PLAN**

### **6.1 Remediation Plan**

Per APCEC Regulation No. 2, Appendix B, Section 3(a)(6), a proposed Remediation Plan is to be included as part of the NOI. The Remediation Plan is to consist of:

- “(A) A description of the existing conditions, including identification of the conditions limiting the attainment of the water quality standards;
- (B) A description of the proposed water quality standard modification, both during and post project;
- (C) A description of the proposed remediation plan;
- (D) The anticipated collateral effects, if any, of the Remediation Plan.”

#### **6.1.1 Existing Conditions**

Regulation No. 2 requires the Remediation Plan to include “a description of the existing conditions, including identification of the conditions limiting the attainment of the water quality standards.” Water quality standards in Holly Creek are currently being met with the exception of the selenium chronic criterion. The ninety-fifth percentile of the existing data is 17 µg/L selenium. The maximum concentration observed to-date has been 23 µg/L. Currently the chronic and acute instream criteria are 5 µg/L and 20 µg/L, respectively, for total recoverable selenium. Analytical techniques for determining selenium concentrations have only recently become sufficient to detect selenium in the Alcoa discharge at concentrations near the current water quality criteria. Thus, Alcoa only recently discovered that the selenium criteria were not being met.

Significant remediation efforts have been conducted in the past to reduce the amount of water containing selenium to be treated. While these remediation efforts have reduced the amount of water containing selenium to be treated, they have not eliminated it.

Water treatment has been occurring on the site since the early 1970s. Current water treatment technologies reduce the selenium concentrations in the discharge but are not adequate to treat the alkaline leachate such that selenium concentrations in the discharge meet selenium

criteria. However, as stated in Sections 13 and 15 of the Fact Sheet accompanying Alcoa's NPDES permit "there is not a currently-available, large-scale, economical treatment system for selenium." Since current water treatment technologies are not adequate and/or cost-effective to treat the alkaline leachate such that selenium concentrations in the discharge meet selenium criteria, Alcoa proposes to evaluate, develop, and implement a new site-specific treatment technology or technologies to meet water quality standards. It is anticipated that this will be an iterative process, based on trial and error, for which significant time will be required.

### **6.1.2 Proposed Water Quality Criteria**

Regulation No. 2 requires the Remediation Plan to include "a description of the proposed water quality standard modification, both during and post project."

#### **6.1.2.1 Proposed Water Quality Criteria During the Project**

Through this EIP Alcoa will seek a temporarily modified chronic selenium criterion of 17 µg/L for Holly Creek. The proposed total recoverable selenium chronic criterion of 17 µg/L is based on the ninety-fifth percentile of the data collected on Alcoa's discharge to-date, and discussions between Alcoa, ADEQ, and EPA. In addition to the fact that those discussions resulted in the requirement of an EIP being included in Alcoa's NPDES permit, the discussions also led to the inclusion of a selenium limit of 17 µg/L in the permit, which represents no change to Holly Creek from the current conditions. This temporary site-specific criterion is requested for the period of this EIP, which is expected to be in effect for 15 to 20 years, or more, while Alcoa implements the Remediation Plan. Reductions in selenium concentrations are occurring with the existing treatment system although the treatment is not sufficient to meet the current instream criteria. As improvements to the treatment system are developed and implemented, the gap between selenium concentrations in the discharge and the instream criteria will close. The length of time the temporary site-specific criterion will be needed is contingent upon whether, and how quickly, treatment technologies can be developed. In the event that significant treatment improvements are made, or other options for reducing the selenium in the discharge become

available within a shorter timeframe, the length of time the temporary site-specific criterion will be needed will be reduced accordingly.

#### **6.1.2.2 Proposed Water Quality Criteria Post-Project**

At the end of the EIP, Alcoa's discharge will meet the water quality criteria for selenium. However, the post-EIP water quality criteria cannot be reliably defined at this time due to 1) the uncertainty of regulatory agreement on the selenium criteria, 2) the lack of proven treatment technologies, and the 3) the complexity of the issues involved (e.g., 100 million cubic yards of residue, inability to eliminate leachate generation, removing low levels of selenium, treating 4 billion gallons of water annually, etc.). As stated previously, EPA's water quality criteria for selenium were adopted by APCEC in the late 1990s, and included a chronic criterion of 5 µg/L and an acute criterion of 20 µg/L. The criteria were based on freshwater aquatic criteria developed by EPA. Currently EPA's criteria for selenium are under review and are expected to change during the course of this EIP. Furthermore, EPA is considering adopting a tissue-based criteria rather than a water quality-based criteria. Alcoa, ADEQ, and EPA are uncertain as to what the tissue-based criteria will be. However, if such criteria are adopted in lieu of the existing criteria, it will become even more difficult to predict the adequacy of a particular treatment approach, since tissue concentrations are a function of bioaccumulation. Tissue testing is atypical for facilities in Arkansas, and preliminary testing has not produced consistent results.

The overarching goals of this EIP are to 1) protect water quality in the streams receiving Alcoa's discharge, and 2) ensure that Alcoa's discharge is in compliance with local, state, and federal statutes, rules, and regulations. If these goals cannot be achieved, then Alcoa will seek to a) develop permanent site-specific selenium criteria that are protective of the existing uses, or b) construct a pipeline directly from Outfall 009 to the Saline River.

#### **6.1.3 Proposed Remediation Plan**

Regulation No. 2 requires the Remediation Plan to include "a description of the proposed remediation plan." Alcoa's proposed Remediation Plan is to take all appropriate actions to develop and implement an economically and technically feasible water treatment technology or

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technologies to reduce the selenium concentrations in Alcoa's discharge so that the applicable water quality criteria for selenium in Holly Creek can be met. This will be accomplished by continuing to evaluate through research, bench-scale studies, and pilot studies those options that show promise in terms of viable selenium reduction. Options for 1) treatment of selenium at its source, 2) after mixing the leachate with the acid mine drainage, and 3) treatment at the discharge will be considered.

The previous remediation efforts conducted to date have demonstrated that the most promising approach for reducing selenium in Alcoa's discharge is to treat the water prior to discharge. Although water treatment has been occurring on the site since the early 1970s, as noted in the Fact Sheet of Alcoa's permit there is no large-scale, economically viable option to treat selenium. Consequently, research and time are needed to develop and implement a treatment technology or technologies to sufficiently treat Alcoa's discharge such that selenium criteria can be met.

The previously investigated treatment technologies are not economical for Alcoa's situation due primarily to the large volume of effluent (an average discharge of 2.5 billion gallons annually) that must be treated, the low concentration of selenium in the water before treatment, and the fact that the form of the selenium present in the discharge is not conducive to treatment.

Treatment technologies that already have been evaluated by Alcoa include physical separation, chemical treatment (hydroxide/sulfide precipitation, sulfate precipitation, ferrous hydroxide, zero-valent iron, adsorption, etc.), and biological systems (reactors, compost filters, constructed wetlands, constructed microbial mats). Although to date no currently known chemical or biological treatment technology is capable of reducing the selenium to meet the current selenium criteria, Alcoa is committed to continue to seek out and evaluate treatment technologies that have the potential to reduce selenium concentrations in the effluent.

Alcoa will also evaluate treatment alternatives relative to the source water as well as at other points throughout the wastewater treatment system. This evaluation will include RO even though use of that technology at this point in time is not economically feasible for treating the

leachate at the source because of the effect of alkalinity of the leachate on the membranes and the effect of scaling upon neutralization of the alkalinity.

Alcoa's research will initially be based on biologically reducing the valence state of the selenium such that precipitation can and will occur. The valence state in which the majority of the selenium currently exists is one that allows the selenium to remain in solution. However, once the valence state is altered from VI to IV the selenium becomes less soluble and will precipitate. If this form of treatment does not allow Alcoa to achieve compliance, then efforts will be made to further enhance the biological treatment in an attempt to increase selenium removal.

Current research suggests that biological forms of treatment will remove significant quantities of selenium. However, other forms of treatment will be researched since biological treatment is not adequate in terms of meeting existing water quality criteria. Given that water quality standards tend to become more restrictive over time, it is anticipated that other forms of treatment will need to be implemented either as a stand-alone unit or in combination with biological treatment. It is impossible to accurately predict the direction that the research will take, but it is conceivable that the biological form of treatment can be modified using various rates, ratios, and types of amendments. It is also conceivable that a combination of chemical and biological treatments can be employed. The optimum combination of the forms of treatment will require significant time to adequately develop and implement.

To the extent that the criteria become tissue-based rather than concentration-based, Alcoa will evaluate options for reducing bioaccumulation opportunities by taking such actions as installing fish barriers and removing older fish from Holly Creek. However, Alcoa may be left no other option than to construct a pipeline directly from Outfall 009 to the Saline River. Alcoa will continue to discuss progress made and potential options for improvement with ADEQ and EPA throughout the life of the EIP.

As noted in Section 5 above, Alcoa has implemented numerous remediation efforts. As technically and economically effective remediation efforts continue to be identified, Alcoa will continue to discuss them with APCEC, ADEQ, and EPA.

It must be understood that, due to the size of the BRDAs, any remediation effort implemented will take years to make a measurable difference in the selenium concentration of the leachate. In that context, it is conceivable that sufficient time has not yet elapsed for the benefits of the past BRDA remediation efforts to be fully realized.

With the exception of constructing a pipeline from Outfall 009 to the Saline River development of treatment technology to reduce selenium concentrations holds the most promise. Thus, to reiterate, Alcoa's proposed Remediation Plan is to take all appropriate actions to develop and implement economically and technically feasible water treatment technology or technologies to reduce the selenium concentrations in Alcoa's discharge so that the applicable water quality criteria for selenium in Holly Creek can be met.

#### **6.1.4 Collateral Effects**

Regulation No. 2 requires the Remediation Plan to describe "the anticipated collateral effects [of the Remediation Plan], if any." Only minimal and limited impacts to Holly Creek, if any, are expected during the EIP. Despite the fact that selenium concentrations have been elevated in the water column and in the tissue of fish taken from Holly Creek, the selenium has had minimal negative impacts to Holly Creek or its limited fishery. The limited fishery observed in Holly Creek is due in large part to the habitat limitations rather than selenium. If selenium concentrations in Alcoa's discharge were to be eliminated the fishery in Holly Creek will continue to be limited due to the lack of sufficient habitat.

The selenium concentrations in the water column of Holly Creek are not expected to increase during the timeframe in which the EIP will be conducted. It is anticipated that the selenium concentration in the fish tissue taken from Holly Creek will decrease over the life of the EIP based upon a) anticipated advancement of treatment technologies, b) implementation of source-reduction strategies, and c) implementation of control strategies.

The potential for fishing, wading, or swimming to occur in Holly Creek are minimal due to the fact that Alcoa owns all the land along both sides of the creek with no intentions of selling any of this land in the foreseeable future and the property has been legally posted. Alcoa will

evaluate the feasibility of installing a fish barrier on Holly Creek in order to minimize the movement of fish between the Saline River and Holly Creek.

As treatment technologies are being evaluated, the anticipated and/or measured effects, if any, on the receiving streams will be carefully studied and reported to ADEQ and APCEC. Although nutrients, DO, TDS, pH values, etc. may be increased/added in the discharge, it is anticipated that such changes on Holly Creek will be of minimal consequence to the fishery or water quality criteria.

There are no anticipated effects to the Saline River as a result of the implementation of this EIP and thus the Saline River is expected to remain unchanged. The Saline River is designated as an Extraordinary Resource Waterbody, an Ecologically Sensitive Waterbody, and a Natural and Scenic Waterbody.

Although the selenium issue was only recently discovered, it is logical to conclude that selenium has been discharged since Alcoa began treating alkaline leachate in the mid-1980s. This conclusion is based on the fact that the source of the selenium is believed to be the alkaline leachate from the BRDAs.

#### **6.1.5 Water Treatment Efforts To Date**

Alcoa contracted with FTN Associates, Ltd. (FTN) to prepare a report of selenium treatment options. This report, titled *Alcoa Inc. – Bauxite Selenium Treatment Report, Bauxite, Arkansas* (June 2009), provides the following:

1. An overview of the selenium issue including information regarding sources of selenium at the site;
2. A study of potential treatment technologies to reduce selenium concentrations at Alcoa's discharge outfalls;
3. A description of bench-scale testing that has been performed;
4. A description of pilot-scale treatability studies that have been completed; and
5. A description of an upscale pilot plant that has recently been put into operation.

All of this work is aimed at determining the feasible means to reduce selenium in discharge waters at the outfalls. The entire report can be found in Appendix A.

A new larger pilot unit is currently being operated. The pilot-scale system is based on biological reduction of the selenium to an insoluble form. The system can be described as an anaerobic biological reactor containing a random plastic media. The plastic media provides a substrate for growth of the bacteria. A carbon source such as methanol, added to the feed water, promotes the anaerobic bacterial activity. Two small-scale biological treatment pilot plants were in operation at two separate locations on the Alcoa and Reynolds sites. The flow rates were approximately 1 gpm of leachate, with an average total selenium removal rate of 65% at the Alcoa site, and 39% at the Reynolds property. The Alcoa pilot plant was in operation for approximately 4 months and the Reynolds pilot plant was in operation for approximately 7 months. The pilot-scale system is intended to provide additional information related to the following:

- Cold weather efficiency;
- The costs of operation of a full-scale system; and
- The ability of the system to achieve the low concentrations required for meeting the water quality criterion in Holly Creek.

Alcoa will continue to actively monitor and report results of this and other research, studies, improvements, and downstream water quality. Treatment options will continue to be evaluated during the EIP and will be implemented as appropriate. It must be remembered that once a viable treatment solution is discovered and perfected, it is expected to take years for Alcoa to treat and discharge the total volume of water at the site due to the large volumes of water that have been and continue to be accumulated at the site.



## **7.0 NPDES PERMIT LIMITS**

Future NPDES permits will need to reflect the approach and schedule of the EIP in order to ensure continuity from one permit writer to another. The permit limit for selenium at Outfall 009 will be a monthly average based on the 95<sup>th</sup> percentile of historical selenium concentration values at the outfall and thus follows the procedure used for Alcoa's 2008 NPDES permit development. These permit limits will then be based on the progress achieved throughout the EIP timeline.

## **8.0 ALTERNATIVES ANALYSIS**

Appendix B of APCEC Regulation No. 2 provides for a third-party rulemaking as part of an EIP. A UAA is typically conducted in support of third-party rulemakings. UAA guidance requires that an evaluation be made of the alternatives to the direct discharge of the water that includes technical and economic considerations. The alternatives to the direct discharge of water to Holly Creek include but are not limited to:

1. No action,
2. Direct discharge to Saline River via dedicated pipeline,
3. Removal/reuse of bauxite residue and/or leachate,
4. Minimize leachate generation (cap improvements), and/or
5. Additional treatment.

### **8.1 No Action**

#### **8.1.1 Description of Alternative**

Alcoa has discharged water into Holly Creek for many years. Although no good background data is available for comparison, there is little evidence suggesting that Holly Creek has been significantly damaged as a result of Alcoa's discharge. Rather, due to the fact that Alcoa's discharge supplies water to an otherwise ephemeral stream (i.e., the creek would otherwise be dry for a portion of the year), taking no action will likely have less impact on the fishery in the creek than an action that would remove the flow from the creek during dry periods (e.g., a direct discharge from Outfall 009 to the Saline River). In addition, the habitat limitations in Holly Creek are such that the creek will remain a limited fishery whether or not selenium is removed from the discharge.

#### **8.1.2 Considerations**

This option can be easily implemented and the cost to Alcoa would be low. However, taking no action is inconsistent with both Alcoa and ADEQ policies, and therefore must be rejected.

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## **8.2 Direct Discharge to Saline River via Dedicated Pipeline**

### **8.2.1 Description of Alternative**

As an alternative to treatment, a pipeline could be installed to convey the entire flow of water currently discharged through Alcoa's Outfall 009 to the Saline River. Holly Creek begins at Alcoa's discharge and flows approximately 3 miles before it converges with the Saline River. Given the volume of Alcoa's discharge and the assimilative capacity of the Saline River, installing a pipeline from the Outfall 009 discharge point to the Saline River is a viable option. By discharging to the Saline River, the water quality issues in Holly Creek would be avoided, and the larger dilution flow associated with the Saline River would mitigate any issues from selenium directly at the point of discharge.

A preliminary engineering design and cost estimate were prepared for this alternative. This conveyance could be achieved with a gravity system consisting of two 30-inch, HDPE, standard dimension ratio (SDR) 26 pipes that would carry the design flow of 20 million gallons per day. The existing ponds above Outfall 009 would be used to equalize flows and control discharge rates to the Saline River so that water quality in the river could be maintained.

The length of the pipeline would be approximately 15,000 linear feet installed in close proximity to the path of Holly Creek. See Section 5 and Appendix B for more detailed information related to this option.

### **8.2.2 Considerations**

The cost of this option is less than the other options, ranging from \$3.6 to \$6.0 million, and it would take less than 2 years to implement. However, if Alcoa were to implement this option, Holly Creek would become a series of pools during dry weather, which may negatively affect the already-limited existing fishery of the creek. Moreover, ADEQ has made its view clear to Alcoa that other options should be evaluated first. Alcoa has chosen not to implement this option at this time but rather to seek relief from the selenium criteria through the EIP.

## **8.3 Residue Removal/Recycle/Reuse**

### **8.3.1 Description of Alternative**

Approximately 100 million cubic yards of residue exists on the Alcoa site. Assuming that the residue is moved a short distance, the residue would likely remain on site by placing it in former mine pits.

The residue could be substituted for agricultural lime or used as a sorbent, cement, road base, additives, etc. Although none of these uses have proven to be economical at this point, Alcoa will continue to seek ways to recycle/reuse the bauxite residue and associated leachate. It is anticipated that even under the most optimistic reuse scenarios, many decades would be required to use the entire volume of residue. It is important that any reuse of the bauxite residue is done carefully and in such a manner that its use results in an overall improvement to the environment.

The leachate could potentially be recycled into a process where alkalinity is needed. However, efforts to recycle/reuse the leachate to date have been unsuccessful because 1) the leachate is weakly alkaline with respect to commercial needs, 2) the leachate contains impurities (e.g., organics) that make it undesirable to an end-user, and 3) transportation costs for the volume of leachate are significant.

### **8.3.2 Considerations**

Technically this option is feasible but would be time-consuming and costly due to the large volume of material to be moved. It is expected that placing the material in former mine pits would result in the continued generation of leachate. Moving the residue offsite would be even more costly due to haul distance alone. Furthermore, an additional cost of disposal would likely be incurred. See Section 5 for more detail on transportation costs. Unless an economical reuse of the material can be found, this option is not practical.

## **8.4 Minimize Leachate Generation (Cap Improvements)**

### **8.4.1 Description of Alternative**

Reducing contact between rainfall and the residue can potentially minimize leachate generation. This is typically accomplished by reducing infiltration through the soil covers by installing flexible membrane liners, improving caps, improving evapotranspiration, improving runoff, etc. Several efforts to reduce infiltration by improving evapotranspiration and runoff have been implemented. The latest BRDA closure included a clay cap. Although it was effective at reducing infiltration, it did not completely eliminate leachate generation.

### **8.4.2 Considerations**

Clay caps will reduce infiltration for a period of time but will not eliminate the generation of leachate from the BRDAs. An adequate volume of suitable clay is not readily available in the immediate area, resulting in significant transportation costs. Synthetic liners typically will reduce the generation of leachate to very low volumes but they have a finite life and are very costly. Section 5 provides more detail on the anticipated cost (> \$53,000,000) of installing a synthetic liner on the BRDAs. The anticipated life of a synthetic liner is not adequate relative to the length of time the residue will continue to produce leachate. Furthermore, even if it were practical to cease all further infiltration into the residue, leachate will continue to be generated for several years, given the volume of leachate that currently exists within the BRDAs and the lag time associated with leachate movement.

Although the alkalinity of the leachate has declined over the past 20 years since closure of the BRDAs began, it still remains elevated. The BRDAs will continue to leach high-alkalinity water that contains selenium for many years based on limited bench test results as well as the stoichiometry of the residue. Given that the residue is highly buffered, a significant but unknown number of pore volumes of rainfall will be required to remove the alkalinity.

Even if the residue were to be isolated in some manner (e.g., geomembrane liner), leachate will continue to be generated for some time. This is due to the time required for the entrained leachate to fully exit the BRDA. This timeframe will become more protracted as the head pressure is reduced.

## **8.5 Evaluation of Treatment Options**

### **8.5.1 Description of Alternative**

The proposed approach is to develop a technically and economically feasible treatment technology or technologies to reduce the selenium in Alcoa's effluent such that the applicable water quality criteria for selenium in Holly Creek can be met. This approach is proposed because Alcoa anticipates that it has the potential to accomplish the end goal of meeting the selenium water quality criteria while having the least negative impact on the receiving streams.

Alcoa proposes to continue to evaluate, through research, bench-scale studies, and pilot studies, those options that show promise in terms of viable selenium reduction. Numerous options for treatment of selenium either at its source, after mixing with the acid mine drainage, or at the discharge have been and will continue to be considered.

Treatment technologies that already have been evaluated include physical separation, chemical treatment (hydroxide/sulfide precipitation, sulfate precipitation, ferrous hydroxide, zero-valent iron, adsorption, etc.), and biological systems (reactors, compost filters, constructed wetlands, constructed microbial mats). Although no chemical or biological treatment is currently known to be capable of meeting criteria/permit limits, Alcoa is committed to continue to seek treatment technologies that have the potential to reduce selenium concentrations in the outfalls to below the applicable water quality standards.

As previously stated, although conventional treatment technologies to meet selenium criteria do exist (e.g., RO and/or ion exchange), they are not economical for treatment of leachate at the Alcoa site. The use of RO is not practical either due to the volume of leachate to be treated and/or the effect of the high alkalinity on the membranes.

Alcoa will continue to actively monitor and report results of this and other research, studies, improvements, and downstream water quality. Treatment options will continue to be evaluated during the EIP and will be implemented as appropriate. It must be noted that once a viable treatment solution is discovered and perfected, it is expected to take years for Alcoa to treat and discharge the total volume of water that has been and continues to be accumulated at the site.

## 8.5.2 Considerations

Alcoa is also unsure of the cost or time requirements for this option. However, it is anticipated that significant dollars will be spent and that 15-20 years or more will be required to find, screen, develop, perfect, construct, and put into operation an acceptable treatment technology. Once such a treatment system is put into operation, it will take an undetermined amount of time (years) for the leachate entrained in the BRDAs to drain, make its way to the treatment system, and be discharged.

Despite the limitations with this option, Alcoa proposes the treatment system option because Alcoa believes that 1) it has the greatest potential of resolving the selenium issues in Alcoa's discharge, and 2) it is the most practical option. Table 8.1 summarizes the alternatives analysis.

Table 8.1. Comparison of alternatives for reducing selenium concentrations in Alcoa's discharge.

<b>Alternative</b>	<b>Estimated Cost (millions)</b>	<b>Relative Level of Effort for Implementation</b>	<b>Relative Long-Term Effectiveness</b>	<b>Relative Benefit to the Environment</b>	<b>Time Required (years)</b>
No Action	\$0	Low	Low	Low	0
Direct Discharge to Saline River	\$3.5 - \$6.2	Low	High	Medium	2
Residue Removal/ Recycle/Reuse	\$100 - \$1,000	High	Low	Low	20 – 100
Minimize Leachate Generation (Cap Upgrade)	\$53.2 - \$100	High	Low	Medium	5 – 15*
Evaluation and Implementation of Treatment Options	\$10 - \$110	High	High	High	15 – 20

\*This timeframe does not include the time required for the leachate currently entrained in the bauxite residue to drain.

## 9.0 EIP OVERALL SCHEDULE

<u>DATE</u>	<u>EVENT</u>
10/05/09	Submit final NOI with Remediation Plan to ADEQ
11/30/09	ADEQ publishes notice of the NOI
12/30/09	End of the initial public comment period on the NOI
09/02/10	ADEQ notifies Alcoa of approval of the project
09/07/10	Alcoa files a Third-Party Request to Amend the Water Quality Standards for Holly Creek <sup>2</sup>
09/24/10	APCEC meeting at which the Third-Party Request is heard
March 2011	Permit renewal application submitted to ADEQ
May 2011	Final approval of the EIP and the temporary modification to the Holly Creek selenium criteria by APCEC <sup>3</sup>
September 2011	EPA comments on the APCEC Regulation No. 2 changes
October 2011	End of the current 3-year permit – renewal as a 5-year permit <ul style="list-style-type: none"><li>• Selenium limit for Outfall 009 based on Holly Creek criterion and inclusion of any associated compliance schedule in permit to provide needed time to meet said limit.</li></ul>
May 2012	First annual report to APCEC <sup>4</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>

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<sup>2</sup> Actual date is dependent upon the date on which ADEQ notifies Alcoa of the approval of the project.

<sup>3</sup> Actual date is dependent upon the date on which the relevant Legislative Committees can review the rulemaking.

<sup>4</sup> Actual date is dependent upon the date on which the EIP receives final APCEC approval.

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May 2013	Second annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e. testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2014	Third annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts;</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2015	Fourth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
March 2016	Permit renewal application submitted to ADEQ
May 2016	Fifth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
October 2016	Permit renewal <ul style="list-style-type: none"><li>• Incremental reduction of permitted interim selenium limit if technically and economically feasible, and inclusion of any associated compliance schedule in permit to provide needed time to meet said limit.</li></ul>

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<sup>5</sup> Actual date is dependent upon the date of the first annual report to APCEC.

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May 2017	Sixth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2018	Seventh annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2019	Eighth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2020	Ninth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
March 2021	Permit renewal application submitted to ADEQ
May 2021	Tenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
October 2021	Permit renewal <ul style="list-style-type: none"><li>• Incremental reduction of permitted interim selenium limit if technically and economically feasible, and inclusion of any associated compliance schedule in permit to provide needed time to meet said limit.</li></ul>

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May 2022	Eleventh annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2023	Twelfth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2024	Thirteenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2025	Fourteenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
March 2026	Permit renewal application submitted to ADEQ
May 2026	Fifteenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>

October 2026	Permit renewal <ul style="list-style-type: none"><li>• Incremental reduction of permitted interim selenium limit if technically and economically feasible, and inclusion of any associated compliance schedule in permit to provide needed time to meet said limit; and</li><li>• Final timeline and tasks to attain compliance with applicable selenium limitations.</li></ul>
May 2027	Sixteenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2028	Seventeenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2029	Eighteenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2030	Nineteenth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>
May 2031	Twentieth annual report to APCEC <sup>5</sup> <ul style="list-style-type: none"><li>• Reporting on status of treatability efforts (i.e., testing, lessons learned, literature searches, etc.);</li><li>• Reporting on status of selenium source mitigation efforts; and</li><li>• Reporting on progress towards permit compliance.</li></ul>

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End of 2031                      Anticipated compliance with applicable selenium limits

This timeline is an estimate and is expected to change since the trajectory of the project cannot be reliably defined at this time. As new information is developed, the timeline and document will be modified accordingly.

## 10.0 REFERENCES

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- MFG. 2000. Hurricane Creek Brown Mud Lakes Hydrogeological Conceptual Model. Prepared for Reynolds Metals Company.

# **APPENDIX A**

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**Engineering Evaluation Review – Selenium Treatment Report  
(with attachments)**

# **ALCOA INC. – BAUXITE SELENIUM TREATMENT REPORT BAUXITE, ARKANSAS**

**JUNE 15, 2009**

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ALCOA INC. – BAUXITE  
SELENIUM TREATMENT REPORT  
BAUXITE, ARKANSAS

Prepared for

Alcoa Inc. – Bauxite  
PO Box 290  
Bauxite, AR 72011-0290

Prepared by

FTN Associates, Ltd.  
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Little Rock, AR 72211

FTN No. 6012-251E

June 15, 2009

## EXECUTIVE SUMMARY

The existing Arkansas and national ambient water quality criterion (chronic) for selenium is 5 µg/L. Discharges from the permitted outfalls at the Alcoa Inc. – Bauxite, Arkansas facility (Alcoa) indicates that selenium concentrations typically range from 3.6 to 17 µg/L from Outfalls 009 and 028 at Holly Creek and Hurricane Creek, respectfully. This report provides:

1. An overview of the selenium issue including information regarding sources of selenium at the site;
2. A study of potential treatment methodologies to reduce selenium concentrations at Alcoa's discharge outfalls;
3. A description of bench-scale testing that has been performed;
4. A description of pilot-scale treatability studies that have been completed; and
5. A description of an upscale pilot plant that is currently being installed.

All of this work is aimed at determining the feasibility of reducing selenium in discharge waters at the outfalls.

From a review of the literature, several methods for treating selenium have been identified and evaluated for potential application at Alcoa. The economics of treating large flow rates, as exist at Alcoa for the treated discharge, discourages the use of many of these methods. In addition, several methods were shown to be ineffective for the treatment of selenium in this application.

A series of bench-scale tests were conducted to demonstrate removal efficiency using different treatment methods applied to different wastewater sources. Based on these tests, a biological reduction process appeared to hold the most promise for treatment of selenium at Alcoa. Some treatment in the pit lakes, almost certainly based on biological activity, has been observed. Biological reduction of the concentrated source of selenium, the bauxite residue disposal area (BRDA) leachate, has been demonstrated to be a potential feasible alternative.

Pilot-scale tests were also conducted using leachate water from the Black Pond on the Reynolds Metals Company side and accumulated leachate water from the New 17 Pit. Both

systems provided significant levels of treatment, but the highest reduction efficiency was achieved with the New 17 Pit water. Several operational problems with this system are discussed in this report and will require further efforts.

The report describes the installation of an upscale pilot unit that is currently being installed. This system is intended to provide additional information related to:

- Cold weather efficiency,
- The costs of operation of a full-scale system, and
- The ability of the system to achieve the low concentrations required for meeting the water quality criterion in Holly Creek.

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ATTACHMENT 3:	Technical Memo - Treatability Test Procedures, Alcoa Selenium Study, June 2007
ATTACHMENT 4:	Alcoa Technical Center Report
ATTACHMENT 5:	Technical Memo - Biological Selenium Reduction Experiment
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## **1.0 OVERVIEW**

### **1.1 Introduction and Purpose**

The existing Arkansas and national ambient water quality criterion (chronic) for selenium is 5 µg/L. Monitoring data from Outfall 009 at the Alcoa Inc. – Bauxite (Alcoa) facility in Bauxite, Arkansas, indicate that selenium concentrations in Holly Creek range from 3.6 µg/L to 17 µg/L. These concentrations consistently exceed the state water quality selenium criterion for Holly Creek. The Hurricane Creek water quality selenium criterion is being met by using a hydrograph-controlled release based on meeting the instream selenium criterion.

Potential options for permit compliance include:

1. Construction of a discharge pipeline to the Saline River,
2. Modifying the existing water quality criterion to allow higher discharge concentrations,
3. Source control, and
4. Treatment methods for selenium reduction.

Items 1, 2, and 3 above are being addressed by other studies. This report provides an overview and summary of the work that Alcoa has undertaken to identify and develop a treatment method to achieve compliance with the effluent standard. This report describes the bench-scale testing and pilot-scale treatability testing that has been performed to date. All of this work is aimed at determining the feasibility of treating selenium in wastewaters prior to discharge from Alcoa.

### **1.2 Background**

Alcoa discharges treated wastewater through National Pollutant Discharge Elimination System (NPDES) Outfalls 009 (to Holly Creek) and 028 (to Hurricane Creek). The total annual discharge volume ranges from 1.4 to 4 billion gallons and is dependent upon weather conditions (wet weather results in higher discharges). The average annual volume discharged through Outfall 009 is 1.96 billion gallons and Outfall 028 is 0.43 billion gallons. Effluent monitoring

data show that selenium exists in the treated effluent at concentrations that typically range from 3 µg/L to 17 µg/L. Selenium has been found to be a constituent in the leachate from the two closed bauxite residue disposal areas (BRDAs) on the site. The BRDA leachate is highly alkaline (from 10 to 20 grams per liter alkalinity) with flows ranging from about 200 gallons per minute (gpm) to over 800 gpm (depending upon weather conditions). Wet weather increases the leachate production. This wet weather effect is particularly evident at the former Reynolds Metals Company (Reynolds) BRDA.

The selenium in the wastewater (BRDA leachate) exists in the form of selenate. The source of the selenium is from the bauxite residue but in relatively low concentrations. The high alkalinity appears to make the selenium more mobile.

With the existing treatment system, water from the BRDAs is combined with acid mine drainage on a proportional basis. Due to the high alkalinity of the BRDA water, sulfuric acid must be added to neutralize the pH of the resulting mixed water. Polymer is added and the resulting floc is allowed to settle in Pond 3. The water from Pond 3 is either discharged through Outfall 009 into Holly Creek or is pumped back to Lake No. 4 on the Reynolds side. Lake No. 4 is used for storage until the water can be released through Outfall 028 to Hurricane Creek. Natural reductions of selenium have been recorded in Lake No. 4 and will be discussed further in subsequent sections of this report.

Alcoa's present NPDES permit (No. AR0000582) requires selenium monitoring and reporting.



Table 1.1. Alcoa selenium wastewater source data.

Wastewater Sources Location		Selenium (µg/L)							
Old Reynolds Metals BRDA Leachate Collection System		11-06-06	05-30-07	06-07-07	06-14-07	06-21-07	09-17-07	09-28-07	Average
RMC BRDA Sump No. 1 and No. 5		<100	24	32	32	46		24	32
RMC BRDA Sump No. 2		<100	91	96	90	100		87	93
RMC BRDA Sump No. 3		370	360	390	380	430		370	383
RMC BRDA Sump No. 4			28	37	38	34		45	36
RMC BRDA Sump No. 6 N/S		<100	40	53	58	58		47	51
RMC BRDA Sump No. 6 W/E		<100	51	73	77	82		74	71
<b>Combined</b>									
<b>Black Pond - RMC BRDA Leachate Collection System</b>			100	170	170	170		160	154
<b>Alcoa BRDA Leachate</b>									
South Seep			75	140	140	130		120	121
Main Seep			170	240	250	230		260	230
East Cooling Pond							2.9		2.9
<b>Treatment Ponds</b>									
Old 17 (Mixture of AMD and BRDA Leachate)		<100	4.1	6.6	5.9	8.2			6.2
Acid Mine Drainage (AMD) Pits									<2.0
New 17 (Combined BRDA Leachate Storage Pond)			96	140	140	140		140	131

### 1.3 Selenium Influent and Effluent Data

As part of this selenium treatability investigation, Alcoa has attempted to define the major sources of selenium in the influent wastewater by initiating a site source-sampling plan. The selenium source investigation identified two main sources of selenium: the Reynolds BRDA Sump No. 3 (average selenium = 383 µg/L) and Alcoa's BRDA Main Seep (average selenium = 230 µg/L). The BRDA leachate collected from both BRDAs is piped and stored in wastewater storage pit New 17. The New 17 pit represents the collective leachate and selenium source average for treatment (average selenium = 131 µg/L). Alcoa monitors the effluent data as part of the existing NPDES permit and is summarized in Table 1.2 with a site map provided in Attachment 1.

Table 1.2. Summary of DMR data over a 2-year period at Alcoa Outfalls 009 and 028.

Frequency	Selenium (µg/L)	
	Outfall 009	Outfall 028
Minimum	7.6	3.6
25 <sup>th</sup> percentile	11.0	7.1
50 <sup>th</sup> percentile	12.0	9.0
95 <sup>th</sup> percentile	15.0	15.0
Maximum	16.0	17.0

## **2.0 SELENIUM TREATMENT METHODS**

Several methods have been evaluated over the past few years for reducing selenium concentrations to acceptable levels in aqueous solutions. These methods generally fall into one of the following categories:

1. Physical separation using reverse osmosis (RO), ion exchange, distillation, etc.;
2. Chemical separation and reduction;
3. Adsorption/absorption techniques;
4. Biological techniques; and
5. Constructed wetlands.

### **2.1 Physical Separation**

Treatment methods that employ physical separation mechanics can be effective in removing selenium. Selenium ions in the selenate oxidation state can be removed by ion exchange or RO. Distillation is another method that would be applicable to an inorganic pollutant with low volatility such as selenium.

These methods are prohibitively expensive when large volumes of an aqueous solution must be treated. With the system at Alcoa, the strong concentrations of dissolved minerals in the BRDA leachate would not allow the use of this technology on this waste stream. For the treated water effluent from Outfall 009, the large volume of water to be treated would make the technology prohibitively expensive.

For instance, the costs of RO for a waste stream of this concentration is estimated to exceed \$0.005 per gallon. For a system that treats over 3 billion gallons per year, the annual cost would be over \$15,000,000 per year. Applying present worth factors to this annual cost would yield a present worth estimate of about \$110 million. Distillation and ion exchange would present similar operating costs (Nitrogen and Selenium Management Program Working Group 2007). Further, all of these methods produce a contaminated regeneration effluent that requires further treatment for selenium fixation or removal before disposal. Thus, the selenium

removal problem would still exist but in a more concentrated solution. Dewatering this solution would prove to be a difficult task, because the solids would still exist as extremely fine particles.

Based on the expected cost, further consideration will not be given in this report to the use of RO, ion exchange, or distillation.

## **2.2 Chemical Treatment**

One method employed to remove or substantially reduce the concentration of soluble inorganic pollutants, such as heavy metals in water, is chemical precipitation of the metals as their oxides or their hydroxides. This precipitation generally is effected by the addition of lime, alum, or an iron salt to the water at an appropriate pH. For selenium, other methods have been tried and will be described in the subsections below.

### **2.2.1 Hydroxide/Sulfide Precipitation Techniques**

It is known that selenium ions can be removed from aqueous systems employing hydroxide chemical precipitation if the selenium is present in the selenite ( $\text{SeO}_3^{-2}$ ) form. Generally, such precipitation methods comprise treating the selenium-containing aqueous system with an iron salt, such as ferric or ferrous sulfate, chloride, or hydroxide, or with aluminum or zinc in some appropriate form such as powder or granules. However, such chemical precipitation methods provide only very limited removal of selenium when it is present in the selenate ( $\text{SeO}_4^{-2}$ ) form (Murphy 1988). Therefore, when selenium is present in the selenate oxidation state ( $\text{Se}^{+6}$ ), other methods generally must be considered for treatment.

Laboratory tests and pilot plant studies have shown that chemical precipitation using traditional hydroxide or sulfide-based reactions is substantially ineffective for removing selenium in the selenate oxidation state from water (Frankenberger 1994). Studies on water having a selenium concentration of 0.03 to 10 mg/L have shown that the conventional chemical precipitation methods remove less than 10% of the selenium from the water according to the United States Environmental Protection Agency (EPA) *Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations* (May 1977, pages 29 through 31).

Some bench-scale treatment tests described in Section 4.0 were performed using the subject water.

### **2.2.2 Ferrous Hydroxide Treatment**

Another chemical method for removing selenium from aqueous solutions involves the use of ferrous hydroxide. Under this patented process, ferrous hydroxide is generated by the addition of ferrous chloride or ferrous sulfate in alkaline water. The ferrous hydroxide solids generated under these conditions react to reduce the selenium ions to elemental selenium. The selenium will then co-precipitate with the ferrous hydroxide solids. According to the literature, this reaction is optimized at a pH of 9.0. Further information is provided on this method in Section 4.0 of this report based on the bench-scale tests that were performed.

### **2.2.3 Chemical Reduction Using Zero-Valent Iron**

Another chemical treatment process to reduce selenium (in the form of selenate ion) is to use the reducing capacity of zero-valent iron (ZVI) filings. ZVI reduces Se(VI) in the form of selenate ion ( $\text{SeO}_4^{2-}$ ) to selenite ion (Se is in the +4 oxidation state) during the corrosion of ZVI to iron oxyhydroxides ( $\text{Fe}_{\text{OH}}$ ). Two mechanisms can be attributed to the rapid removal of Se(VI) from the solutions. One is the reduction of Se(VI) to Se(IV), followed by rapid adsorption of Se(IV) to  $\text{Fe}_{\text{OH}}$ . The other is the adsorption of Se(VI) directly to  $\text{Fe}_{\text{OH}}$ , followed by its reduction to Se(IV). This is a low-cost technology if implemented in a passive manner and could be attractive if the technology is able to treat the complex matrices (such as Reynolds sump water) without any pH adjustment and dilution. Further evaluation is provided in Section 4.0 of this report based on the treatability data.

### **2.2.4 Sulfate Precipitation**

An alternative treatment process would precipitate the selenium as metal selenate or metal selenite by co-precipitation with a soluble sulfate, which encapsulates the metal selenate or metal selenite. The process can be carried out in a batch or continuous manner. While any metal salt and any soluble sulfate could theoretically be used, the process has been demonstrated with

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the use of barium chloride and ferrous sulfate. The company holding the patent for this process claims to have the capability to apply this treatment to wastewater received at their treatment facility in Oklahoma. A large-scale, onsite application of this process has not been demonstrated. At this point, the process would have to be considered experimental, at least in terms of the subject application, and will not be given further consideration in this report (Centofanti 2001).

### **2.2.5 Adsorption**

Literature published to date by EPA and others report removal efficiency of greater than 98% of selenium with ALCOA F-1 alumina. F-1 alumina has an inherently low chemisorptions capacity, which means that a large amount of this material would be required per volume of water treated. The literature does not describe other successful applications of adsorption techniques for treating selenium-contaminated water. In addition, many problems (e.g., algae buildup and used adsorbent disposal) could be anticipated with pumping high flows of the Alcoa water through adsorption columns. The costs appear to be comparable to those associated with ion exchange as described in Section 2.1 of this report. For this reason, this technology will not be given further consideration in this report.

## **2.3 Biological Systems**

Treating wastewater contaminated with selenium has been studied for many years in California. Most of this work is a result of the attention focused on treatment of agricultural drainage water in the San Joaquin Valley. This valley is generally low-lying and requires drainage in order to avoid high salinity in crop root zones. A major scheme to drain off subsurface water after use for irrigation was frustrated by discovery of high levels of contaminants in the water. The drainage water is brackish, and has a relatively high concentration of salts and potentially toxic elements, with selenium representing a particular problem.

Several biological methods have been developed in California to remove selenium. Selenium can be removed in any biological system in which reducing activity occurs. The method causes the selenium to be converted to insoluble forms of selenium, including elemental

selenium, which can be captured or entrained by larger particles. Conversion of the selenium to a filterable form is also accompanied by conversion to volatile selenium compounds, typically including hydrogen selenide and methyl selenide. Such compounds can generally be eliminated from the discharge of the system through simple aeration (Frankenberger 1994).

The water to be treated by a biological process is normally spiked with a food source for the biomass, especially an assimilable carbon source. Free oxygen must be eliminated from the system so that the biological conversion proceeds in an anaerobic or anoxic state. After carrying out the biological conversion, the selenium exists in different forms, including:

1. Selenium that has become organically bound (probably in the form of a soluble complex compound);
2. Selenium that has in some way been captured by larger particles;
3. Selenium that has been captured in some way by the biomass retained in the reactor;
4. Selenium in the form of volatile organic; and
5. Inorganic selenium compounds.

For example, the selenium that has been captured by larger particles is removed by filtration. The volatile selenium compounds are allowed to escape as gas from the water.

Biological methods are especially suited for removing the selenate form of selenium from water that contains a high concentration of sulfate. This is similar to the situation at Alcoa.

The reaction mechanism is not known, though it is possible that during fermentation extra-cellular amino acids form organic complexes with the selenium. These organic complexes are subsequently assimilated by the microorganisms in the biomass. Precipitation or co-precipitation may also occur. The particles might contain one or more organic complexes, some of which may be in suspension or some in solution. The selenium compounds may also absorb or adsorb on the surface of microbial cells, which subsequently can be removed by precipitation. The biological system can be operated so that sulfate is not removed or reduced. With wastewater containing high concentrations of sulfate, such as exists in the mines at Alcoa, this is a critical factor.

Selenate is a known competitive inhibitor of sulfate reduction, having a 40-fold greater affinity for the enzyme uptake system than the sulfate ions. Generally, the growth of the biomass needs to be promoted by supplementing the selenium-containing water with an organic source and possibly, nutrients. The organic feed can include a readily biodegradable organic compound, for example methanol, ethanol, or a mixture of organic wastes. Nitrogen and phosphorous may have to be added in order to generate and sustain the necessary biochemical activity, if they are not already sufficiently present in the water to be treated. The system must be operated so that there is only a small residual of nitrate-nitrogen left in the reactor at the outlet (less than 1 mg/L). Residual nitrate-nitrogen in the reactor will interfere with the selenate reduction process.

The bacterial biomass will be heterotrophic but will not be of a specific strain and is unlikely to be a pure culture. The biomass may initially be composed of organisms growing from natural contamination. Suitable bacteria are likely to include strains belonging to the genera *Hyphomicrobium*, *Corynebacterium*, *Salmonella*, *Pseudomonas*, and *Bacillus*. There is no need for special seeding of the reactor unless the water is sterile, but in practice it is possible to save time by seeding with sludge from a sewage treatment plant, preferably from an anoxic nitrate-removing reactor or an ordinary activated sludge reactor.

In a large-scale reactor exposed to sunlight, such as a pit or lagoon, it is possible to provide a carbon source by developing an algae culture in the water rather than adding a synthetic feed such as methanol. This method was demonstrated in the San Joaquin Valley for selenium removal from subsurface drainage water. The basic concept is to grow an algal biomass that will provide the carbon source for native selenium-reducing bacteria, such as *Pseudomonas* and *Bacillus*. The algae require only sunlight, carbon dioxide, nutrients, and a circum-neutral aqueous environment to develop. In most natural systems, the most limiting factor for the growth of algae is nutrients primarily in the form of nitrogen and phosphorus. These nutrients can readily be added to the water using fertilizers or some waste products.



The pit lakes that exist at Alcoa could potentially be used as the biological reactor. Other alternatives for the use of biological systems could also be developed. Specific treatment systems that depend on biological methods for selenium removal include:

1. Biological reactors,
2. Compost filters,
3. Constructed wetlands, and
4. Constructed microbial mats.

### **2.3.1 Biological Reactors**

Biological reactors generally include systems comprised of tanks and mechanical equipment. The system can take the form of a single or multi-stage reactor that encourages anoxic conditions. Suitable reactor types include fixed-bed reactors, fluidized-bed reactors, sludge-blanket reactors, and stirred reactors. The use of these systems generally provides more control of flow rates and operating conditions. The capital cost of these systems is a major drawback. Bench-scale tests involving biological reactors were conducted and are described in Section 4.0.

### **2.3.2 Compost Filters**

Spent mushroom compost filters provide the necessary biological substrate to degrade selenium in the +6 oxidation state to selenite where selenium is in the +4 oxidation state. Carbon substrate acts as electron donor while nitrogen and phosphorus in the compost media provide the necessary nutrients to sustain the anaerobic reduction process. These filters could be applicable for selenium removal from neutralized BRDA leachate or from the final pond effluent. Additional information is provided on compost filters in Section 4.0.

### **2.3.3 Constructed Wetlands**

It has been found that flow-through wetland areas populated with certain plant species, such as cattail and bulrush, provide treatment for selenium. Even wetland cells with no plant species, colonized by naturally occurring algae and other microbes, can be effective. As a

wetland system matures and organic debris and microbial biomass builds up, the wetland's ability to remove selenium improves. Selenium is incorporated into plant tissue, volatilized into the atmosphere or tied up with the sediment particles of the wetland.

#### **2.3.4 Constructed Microbial Mats**

Constructed microbial mats represent a patented wastewater treatment process that can be applied to shallow ponds. This technology has been demonstrated to reduce heavy metals in situations involving large volumes of water (e.g., removal of manganese from acid coal mine drainage). A specific application to selenium-bearing wastewater has not been completed. However, many of the same principles will apply.

When applied to shallow ponds for treatment of large volumes of wastewater, the mats are generally floating and cover the surface of the pond. Different bacteria and other organisms create both oxidizing and reducing environments within the mat's substrate. This is similar to the processes that occur in a wetland system. The applicability of biomats to this wastewater requires bench scale testing conducted by the owner of the patent. The results of this study are presented in Section 4.0 of this report.

### 3.0 ALCOA'S EXPERIENCE

As discussed, it has been determined that the primary source of selenium at the Alcoa site is highly alkaline leachate from the two BRDA process storage areas. These BRDAs are no longer active and have already been closed, but the alkaline leachate from them must be collected and treated. The water from these BRDAs has selenium concentrations in the range of 100 to 450 µg/L. The selenium in the leachate most likely exists as the selenate form ( $\text{SeO}_4^{-2}$ ).

After treatment through the existing process, selenium concentrations are reduced (primarily by dilution) to approximately 10 µg/L to 20 µg/L. Selenium reduction has been observed in a large pit at the site that stores the treated water prior to discharge. It is likely that biological treatment is the primary method of treatment for this particular selenium reduction.

In this pit, it is theorized that the upper layer of water supports a growth of algae that converts carbon dioxide into cellular mass. The upper stratum of the pit remains in an aerobic state with free oxygen available for bacterial respiration. As the algae matures and dies, the cells sink to the lower levels of the pit. Through bacterial action, the free oxygen in the lower levels is consumed and anoxic conditions result. As described previously, the anoxic conditions are necessary for the selenium to be converted into an insoluble form or to be absorbed in the cell mass that will sink to the bottom of the pit lake. Figure 3.1 shows a diagram that represents the different reactions that take place in the pit. Laboratory tests of the water taken from the middle and lower levels of the pit at Alcoa have confirmed the reduced concentrations of selenium compared to influent concentration. As expected, the sediments in the pit contain elevated concentrations of selenium.

This treatment system, which occurs naturally, is actively being used to help reduce selenium concentration. However, the dynamics of the process do not allow for the complete treatment of all of the water at Alcoa. Also, the effluent water, even for low flow rates, does not meet effluent limitations for selenium.

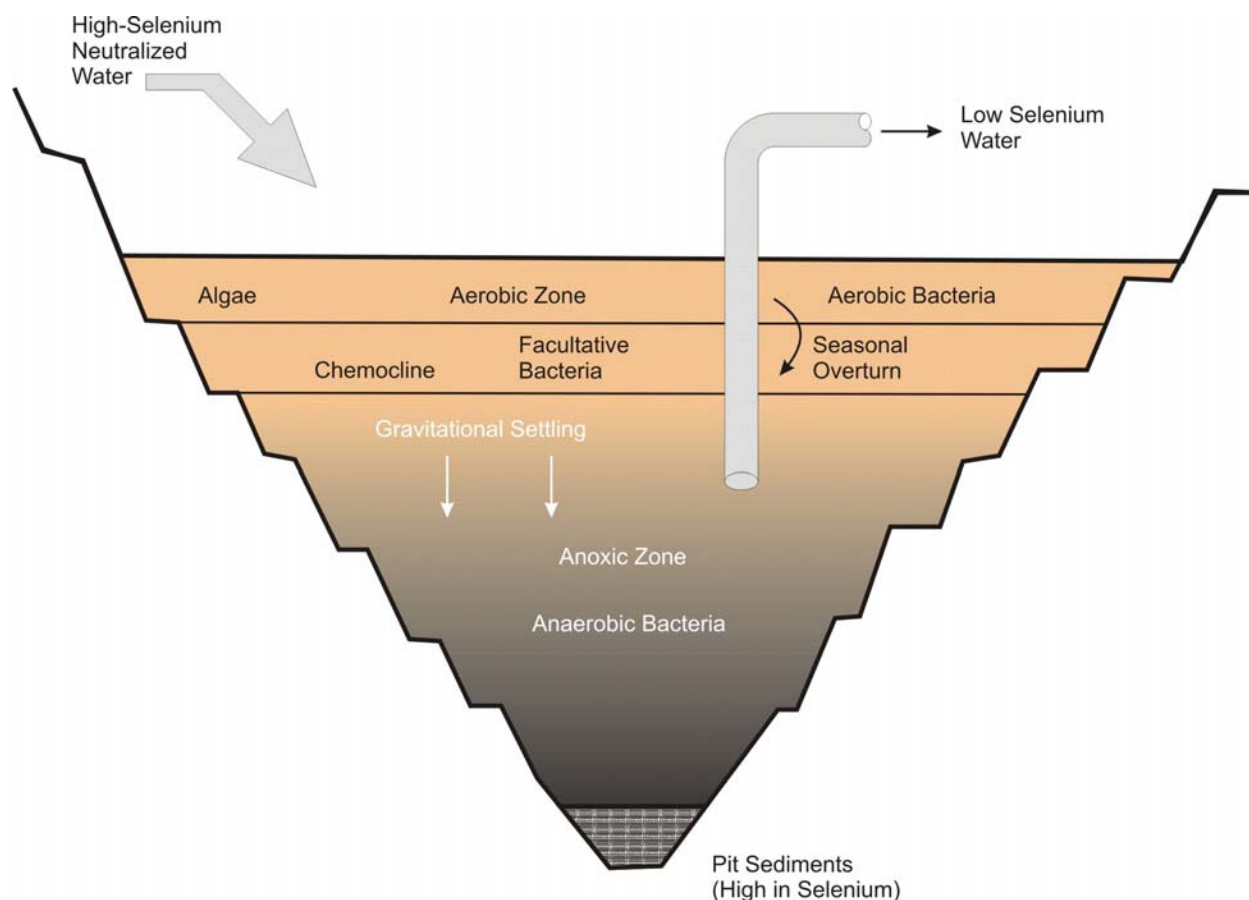


Figure 3.1. Bacteria dynamics of an existing pit lake.

It is expected that the natural reduction of selenium that is observed in the pit can be replicated. A synthetic carbon source, such as methanol, could be added to the water to provide carbonaceous feedstock for the bacterial growth. The additional loading of carbonaceous material should more quickly drive the water to an anoxic condition. The addition of nutrients such as nitrogen and phosphorus may also be required to optimize the reaction.

The second approach would be to utilize algae grown in one of the pits as a carbon source. As discussed above, algae only requires sunlight, nutrients, and carbon dioxide in a circum-neutral environment. In the existing pit, at least one of these parameters is limiting the amount of algae that is produced. If this limitation were removed, additional algae may be

produced which could be used to drive the required anoxic reactions. The most likely limitation in the pit lake system is the low levels of nutrients that occur in the water.

There are disadvantages and potential problems with the application of the biological reaction process, particularly as a post-treatment polishing step:

1. Post-neutralization treatment would mean that all of the water would require treatment (approximately 3 to 4 billion gallons per year).
2. Concentrations of suspended solids and biochemical oxygen demand (BOD) might increase to levels that represent discharge violations;
3. The process might be inefficient during cold weather/low sunlight;
4. Dissolved oxygen (DO) levels in the discharge water might be extremely low and require re-aeration; and
5. There is no evidence that the low levels required for meeting water quality criteria in Holly Creek can be obtained with a biological system.

To develop more information regarding the potential application of biological treatment, a series of bench-scale testing was performed. The results of this testing are provided in Section 4.0 of this report.

## **4.0 BENCH-SCALE TESTING**

Based on the screening analysis, bench-scale tests were used to determine the applicability of some of the specific treatment methods discussed in Section 2.0. Bench-scale testing was performed for both chemical and biological systems. The range of systems tested included:

1. Treatment using various chemical precipitation processes,
2. Chemical treatment using ferrous iron precipitation,
3. Chemical reduction of BRDA leachate using ZVI and anaerobic reduction of selenate using spent mushroom compost,
4. Biological reduction treatment for Pond 3 water,
5. Biological reduction treatment for New 17 water,
6. Biological reduction treatment using water from Black Pond and Sump 3 (Reynolds side), and
7. BioMats using water from Pond 3 and New 17 Pond.

### **4.1 Chemical Reducing Reagents**

Several chemical reagents were tested in a series of bench-scale tests to determine if any reduction could be achieved. In general, the chemicals used were known to be strong chemical reducing agents. Attachment 2 includes a discussion of the materials and methods used in this testing and the subsequent results.

The testing results did not show any evidence that these reagents could be used to reduce selenium values. As discussed previously, these results agree with research on the subject from the literature. A separate test protocol has been established for the use of ferrous hydroxide, which has been shown to reduce selenium under specific circumstances, as discussed below.

### **4.2 Ferrous Hydroxide Precipitation**

A specific treatment protocol using ferrous-based products has been demonstrated to reduce selenium. The protocol involves the generation of ferrous hydroxide that reacts with the

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selenate or selenite ions to form elemental selenium. The elemental selenium is insoluble and can be removed by filtration or settling.

Ferrous hydroxide can be generated from ferrous sulfate or ferrous chloride under alkaline conditions. A specific protocol is available from the literature although a patent appears to apply to this process.

Bench-scale tests were conducted using the ferrous hydroxide method. A complete description of the tests and results are provided in Attachment 3. The tests were conducted on New 17 water. As shown in Attachment 3, the bench tests did not show any significant reduction of selenium. It is suspected that the water chemistry at Alcoa prevents the formation of elemental selenium due to competing reactions from other chemical species in the water.

Based on the results of this bench-scale testing, no further consideration was given to chemical precipitation methods.

#### **4.3 Zero-Valent Iron/Mushroom Compost**

A research team from the Alcoa Technical Center (ATC) performed bench-scale tests using two different treatment technologies. A 50% ZVI-sand media and a spent mushroom compost media were used in fixed bed columns to treat dissolved selenium in the concentrated leachate from Arkansas mine waters. Approximately 20% to 45% of the dissolved selenium was removed from the mine waters using ZVI technology.

The ZVI technology removed selenium from the highly complex Reynolds sump water matrix at a rate of around 30%, without any pH adjustment. Reduction of selenium at this source location could ultimately reduce the total selenium load in the downstream final effluent.

The spent mushroom compost columns resulted in removing around 30% of the dissolved selenium from the mine waters (New 17 and Alcoa Main Seep) after pH neutralization using sulfuric acid.

The report from ATC that covers both tests is provided in Attachment 4. Based on the preliminary results provided in the report, further development of the ZVI and the compost media were not considered as viable options.

#### **4.4 Biological Reduction Treatment for Pond 3 (Effluent) Water**

As discussed previously, biological treatment methods appear to hold potential for the removal of selenium. A series of bench-scale tests were used to test the relative effectiveness of biological methods. The initial test was conducted using Pond 3 water. Anoxic conditions were created in a series of jars using molasses as a biological oxygen demand. In this way, the DO concentrations were reduced to very low levels approaching zero. Attachment 5 provides a description of the protocol and the results of this testing.

The results indicate treatment efficiencies of about 45% removal of selenium. This efficiency is comparable to results that are seen in the deep holding pits at Alcoa.

The results of this test were significant in determining that natural conditions could be replicated in a series of bottles. Using similar setups, the effect of pH, the dose of carbonaceous material, dissolved solids content, and other parameters could be studied. Based on the results of this test, a series of follow-up tests were conducted and are discussed in Section 4.5.

#### **4.5 Biological Reduction Treatment for New 17 Water**

Using the biological reduction test methods described above, a series of bench-scale tests were conducted using acid mine drainage from Old 17 pond and the leachate from New 17 pond. These two sources of water were mixed in various dilutions and adjusted pH (pH <9 su) settings to determine the effect on the biological treatment process. The procedures used in this test and the results are provided in Attachment 6.

The primary result of this testing indicated that the biological process was immune to the concentration of the dissolved solids in the test (up to the high concentration existing in New 17). A correlation did exist with the final adjusted pH setting. These results suggest that the biological process can be conducted using leachate water without further dilution. This would significantly reduce the cost of the treatment process since the hydraulic rate would be much lower. Based on this result, another bench-scale test was devised to test the treatability of water from the Reynolds side of the plant (Sump 3 and the Black Pond), discussed in Section 4.6.



#### **4.6 Biological Reduction Treatment Using Water from Black Pond and Sump 3**

The basic protocol shown for the New 17 water in Section 4.4 was applied to two sources of water from the Reynolds side of the facility. This included water directly from the Black Pond, which collects all of the leachate water on the Reynolds side. It also included a sample from Sump 3, which was known to contain a significant portion of the overall selenium load. This treatment required that the pH of the sources was adjusted to <9 su.

This testing procedure also was designed to study the effect of nutrients and the dose of a carbon source. For each sample, the samples were spiked with a seed of activated sludge from the local domestic wastewater treatment plant.

The test results indicated a removal of selenium of up to 78% for the Black Pond water and 62% removal for the Sump 3 water (the addition of nutrients did not seem to improve the treatability results).

#### **4.7 BioMats Using Water from Pond 3 and New 17 Pond**

PLANTECO Environmental Consultants, LLC (PLANTECO) was enlisted to run a bench-scale test using their proprietary technology commonly referred to as biomats. Constructed microbial mats or biomats can be applied to shallow ponds and provide zones of aerobic and anaerobic biological activity. It has been documented that biomats can be effective for the removal of heavy metals. While a full-scale system of this type has not been established, there is evidence that biomats could be effective for the treatment of selenium. The report by PLANTECO is included as Attachment 7. PLANTECO reported significant problems with analytical tests of the treated wastewater. The revised Table 1 from that report is also included in Attachment 7 to provide the results of split samples tested by American Interplex.

The report from PLANTECO suggests that reduced concentrations of selenium can be obtained with the use of biomats. The table of results from the report indicates reductions of selenium when applied to the concentrated leachate, but not as high as obtained with other biological treatment systems. Test results on the Pond 3 water did not appear to be effective based on the analysis of the split samples by American Interplex.

PLANTECO has provided an estimated cost for conducting pilot-scale tests. The total cost for conducting a 12-month pilot study using microbial mats, including a 15% contingency, would be \$291,500 (email from Walter O'Neill to R. Robbins dated October 17, 2007). Based on the cost of the pilot system and the limited selenium reductions, the decision was made to concentrate efforts on other biological treatment systems.

## 5.0 PILOT-SCALE TESTING

Based on the results of the bench-scale tests, attention was focused on designing and implementing a pilot-scale treatment system on the concentrated leachate from the site. The bench-scale treatability results indicate that treating the concentrated leachate has the greatest potential for reducing the selenium discharge mass. Treating only the concentrated leachate, as opposed to the entire flow of leachate plus acid mine drainage, will reduce the size of the treatment system.

### 5.1 Small-Scale Pilot Plant Systems

A study was made using two small-scale pilot treatment systems that would each treat about 1 gpm of concentrated leachate. These systems had a similar design consisting of a small neutralization tank that was set up to reduce the pH of the leachate water. Following the neutralization tank was a 1,000-gallon biological reaction tank that was dosed with the carbon source (methanol). The water flow from the biological reactor overflowed to a ditch lined with an high-density polyethylene (HDPE) liner. The ditch was filled with crushed rock. A diagram of the system is shown on Figure 5.1.

These pilot-scale systems were set up to treat water from the accumulation pond (Black Pond) on the Reynolds side and from the final storage pit (New 17) prior to treatment on the Alcoa side. A photo of the system installed on the Reynolds side is shown as Figure 5.2.

The pilot system on the Reynolds side was operated from April 2008 thru December 2008. The removal of selenium across the entire treatment train varied from 14% to 49% (Table 5.1). The removal efficiencies from the Reynolds side were not as high as on the Alcoa side at New 17 pit. Water from the Reynolds side is collected from leachate sumps at the BRDA. It is known that the chemistry of the leachate from the Reynolds side is significantly different as it contains a high concentration of silica. It is not known if this silica concentration is the primary cause of the lower treatment efficiency.

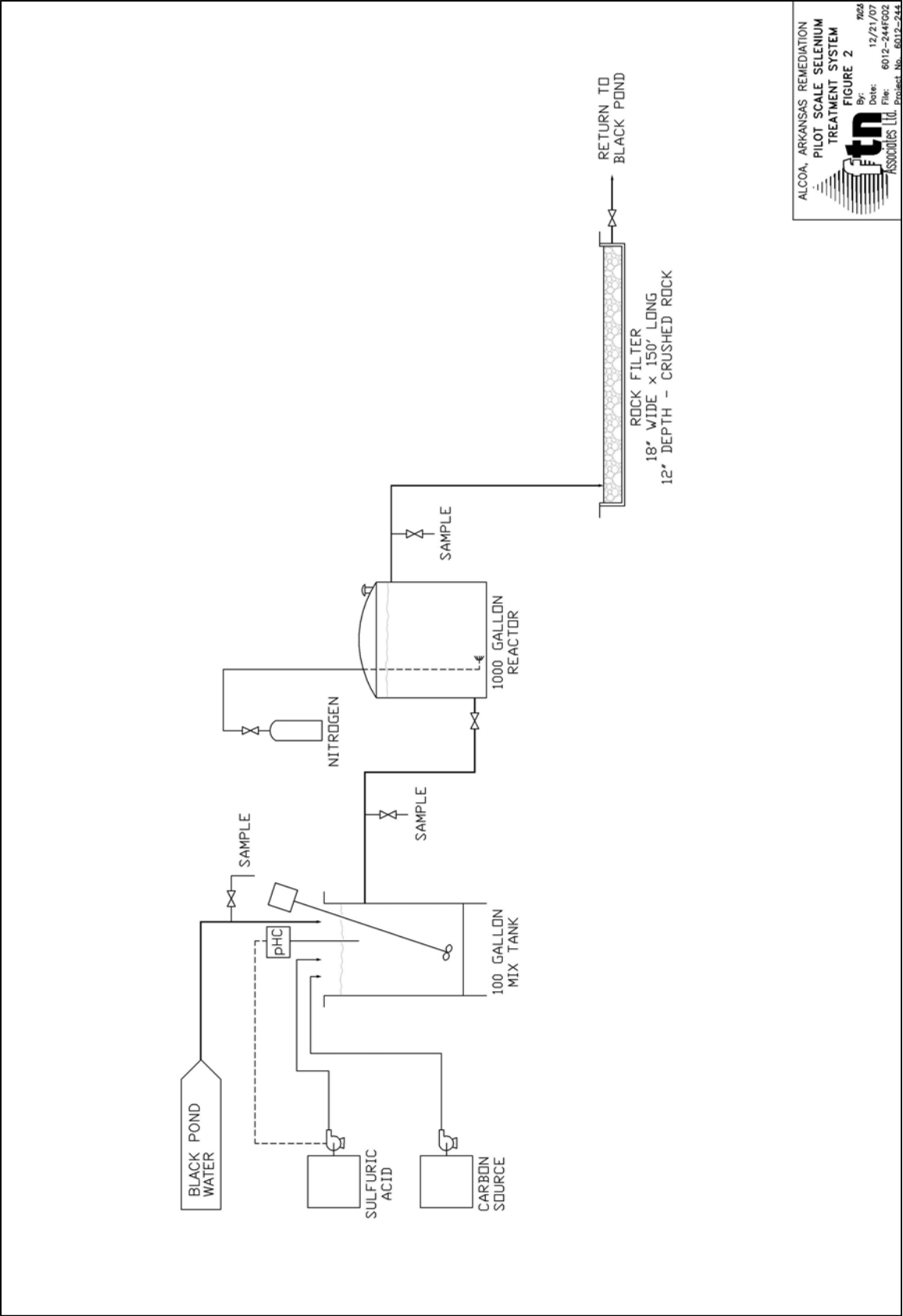


Figure 5.1. Pilot-scale selenium treatment system.



Figure 5.2. Pilot-scale treatment system installed on the Reynolds site.

Table 5.1. Results from the bioreactor pilot selenium treatment system operated on the former RMC property.

[illegible]

\*Reactor tank capacity is 1,000 gallons.

On the Alcoa side, the pilot system is fed from the New 17 pit and includes the leachate from the BRDA sumps of the Alcoa side and the Reynolds side. Thus the water in New 17 pit is an accumulation of all of the leachate water from the Alcoa reclamation areas.

As it is pumped from the New 17 pit to the existing precipitation treatment system, the water is dosed with carbon dioxide gas. This treatment is used to bring the pH of the New 17 pit water to a pH below 9.0.

The test results from the Alcoa side pilot system (Table 5.2) showed a higher level of treatment than shown on the Reynolds side.

During the operation of the selenium pilot treatment plants, both the pilot unit at the Reynolds property and the pilot unit located near the New 17 pond systems were affected by operational problems that affected the selenium treatment efficiency.

On a few occasions at the Reynolds pilot unit, the pH of the system would rise above the desired range and kill or cause the microbes to go dormant. The influent was a gravity fed system, and a couple of power outages resulted in a loss of acid feed while the influent kept flowing through the system, thus causing the high pH issue.

Also, lowering the pH of the water caused the suspended solids in the water to precipitate. This created a coating on all surfaces in contact with the water: pH probes, inner tanks, and inner pipes. The pH probe and pipe between mix tank, and reactor tank required cleaning on a regular basis.

At the New 17 pilot unit, the influent supply comes from a pressurized pipeline at a point downstream of the carbon dioxide injection point. The pilot plant's influent fed into a small tank for transfer to the pilot unit. A pump fed from this small tank into the treatment system's mix tank. With the lower pH, the suspended solids in the water would precipitate, creating buildup on the transfer pump and influent supply lines. This situation caused the pump flow to be inconsistent and/or on occasion having no flow. The feed pump and supply lines required cleaning on a regular basis.

While these problems were problematic for a small-scale operation, it is expected that the issues could be addressed with proper design considerations or operating procedures in a full-scale system.

[illegible]

5-6



## **5.2 Upscale Pilot Treatment**

The design and application of a larger pilot plant system has been reviewed with ADEQ and is currently being installed. A schematic diagram showing the basic design of this treatment system is shown on Figure 5.3.

This pilot system would build on some of the information gathered in the final round of sampling. It will also provide treatment for a significantly higher flow rate (up to about 30 gpm).

The information from this pilot-scale unit should determine the ability of a biological system to provide significant treatment of selenium.

## **5.3 Full-Scale Operation**

Assuming that a biological system would be installed to significantly reduce selenium concentrations and based solely on the cost of other biological systems, it is expected that there would be approximately \$0.5 million in additional operational costs, primarily related to the cost of organic feed chemicals and additional manpower requirements. Applying a present worth factor to the operating cost increase provides a total present worth of the biological system of about \$10 million. The current pilot-scale tests should provide information to substantiate these values.

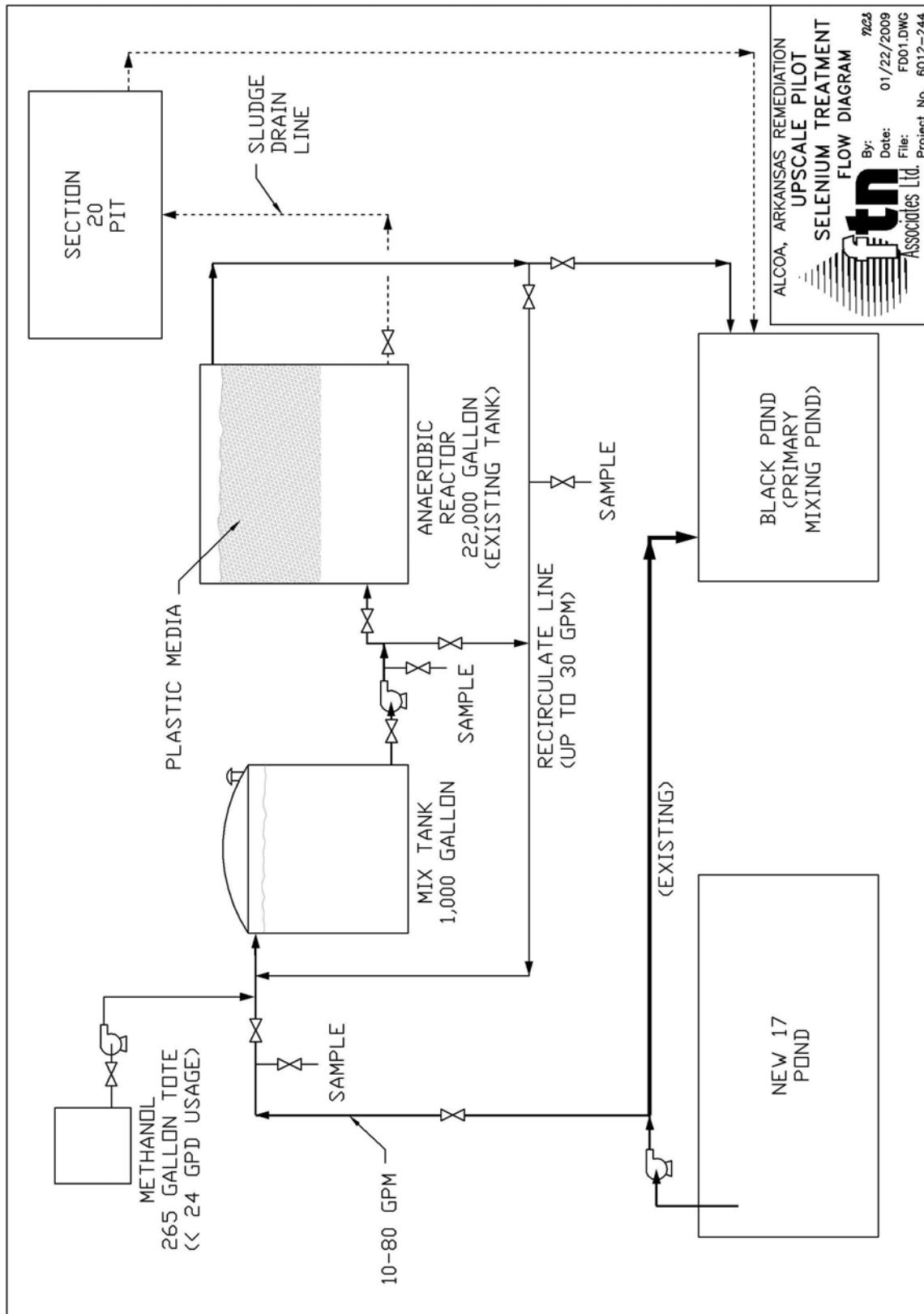


Figure 5.3. Upscale pilot selenium treatment flow diagram.

## 6.0 CONCLUSIONS

From a review of the literature, several methods for treating selenium have been identified and evaluated for potential application at Alcoa. The economics of treating large-flow rates, such as exist at Alcoa for the treated discharge, would discourage the use of most of these methods. Also, several methods were shown to be ineffective for the treatment of selenium in this application.

A series of bench-scale were conducted to demonstrate removal efficiency using different treatment methods applied to different wastewater sources. Based on these tests, a set of pilot-scale tests were conducted. With these pilot-scale tests, biological treatment of the concentrated source of selenium, the BRDA leachate, has been demonstrated to be a feasible alternative.

An expanded pilot-scale test program is being developed to further demonstrate the feasibility of a full-scale system. A larger pilot-scale system is being installed that can potentially treat up to 30 to 60 gpm of the concentrated leachate water. This larger scale pilot system will help better evaluate the rate of treatment, costs and other system dynamics involved with a full-scale system.

Despite some of the success of the biological treatment method for selenium removal, there are still significant concerns that have not been fully addressed:

- The process might be inefficient during cold weather;
- The costs of a full-scale system; and
- There is no evidence that the low levels required for meeting the water quality criterion in Holly Creek can be obtained with a biological system.

## 7.0 REFERENCES

- Baldwin, R.A., J.C. Stauter, and D.L. Terrell. August 1930. Process for the Removal of Selenium from Aqueous Systems. Kerr-McGee Nuclear Corporation. 4405464 Patent.
- Centofanti, L., R. Self, and T.W. Yarbrough. September 2001. Methods for Removing Selenium from a Waste Stream. Perma-Fix Environmental Services, Inc. 6251283 Patent.
- Environmental Protection Agency (EPA). May 1977. Manual of Treatment Techniques for Meeting the Interim Primary Drinking Water Regulations. pp. 22-31. US Environmental Protection Agency, Office of Water. Washington, DC.
- EPA. August 1980. Selenium Removal from Ground Water Using Activated Alumina [EPA Publication No. 600/280153]. US Environmental Protection Agency, Office of Water. Washington, DC.
- Frankenberger, W.T., and S. Benson. 1994. Selenium in the Environment. Marcel Dekker, Inc.
- Murphy, A.P. 1988. Removal of Selenate from Water by Chemical Reduction. Industrial and Engineering Chemical Research, Vol. 27.
- Nitrogen and Selenium Management Program Working Group. March 2007. Identification and Assessment of Selenium and Nitrogen Treatment Technologies and Best Management Practices.
- Twidell, L.G., J. McCloskey, P. Miranda, and M. Gale. February 2000. Technologies and Potential Technologies for Removing Selenium from Process and Mine Wastewaters. Proceedings Minor Elements 2000, SME, Salt Lake City. pp 53-66.

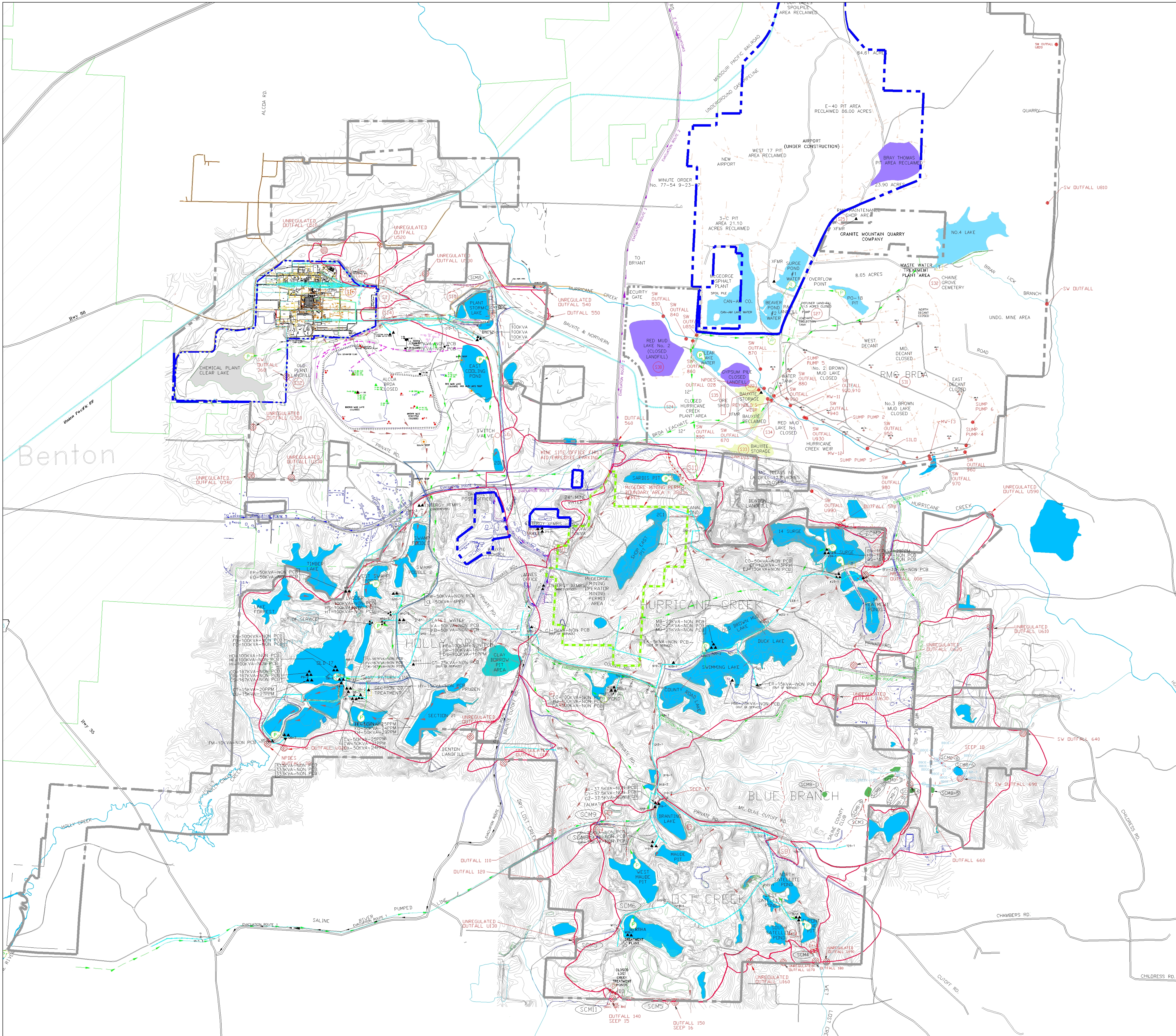
# **ATTACHMENT 1**

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**Site Map**



R:\CAD\CAD\_POR\6012-250.0\MASTER DRAWING\MASTER-6012-250-SW01.DWG



**GRAPHIC LEGEND**

- SURFACE MINE
- 2B1 TYPICAL PIT DESIGNATION
- DRAINAGE BASIN BOUNDARY
- OUTFALL
- DRAINAGE DIRECTION
- APPROXIMATE PROPERTY LINE
- APPROXIMATE PROPERTY LINE
- APPROXIMATE PROPERTY LINE
- STORAGE AREA
- ML MATERIAL LOADING AND UNLOADING AREA
- SCM STRUCTURAL CONTROL MEASURE
- P PUMP
- CULVERT
- ▲ FILL BERM
- PIPE LINE
- ▲ TRANSFORMER
- POWERLINE

**LEGEND**

**STORAGE AREAS:**

- S1 -ERECTION SIDE MATERIAL LAYDOWN AREA
- S2 -MATERIAL LAYDOWN AREA
- S3 -RECLAIMED MINE SPOIL PILE
- S4 -MINE SPOIL PILES
- S5 -MINE SPOIL PILES
- S6 -MINE SPOIL PILES
- S7 -MINE SPOIL PILES
- S8 -BORROW PIT
- S9 -MINE SPOIL PILES AND BAUXITE STORAGE
- S10 -RECLAIMED GRAVEL/CLAY BORROW AREA (WOOD ASH AMENDED SOILS)
- S11 -RECLAIMED MINE SPOIL PILES
- S12 -ALCOA OLD PLANT LANDFILL
- S13 -MATERIAL LAYDOWN AREA
- S14 -CONTRACTORS STORAGE AREA
- S15 -RECLAIMED 1999
- S16 -FILTER PLANT SLUDGE POND
- S17 -ACIDIC SEEP FLOW
- S22 -RMC BAUXITE STORAGE AREA
- S24 -RMC OLD PLANT SITE
- S25 -RMC MAINTENANCE SHOP
- S27 -R&D POTLINER LANDFILL
- S30 -RED MUD LAKE NO.2 CLOSED
- S31 -RMC BRDA LANDFILL
- S32 -RMC OLD TREATMENT PLANT
- S33 -RMC BAUXITE STORAGE AREA
- S34 -RED MUD LAKE NO.1 CLOSED
- S35 -RMC ORE SHED

**STRUCTURAL CONTROL MEASURES:**

- SCM1 -BERMED AREA TO DIVERT ACID MINE DRAINAGE FROM LEAVING SITE THROUGH STORMWATER OUTFALL 110
- SCM2 -DITCH CUT AROUND SPOIL PILE (S3) TO DIVERT ACID MINE RUNOFF INTO PIT 2B2
- SCM3 -LEVEE ON NORTH END OF PIT 4A1
- SCM4 -LEVEE ON SOUTH END OF PIT 4A5
- SCM5 -SERIES OF BERMS AND DITCHES TO DIVERT STORM WATER RUNOFF INTO PIT 4A9
- SCM6 -LEVEE TO HOLD ACID MINE DRAINAGE AND STORM WATER RUNOFF
- SCM7 -LARGE SUMP AND SMALL WEIR TO CONTAIN STORMWATER RUNOFF WATER PUMPED INTO STORMWATER PONDS
- SCM8 -MULTIPLE SEDIMENTATION BASINS THROUGHOUT THE BLUE BRANCH RECLAMATION
- SCM9 -SERIES OF BERMS, DITCHES AND RETENTION BASIN THAT COLLECTS SEDIMENT FROM RUNOFF AND DIVERTS IT INTO 4B1.
- SCM10 -SEDIMENT AND FLOW CONTROL BERM
- SCM11 -SEEP COLLECTION PONDS

**SW OUTFALL NAMED:**

LOST CREEK 100-200  
HOLLY CREEK 300-490  
HURRICANE CREEK 500-990

**INDEX**

**Scale in Feet**

0 1200

**Arkansas Remediation**  
**ALCOA**

**STORMWATER SITE MAP**

**ftn Associates Ltd.**  
water resources/environmental consultants

**DRAWN BY:** FILE NAME: SCALE: SHEET NO.  
MASTER-6012-250-SW01.DWG 1" = 1200' 1

**APPROVED BY:** PROJECT NO. DATE: 02/12/07 OF 9  
6012-250



## **ATTACHMENT 2**

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**Technical Memo – Treatability Test Procedures,  
Alcoa Selenium Study,  
January 2007**

## **TECHNICAL MEMO**

**DATE:** 1/12/07

**TO:** Files

**FROM:** Jimmy Rogers

**RE:** Treatability Test Procedures  
Alcoa Selenium Study  
Chemical Treatment

---

### **INTRODUCTION**

In order to discover a way to reduce the Selenium in the water to be discharged from Alcoa's site a series of experiments have been preformed. The possible treatment options are being preformed in small scale experiments in the hopes of finding an option that can be tested in a pilot experiment program that would be implemented on site at a large scale. The first phase of this experimental process is to use chemical methods in the hopes of drawing the Selenium out of solution and into a floc that can be separated from the discharge water.

### **MATERIALS AND METHODS**

Alkaline water from New 17 (water to be treated) was first mixed with varying percentages of acid mine drainage from Sec 21. Initial mixtures were 100%, 50%, 25%, and 10% of New 17 water. As the experiment progressed the percentages were adjusted based on results. Also, several of the samples used raw stand-pipe water instead of New 17; these samples are indicated as such. Each mixture was stirred until well mixed. Next each mixture was neutralized using 10N H<sub>2</sub>SO<sub>4</sub> to reach an approximated pH of 7.00. In situ readings were taken between each step in this process. Several different reagents were used in varying amounts to treat the mixture. Reagents were added to each mixture while the mixture was constantly being stirred. After treatment in situ measurements were recorded and selected samples were submitted for analysis. Samples were collected after allowing the treated mixture to sit for at least 30 minutes. After this time a syringe was used to draw the water off the surface of the sample without disturbing the flocculent which had developed and sunk to the bottom of the sample container. The table below shows each experiment sample; the mixture percent of New 17 (or raw stand pipe water where applicable); the initial and final pH and ORP readings; the reagent used and total amount added; and the laboratory analysis results (where applicable).



Sample	Mixture % of New 17	Initial pH	Initial ORP	H2SO4 Added ml	Reagent	Reagent Added (mg/l)	Final pH	Final ORP	Total SE (mg/l)	Dissolved SE (mg/l)
A	100	12.73	-172	26	Iron (II) Sulfate Heptahydrate	30	7.09	4	0.14	0.12
B	50	12.39	-128	11.9	Iron (II) Sulfate Heptahydrate	30	6.77	36		
C	25	11.88	-51	4.9	Iron (II) Sulfate Heptahydrate	30	6.3	120	0.3	0.28
D	10	9.6	104	0.6	Iron (II) Sulfate Heptahydrate	30	5.22	300		
E	100	12.47	109	25.65	Zinc, granule, 20 mesh	30	n/a	n/a		
F	25	n/a	n/a	n/a	n/a	n/a	n/a	n/a		
G	100	12.48	112	25.8	Sodium bisulfite	30	6.45	241	0.16	0.16
H	25	11.71	118	4.9	Sodium bisulfite	30	6.19	289	0.04	0.039
I	100	12.45	91	25.9	Copper (II) Sulfate	30	6.1	384	0.12	0.12
J	25	11.68	139	5	Copper (II) Sulfate	30	5.56	482	0.021	0.026
K	100	12.46	127	26.5	Calcium Hydroxide	30	9.66	246	0.15	0.15
L	25	11.66	164	4.95	Calcium Hydroxide	30	12.36	115	0.036	0.035
M	100	12.64	134	26.4	Iron (III) Chloride	30	6.52	358	0.15	0.13
N	25	11.85	182	5.7	Iron (III) Chloride	30	2.96	787	0.035	0.028
O	100	12.87	152	26.65	Copper Sulfate crystals	10	6.37	407	0.16	0.14
P	100	12.92	137	26.6	Copper Sulfate crystals	20	6.45	360	0.13	0.13
Q	100	12.82	108	27.1	Copper Sulfate crystals	30	6.18	368	0.13	0.12
R	100	12.75	98	26.9	Copper Sulfate crystals	40	6.1	365	0.13	0.12
S	25	11.92	130	5.4	Copper Sulfate crystals	10	6.07	398	0.03	0.033
T	25	12	151	5.35	Copper Sulfate crystals	20	5.93	386	0.027	0.031
U	25	11.95	142	5.45	Copper Sulfate crystals	30	5.8	382	0.026	0.028
V	25	11.97	135	5.5	Copper Sulfate crystals	40	5.7	383	0.028	0.024
W	100	7.15	309	n/a	Copper Sulfate crystals	10	5.47	370	<0.02	<0.02
X	100	7.24	307	n/a	Copper Sulfate crystals	20	5.53	379	<0.02	<0.02
Y	100	7.35	293	n/a	Copper Sulfate crystals	30	5.42	374	<0.02	<0.02
Z	100	7.39	298	n/a	Copper Sulfate crystals	40	5.29	385	<0.02	<0.02

Stand Pipe  
Water Used at  
100% for W-Z

## **RESULTS**

Throughout the experiment results varied depending on several contributing factors including: the percentage of New 17 water in the mixture, the reagent used, and the amount of reagent added. Raw New 17 water has a Selenium concentration of 0.16 mg/l. In the initial samples (A-N) Copper (II) Sulfate showed the most promise for a reduction in selenium. Samples O-Z used Copper Sulfate crystals at varying amounts in an effort to further reduce the selenium and find the optimal conditions for this reduction. Due to using high amounts of the Cu the laboratory was unable to perform low level Se analysis when treating the raw stand-pipe water.

## **CONCLUSION**

Thus far in the experimental procedure, no working Selenium reduction methods have been discovered. Though there was reduction of the Se with the use of the Copper Sulfate crystals, the resulting increase of the Cu concentration in the water makes this Se reduction method nonviable. Other options are impractical from an economic standpoint. Further experiments are currently underway to find a suitable solution to the Selenium problem.

JJR/kdw



Alcoa Inc.  
ATTN: Mr. Pat Keogh  
Post Office Box 290  
Bauxite, AR 72011-0290

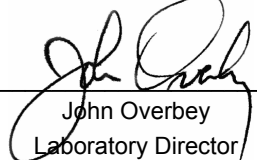
Dear Mr. Pat Keogh:

Project Description: Seventeen (17) water sample(s) received on December 1, 2006  
Arkansas Remediation  
Alcoa SE  
6012-244  
P.O. No. 190009011

This report is the analytical results and supporting information for the samples submitted to American Interplex Corporation (AIC) on December 1, 2006. The following results are applicable only to the samples identified by the control number referenced above. Accurate assessment of the data requires access to the entire document. Each section of the report has been reviewed and approved by the appropriate laboratory director or a qualified designee.

Data has been validated using standard quality control measures performed on at least 10% of the samples analyzed. Quality Assurance, instrumentation, maintenance and calibration were performed in accordance with guidelines established by the cited methodology.

**AMERICAN INTERPLEX CORPORATION**

By \_\_\_\_\_  
John Overbey  
Laboratory Director

Enclosure(s): Chains of Custody

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ATTN: Mr. Rex Robbins  
rmr@ftn-assoc.com



Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

CASE NARRATIVE

SAMPLE RECEIPT

Received Temperature: 1°C

Receipt Verification:	Complete Chain of Custody	Y
	Sample ID on Sample Labels	Y
	Date and Time on Sample Labels	Y
	Proper Sample Containers	Y
	Within Holding Times	Y
	Adequate Sample Volume	Y
	Sample Integrity	Y
	Proper Temperature	Y
	Proper Preservative	Y

QUALIFIERS

Qualifiers	Definition
D	Result is from a secondary dilution factor

References:

"Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79-020 (Mar 1983) with updates and supplements EPA/600/5-91-010 (Jun 1991), EPA/600/R-92-129 (Aug 1992) and EPA/600/R-93-100 (Aug 1993).

"Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846)", Third Edition.

"Standard Methods for the Examination of Water and Wastewaters", 20th edition, 1998.

"American Society for Testing and Materials" (ASTM).

"Association of Analytical Chemists" (AOAC).

"Self-Davis and Moore" (2000).

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### ANALYTICAL RESULTS

AIC No. 105432-1

Sample Identification: New 17 11/28/06 1010

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	0.011	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.16	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	0.011	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.16	0.02	mg/l	S19377	D

AIC No. 105432-2

Sample Identification: New 17, 100% neutral 11/28/06 1045

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	0.039	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.16	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	0.038	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.16	0.02	mg/l	S19377	D

AIC No. 105432-3

Sample Identification: New 17, 25% neutral 11/28/06 1052

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	0.31	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.043	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	0.12	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.038	0.02	mg/l	S19377	D

AIC No. 105432-4

Sample Identification: M-100% New 17, 30 mg/1 Fe 11/28/06 1035

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	0.11	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.15	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	0.052	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.13	0.02	mg/l	S19377	D

AIC No. 105432-5

Sample Identification: N-25% New 17, 30 mg/1 Fe 11/28/06 1110

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	0.14	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.035	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	0.13	0.01	mg/l	S19377	D
Selenium	EPA 200.8	0.028	0.02	mg/l	S19377	D

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### ANALYTICAL RESULTS

AIC No. 105432-6

Sample Identification: O-100% New 17, 10 mg/1 Cu 12/1/06 0855

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	190	6	mg/l	S19377	D
Selenium	EPA 200.8	0.16	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	77	6	mg/l	S19377	D
Selenium	EPA 200.8	0.14	0.02	mg/l	S19377	D

AIC No. 105432-7

Sample Identification: P-100% New 17, 20 mg/1 Cu 12/1/06 0930

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	260	6	mg/l	S19377	D
Selenium	EPA 200.8	0.13	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	110	6	mg/l	S19377	D
Selenium	EPA 200.8	0.13	0.02	mg/l	S19377	D

AIC No. 105432-8

Sample Identification: Q-100% New 17, 30 mg/1 Cu 12/1/06 0950

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	350	6	mg/l	S19377	D
Selenium	EPA 200.8	0.13	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	220	6	mg/l	S19377	D
Selenium	EPA 200.8	0.12	0.02	mg/l	S19377	D

AIC No. 105432-9

Sample Identification: R-100% New 17, 40 mg/1 Cu 12/1/06 1015

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	410	6	mg/l	S19377	D
Selenium	EPA 200.8	0.13	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	280	6	mg/l	S19377	D
Selenium	EPA 200.8	0.12	0.02	mg/l	S19377	D

AIC No. 105432-10

Sample Identification: S-25% New 17, 10 mg/1 Cu 12/1/06 1035

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	180	6	mg/l	S19377	D
Selenium	EPA 200.8	0.030	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	120	6	mg/l	S19377	D
Selenium	EPA 200.8	0.033	0.02	mg/l	S19377	D

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Bauxite, AR 72011-0290

### ANALYTICAL RESULTS

AIC No. 105432-11

Sample Identification: T-25% New 17, 20 mg/1 Cu 12/1/06 1100

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	360	6	mg/l	S19377	D
Selenium	EPA 200.8	0.027	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	280	6	mg/l	S19377	D
Selenium	EPA 200.8	0.031	0.02	mg/l	S19377	D

AIC No. 105432-12

Sample Identification: U-25% New 17, 30 mg/1 Cu 12/1/06 1115

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	570	6	mg/l	S19377	D
Selenium	EPA 200.8	0.026	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	500	6	mg/l	S19377	D
Selenium	EPA 200.8	0.028	0.02	mg/l	S19377	D

AIC No. 105432-13

Sample Identification: V-25% New 17, 40 mg/1 Cu 12/1/06 1140

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	810	6	mg/l	S19377	D
Selenium	EPA 200.8	0.028	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	720	6	mg/l	S19377	D
Selenium	EPA 200.8	0.024	0.02	mg/l	S19377	D

AIC No. 105432-14

Sample Identification: W-100% Stand Pipe, 10 mg/1 Cu 12/1/06 1155

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	410	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	300	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D

AIC No. 105432-15

Sample Identification: X-100% Stand Pipe, 20 mg/1 Cu 12/1/06 1210

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	900	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	790	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D

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ANALYTICAL RESULTS

AIC No. 105432-16

Sample Identification: Y-100% Stand Pipe, 30 mg/1 Cu 12/1/06 1125

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	1400	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	1200	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D

AIC No. 105432-17

Sample Identification: Z-100% Stand Pipe, 40 mg/1 Cu 12/1/06 1240

Analyte	Method	Result	RL	Units	Batch	Qualifier
Copper	EPA 200.8	1900	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D
Dissolved:						
Copper	EPA 200.8	1700	6	mg/l	S19377	D
Selenium	EPA 200.8	< 0.02	0.02	mg/l	S19377	D



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### SAMPLE PREPARATION REPORT

AIC No. 105432-1

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06	0950 263	04DEC06	1327 235	10	S19377	D
Dissolved: Metals	04DEC06	0950 263	04DEC06	1320 235	10	S19377	D

AIC No. 105432-2

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06	0950 263	04DEC06	1340 235	10	S19377	D
Dissolved: Metals	04DEC06	0950 263	04DEC06	1334 235	10	S19377	D

AIC No. 105432-3

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06	0950 263	04DEC06	1354 235	10	S19377	D
Dissolved: Metals	04DEC06	0950 263	04DEC06	1347 235	10	S19377	D

AIC No. 105432-4

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06	0950 263	04DEC06	1407 235	10	S19377	D
Dissolved: Metals	04DEC06	0950 263	04DEC06	1400 235	10	S19377	D

AIC No. 105432-5

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06	0950 263	04DEC06	1420 235	10	S19377	D
Dissolved: Metals	04DEC06	0950 263	04DEC06	1413 235	10	S19377	D

AIC No. 105432-6

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06	0950 263	05DEC06	1059 235	1000	S19377	D
Metals	04DEC06	0950 263	04DEC06	1447 235	10	S19377	D
Dissolved: Metals	04DEC06	0950 263	05DEC06	1052 235	1000	S19377	D
Metals	04DEC06	0950 263	04DEC06	1440 235	10	S19377	D

AIC No. 105432-7

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06	0950 263	05DEC06	1112 235	1000	S19377	D
Metals	04DEC06	0950 263	04DEC06	1500 235	10	S19377	D
Dissolved: Metals	04DEC06	0950 263	05DEC06	1106 235	1000	S19377	D
Metals	04DEC06	0950 263	04DEC06	1453 235	10	S19377	D

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### SAMPLE PREPARATION REPORT

AIC No. 105432-8

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1126	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1513	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1119	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1507	235	10	S19377	D

AIC No. 105432-9

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1139	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1527	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1132	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1520	235	10	S19377	D

AIC No. 105432-10

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1152	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1540	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1146	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1534	235	10	S19377	D

AIC No. 105432-11

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1219	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1607	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1212	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1600	235	10	S19377	D

AIC No. 105432-12

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1232	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1620	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1226	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1613	235	10	S19377	D

AIC No. 105432-13

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1246	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1633	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1239	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1627	235	10	S19377	D

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### SAMPLE PREPARATION REPORT

AIC No. 105432-14

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1259	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1647	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1252	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1640	235	10	S19377	D

AIC No. 105432-15

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1312	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1700	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1306	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1653	235	10	S19377	D

AIC No. 105432-16

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1339	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1727	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1332	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1720	235	10	S19377	D

AIC No. 105432-17

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	04DEC06 0950	263	05DEC06 1352	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1740	235	10	S19377	D
Dissolved:							
Metals	04DEC06 0950	263	05DEC06 1346	235	1000	S19377	D
Metals	04DEC06 0950	263	04DEC06 1733	235	10	S19377	D

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LABORATORY CONTROL SAMPLE RESULTS

Analyte	Spike Amount	% Recovery	% Recovery Limits	RPD	RPD Limit	Batch	Qualifier
Copper	0.05 mg/l	99.2/98.6	85-115	0.667	20	S19377	
Selenium	0.05 mg/l	98.2/98.6	85-115	0.461	20	S19377	

MATRIX SPIKE SAMPLE RESULTS

Analyte	Spike Amount	% Recovery	% Recovery Limits	RPD	RPD Limit	Batch	Qualifier
Copper	0.05 mg/l	92.8/93.3	75-125	0.559	20	S19377	
Selenium	0.05 mg/l	99.0/99.2	75-125	0.215	20	S19377	

LABORATORY BLANK RESULTS

Analyte	Method	Result	Units	RL	QC Sample	Qualifier
Copper	EPA 200.8	< 0.001	mg/l	0.001	S19377-1	
Selenium	EPA 200.8	< 0.002	mg/l	0.002	S19377-1	
Selenium	EPA 200.8	< 0.002	mg/l	0.002	S19377-1	

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QUALITY CONTROL PREPARATION REPORT

LABORATORY CONTROL SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	04DEC06 0950	263	04DEC06 1213	235		S19377-2	
Metals	04DEC06 0950	263	04DEC06 1220	235		S19377-3	

MATRIX SPIKE SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	04DEC06 0950	263	04DEC06 1227	235		S19377-4	
Metals	04DEC06 0950	263	04DEC06 1233	235		S19377-5	

LABORATORY BLANKS

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	04DEC06 0950	263	04DEC06 1207	235		S19377-1	



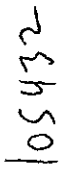
105432

Date 12-1-06	Project Name Alcoa SE	Project No. 6012-244	Project Manager (Print) RMR	Page 1 of 3
Report / Bill to:		Submitted by:		
Arkansas Remediation (Exp)		FTN Associates, Ltd.		
Project Ref: (Exp)		3 Innwood Circle, Suite 220		
Phone:		Little Rock, AR 72211		
		(501) 225-7779 • Fax (501) 225-6738		
Sampler Signature(s) <i>Jimmy Rogers</i>		Recorded By (Print) Jimmy Rogers		
SAMPLE DESCRIPTION				
Sample Identification	Date	Time	Matrix* W S O	No. of Containers
New 17	11/28/06	1010	X	2
New 17, 100%, neutral	11/28/06	1045	X	2
New 17, 25%, neutral	11/28/06	1052	X	2
M - 100% New 17, 30 mg/l Fe	11/28/06	1035	X	2
N - 25% New 17, 30 mg/l Fe	11/28/06	1110	X	2
O - 100% New 17, 10 mg/l Cu	12/1/06	0855	X	2
P - 100% New 17, 20 mg/l Cu	12/1/06	0930	X	2
Q - 100% New 17, 30 mg/l Cu	12/1/06	0950	X	2
		Container Type	Preservative	
		P	N	
* Matrix: W = Water S = Soil O = Other G = Glass P = Plastic H = HCl to pH2 NO = None S = Sulfuric acid pH2 N = Nitric acid pH2 B = NaOH to pH12 V = VOA vials				
Relinquished By (Signature) <i>Jimmy Rogers</i>	Print Name Jimmy Rogers	Date 12/1/06	Time 1430	Received By (Signature)
Relinquished By (Signature)	Print Name	Date	Time	Received By Laboratory (Signature)
				<i>Eugene Hampton</i>
Laboratory Remarks:				
Sampler Remarks: *ALCOA LIST jir@ftn-assoc.com				



105432

Date 12-1-06	Project Name Alcoa SE	Project No. 6012-244	Project Manager (Print) RMR		Page 2 of 3	
Report / Bill to:			Submitted by:			
Arkansas Remediation (Exp)			FTN Associates, Ltd.			
Project Ref: (Exp)			3 Innwood Circle, Suite 220			
Phone:			Little Rock, AR 72211			
			(501) 225-7779 • Fax (501) 225-6738			
Sampler Signature(s) 			Recorded By (Print) Jimmy Rogers			
SAMPLE DESCRIPTION						
Sample Identification	Date	Time	Matrix*		No. of Containers	
			W	S	O	
R - 100% New 17, 40 mg/l Cu	12/1/06	1015	X		2	
S - 25% New 17, 10 mg/l Cu	12/1/06	1035	X		2	
T - 25% New 17, 20 mg/l Cu	12/1/06	1100	X		2	
U - 25% New 17, 30 mg/l Cu	12/1/06	1115	X		2	
V - 25% New 17, 40 mg/l Cu	12/1/06	1140	X		2	
W - 100% stand pipe, 10 mg/l Cu	12/1/06	1155	X		2	
X - 100% stand pipe, 20 mg/l Cu	12/1/06	1210	X		2	
Y - 100% stand pipe, 30 mg/l Cu	12/1/06	1125	X		2	
			Container Type			
			Preservative			
			N			
* Matrix: W = Water S = Soil O = Other G = Glass P = Plastic H = HCl to pH2 NO = None S = Sulfuric acid pH2 N = Nitric acid pH2 B = NaOH to pH12 T = Sodium Thiosulfate Z = Zinc acetate						
Relinquished By (Signature) 	Print Name Jimmy Rogers	Date 12/1/06	Time 1422	Received By (Signature) 	Print Name Eugene Hampton	
Relinquished By (Signature)	Print Name	Date	Time	Received By Laboratory (Signature)	Print Name	
					12-1-06 1422	
Sampler Remarks: *ALCOA LIST jlr@ftn-assoc.com						



5



# **ATTACHMENT 3**

---

**Technical Memo – Treatability Test Procedures,  
Alcoa Selenium Study,  
June 2007**

## TECHNICAL MEMO

**TO:** Files

**FROM:** Rex Robbins

**RE:** Treatability Test Procedures  
Alcoa Selenium Study  
Chemical Treatment using Ferrous-based Reagents

**DATE:** 6/18/07

---

This treatability test is designed to determine the ability of ferrous hydroxide to react with and settle selenium contained in samples of Alcoa leachate. Two ferrous-based reagents ( $\text{FeCl}_3$  and  $\text{FeSO}_4$ ) will be reacted with the partially neutralized leachate water to form ferrous hydroxide. According to the literature, it can be expected that the ferrous hydroxide will form an insoluble magnetite containing selenium that can be settled or filtered from the water. The test will give some information regarding the relative efficiency of  $\text{FeCl}_3$  vs.  $\text{FeSO}_4$ , and the importance of initial pH in the formation of the ferrous hydroxide.

### Materials/Equipment:

1. 4 gallons of New 17 water,
2. 50 grams of  $\text{FeCl}_3$ ,
3. 50 grams of  $\text{FeSO}_4$ ,
4. 10N Sulfuric acid for adjusting pH,
5. Titration apparatus,
6. 6 – 1-liter wide mouth Nalgene or plastic bottles,
7. Magnetic stirrer with plastic coated magnets, and
8. 13 – un-preserved bottles for selenium analysis (From AIC).

### Procedures:

- Collect samples of raw water into an un-preserved bottle for analysis. From the same container, pull three 1-liter aliquots into the 1-liter bottles and do titrations using 10N sulfuric acid. Record the quantity of acid needed to reach pH 9, 10 and 11. Re-adjust as needed after one hour and record total quantity of acid for each pH endpoint.

- Fill two sets of 1-liter bottles according to Table 1 (total of six bottles with two of each pH). For labeling, add the initials FeCl<sub>3</sub> to one set and FeSO<sub>4</sub> to the other set. To one set of bottles, add 2 grams of FeCl<sub>3</sub> and to the other set, add 2 grams of FeSO<sub>4</sub>. After adding ferrous reagent to all of the bottles, individually set up each bottle on the magnetic stirrer and adjust pH back to pH 9.0 for each sample. Allow each bottle to mix for about 10 minutes, then recap and allow at least one hour of unstirred reaction/settling time. Decant water from each 1-liter bottle into an unpreserved sample bottle.

Table 1. Sample Labels.

	<b>FeCl<sub>3</sub></b>	<b>FeSO<sub>4</sub></b>
pH 9	9A-FeCl <sub>3</sub>	9B-FeSO <sub>4</sub>
pH 10	10A-FeCL3	10B-FeSO <sub>4</sub>
pH 11	11A-FeCl <sub>3</sub>	11B-FeSO <sub>4</sub>

Place all samples in refrigerator or on ice. Initially, submit the two raw samples and samples 10A-FeCl<sub>3</sub> and 10A-FeSO<sub>4</sub> to American Interplex for testing for dissolved and total selenium. Arrange for 2-day turnaround on initial sample results. If testing shows significant reduction of selenium, the remaining samples will be analyzed.

JJR/ack

# Alcoa Selenium Chemical Treatability Test Study Results

Selenium Treatment with ferrous hydroxide

Source Data		
Sample	Initial pH	Selenium (mg/L)
New 17 Untreated	12.49	0.13
New 17 Acid Treat Only	12.49	0.14

Experimental Data										
Sample	Initial pH	Acid	Acid Added (mL)	Intermediate pH	Chemical Addition	pH After Chemical Addition	Acid Added (mL) [part 2]	Final pH	Selenium (mg/L)	Selenium % Reduction
9A	12.49	Alcoa H <sub>2</sub> SO <sub>3</sub>	3.7	8.9	2 g/L FeCl <sub>3</sub>	7.62	33*	8.98	0.12	7.69%
9B	12.49	Alcoa H <sub>2</sub> SO <sub>4</sub>	3.7	8.98	2 g/L FeSO <sub>4</sub>	7.75	24*	8.98	0.12	7.69%
10A	12.49	Alcoa H <sub>2</sub> SO <sub>4</sub>	3	10.02	2 g/L FeCl <sub>3</sub>	8.88	0	8.88	0.12	7.69%
10B	12.49	Alcoa H <sub>2</sub> SO <sub>4</sub>	3.1	10	2 g/L FeSO <sub>4</sub>	9.41	0.2	8.79	0.13	0.00%
11A	12.49	Alcoa H <sub>2</sub> SO <sub>4</sub>	2.5	10.99	2 g/L FeCl <sub>3</sub>	10.07	0.5	8.99	0.14	-7.69%
11B	12.49	Alcoa H <sub>2</sub> SO <sub>4</sub>	2.5	11	2 g/L FeSO <sub>4</sub>	10.34	0.6	8.99	0.13	0.00%

**\*Note:**

Values with an asterisk indicate that the pH was increased by adding that number of mL of 0.5 N NaOH

**Procedures:**

Raw water samples from New 17 were collected into (6) one liter containers. The pH was then adjusted using 93% concentrated sulfuric acid: two bottles were lowered to a pH of 9, two bottles were lowered to a pH of 10, and two were lowered to a pH of 11. The bottles were then allowed to sit for an hour and reobserve the pH (readjusting as needed). There was no observed change in pH in any bottle. Chemical treatment was then administered. To the "A" bottles a dose of 2 g/L of FeCl<sub>3</sub> was added. To the "B" bottles a dose of 2 g/L of FeSO<sub>4</sub> was added. Then each sample's pH was adjusted accordingly to reach a final pH of 9. After this treatment each sample was allowed to mix on the magnetic stirrer for 10 minutes. Then each sample was allowed at least one hour for reaction/settling time. Water was then decanted into sample bottles and sent to the lab for analysis.

# **ATTACHMENT 4**

---

**Alcoa Technical Center Report**

Current Report is:

- ☐ Initiation Report  
☐ Progress Report  
☒ Final Report

## RD&E Report

<b>Title:</b>	Arkansas Waste Water Selenium Removal Treatability Study – Final Report
<b>Authors:</b>	Rajat Ghosh, Dennis Fulmer, Robin Weightman and Jaw Fu
<b>Report No.:</b>	07-218 <small>(One number is assigned for all 3 sections – Initiation, Progress and Final Report)</small>
<b>Initiation Report Date:</b>	
<b>Progress Report Dates:</b>	
<b>Final Report Entry Date:</b>	12/10/07

### Abstract

Treatability studies for removal of Selenium from Arkansas Bauxite Mine leachates were performed using two different treatment technologies; a 50% Zero-Valent Iron (ZVI)-sand media and a Spent Mushroom Compost media. Both technologies used fixed bed columns. Approximately, 20-45% of the dissolved selenium was removed from the mine waters using ZVI technology while the spent mushroom compost columns resulted in removal of around 30%. It's notable that 30% selenium removal was achieved from the highly complexed RMC Sumpwater matrix using ZVI technology without any pH adjustment. Reduction of selenium at this source location could ultimately reduce the total selenium load in the downstream final effluent. In addition to the treatment technologies, an analytical method detection limit study was also conducted in order to evaluate the practical quantitation limit for selenium in the site specific matrix (waters) of interest. Evaluation by a single laboratory suggests practical quantification limits are almost a factor of 2 or higher than the 5 ppb detection limit cited in the EPA 40 CFR method. Finally, split analysis of spiked BRDA and final effluent samples by two independent laboratories indicate inter-laboratory variability in Se recovery with the lowest recovery (61% for New 17 spike) recorded by the local laboratory routinely used by Alcoa. As a perspective, the acceptable spike recovery for EPA contract laboratory is within 85-110% of the spiked amount for an aqueous matrix.

### Keywords

Selenium, ZVI, compost, NMF, MDL

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## Background

Previous treatment of Se containing wastewater at ATC through elemental iron-sand column has proved successful in removing 90% of the influent Se from average influent concentration of 7.5 ppm down to detection level concentrations of around 0.5 ppm. Given the past success, ATC proposed to use elemental iron-sand reduction technology for treating Se from the bauxite residue leachate at the Arkansas site following pH adjustment. Zero-valent iron (ZVI) reduces Se(VI) in the form of selenate ion ( $\text{SeO}_4^{2-}$ ) to selenite ion (Se is in the +4 oxidation state) during the corrosion of ZVI to iron oxyhydroxides ( $\text{Fe}_{\text{OH}}$ ). Two mechanisms can be attributed to the rapid removal of Se(VI) from the solutions. One is the reduction of Se(VI) to Se(IV), followed by rapid adsorption of Se(IV) to  $\text{Fe}_{\text{OH}}$ . The other is the adsorption of Se(VI) directly to  $\text{Fe}_{\text{OH}}$ , followed by its reduction to Se(IV). In addition, ATC had previously performed fixed bed column studies with mushroom compost to evaluate the potential for anaerobic reduction of selenate following pH adjustment of the residue leachate in the range of 8.

## Project Objective(s)

The objectives of this project are as follows:

- To assess the potential for ZVI/sand media to treat Se containing bauxite residue leachate to concentrations less than 10 ppb in ex-situ fixed bed columns or in-situ interception trench configuration
- To assess the potential of natural compost media in promoting anaerobic degradation of selenium in ex-situ fixed bed columns
- To evaluate the practical quantitation limit for Se in the site specific matrix of interest; this will enable Alcoa to establish the accuracy of Se analysis near the action level
- To evaluate the accuracy of the Se analysis at the concentrations of the site water

## Experimental Plan/Project Approach

### Initial Characterization

All four waste media (final effluent, Alcoa BML or Main Seep, New 17 and RMC sumpwater) were characterized for total and dissolved Se, pH and ORP. Table 1 provides the absolute Selenium concentration of the four streams as analyzed by two independent laboratories.

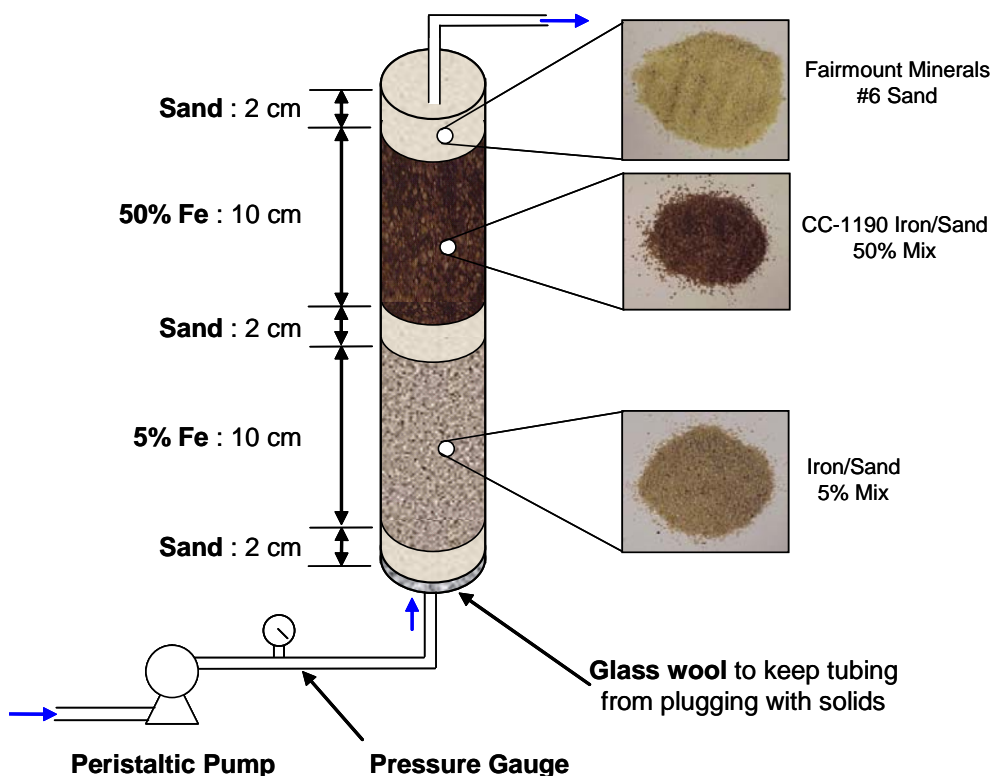


**Table 1.** Initial Characterization of Arkansas Wastewaters for Selenium

Sample ID	Laboratory	
	Test America	American Interplex
#3 Pond Final Effluent	12.1 ug/L	14 ug/L
RMC Sumpwater	310 ug/L	400 ug/L
Alcoa Main Seep	206 ug/L	260 ug/L
New 17	112 ug/l	140 ug/L

### *ZVI/Sand Treatment*

The objective of this study was to evaluate the feasibility of Alcoa's ZVI/sand treatment technology to reduce selenate ion from multiple waste streams generated at Alcoa's Arkansas facility. The study was performed in fixed bed columns with 1 inch in diameter and approximately 26 cm in length. The conceptual column design is provided in Figure 1.

**Figure 1.** ZVI/Sand Column Treatability Schematic

As shown in Figure 1, each column had a 10 cm layer of redox control media containing 5 wt% CC-1190 ZVI mixed with 95 wt% Global #6 sand followed by a 10 cm layer of actual treatment media comprised of 50 wt% CC-1190 mixed 50 wt% Global #6. Each column was subjected to specific waste media treatment, namely, the RMC sumpwater with Se in the range of 400  $\mu\text{g/L}$ ; the Alcoa Main Seep with Se in the range of 300  $\mu\text{g/L}$ ; and the combined Alcoa + RMC BRL (New 17) where Se is in 200  $\mu\text{g/L}$  range. Note, for the treatment of New 17 leachate and Alcoa Main Seep, pH was adjusted to below 8 using sulfuric acid prior to column treatment. As for the

RMC Sumpwater, attempts to adjust the pH below 8 resulted in the formation of Al/Fe/Si hydroxide gel which was difficult to remove. As a result, RMC Sumpwater was run through the column without any pH adjustment.

The columns were started at a flow rate of 1 mL/min (0.05 gpm/ft<sup>2</sup>) and was slowly increased to 5 mL/min (0.25 gpm/ft<sup>2</sup>) after a day and then to a final flow rate of 10 mL/min (0.5 gpm/ft<sup>2</sup>) after the second day. On the last day of the five day column operation, the flow rate was increased to 20 mL/min (1 gpm/ft<sup>2</sup>) for few hours prior to termination of the testing. A detailed sampling schedule is provided in Table 2.

**Table 2.** Sampling Schedule for the ZVI Treatment Column

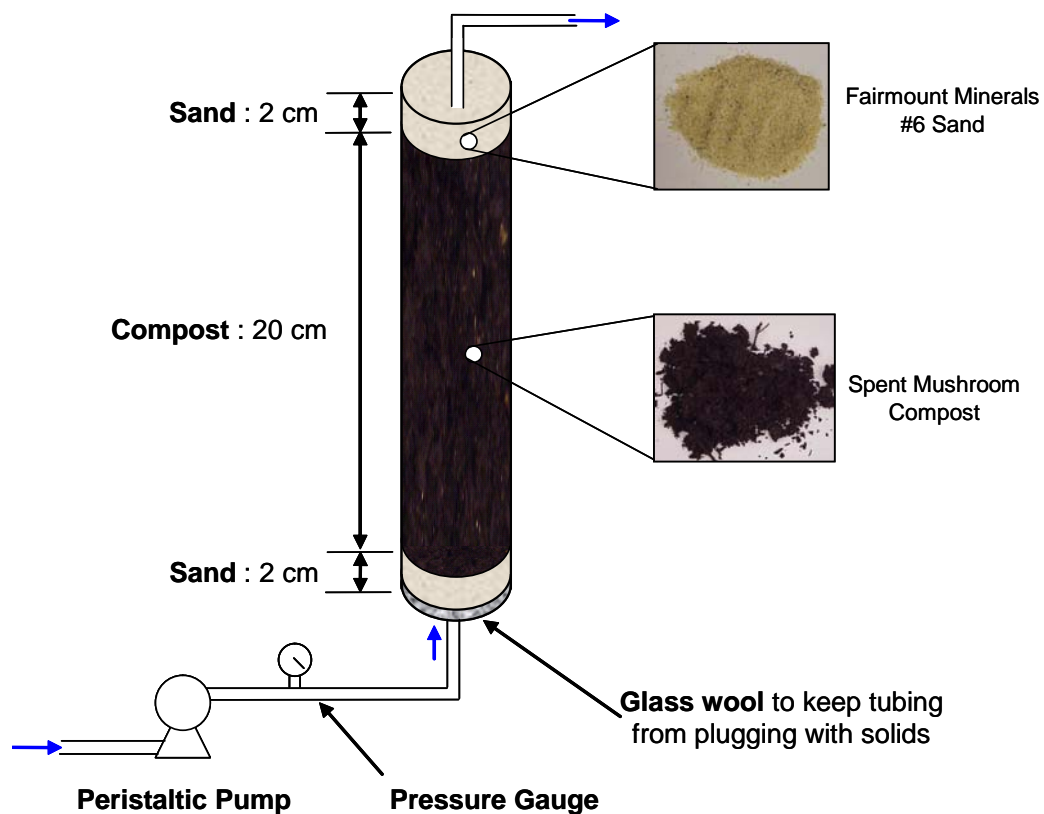
Sampling Parameters	Sampling Schedule				
	Day 1	Day 2	Day 3	Day 4	Day 5
Total Se	Inf, Eff	Eff	Eff	Eff	Inf, Eff
Dissolved Se	Inf, Eff	Eff	Eff	Eff	Inf, Eff
pH	Inf, Eff	Inf, Eff	Inf, Eff	Inf, Eff	Inf, Eff
ORP	Inf, Eff	Inf, Eff	Inf, Eff	Inf, Eff	Inf, Eff

A second column study was also undertaken, where the same three waters were passed through similar ZVI/sand columns as depicted in Figure 1 with the only exception of increasing the mass of ZVI in the active treatment layer from 50% to 75%. The purpose of this study was to evaluate the effect of increased Fe content on Selenium reduction.

### *Spent Mushroom Compost Treatment*

The objective of this study was to evaluate the feasibility of promoting anaerobic reduction of selenate in fixed bed columns using 100% spent mushroom compost as the degrading medium. The study was performed in fixed bed columns with 1 inch in diameter and approximately 24 cm in length. The conceptual column design is provided in Figure 2. As shown in Figure 2, each column had a 20 cm layer of spent mushroom compost media. Each column was subjected to specific waste media treatment, namely, the Alcoa Main Seep with Se in the range of 300 µg/L and the combined Alcoa + RMC BRL (New 17) where Se is in 140 µg/L range. Note, for the treatment of New 17 leachate and Alcoa Main Seep, pH was adjusted to below 8 using sulfuric acid prior to column treatment. As for the RMC sumpwater, attempt to adjust the pH below 8 resulted in the formation of Al/Fe hydroxide gel which was difficult to remove. As a result, the RMC sumpwater was not used for the compost study.

The columns were operated in the upflow mode at a flow rate of 1 mL/min (0.05 gpm/ft<sup>2</sup>). The same sampling schedule as depicted in Table 1 was adopted here also.



**Figure 2.** Spent Mushroom Compost Column Schematic

### *MDL/PQL Study*

The objective of this study was to determine the practical quantitation limit (PQL) for Se in the site specific matrix of interest. This study will also help to establish the accuracy of Se analysis near the action level. Note, the MDL for an analytical method that analytical laboratory usually uses is usually established by performing a random spiking study on clean water matrix, not on the site specific matrix of interest. The rest of this section provides the detailed approach to perform the MDL/PQL study.

1. The Alcoa Final Effluent sample was separated into 6 separate aliquots of 500 mL each.
2. Each aliquot was spiked as follows:
  - A. 0.0 ppb
  - B. 2.0 ppb
  - C. 5.0 ppb
  - D. 10.0 ppb
  - E. 20.0 ppb
  - F. 40.0 ppb

Please note the permit limit is 5.0 ppb.

3. Each spiked sample was separated into 7 different aliquots of 50 mL each by ATC.
4. All 42 samples were randomized (6 different concentrations  $\times$  7 replicates) by ordering them in a random fashion by ATC.

5. The samples were then shipped to Test America where analysis was performed by an external lab/operator with no knowledge of the concentration levels.
6. Instrument used for analysis: ICP-MS (Method SW 846 6020)
7. Results were reported back to ATC where statistical modeling was performed to determine the MDL/PQL for this method for Se for this water matrix.

### *Matrix Spike Study*

The objective of this study was to evaluate the accuracy of the Se analysis at the concentrations of the site water. To accomplish this, a matrix spike study was conducted where the final effluent (prior to discharge) and the BRDA leachate (New 17) were individually spiked with 500 ppb of Se. The resultant solution was then analyzed to evaluate the recovery efficiency. Split analysis was performed between Test America and American Interplex Corporation, both of which are contract laboratories certified for the State of Arkansas. ATC supplied Test America with the original and spiked samples for both the media while only the spiked samples were sent to American Interplex. The purpose of this analysis was to determine the inter-lab variability in the accuracy of the test results as well as to evaluate the quality of the historical data collected.

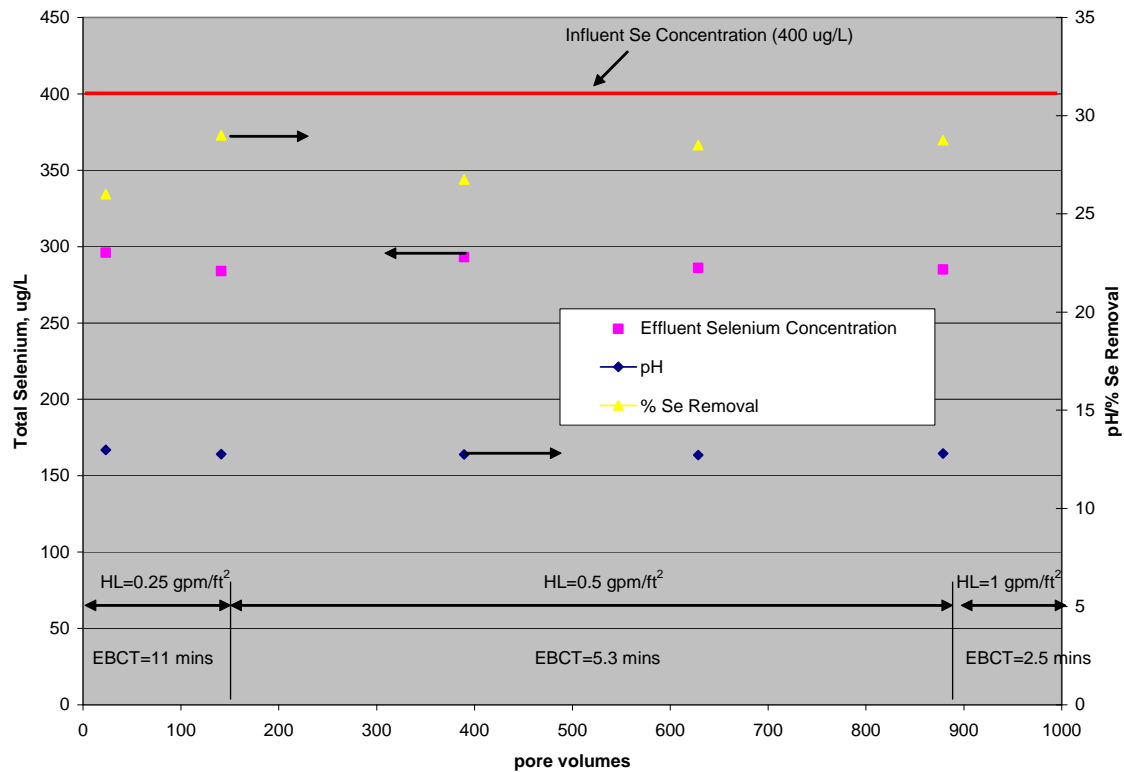
### **Schedule**

The entire study was conducted over a period of two months, starting September 15, 2007. ZVI/sand treatment column study was conducted for two weeks followed by the spent mushroom compost column study. The MDL/PQL study commenced following the compost column study. Due to technical difficulties, the Matrix Spike study was delayed until the first week in November.

### **Technical Results or Findings**

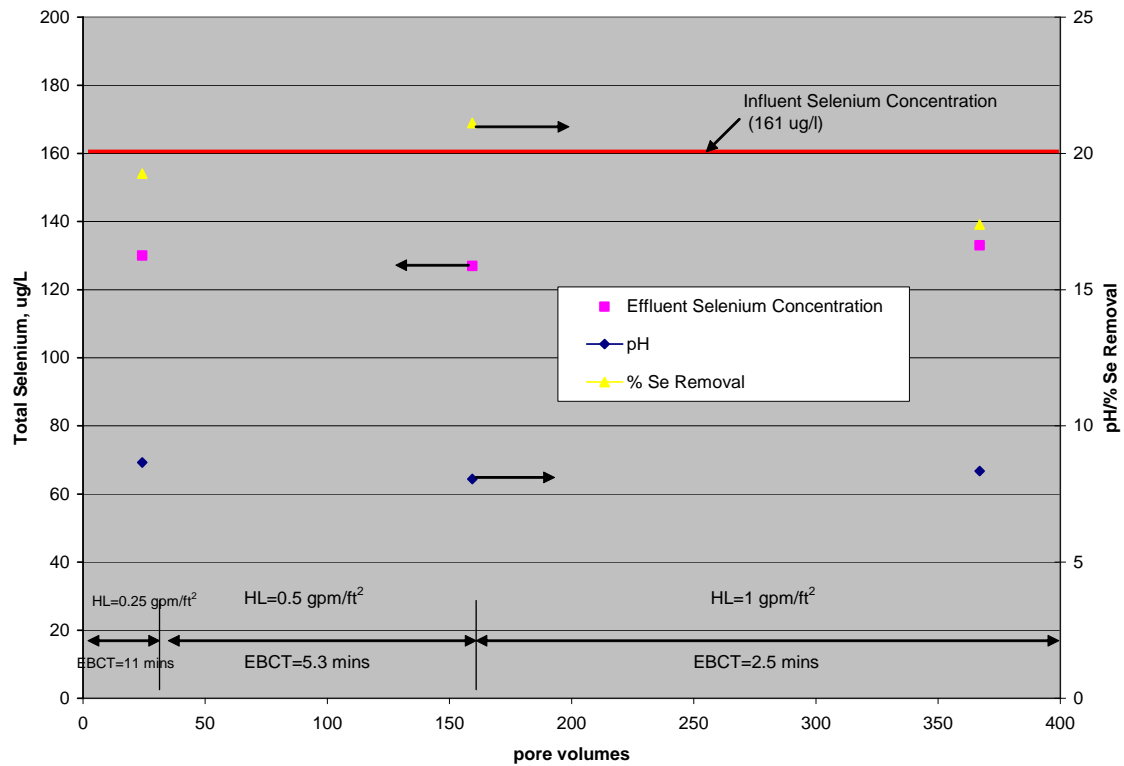
#### *50% ZVI/Sand Treatment*

Figure 3 provides the results of the selenium removal from the RMC sumpwater using 50% ZVI-Sand treatment study without any pH adjustment. As shown in the figure, the column ran without any hydraulic issues and was able to remove ~28% of the influent Se on a consistent basis. Although the column was subjected to three different hydraulic loading rates, this did not alter the Se removal efficiency through the column, indicating establishment of some kind of equilibrium condition.



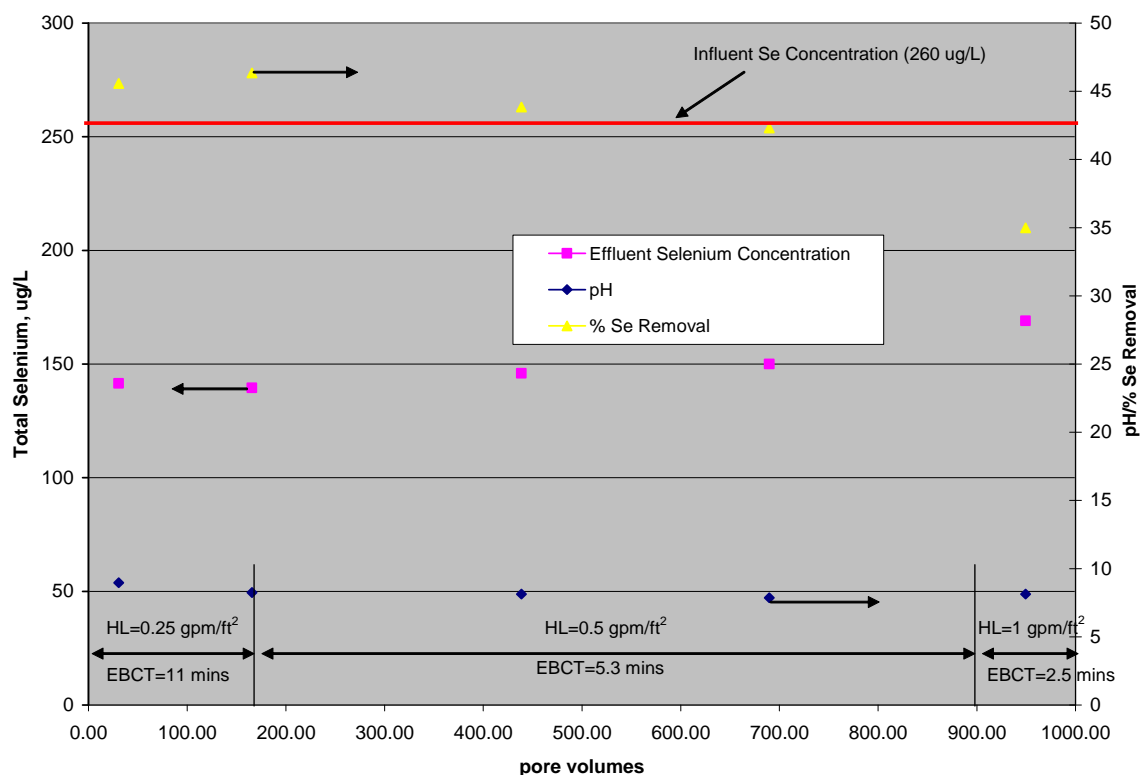
**Figure 3.** Selenium Removal from RMC Sumpwater using 50% ZVI

Figure 4 presents the selenium removal from the New 17 water using 50% ZVI-Sand treatment following pH adjustment of the leachate around 8 s.u. As shown in Figure 4, the ZVI/sand media was able to remove ~20% of the total influent Se mass over 400 pore volumes of operation. Like the previous test, the increase in the hydraulic loading did not affect the Se removal efficiency. However, increased pressure drop was noticeable across the reactive media after 400 pore volumes of operation after which the column test was terminated.



**Figure 4.** Selenium Removal from New 17 using 50% ZVI

Perhaps the best removal efficiency was evidenced with the Alcoa Main Seep influent following pH adjustment of the leachate below 8 s.u. As shown in Figure 5, the average Se removal efficiency was around 45%, with efficiency decreasing as a function of increased hydraulic loading. This column showed no signs of hydraulic issues over the course of its operation.



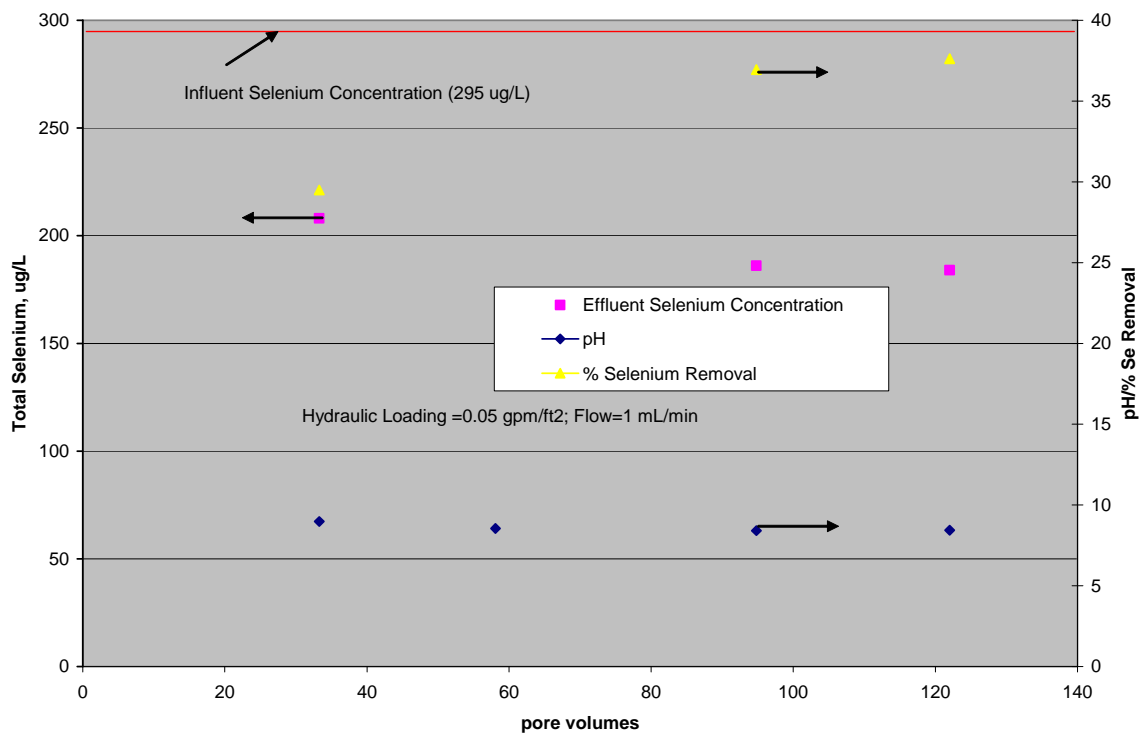
**Figure 5.** Selenium Removal from Alcoa Main Seep using 50% ZVI

### *75% ZVI/Sand Treatment*

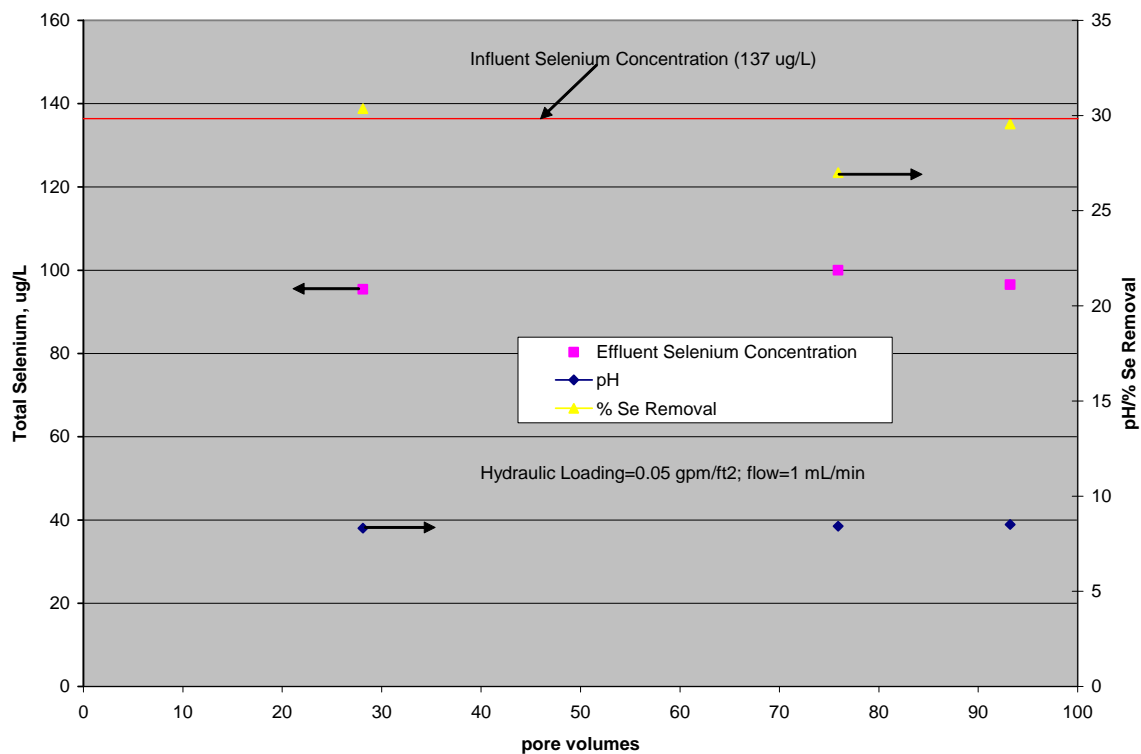
Figure 6 shows the selenium removal profile for Alcoa Main Seep with 75% ZVI in the reaction zone. As shown in this figure, removal efficiency actually dropped at the higher Fe levels from an average level of 43% to 37% with corresponding release of dissolved Fe in the effluent. Similar drop in efficiency was noticeable with RMC sumpwater as well as New 17 effluent. The use of higher Fe percentage is therefore not foreseen as a viable option to consider for treating Selenium from the mud lakes.

### *Spent Mushroom Compost Treatment*

Because of the formation of Al/Fe/Si hydroxide gel upon pH adjustment to neutral pH range, the RMC Sumpwater could not be used in the compost treatment study. The other two matrices, namely, the Alcoa Main Seep and the New 17 sample were adjusted to pH<8 using sulfuric acid and then introduced into the columns containing spent mushroom compost operated at hydraulic loading rates of 0.05 gpm/ft<sup>2</sup> which is considered typical for engineered natural media filtration systems (ATC Report RDE 07-153). Figure 7 shows the selenium removal data from the New 17 sample using 100% spent mushroom compost. As shown in Figure 7, approximately 30% Selenium was removed in course of the 100 pore volumes of column operation. Similar removal efficiencies were noticeable in the case of Alcoa Main Seep sample, the results of which are provided in Figure 8.

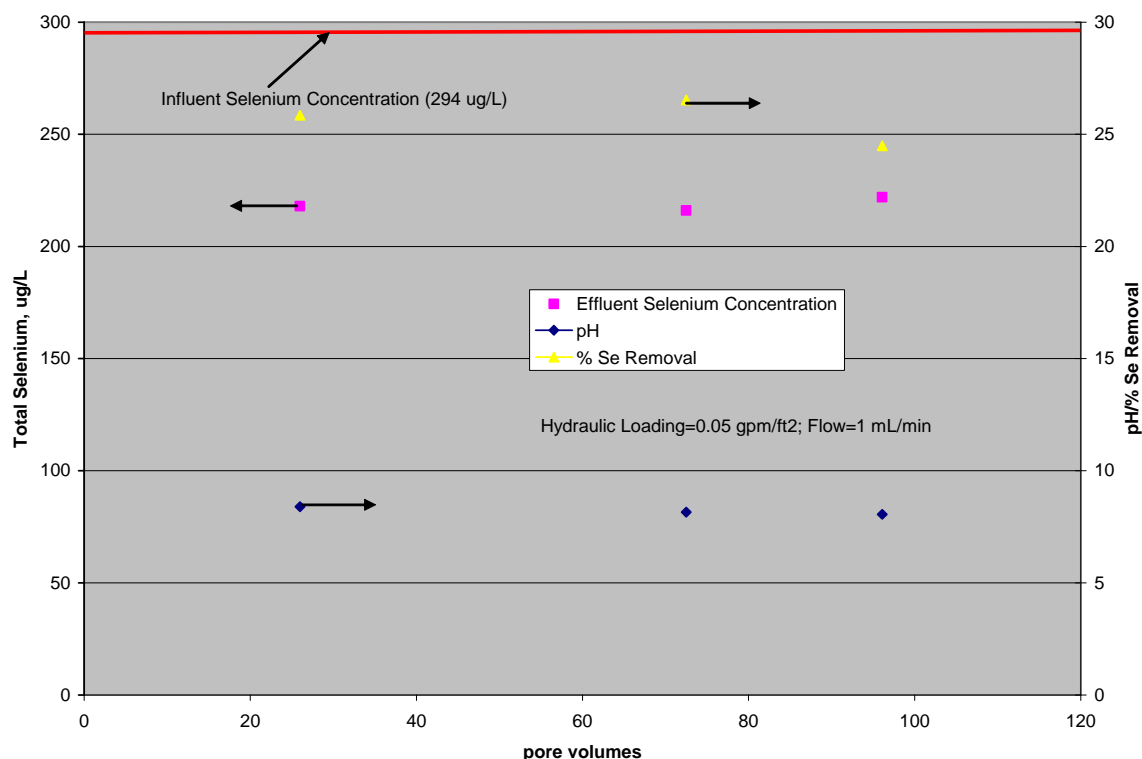


**Figure 6.** Selenium Removal from Alcoa Main Seep using 75% ZVI



**Figure 7.** Selenium Removal from New 17 sample using 100% Spent Mushroom Compost





**Figure 8.** Selenium Removal from New 17 sample using 100% Spent Mushroom Compost

### MDL/PQL Study

Table 3 presents the results of the MDL/PQL analysis for Se from randomly generated spiked samples. As shown in Table 3, the overall bias was 11.5  $\mu\text{g/L}$  and the detection limit ranges from 11.25  $\mu\text{g/L}$  to 13.4  $\mu\text{g/L}$  depending upon the nominal false positive and negative rate. Note, the EPA 40 CFR MDL is 6  $\mu\text{g/L}$  and site specific action level is 5  $\mu\text{g/L}$ . Therefore, the matrix specific MDL is almost twice as high as the EPA MDL number. The Practical Quantitation Limit (PQL) or Sample Reporting Limit is 3 times the MDL and should be around 37 ppb (3Gaverage MDL).

**Table 3.** MDL Study Results

Statistical Parameters	Values, $\mu\text{g/L}$
Bias	11.5
MDL assuming 2.5% false +ve/false -ve rate	11.25
MDL assuming 1% false +ve/false -ve rate	13.4

### Matrix Spike Study

Table 4 presents the results of the matrix spike study. As shown in Table 4, the spike recovery ranged from 88% to 90% for the Final Pond Effluent while the recovery for the New 17 sample

was between 61 and 83%. As a perspective, the acceptable spike recovery for EPA contract laboratory is within 85-110% of the spiked amount for an aqueous matrix. It appears that the lowest recovery for both the spiked matrices were from the American Interplex Corporation, the laboratory routinely used by Alcoa for analysis dissolved Se from the site. This inter-laboratory variability could be attributed to the complex nature of matrix which is evident by the high reporting limit for these samples as reported by American Interplex (RL=70 ppb) and Test America (RL=50 ppb) as well as the inter-laboratory variability in precision and analytical data quality.

**Table 4.** Matrix Spike Study Results (Spike Value = 500 ppb)

Sample ID	Baseline Concentration, ppb	Test America		American Interplex	
		Concentration, ppb	Recovery (% of original spike)	Concentration, ppb	Recovery (% of original spike)
Final Pond	18	468	90	460	88.4
New 17	124	540	83.2	430	61.2

## Discussion

The 50% ZVI-sand treatment technology has been shown to remove approximately 20% Se from the New 17 sample upon pH adjustment and almost 45% Se from Alcoa Main Seep following pH adjustment. Varying the hydraulic loading rates did not amount to any significant change in the removal rates, which is indicative of equilibrium conditions. The relatively low removal of Se from these matrices is reflective of the presence of other anions such as sulfates, which competes with selenate as electron acceptors. The RMC sumpwater however, was run without any pH adjustment and resulted in ~28% removal of Selenium without causing any hydraulic issues over 1000 pore volumes of operation. The high pH of the influent coupled with low redox potential (-90 mV) created a reducing environment conducive to low rate of ZVI oxidation to Fe(II) as well as resulting oxidation to Fe(III) which caused limited reduction of selenate but resulted in no hydraulic issues whatsoever, primarily due to the absence of hydrous ferric oxide formation. Also, the presence of other counter anions, such as sulfates (~0.66 g/L) which competes with selenate for electron acceptance attributed to limited reduction of selenate. Increasing the iron percentage did not attribute to any enhanced removal of selenate primarily because of the limited iron dissolution at the alkaline pH of the system coupled with the presence of the counter anions.

Increase in the selenate reduction is possible by decreasing the pH of influent to a near neutral regime (e.g., 9<pH<10) which will increase the rate of iron corrosion reaction and thereby increasing reducing capacity of the system. However, one should allow sufficient time for the pH adjusted influent to settle prior to ZVI treatment because of the formation of the silica gel upon lowering the pH of the RMC sumpwater. Application of compost aided anaerobic reduction of selenate resulted in approximately 30% removal of selenium from Alcoa Main Seep and New 17 samples following pH adjustment. Once again low removal of selenium seen in these compost columns could be reflective of the loading rates (residence time effect) as well as the presence of other counter anions, such as sulfates which is conducive to anaerobic reduction process.

The MDL/PQL study has revealed certain positive bias in the analysis of the samples near the method detection limit of selenium. This analysis reports a MDL which is almost a factor of 2 higher than the EPA 40CFR reported MDL for selenium analysis. This could be due to the nature of the matrix or due to analytical method interferences near the detection level of the instrument. Thus, it is not possible to reliably detect or quantify the selenium concentrations at this Outfall to the water quality criterion (chronic) for the outfall (5 µg/L). Hence, it is recommended that for the next round of permit negotiation, Alcoa should use this information to request an increase in their compliance limit to a site-specific MDL/PQL value.

The complex nature of the mine waters is further elucidated by the matrix spike recovery study where split sample analysis from two independent laboratories indicate significant analytical variability in spike recoveries on the BRDA sample (New 17). This is indicative of the high reporting limit (RL) reported by the individual laboratories which ranges from 10 to 14 times the water quality criterion (chronic) for the outfall (5 µg/L). American Interplex, the regular site laboratory had, in one case only 60% recovery, indicating that in some cases reported Se concentrations may be significantly under estimated.

## **Recommendations**

The following recommendations are made based on the results of the bench-scale treatability study:

- Retest RMC Sumpwater with 30-50% ZVI in bench-scale columns with pH of the influent adjusted ~10; this should allow for higher rate of ZVI corrosion and hence increased reducing activity which should result in higher Se removal. However, pH adjusted influent should be allowed to settle in a tank prior to treatment through the column in order to avoid the clogging of the column by silica gel formed upon lowering the pH of the RMC sumpwater. Also, because of the potential of sludge generation, some testing on determining optimum sludge production and sludge settling rates is necessary for final costing purposes
- Perform a ZVI pilot to treat a portion of the concentrated Se stream from the sumpwater on the Reynold's side without any pH adjustment of the influent. Partial treatment of Se from this source coupled with downstream dilution should be able to significantly reduce the total Se mass loading to the outfall thereby helping the site to meet compliance standards.
- Use the results of the MDL/PQL study as the basis to negotiate a higher permit limit. If necessary, perform a more comprehensive MDL/PQL study involving multiple laboratories following proper QA/QC guidelines and communicate the results of the analysis to Arkansas Department of Environmental Quality. This is essential to demonstrate to the regulatory agency that currently it is not possible to reliably detect or quantify the selenium concentrations at this Outfall to the water quality criterion (chronic) for the outfall (5 µg/L).

- As far as the current laboratory in use, perform an audit to understand the issue of poor recovery, whether it is related to the poor quality of analysis; if necessary need to change laboratory for routine sample analysis.

## **References**

RDE 07-153, Treatment of Water Containing Low Levels of PCBs Using Natural Media Filtration, ATC, 2007

# **ATTACHMENT 5**

---

**Technical Memo – Biological Selenium Reduction Experiment**



water resources / environmental consultants

3 Innwood Circle • Suite 220 • Little Rock, AR 72211 • (501) 225-7779 • Fax (501) 225-6738

**DATE:** March 26, 2007

**TO:** Mr. Pat Keogh  
Alcoa, Inc.

**FROM:** Rex Robbins, PE  
FTN Associates, Ltd.

**SUBJECT:** Selenium Treatment Experiments *RMR*  
FTN No. 6012-244

---

## INTRODUCTION

FTN Associates, Ltd. (FTN) and Alcoa have performed a series of experiments to determine the feasibility of reducing selenium in the water discharged from Alcoa's site. Several treatment options have been studied in small-scale experiments in anticipation of finding an option that could be tested in a pilot-scale experimental program.

American Interplex determined that the selenium in the samples from Alcoa exists primarily as Se+6, which is the highly soluble selenate form. If a chemical reducing agent or a biological method could be identified that would convert the existing selenate to the selenite form, the subsequent removal of the suspended selenium using filtration or precipitation would be straightforward.

The first phase of the bench-scale testing involved the use of chemical techniques that have been applied with success for the treatment of heavy metals. Much of this testing involved the use of chemical reagents that produce reducing conditions in water.

Several reagents were obtained and tested including sodium bisulfite, iron sulfate, copper sulfate, iron chloride, and granular zinc. For this initial test, a standard dose of each reagent was applied to samples of neutralized leachate water and water from 3-Pond. Insitu measurements were made, including the oxidation-reduction-potential (ORP). The treated water was observed for changes to physical characteristics, such as color and the appearance of any suspended solids. Samples of decanted water were collected from each beaker and sent to American Interplex for testing for soluble and total selenium. The results of the laboratory testing did not indicate any significant differences in selenium concentrations between the treated and untreated samples.

It should be noted that the results using chemical reagents seem to be consistent with the literature on this subject. While some experimental methods have been described for selenium treatment, the literature search conducted as part of this study did not reveal any successful applications of chemical treatment that was specific for the selenate form of selenium.

The second phase of the experimental process was to test biological methods as a means to convert the dissolved selenium to an insoluble form that can be separated from the water. The literature indicates that biological processes have been applied for reducing selenium concentrations even when the selenium exists as the selenate form.

In the initial biological testing, water from 3-Pond was collected into two five-gallon plastic carboys. One carboy was used as the control (1A) container and the second was used as the experimental (1D) container. The test sample was spiked with fresh activated sludge obtained from a local municipal wastewater treatment plant. An organic feedstock (molasses) was added as a food source to the experimental container. Initially, only 2-3 drops of molasses was used.

Over the course of several days, dissolved oxygen and pH values were recorded for both containers. The initial experiments (1A and 1D) were repeated (1A.2 and 1D.2) with a change in the amount of molasses added. A higher dose of molasses was necessary to reduce the dissolved oxygen levels during the test.

The following table provides analytical results for each of the four samples as well as a raw 3-Pond water sample submitted on February 2, 2007.

During the initial experiment the dissolved oxygen did not drop as rapidly or as low as anticipated. This is possibly due to the amount of food provided to the system in the form of molasses. It may also have resulted from the lack of mixing in the system, which minimized the contact of bacteria, oxygen and food. When the amount of food was increased for the second run of the experiment, the dissolved oxygen dropped much more rapidly and remained at a low level. The selenium results reflect a significant difference between the two experiments. Very little reduction was seen in the first experiment and approximately 50% reduction was seen in the second experiment.

Table 2. Selenium Concentrations.

	Raw	1A	1D	1A.2	1D.2
Total Selenium (mg/l)	0.013	0.011	0.01	0.014	0.0082
Dissolved Selenium (mg/l)	0.012	0.011	0.0096	0.013	0.0057

## CONCLUSIONS AND RECOMMENDATIONS

Based on this preliminary and simple testing approach, biological treatment has demonstrated the potential for treating selenium at the Alcoa facility. Further experimentation is needed to more fully evaluate the conditions and mixing needed for the process to work optimally.

1. Complete additional bench-scale biological treatment experiments to calculate the effect of carbon feedstock dose and retention time. The potential for algae to provide the carbon source for this process also needs to be investigated. This information is necessary to develop the design of a pilot-scale test.

Mr. Pat Keogh  
March 26, 2007  
Page 3

2. Design the pilot scale system. Provide the design, project budget, and operating protocols for the pilot test to Alcoa for review and comments.
3. Construct and run the pilot-scale biological treatment system.
4. Summarize pilot scale data and complete a summary technical memorandum that provides conclusions of the potential success of the treatment process to either reduce discharge selenium concentrations or reduce selenium mass (a quantifiable reduction) in the water collection and treatment system at Alcoa Bauxite. Provide associated budget (capital and O&M) estimates to design/construct the full-scale system.
5. Alcoa and FTN meeting to discuss the results and the potential full-scale system.
6. Present the treatability testing summary information and data to ADEQ and discuss future steps to manage and monitor selenium at the site (i.e., integrate these data into the proposed management approach on a timeframe that will coordinate with NPDIS permit requirements).

RMR/jsl

R:\WP\_FILES\6012-244\M - P KEOGH 03-26-07\CORRESPONDANCE\M- P KEOGH 3-26-07.DOC







Alcoa Inc.  
ATTN: Mr. Pat Keogh  
Post Office Box 290  
Bauxite, AR 72011-0290

Dear Mr. Pat Keogh:

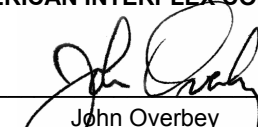
Project Description: Two (2) water sample(s) received on February 26, 2007  
Alcoa SE  
6012-244b  
P.O. No. 190030460

This report is the analytical results and supporting information for the samples submitted to American Interplex Corporation (AIC) on February 26, 2007. The following results are applicable only to the samples identified by the control number referenced above. Accurate assessment of the data requires access to the entire document. Each section of the report has been reviewed and approved by the appropriate laboratory director or a qualified designee.

Data has been validated using standard quality control measures performed on at least 10% of the samples analyzed. Quality Assurance, instrumentation, maintenance and calibration were performed in accordance with guidelines established by the cited methodology.

**AMERICAN INTERPLEX CORPORATION**

By \_\_\_\_\_

  
John Overbey  
Laboratory Director

Enclosure(s): Chain of Custody

PDF cc: FTN Associates, Ltd.  
ATTN: Mr. Matt Burnham  
mwb@ftn-assoc.com

FTN Associates, Ltd.  
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Alcoa Inc.  
ATTN: Mr. Pat Keogh  
patrick.keogh@alcoa.com

FTN Associates, Ltd.  
ATTN: Mr. Jimmy Rogers  
jjr@ftn-assoc.com

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

CASE NARRATIVE

SAMPLE RECEIPT

Received Temperature: 1°C

Receipt Verification:	Complete Chain of Custody	Y
	Sample ID on Sample Labels	Y
	Date and Time on Sample Labels	Y
	Proper Sample Containers	Y
	Within Holding Times	Y
	Adequate Sample Volume	Y
	Sample Integrity	Y
	Proper Temperature	Y
	Proper Preservative	Y

COMMENTS

There were no qualifiers for this data and all samples met quality control criteria.

References:

"Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79-020 (Mar 1983) with updates and supplements EPA/600/5-91-010 (Jun 1991), EPA/600/R-92-129 (Aug 1992) and EPA/600/R-93-100 (Aug 1993).

"Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846)", Third Edition.

"Standard Methods for the Examination of Water and Wastewaters", 20th edition, 1998.

"American Society for Testing and Materials" (ASTM).

"Association of Analytical Chemists" (AOAC).

"Self-Davis and Moore" (2000).

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290ANALYTICAL RESULTS

AIC No. 107612-1

Sample Identification: 3 Pond Bio 1A.2 2/26/07/0730

Analyte	Method	Result	RL	Units	Batch	Qualifier
Selenium	EPA 200.8	0.014	0.002	mg/l	S19904	
Dissolved: Selenium	EPA 200.8	0.013	0.002	mg/l	S19904	

AIC No. 107612-2

Sample Identification: 3 Pond Bio 1D.2 2/26/07/0730

Analyte	Method	Result	RL	Units	Batch	Qualifier
Selenium	EPA 200.8	0.0082	0.002	mg/l	S19904	
Dissolved: Selenium	EPA 200.8	0.0057	0.002	mg/l	S19904	



Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

SAMPLE PREPARATION REPORT

AIC No. 107612-1

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	27FEB07	1219 117	27FEB07	1650 117		S19904	
Dissolved: Metals	27FEB07	1219 117	27FEB07	1643 117		S19904	

AIC No. 107612-2

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	27FEB07	1219 117	27FEB07	1703 117		S19904	
Dissolved: Metals	27FEB07	1219 117	27FEB07	1656 117		S19904	

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

LABORATORY CONTROL SAMPLE RESULTS

Analyte	Spike Amount	% Recovery	% Recovery Limits	RPD	RPD Limit	Batch	Qualifier
Selenium	0.05 mg/l	104	85-115	-	20	S19904	

MATRIX SPIKE SAMPLE RESULTS

Analyte	Spike Amount	% Recovery	% Recovery Limits	RPD	RPD Limit	Batch	Qualifier
Selenium	0.05 mg/l	102/101	75-125	0.682	20	S19904	

LABORATORY BLANK RESULTS

Analyte	Method	Result	Units	RL	QC Sample	Qualifier
Selenium	EPA 200.8	< 0.002	mg/l	0.002	S19904-1	

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

QUALITY CONTROL PREPARATION REPORT

LABORATORY CONTROL SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	27FEB07	1220 117	27FEB07	1503 117		S19904-2	

MATRIX SPIKE SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	27FEB07	1220 117	27FEB07	1510 117		S19904-3	
Metals	27FEB07	1220 117	27FEB07	1517 117		S19904-4	

LABORATORY BLANKS

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	27FEB07	1220 117	27FEB07	1457 117		S19904-1	



107612

Date 2/26/07	Project Name Alcoa SE	Project No. 6012-244b	Project Manager (Print) RMR	Page 1 of 1
Report / Bill to: ALCOA	Submitted by: FTN Associates, Ltd. 3 Innwood Circle, Suite 220 Little Rock, AR 72211 (501) 225-7779 • Fax (501) 225-6738			Lab Turn-Around-Time <input type="checkbox"/> 24 Hours <input type="checkbox"/> 48 Hours <input checked="" type="checkbox"/> Normal <input type="checkbox"/> Other: Due: ____/____/____
Phone:				
Sampler Signature(s) <i>Jim Rogers</i>	Recorded By (Print) Jimmy Rogers			
SAMPLE DESCRIPTION				
Sample Identification	Date	Time	Matrix* W S O	No. of Containers
3 Pond bio 1A.2	2/26/07	0730	X	2
3 Pond bio 1D.2	2/26/07	0730	X	2
Total Selenium				
			X	
			X	
SE, DISS				
			X	
			X	
Detection Limits				
Parameter				Detection Limit
				Low Level SE
Container Type				
			P	
Preservative				
			N	
* Matrix: W = Water S = Soil O = Other G = Glass P = Plastic H = HCl to pH2 T = Sodium Thiosulfate NO = None S = Sulfuric acid pH2 B = NaOH to pH12 Z = Zinc acetate V = VOA vials N = Nitric acid pH2				
Relinquished By (Signature) <i>Jim Rogers</i>	Print Name Jimmy Rogers	Date 2/26/07	Time 0730	Received By (Signature) <i>Jimmy Rogers</i>
Relinquished By (Signature) <i>Jim Rogers</i>	Print Name Jimmy Rogers	Date 2/26/07	Time 0730	Received By Laboratory (Signature) <i>Jimmy Rogers</i>
Laboratory Remarks: Jimmy Day				
Sampler Remarks: *ALCOA LIST jir@ftn-assoc.com				



Alcoa Inc.  
ATTN: Mr. Pat Keogh  
Post Office Box 290  
Bauxite, AR 72011-0290

Dear Mr. Pat Keogh:

Project Description: Two (2) water sample(s) received on February 12, 2007  
Alcoa SE  
6012-2446  
P.O. No. 190030460

This report is the analytical results and supporting information for the samples submitted to American Interplex Corporation (AIC) on February 12, 2007. The following results are applicable only to the samples identified by the control number referenced above. Accurate assessment of the data requires access to the entire document. Each section of the report has been reviewed and approved by the appropriate laboratory director or a qualified designee.

Data has been validated using standard quality control measures performed on at least 10% of the samples analyzed. Quality Assurance, instrumentation, maintenance and calibration were performed in accordance with guidelines established by the cited methodology.

**AMERICAN INTERPLEX CORPORATION**

By \_\_\_\_\_

A handwritten signature in black ink, appearing to read 'John Overbey', written over a horizontal line. Below the signature, the text 'John Overbey' and 'Laboratory Director' are printed.

John Overbey  
Laboratory Director

Enclosure(s): Chain of Custody

PDF cc: FTN Associates, Ltd.  
ATTN: Mr. Matt Burnham  
mwb@ftn-assoc.com

FTN Associates, Ltd.  
ATTN: Mr. Nathan Siria  
njs@ftn-assoc.com

Alcoa Inc.  
ATTN: Ms. Jennifer Mitchell  
jennifer.mitchell2@alcoa.com

FTN Associates, Ltd.  
ATTN: Mr. Jim Malcolm  
jtm@ftn-assoc.com

Alcoa Inc.  
ATTN: Mr. Pat Keogh  
patrick.keogh@alcoa.com

FTN Associates, Ltd.  
ATTN: Mr. Jimmy Rogers  
jjr@ftn-assoc.com



Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

CASE NARRATIVE

SAMPLE RECEIPT

Received Temperature: 4°C

Receipt Verification:	Complete Chain of Custody	Y
	Sample ID on Sample Labels	Y
	Date and Time on Sample Labels	Y
	Proper Sample Containers	Y
	Within Holding Times	Y
	Adequate Sample Volume	Y
	Sample Integrity	Y
	Proper Temperature	Y
	Proper Preservative	Y

COMMENTS

There were no qualifiers for this data and all samples met quality control criteria.

References:

"Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79-020 (Mar 1983) with updates and supplements EPA/600/5-91-010 (Jun 1991), EPA/600/R-92-129 (Aug 1992) and EPA/600/R-93-100 (Aug 1993).

"Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846)", Third Edition.

"Standard Methods for the Examination of Water and Wastewaters", 20th edition, 1998.

"American Society for Testing and Materials" (ASTM).

"Association of Analytical Chemists" (AOAC).

"Self-Davis and Moore" (2000).

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

ANALYTICAL RESULTS

AIC No. 107236-1

Sample Identification: 3 Pond bio 1A 2/12/07 / 0800

Analyte	Method	Result	RL	Units	Batch	Qualifier
Selenium	EPA 200.8	0.011	0.002	mg/l	S19799	
Dissolved: Selenium	EPA 200.8	0.011	0.002	mg/l	S19799	

AIC No. 107236-2

Sample Identification: 3 Pond bio 1D 2/12/07 / 0800

Analyte	Method	Result	RL	Units	Batch	Qualifier
Selenium	EPA 200.8	0.010	0.002	mg/l	S19799	
Dissolved: Selenium	EPA 200.8	0.0096	0.002	mg/l	S19799	

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

SAMPLE PREPARATION REPORT

AIC No. 107236-1

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	13FEB07	1040 117	13FEB07	1451 117		S19799	
Dissolved: Metals	13FEB07	1040 117	13FEB07	1458 117		S19799	

AIC No. 107236-2

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	13FEB07	1040 117	13FEB07	1511 117		S19799	
Dissolved: Metals	13FEB07	1040 117	14FEB07	1902 117		S19799	

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

SAMPLE DUPLICATE RESULTS

AIC No. 107236-1

Analyte	Method	Sample Result	Duplicate Result	Units	RPD	RPD Limit	Batch	Qualifier
Selenium	EPA 200.8	0.011	0.011	mg/l		-	S19799	

LABORATORY CONTROL SAMPLE RESULTS

Analyte	Spike Amount	% Recovery	% Recovery Limits	RPD	RPD Limit	Batch	Qualifier
Selenium	0.05 mg/l	102	85-115	-	20	S19799	

LABORATORY BLANK RESULTS

Analyte	Method	Result	Units	RL	QC Sample	Qualifier
Selenium	EPA 200.8	< 0.002	mg/l	0.002	S19799-1	

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

QUALITY CONTROL PREPARATION REPORT

DUPLICATE SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	13FEB07	1041 117	13FEB07	1445 117		S19799-5	

LABORATORY CONTROL SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	13FEB07	1041 117	13FEB07	1425 117		S19799-2	

MATRIX SPIKE SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	13FEB07	1041 117	13FEB07	1438 117		S19799-4	

LABORATORY BLANKS

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	13FEB07	1041 117	13FEB07	1418 117		S19799-1	





Alcoa Inc.  
ATTN: Mr. Pat Keogh  
Post Office Box 290  
Bauxite, AR 72011-0290

Dear Mr. Pat Keogh:

Project Description: One (1) water sample(s) received on February 20, 2007  
Alcoa SE  
6012-244b  
P.O. No. 190030460

This report is the analytical results and supporting information for the sample submitted to American Interplex Corporation (AIC) on February 20, 2007. The following results are applicable only to the sample identified by the control number referenced above. Accurate assessment of the data requires access to the entire document. Each section of the report has been reviewed and approved by the appropriate laboratory director or a qualified designee.

Data has been validated using standard quality control measures performed on at least 10% of the samples analyzed. Quality Assurance, instrumentation, maintenance and calibration were performed in accordance with guidelines established by the cited methodology.

**AMERICAN INTERPLEX CORPORATION**

By \_\_\_\_\_

A handwritten signature in black ink, appearing to read 'John Overbey', written over a horizontal line.

John Overbey  
Laboratory Director

Enclosure(s): Chain of Custody

PDF cc: FTN Associates, Ltd.  
ATTN: Mr. Matt Burnham  
mwb@ftn-assoc.com

FTN Associates, Ltd.  
ATTN: Mr. Nathan Siria  
njs@ftn-assoc.com

Alcoa Inc.  
ATTN: Ms. Jennifer Mitchell  
jennifer.mitchell2@alcoa.com

FTN Associates, Ltd.  
ATTN: Mr. Jim Malcolm  
jtm@ftn-assoc.com

Alcoa Inc.  
ATTN: Mr. Pat Keogh  
patrick.keogh@alcoa.com

FTN Associates, Ltd.  
ATTN: Mr. Jimmy Rogers  
jjr@ftn-assoc.com

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

CASE NARRATIVE

SAMPLE RECEIPT

Received Temperature: 1°C

Receipt Verification:	Complete Chain of Custody	Y
	Sample ID on Sample Labels	Y
	Date and Time on Sample Labels	Y
	Proper Sample Containers	Y
	Within Holding Times	Y
	Adequate Sample Volume	Y
	Sample Integrity	Y
	Proper Temperature	Y
	Proper Preservative	Y

COMMENTS

There were no qualifiers for this data and all samples met quality control criteria.

References:

"Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79-020 (Mar 1983) with updates and supplements EPA/600/5-91-010 (Jun 1991), EPA/600/R-92-129 (Aug 1992) and EPA/600/R-93-100 (Aug 1993).

"Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846)", Third Edition.

"Standard Methods for the Examination of Water and Wastewaters", 20th edition, 1998.

"American Society for Testing and Materials" (ASTM).

"Association of Analytical Chemists" (AOAC).

"Self-Davis and Moore" (2000).





Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

ANALYTICAL RESULTS

AIC No. 107468-1

Sample Identification: 3 Pond 2/20/07/1034

Analyte	Method	Result	RL	Units	Batch	Qualifier
Selenium	EPA 200.8	0.013	0.002	mg/l	S19856	
Dissolved: Selenium	EPA 200.8	0.012	0.002	mg/l	S19856	



Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

SAMPLE PREPARATION REPORT

AIC No. 107468-1

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	21FEB07	1206 263	22FEB07	1419 117		S19856	
Dissolved: Metals	21FEB07	1206 263	22FEB07	1412 117		S19856	

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

LABORATORY CONTROL SAMPLE RESULTS

Analyte	Spike Amount	% Recovery	% Recovery Limits	RPD	RPD Limit	Batch	Qualifier
Selenium	0.05 mg/l	100	85-115	-	20	S19856	

MATRIX SPIKE SAMPLE RESULTS

Analyte	Spike Amount	% Recovery	% Recovery Limits	RPD	RPD Limit	Batch	Qualifier
Selenium	0.05 mg/l	97.1/96.7	75-125	0.386	20	S19856	

LABORATORY BLANK RESULTS

Analyte	Method	Result	Units	RL	QC Sample	Qualifier
Selenium	EPA 200.8	< 0.002	mg/l	0.002	S19856-1	

Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

QUALITY CONTROL PREPARATION REPORT

LABORATORY CONTROL SAMPLES

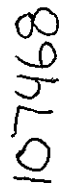
Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	21FEB07	1206 263	22FEB07	1209 117		S19856-2	

MATRIX SPIKE SAMPLES

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	21FEB07	1206 263	22FEB07	1216 117		S19856-3	
Metals	21FEB07	1206 263	22FEB07	1222 117		S19856-4	

LABORATORY BLANKS

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	QC Sample	Qualifier
Metals	21FEB07	1206 263	22FEB07	1202 117		S19856-1	

Revision Date 11/22/02

## **ATTACHMENT 6**

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**Technical Memo – Biological Treatability Test Procedures at New 17**

## **TECHNICAL MEMO**

**TO:** Files

**FROM:** Rex Robbins

**RE:** Biological Treatability Test Procedures  
Alcoa Selenium Study

**DATE:** 5/23/07

---

### **PURPOSE:**

This treatability test will apply microbes operating in an anoxic environment to reduce selenate to selenite (and/or elemental selenium). Similar testing has demonstrated that this reaction can be successfully applied to the treated water from Pond 3 at the Alcoa facility. This series of tests will utilize leachate water collected from the New 17 pit. Acid Mine Drainage (AMD) will be used as a diluent for some of the test setups. Once formed, it is expected that the selenite or selenium can be filtered from the water.

The tests will give some information regarding the relative effect of dilution using AMD and the effect of different pH endpoints on the microbial activity and selenium reduction.

### **EQUIPMENT/SUPPLIES:**

1. Three 40-gallon plastic drums,
2. Nine 5-gallon bottled-water carboys,
3. One 7-gallon water tote,
4. 10N sulfuric acid,
5. 40 gallons of New 17 water,
6. 20 gallons of Old 17 water,
7. 5 gallons from Pond 3,
8. 2 gallons – Activated sludge from municipal wastewater plant, and
9. 500 mls – molasses.

### **PROCEDURE:**

- About 25 gallons of leachate water from the New 17 pit will be placed in each of two drums. The other drum will be used to collect about 20 gallons of acid mine

drainage (AMD) collected from Old 17. The sample of activated sludge will be pulled within two days of the test setup and kept refrigerated until mixing. Samples of the leachate water and the AMD will be collected and analyzed for total selenium and TDS.

- Mixtures of leachate and AMD will be prepared in 7-gallon water totes according to the following schedule.
  - a. Samples 1a and 1b - 6 gallons of leachate water,
  - b. Samples 2a and 2b - 5 gallons of leachate and 1 gallons of AMD,
  - c. Samples 3a and 3b - 3 gallons of leachate and 3 gallons of AMD,
  - d. Samples 4a and 4b - 2 gallons of leachate and 4 gallons of AMD, and
  - e. Sample 5 - 5 gallons from Pond 3.

For each sample (1-4), sulfuric acid will be added into the water tote containing the mixture to lower the pH. The water will be mixed with a paint stirrer or by shaking the tote. For the “a” samples, the pH will be lowered to pH 7.5 using 10N sulfuric acid. For the “b” samples, the pH will be stabilized at pH 8.5, using acid as needed. The mixer will then be turned off and any precipitated solids will be allowed to settle for at least two hours.

Water will be poured from the tote into a 5-gallon carboy. Each carboy will be filled with the decanted water with as few solids carryover as possible. About 500 mls of water will be removed from each carboy and replaced with 500 mls of activated sludge.

Each carboy will be prepared by adding a dose of molasses equal to about 50 mg/L. (Each carboy will be capped allowing the least possible head space). The test will be run for 14 days minimum with periodic checks for in situ readings. In situ readings should be taken after 24 hours, and after 3, 7, and 14 days. During this time and for the extent of the test, each of the 10 carboys will be inverted gently at least once a day to allow mixing. At the end of the 14 days, the carboys will be opened, in situ readings (dissolved oxygen and pH) will be taken, and samples collected.

Based on the in situ readings, samples will be submitted to American Interplex for testing for dissolved and total selenium.

JJR/ack



Alcoa Arkansas Remediation Selenium Treatability Study  
Biological Treatability  
Test Study Results

Source Data	Selenium (mg/L)
New 17 untreated	0.13
AMD	<.005 ug
Pond 3 (existing treatment system)	0.0077

Experimental Results	Mixture Ratio				Initial pH	Acid	Acid Added (mL)	mL of Acid Added/ 1 gal New 17	Final pH	Initial Selenium (mg/L)	Selenium after 21 days (mg/L)	Selenium % Removal (Adjusted for any mixture)
Carboy	New 17 (gal)	Acid Mine Drainage (gal)	Activated Sludge	Molasses								
1A	6	0	500 mL	50 mg/L	12.8	10 N H <sub>2</sub> SO <sub>4</sub>	298.5	-----	7.55	0.1300	0.058	55.38%
1B	6	0	500 mL	50 mg/L	12.46	Alcoa H <sub>2</sub> SO <sub>4</sub>	82	13.67	8.47	0.1300	0.066	49.23%
2A	5	1	500 mL	50 mg/L	12.27	Alcoa H <sub>2</sub> SO <sub>4</sub>	73.5	14.70	7.53	0.1083	0.05	53.85%
2B	5	1	500 mL	50 mg/L	12.37	Alcoa H <sub>2</sub> SO <sub>4</sub>	72.25	14.45	8.49	0.1083	0.052	52.00%
3A	3	3	500 mL	50 mg/L	12.1	Alcoa H <sub>2</sub> SO <sub>4</sub>	42.5	14.17	7.53	0.0650	0.032	50.77%
3B	3	3	500 mL	50 mg/L	12.12	Alcoa H <sub>2</sub> SO <sub>4</sub>	41.5	13.83	8.51	0.0650	0.031	52.31%
4A	2	4	500 mL	50 mg/L	11.97	Alcoa H <sub>2</sub> SO <sub>4</sub>	27.25	13.63	7.46	0.0433	0.023	46.92%
4B	2	4	500 mL	50 mg/L	11.98	Alcoa H <sub>2</sub> SO <sub>4</sub>	26.5	13.25	8.57	0.0433	0.025	42.31%

**Procedures:**

Water was added to totes in the described mixture ratio above. For each sample (1-4) sulfuric acid was added to stabilize the pH at 7.5 for "A" carboys and 8.5 for "B" Carboys. Solids were allowed to settle overnight. Water was then decanted to carboys from the totes. In addition to the water from the totes the carboys also contained 500 mL of activated sludge and 50 mg/L of molasses. Carboys were held at zero head space. The carboys were capped on June 19, 2007 and samples were taken July 10, 2007. In-Situ readings can be found on the accompanying sheets.

Sample	Temp.	DO	SpC	pH	ORP
1A	22.79	0.21	15261	7.36	-217
1B	22.74	0.34	15389	8.03	-228
2A	22.85	0.4	13230	7.24	-226
2B	22.87	0.31	12182	8.12	-263
3A	22.74	0.73	8683	7.26	-209
3B	22.76	0.4	8755	7.9	-218
4A	22.74	0.25	6178	7.14	-189
4B	22.7	0.35	6138	7.77	-240
3 Pond	22.81	0.54	2534	7.2	-161

Date: June 21, 2007

In-Situ Readings on Carboys listed above

# **ATTACHMENT 7**

---

**Technical Memo – PLANTECO Report**

# **Using Microbial Mats to Remove Selenium from Acid Mine Drainage - Bench-Scale Treatability Tests**

**Bench Scale Treatability Study Report Prepared for:**



**FTN Associates, LTD.**

**3 Innwood Circle  
Little Rock, AR 72211  
PHONE: (501) 225-7779**

**Submitted by:**



**PLANTECO Environmental Consultants, LLC**

**337 South Milledge, Suite 202**

**Athens, Georgia 30605**

**Phone: (706) 316-3525**

**Fax: (706) 542-6803**

**September 3<sup>rd</sup>, 2007**

## **Background**

### **What are Constructed Microbial Mats (CMM)?**

Constructed microbial mats consist of biological organisms that self-associate to form a complex ecosystem capable of removing contaminants from the environment. The constructed microbial mat comprises cyanobacteria and purple autotrophic bacteria and other microorganisms organized into a layered structure which is held together with slime, and has an organic nutrient source provided (Figures 1 & 2). Like the other active microbial systems, the microbial mats are able to simultaneously sequester heavy metals and degrade organic contaminants. The overall oxygen concentration in the system can be controlled by manipulation of the activity of oxygen producing phototrophic bacteria using lighting intensity (Figure 3). Together with different metabolic zones (micro-environments) within the mat, a variety of bioremediation reactions are enabled, such as anoxic bioreduction of metals (e.g. Cr(VI) to Cr(III), Se(IV or VI) to Se(0)), metabolism of perchlorate and explosives, sequestration and metabolism of petrochemicals, dechlorination of trichlorethylene, or nitrification under highly oxic conditions.

*Microbial Aquatic Treatment Systems (MATS)* have been tested at the pilot level, applying the following treatment designs (Patent US6033559):

- Floating mats on ponds, with low-flow or batch mode, can treat large volumes of water economically (e.g. removal of manganese from acid coal mine drainage).
- Dry mat has been used as biosorbents for removal of organics and metals from water.
- Mats immobilized as biofilms on vertical boards have been tested for the final polishing treatment of radioactive water.
- Mat microbes have also been immobilized in silica particles and tested for the removal of a menu of radionuclides, including plutonium and uranium. With the words of a co-inventor of biomats, “this immobilization represents an important advance of the technology in terms of the rates of removal and ease of engineering and management”.

The distinguishing feature and advantage of MATS, compared with all other systems using active microorganisms, is the integration of photosynthetic bacteria into the microbial consortium, creating a self-sustainable system with minimal need for supplemental nutrition.

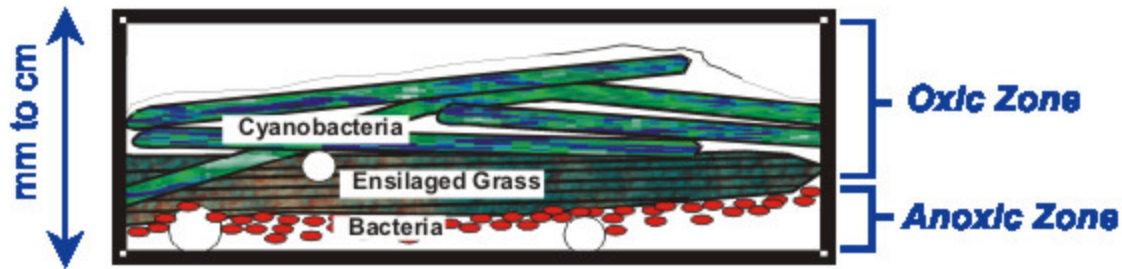


Figure 1. Schematic Cross-Section of Microbial Mat



Figure 2. Microbial Mat

### Mechanisms of Metal Removal in Microbial Mats Treatment Systems

Previous research has proven that mats will adsorb and sequester a variety of metals including As, Mn, Fe, Pb, Al, Zn, Th, Se, and Cu, and they have been successfully tested on waste streams generated at multiple mine sites, including acid mine drainage (Bender et al 2000; Bender and Phillips, 1995; Bender et al 1994<sup>1</sup>; Bender et al 1994<sup>2</sup>; Phillips, et al, 1993; Bender et al 1991; Bender and Ibeanusi 1987). The CMM have also effectively removed dissolved uranium and mercury from wastewater (Bender et al, 2000; O’Niell and Noakes, unpublished).

Mats can remove metals, metaloids, radionuclides, and oxyanions from water through several different mechanisms:

- Ion exchange/sorption – Mats provide huge negatively charged surface area for binding positively charged metals, and surface binding and ion exchange mechanisms are involved in the metal removal process. Once all the binding sites are filled with metals, a period of regrowth is needed to rejuvenate the mats.
- Reduction – Many metals (e.g.,  $U^{6+}$ ,  $Cr^{6+}$ , and  $Se^{6+}$ ) must be reduced for removal to occur. Metals are reduced in the anoxic reducing zones created in mats at night or in mats maintained in dark or low light conditions. Once these metals are reduced they will precipitate as oxides, hydroxides or sulfides.

- Oxidation – Some metals (e.g., manganese) are oxidized and precipitated. Mats are photosynthetic and can saturate the water with oxygen during daylight hours.
- Biofloculants – Mats produce negatively charged carbohydrate molecules that act as biofloculants to bind metals and cause them to precipitate out of the water column.

Initial tests conducted by PLANTECO indicate that mats will remove selenium from the aqueous phase, but additional research is needed. In sediment water systems, selenium exists as either a water soluble selenate ( $\text{Se}^{6+}$ ) or water insoluble selenite ( $\text{Se}^{4+}$ ) or elemental selenium ( $\text{Se}^0$ ). The water soluble selenate would likely be most common in the AMD. In the CMM treatment system, the positively charged ion would be attracted to the negatively charged mat surface where it will be bound and removed from the waste stream. Under the anoxic zone of the CMM, selenate will act as a terminal electron acceptor and be reduced to insoluble selenite or selenium, and precipitated out of the waste stream. The conditions needed for the reduction of selenate are present within mat systems: low oxygen levels (anaerobic reducing conditions) are created within certain portions of the mat and in the dark or low light conditions, sulfate reducing zone and the exudation of reductase enzymes.

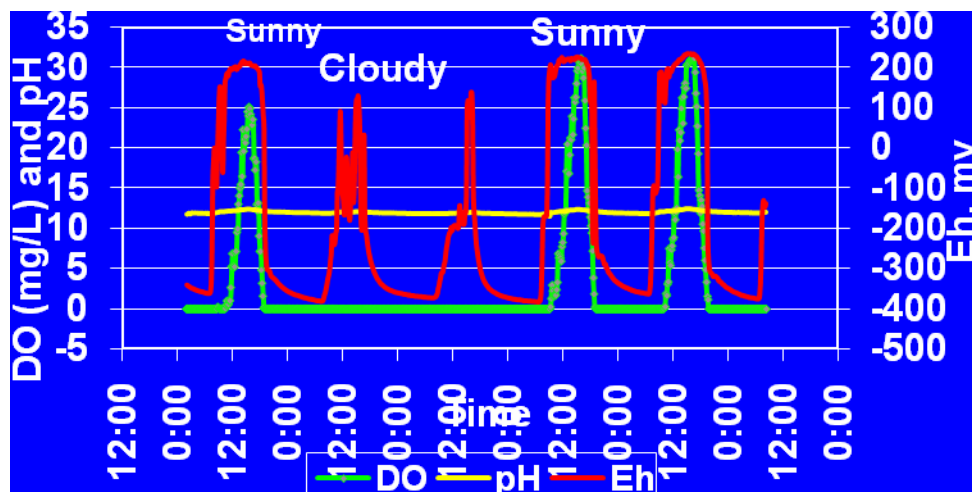


Figure 3. Changes in DO, pH and Eh levels in a microbial Mat bioreactor

**Microbial Mats and Biodegradation of Organic Compounds** - The mats are photoautotrophs that can saturate the aqueous phase with oxygen (12 mg/L) during the daylight hours and have the potential to degrade organics through oxidative pathways. At night the mats consume the oxygen and provide an environment where organic contaminants can be reductively degraded (Nzengung et al, 2002; O’Niell and Nzengung, 2000; O’Niell et al, 2000<sup>1</sup>; O’Niell et al, 2000<sup>2</sup>; O’Niell et al, 1998; Murray et al, 1997;

O’Niell et al, 1997). Microbial mats have been shown to adsorb dissolved phase organic contaminants from water in a matter of seconds to minutes (O’Niell, et al, 2000). Thus, microbial mats can also be used as biosorbents for anthropogenic organic contaminants in water.

**Pilot Scale Application of Microbial Mats for Selenium Removal** – Extensive experiments have NOT been conducted to establish the most effective methods of implementing microbial mat technology for selenium removal from wastewater. PLANTECO proposes the following conceptual treatment systems:

#### A. For lower volumes of waste water

Solar-powered “plate and shelf” bioreactor (Figures 4 and 5) – This bioreactor was developed and tested for removal of contaminants at a remote location. It consists of a 2m x 1m x 1m Plexiglas® box with 5 removable shelves. The cyanobacteria are grown on synthetic fiber mats that fit onto each of the shelves. A solar-powered pump is used to transfer the contaminated water into the top of the reactor. The water flows by gravity through each of the layers of mat, the metals and other contaminants are removed and clean water flows through an outlet at the base.

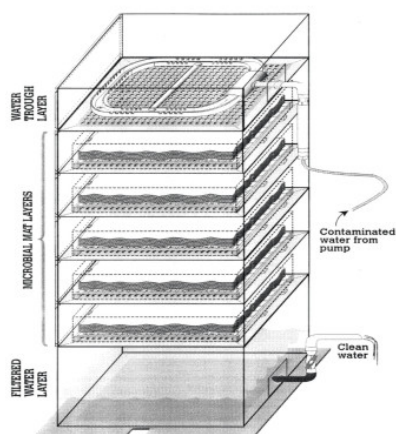


Figure 4. Schematic of Microbial Mat Bioreactor



Figure 5. Photo of

#### B. Shallow Lagoon Treatment Wetlands

This technique would be used to treat larger volumes of the mine wastewater in shallow ponds. Mine wastewater will be mostly treated in the front end of the wetland where floating microbial mats would remove the selenium (Figure 6). Treated water leaving the floating CMM front-end of the shallow pond will flow through an area planted with aquatic plants to polish-up the water. Terrestrial plants known to



remove selenium would also be planted in the wetland to further enhance selenium removal. Data from the bench scale treatability tests will provide preliminary data for estimation of the treatment volume for each of the currently unused ponds.

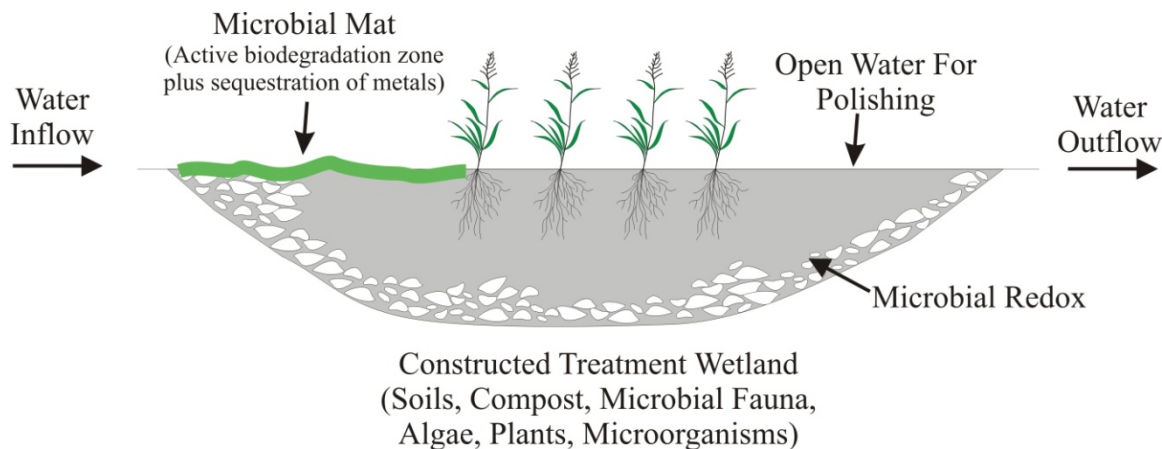


Figure 6. Conceptual Design of a Microbial Mat/Constructed Treatment Wetland

**Advantages of Microbial Mat Systems** – The microbial mat bioremediation system provides several unique advantages over conventional techniques:

- i. **Low cost** - microbial mat can be “farmed” at very low costs. Ensilaged grass and silica bead are both very inexpensive components.
- ii. **Solar driven** – fewer power requirements to implement technology.
- iii. **Minimal required training** - the application of the technology does not require any special skills.
- iv. **Low maintenance** – a simplified treatment system can be designed using either minimal or no moving parts.
- v. **Ease of application** - technology is easily transported to other locations in the country.
- vi. **Applicable to harsh environmental conditions** – Mats can survive in cold temperatures and will flourish in temperatures above 25°C with abundant sunlight. They can be dried and will reform upon rehydration, and are unaffected by high concentrations of many contaminants. Unlike many plants or algae, microbial mats can survive high, often phyto-toxic concentrations of metals or organic contaminants.
- vii. **Reduction of waste byproducts and sludge** – because microbial mat can be dried to 1-2% of its wet volume, it will not produce as much waste as coagulation/precipitation processes, adsorption processes or ion exchange processes. It should be possible to recycle the vitric crust of the dried mat/silica gel based treatment system to reduce disposal costs or the need to landfill the byproduct

**Limitations of Microbial Mat Systems** – Although maintenance requirements for the mat systems are minimal, a long-term application of the system will require periodic maintenance. Mats are living organisms, and any biological system can be invaded by competing species. The primary species that may interfere with mat growth is freshwater algae. The salinity of the wastewater can be increased to control freshwater algae and alternatively algacides can provide spot control measures.

**Constructed Microbial Mats Treatment Methodology** – The two tasks performed under this contract are listed below.

***Task 1 - Baseline Characterization of the Mine Leachate.***

FTN Associate Limited provided PLANTECO with three 5 gallon buckets containing mine leachate samples labeled as follows:

1. Pond 3 water (untreated)
2. Leachate with FeSO<sub>4</sub> added then neutralized to pH = 8.5.
3. Leachate neutralized to pH = 8.5

The leachate samples were analyzed for selenium (Se), aluminum (AL), iron (Fe), manganese (Mn) and zinc (Zn) by ICP/MS and IC/EOS. Prior to analyzing for the metals of concern, the water samples were filtered with a 0.45 µm filter and acid digested. The results for the baseline characterization are included in Table 1.

***Task 2 – Bench Scale Tests.***

Constructed microbial mats (CMM) used in the bench scale treatability tests were grown on coconut fiber and synthetic fabric, respectively. Two types of batch treatments were performed in glass bioreactors. Specifically, the treatments involved:

- A. Floating constructed microbial mats on leachate in rectangular tanks: The CMM were grown on synthetic fiber and transferred to each tank after the mat had completely formed. This design simulates treatment in low-flow ponds or batch mode in large static ponds. The pictures below show the set-up of the treatments for each of the three types of mine leachate.
- B. Submerged CMM in conical flasks: The CMM was grown on coconut fiber and transferred to the flasks after the CMM had fully formed.

Aqueous phase samples were taken from each tank filtered to remove the microbial mats particles in suspension and digested with nitric acid. The digested samples were analyzed by ICP-MS and ICP-OES for five metals: Al, Fe, Mn, Se, and Zn. The regulatory driver for the leachate treatment was Se. Two separate laboratories analyzed the treated and untreated samples by ICP-MS, while one laboratory analyzed the samples by both ICP-MS and ICP-OES. The pH of the samples were taken during the treatment and since all pH measurements were taken during daylight hours when the microbial mats were photosynthesizing and producing oxygen (O<sub>2</sub>), the pH values were generally above 8.5. The pH values during daylight hours in CMM reactors are expected to be high as shown in Figure 3 above.

## Mat Growing on Coconut Fiber



08/20/07

Confidential

## Static Mat/Leachate Tests in Tanks



08/20/07

Confidential

## Initially Mats Were Setup In Tanks - Tank A - Untreated Pond 3



08/20/07

Confidential

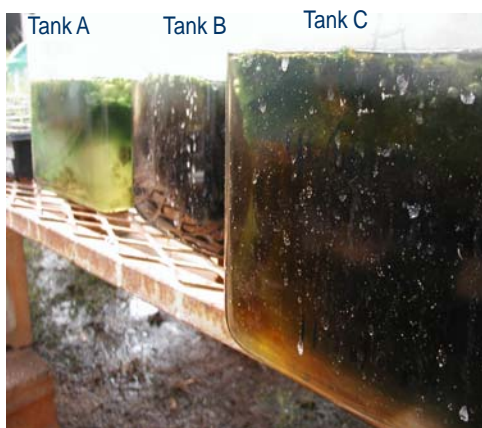
## C - Leachate Neutralized to pH 8.5



08/20/07

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## Three Mat Tanks after 28 Days Note Healthy Growth in Tanks A & C



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## Closeup of Tank A



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### Flask with Leachate



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### Mat Flasks After 48 Hours Notice Growth/Precipitate at Bottom of Mat



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### Flasks with Mat Added Start of Test



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### Mat Flasks After 48 Hours



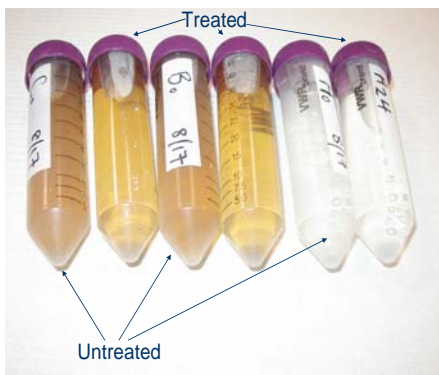
08/20/07

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Environmental Consulting, LLC

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### Untreated and Treated Samples Mat Flask Tests After 48 Hours



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## **Results**

The CMM in each tank continued to grow in each of the leachate. Although the CMM continues to grow and increase the amount of biomass, the healthiest growth was observed in the untreated leachate from Pond 3. Visual inspection of the reactors showed the formation of a brownish precipitate at the bottom of the CMM and a decrease in the intensity of the leachate color after about 48 hours.

The first two laboratories that analyzed the treated and untreated samples had inconsistent results and very poor reproducibility. As a result, the results from those laboratories are not reported. The results from the third laboratory (Savannah River Ecology Laboratory – SREL) were more consistent and reproducible than the previous two laboratories.

The results of ICP-MS and ICP-OES analysis of the treated and untreated samples filtered to 0.22  $\mu\text{m}$  and acidified to 1%  $\text{HNO}_3$  just prior to analysis are presented in Table 1. The concentrations of Al, Mn and Fe were measured by ICP-OES and Zn and Se by ICP-MS. Duplicate samples were analyzed to determine reproducibility. The reproducibility was good for all elements except for Zn.

For treatments in which the CMM was fully acclimatized with the leachate, it was observed that the CMM removed 90% of the initial selenium in leachate with  $\text{FeSO}_4$ , 60% in Pond 3 leachate, and 65% in leachate neutralized to  $\text{pH} = 8.5$ . The removal efficiency generally improved with the iron content of the leachate as would be predicted for CMM dominated by sulfate reducing bacteria.

The relatively low Se removal in treatments incubated with the microbial mats for only 48 hours was attributed to the short incubation time, which may not be sufficient for the redox zones of the microbial mat to reform. Recall that the sulfate reducing zone is the most effective redox zone for removal of the trace metals from solution.

It is likely that the CMM removed the trace metals from the leachate with a higher efficiency, but can not be confirmed due to the analytical challenges (poor accuracy due to interferences) encountered during the analysis by different laboratories. The analytical chemist who analyzed the samples using both ICP-MS and ICP-OES remarked that the high salt and organic content of the microbial mat treated samples could have positively biased the Se results.

“... These samples are way too salty for reliable ICP-MS analysis and they are almost too salty to analyze by ICP-OES. There is so much Na that the plasma turns bright orange. On the other hand, some of your concentrations are very low and if the samples were sufficiently diluted some of the elements would drop below the detection limits and certainly below the quantitation limits. We obtained marginal quality control values, but I wouldn't say that I am 100% confident of the accuracy. There are labs that can use a flow injection system to separate the trace elements from the Na, K, and Ca to analyze such salty samples (usually marine labs; you might want to call Skidaway Oceanographic Institute). Also, because there is so much organic carbon in some of the samples, the measured Se concentration may be

positively biased by 10-15% (organic carbon enhances the signal intensity for Se). The way we typically correct for this is by using the method of standard additions, but we didn't have sufficient sample volume to do it this time. ...”

Table 1: Summary of Results from Batch Treatment of Mine Waste using Microbial Mats.

<b>Sample Description</b>	<b>Se ug/L</b>	<b>Fe ug/L</b>	<b>AL ug/L</b>	<b>Mn ug/L</b>	<b>Zn ug/L</b>
Ao	24.50	1.90	46.01	0.43	4.07
A48 hours	26.79	3.01	6.73	6.04	8.20
A23 days	9.47 (9.63)	3.48 (BDL)	29.79 (34.13)	4.26 (3.92)	44.28 (35.92)
Bo	254.55	257.03	346.34	7.67	7.54
B48 hours	229.03	301.11	620.42	26.09	15.17
B23 days	24.74 (24.29)	507.50 (468.46)	243.76 (248.69)	2879.63 (2850.17)	22.78 (36.63)
Co	246.50	28.93	109.60	11.49	18.34
C48 hours	223.60	20.46	234.96	23.09	18.53
C23 days	85.04 (89.98)	15.57 (14.04)	171.34 (167.05)	298.72 (296.15)	30.92 (31.76)
Spike Recovery	111%	118%	107%	99%	85%
M/WL	77	238.61	308.21	257.61	68
IDL	0.65	1.52	2.96	0.38	1.04
IQL	1.95	4.56	8.88	1.15	3.12

Ao = Pond 3 leachate (untreated); Bo = Leachate with FeSO<sub>4</sub> added then neutralized to pH = 8.5;  
Co = Leachate neutralized to pH = 8.5.

## **Recommendations**

Despite the analytical challenges, PLANTECO believes that the microbial mats are potentially effective for removing Se from leachate. A more efficient conceptual treatment design may involve a series of interconnected shallow slow flow-through treatment ponds or treat-and discharge pond where the CMM are floated. The highest Se removal efficiency will occur if the treated leachate treated with the CMM contains high dissolved iron. The pH of the water should not matter since the microbial mats will survive and grow in extreme pH water containing high dissolved concentration of metals. Once the microbial mats have acclimatized with the leachate over several weeks, the Se removal efficiency should significantly improve. An analytical method that does not positively bias the concentration of Se in the CMM treated water should be used to confirm treatment to compliance levels.

Table 1. Summary of Selenium Results including split samples.

Treatment of Mine Waste Using Microbial Mats.

Sample Description	Se µg/L	FTN Splits Se µg/L	Removal Eff. Planteco	Removal Eff. Split
A0	24.50	16 <sup>1</sup>		
A48 hours	26.79	46	Ind. <sup>3</sup>	Ind. <sup>3</sup>
A23 days	9.47 (9.63)	16	61%	Ind. <sup>3</sup>
B0	254.55	130 <sup>2</sup>		
B48 hours	229.03	50	10%	61%
B23 days	24.74 (24.29)	23	91%	82%
C0	246.50	130 <sup>2</sup>		
C48 hours	223.60	60	9%	54%
C23 days	85.04 (89.98)	26	65%	80%

A0 = Pond 3 water (untreated); B0 = Leachate (New 17) with FeSO<sub>4</sub> added then neutralized to pH = 8.5; C0 = Leachate (New 17) neutralized to pH = 8.5.

Notes:

1. Expected maximum selenium concentration in Pond 3 based on previous sample results.
2. Expected selenium concentration in New 17 based on previous sample results.
3. Indeterminate.



Alcoa Inc.  
ATTN: Mr. Pat Keogh  
Post Office Box 290  
Bauxite, AR 72011-0290

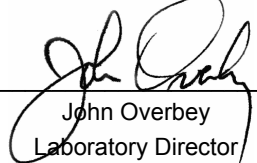
Dear Mr. Pat Keogh:

Project Description: Six (6) water sample(s) received on September 12, 2007  
6012-244b  
Alcoa SE Treatability Experiment-PlantCo  
P.O. No. 190030460

This report is the analytical results and supporting information for the samples submitted to American Interplex Corporation (AIC) on September 12, 2007. The following results are applicable only to the samples identified by the control number referenced above. Accurate assessment of the data requires access to the entire document. Each section of the report has been reviewed and approved by the appropriate laboratory director or a qualified designee.

Data has been validated using standard quality control measures performed on at least 10% of the samples analyzed. Quality Assurance, instrumentation, maintenance and calibration were performed in accordance with guidelines established by the cited methodology.

**AMERICAN INTERPLEX CORPORATION**

By  By KW  
John Overbey  
Laboratory Director

Enclosure(s): Chain of Custody

PDF cc: FTN Associates, Ltd.  
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Alcoa Inc.  
Post Office Box 290  
Bauxite, AR 72011-0290

CASE NARRATIVE

SAMPLE RECEIPT

Received Temperature: 21°C

Receipt Verification:	Complete Chain of Custody	N
	Sample ID on Sample Labels	Y
	Date and Time on Sample Labels	N
	Proper Sample Containers	Y
	Within Holding Times	Y
	Adequate Sample Volume	Y
	Sample Integrity	Y
	Proper Temperature	Y
	Proper Preservative	Y

COMMENTS

There were no qualifiers for this data and all samples met quality control criteria.

References:

"Methods for Chemical Analysis of Water and Wastes", EPA/600/4-79-020 (Mar 1983) with updates and supplements EPA/600/5-91-010 (Jun 1991), EPA/600/R-92-129 (Aug 1992) and EPA/600/R-93-100 (Aug 1993).

"Test Methods for Evaluating Solid Waste Physical/Chemical Methods (SW846)", Third Edition.

"Standard Methods for the Examination of Water and Wastewaters", 20th edition, 1998.

"American Society for Testing and Materials" (ASTM).

"Association of Analytical Chemists" (AOAC).

"Self-Davis and Moore" (2000).

Alcoa Inc.  
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Bauxite, AR 72011-0290

### ANALYTICAL RESULTS

AIC No. 112841-1  
Sample Identification: AF 9/10/07

Analyte	Method	Result	RL	Units	Batch	Qualifier
Dissolved: Selenium	EPA 200.7	0.046	0.002	mg/l	S21273	

AIC No. 112841-2  
Sample Identification: BF 9/10/07

Analyte	Method	Result	RL	Units	Batch	Qualifier
Dissolved: Selenium	EPA 200.8	0.050	0.002	mg/l	S21273	

AIC No. 112841-3  
Sample Identification: CF 9/10/07

Analyte	Method	Result	RL	Units	Batch	Qualifier
Dissolved: Selenium	EPA 200.7	0.060	0.002	mg/l	S21273	

AIC No. 112841-4  
Sample Identification: AT 9/10/07

Analyte	Method	Result	RL	Units	Batch	Qualifier
Dissolved: Selenium	EPA 200.7	0.016	0.002	mg/l	S21273	

AIC No. 112841-5  
Sample Identification: BT 9/10/07

Analyte	Method	Result	RL	Units	Batch	Qualifier
Dissolved: Selenium	EPA 200.7	0.023	0.002	mg/l	S21273	

AIC No. 112841-6  
Sample Identification: CT 9/10/07

Analyte	Method	Result	RL	Units	Batch	Qualifier
Dissolved: Selenium	EPA 200.8	0.026	0.002	mg/l	S21273	

Alcoa Inc.  
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Bauxite, AR 72011-0290

SAMPLE PREPARATION REPORT

AIC No. 112841-1

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Dissolved: Metals	13SEP07	1446 268	18SEP07	2132 117		S21273	

AIC No. 112841-2

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	13SEP07	1446 268	24SEP07	1409 117		S21273	

AIC No. 112841-3

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	13SEP07	1446 268	19SEP07	1656 117		S21273	

AIC No. 112841-4

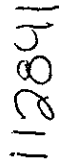
Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	13SEP07	1446 268	18SEP07	2140 117		S21273	

AIC No. 112841-5

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	13SEP07	1446 268	18SEP07	2143 117		S21273	

AIC No. 112841-6

Analyte	Date/Time Prepared By		Date/Time Analyzed By		Dilution	Batch	Qualifier
Metals	13SEP07	1446 268	24SEP07	1417 117		S21273	



1 2 3 4 5 6

# **ATTACHMENT 8**

---

**Technical Memo – Biological Treatability Test Procedures at  
Sump 3 and Black Pond**

## **TECHNICAL MEMO**

**TO:** Files

**FROM:** Rex Robbins

**RE:** Biological Treatability Test Procedures  
Alcoa Selenium Study

**DATE:** 8/10/07

---

### **PURPOSE:**

This treatability test will apply microbes operating in an anoxic environment to reduce selenate to selenite (and/or elemental selenium). Similar testing has demonstrated that this reaction can be successfully applied to the treated water from Pond 3 and to the concentrated leachate in the New 17 pit. Once formed, it is expected that the selenite or selenium can be filtered from the water.

The tests will give some information regarding the relative effect of nutrients, biological solids seeding, and the addition of a carbon source.

### **EQUIPMENT/SUPPLIES:**

1. Three 40-gallon plastic drums,
2. Eight 5-gallon bottled-water carboys,
3. Two 7-gallon water tote,
4. 10N sulfuric acid,
5. 30 gallons of water from Black Pond (Reynold's side),
6. 30 gallons of water from Sump 3 (Reynold's side),
7. 2 gallons – Activated sludge from municipal wastewater plant, and
8. 500 mls – molasses.

### **PROCEDURE:**

- About 25 gallons of leachate water from the Black Pond will be collected in a drum. Also, about 25 gallons of water from Sump 3 will be collected in a drum. The sample of activated sludge will be pulled within two days of the test setup and kept refrigerated until mixing. Samples of the Black Pond water and Sump 3

water will be collected and analyzed for total selenium. The following test samples will be set up in 5 gallon bottles as described in previous documentation.

1. Sample 1 – Black Pond Control,
  2. Sample 2 – Black Pond with Activated Sludge Seed,
  3. Sample 3 - Black Pond with Seed and Carbon,
  4. Sample 4 – Black Pond with Seed and Nutrient,
  5. Sample 5 – Black pond with Seed and nutrient (open top),
  6. Sample 6 – Sump 3 Control,
  7. Sample 7 – Sump 3 with Activated Sludge Seed,
  8. Sample 8 - Sump 3 with Seed and Carbon,
  9. Sample 9 – Sump 3 with Seed and Nutrient, and
  10. Sample 10 – Sump 3 with Seed and nutrient (open top).
- For each sample (1-10), sulfuric acid will be added to the container to lower the pH to about 8.5. The water will be mixed with a paint stirrer or by shaking the tote. The mixing will then stop and any precipitated solids will be allowed to settle for at least two hours.
  - Water will be poured from the tote into a 5-gallon carboy. Each carboy will be filled with the decanted water with as few solids carryover as possible.
  - For samples requiring seed, about 500 mls of water will be removed from carboy and replaced with 500 mls of activated sludge. For samples requiring carbon addition, a dose of molasses equal to about 50 mg/L will be added. (The carboys will be capped allowing the least possible head space). The open top test will be conducted in an unsealed five-gallon paint bucket. The test will be run for 14 days minimum with periodic checks for in situ readings. In situ readings should be taken after 24 hours, and after every few days (the exact schedule is not critical). During this time and for the extent of the test, each of the 10 carboys will be inverted gently at least once a day to allow mixing. At the end of each week, for a period of 4 weeks, the carboys will be opened, in situ readings (dissolved oxygen and pH) will be taken, and samples collected.
  - Based on the in situ readings, samples will be submitted to American Interplex for testing for dissolved and total selenium.

Alcoa Arkansas Remediation Selenium Treatability Study  
Biological Treatability  
Test Study Results

Source Data	Selenium, Total (mg/L)	Selenium, Dissolved (mg/L)
RMC Black Pond untreated	0.21	0.21
RMC Sump Pump #3	0.45	0.42

RMC Black Pond Treatability Experiment		Control (No Treatment)		Seed		Seed + Carbon		Seed + Nutrients		Seed + Nutrients + Open Top	
Date	Form	mg/L	% Removal	mg/L	% Removal	mg/L	% Removal	mg/L	% Removal	mg/L	% Removal
After 1 Week	Total	0.21	0%	0.16	24%	0.14	33%	0.16	24%	0.17	19%
23-Aug-07	Dissolved	0.21	0%	0.095	55%	0.09	57%	0.18	14%	0.17	19%
After 2 Weeks	Total	0.16	24%	0.14	33%	0.084	60%	0.11	48%	0.15	29%
30-Aug-07	Dissolved	0.13	38%	0.056	73%	0.049	77%	0.047	78%	0.13	38%
After 3 Weeks	Total	0.17	19%	0.1	52%	0.09	57%	0.12	43%	0.11	48%
7-Sep-07	Dissolved	0.13	38%	0.11	48%	0.056	73%	0.079	62%	0.11	48%
After 4 Weeks	Total	0.16	24%	0.1	52%	0.078	63%	0.1	52%	0.14	33%
13-Sep-07	Dissolved	0.11	48%	0.066	69%	0.05	76%	0.076	64%	0.11	48%
Maximum Removal	Total		24%		52%		63%		52%		48%
	Dissolved		48%		73%		77%		78%		48%

RMC Sump # 3 Treatability Experiment		Control (No Treatment)		Seed		Seed + Carbon		Seed + Nutrients		Seed + Nutrients + Open Top	
Date	Form	mg/L	% Removal	mg/L	% Removal	mg/L	% Removal	mg/L	% Removal	mg/L	% Removal
After 1 Week	Total	0.41	9%	0.37	18%	0.37	18%	0.38	16%	0.42	7%
23-Aug-07	Dissolved	0.39	7%	0.19	55%	0.3	29%	0.36	14%	0.41	2%
After 2 Weeks	Total	0.35	22%	0.3	33%	0.29	36%	0.31	31%	0.38	16%
30-Aug-07	Dissolved	0.32	24%	0.19	55%	0.2	52%	0.18	57%	0.31	26%
After 3 Weeks	Total	0.41	9%	0.27	40%	0.31	31%	0.32	29%	0.3	33%
7-Sep-07	Dissolved	0.23	45%	0.16	62%	0.2	52%	0.16	62%	0.31	26%
After 4 Weeks	Total	0.32	29%	0.28	38%	0.32	29%	0.27	40%	0.28	38%
13-Sep-07	Dissolved	0.27	36%	0.22	48%	0.23	45%	0.25	40%	0.28	33%
Maximum Removal	Total		29%		40%		36%		40%		38%
	Dissolved		45%		62%		52%		62%		33%



# Insitu Readings from Biological Testing

ID	Date	Temp	pH	DO	SPC	ORP
Black Pond - Control	8/16/2007	31.38	8.11	6.13	18795	
Black Pond - Seed	8/16/2007	31.19	8.45	4.57	18805	
Black Pond - Seed + Carbon	8/16/2007	29.56	8.45	3.12	18419	
Black Pond - Seed + Nutrient	8/16/2007	31.11	8.36	2.84	18448	
Black Pond - Seed + Nutrient outside	8/16/2007	31.27	8.39	6.25	18476	
Sump 3 - Control	8/16/2007	29.63	8.06	4.39	23697	
Sump 3 - Seed	8/16/2007	29.61	8.02	4.19	22867	
Sump 3 - Seed + Carbon	8/16/2007	29.53	8.36	2.64	23036	
Sump 3 - Seed + Nutrient	8/16/2007	29.34	8.35	3.97	22979	
Sump 3 - Seed + Nutrient outside	8/16/2007	29.65	9.15	3.08	23576	
Black Pond - Control	8/20/2007	25.36	8.39	0.15	18973	
Black Pond - Seed	8/20/2007	25.28	8.69	0.14	18580	
Black Pond - Seed + Carbon	8/20/2007	24.64	8.12	0.15	18458	
Black Pond - Seed + Nutrient	8/20/2007	24.99	8.73	0.12	18597	
Black Pond - Seed + Nutrient outside	8/20/2007	29.63	8.72	0.18	18855	
Sump 3 - Control	8/20/2007	24.51	8.5	0.14	23949	
Sump 3 - Seed	8/20/2007	25.06	8.46	0.32	22865	
Sump 3 - Seed + Carbon	8/20/2007	24.79	8.7	0.14	22932	
Sump 3 - Seed + Nutrient	8/20/2007	25.28	8.8	0.15	22686	
Sump 3 - Seed + Nutrient outside	8/20/2007	29.71	9.16	0.09	25660	
Black Pond - Control	8/23/2007	23.55	8.33	0.13	19399	-136
Black Pond - Seed	8/23/2007	23.75	8.56	0.07	18954	-257
Black Pond - Seed + Carbon	8/23/2007	23.54	7.99	0.17	19020	-229
Black Pond - Seed + Nutrient	8/23/2007	53.53	8.67	0.07	19044	-280
Black Pond - Seed + Nutrient outside	8/23/2007	34.57	8.75	0.05	19557	-245
Sump 3 - Control	8/23/2007	23.52	8.51	0.12	24230	-273
Sump 3 - Seed	8/23/2007	23.57	8.45	0.03	23762	-306
Sump 3 - Seed + Carbon	8/23/2007	23.54	8.69	0.04	23561	-310
Sump 3 - Seed + Nutrient	8/23/2007	23.77	8.77	0.13	23692	-256
Sump 3 - Seed + Nutrient outside	8/23/2007	33.39	9.1	0.09	24862	-325
Black Pond - Control	8/30/2007					
Black Pond - Seed	8/30/2007					
Black Pond - Seed + Carbon	8/30/2007					
Black Pond - Seed + Nutrient	8/30/2007					
Black Pond - Seed + Nutrient outside	8/30/2007					
Sump 3 - Control	8/30/2007					
Sump 3 - Seed	8/30/2007					
Sump 3 - Seed + Carbon	8/30/2007					
Sump 3 - Seed + Nutrient	8/30/2007					
Sump 3 - Seed + Nutrient outside	8/30/2007					
Black Pond - Control	9/7/2007	23.1	8.2	0.1	20600	-197
Black Pond - Seed	9/7/2007	23	8.41	0.1	20200	9225
Black Pond - Seed + Carbon	9/7/2007	22.8	7.6	0.1	20100	-191

Black Pond - Seed + Nutrient	9/7/2007	22.8	8.6	0.1	20300	-237
Black Pond - Seed + Nutrient outside	9/7/2007	26.5	8.6	0.1	21000	-91
Sump 3 - Control	9/7/2007	22.7	8.4	0.1	25800	-214
Sump 3 - Seed	9/7/2007	22.7	8.2	0.1	25000	-229
Sump 3 - Seed + Carbon	9/7/2007	22.8	8.4	0.1	25100	-252
Sump 3 - Seed + Nutrient	9/7/2007	22.8	8.7	0.1	25200	-253
Sump 3 - Seed + Nutrient outside	9/7/2007	27	8.9	0.1	25800	-160
Black Pond - Control	9/13/2007	23.42	8.3	0.08	16309	
Black Pond - Seed	9/13/2007	23.5	8.4	0.12	15926	
Black Pond - Seed + Carbon	9/13/2007	23.14	7.68	0.07	15914	
Black Pond - Seed + Nutrient	9/13/2007	23.2	8.58	0.1	16033	
Black Pond - Seed + Nutrient outside	9/13/2007	22.27	8.51	0.83	16666	
Sump 3 - Control	9/13/2007	23.19	8.49	0.05	20370	
Sump 3 - Seed	9/13/2007	23.18	8.29	0.04	19867	
Sump 3 - Seed + Carbon	9/13/2007	23.14	8.55	0.06	19786	
Sump 3 - Seed + Nutrient	9/13/2007	23.2	8.76	0.04	19934	
Sump 3 - Seed + Nutrient outside	9/13/2007	22.36	9.05	0.42	20627	

## **APPENDIX B**

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**Engineering Evaluation Review – Pipeline from Alcoa’s Outfall 009  
to the Saline River**

## **ENGINEERING EVALUATION REVIEW – PIPELINE FROM ALCOA OUTFALL 009 TO THE SALINE RIVER**

As an alternative to modifying the existing treatment system, a pipeline could be installed to convey the entire flow of water currently discharged through Outfall 009 at Alcoa. Rather than discharging to Holly Creek, and then to the Saline River, the discharge would be directly to the Saline River. In this way, the water quality issues in Holly Creek would be avoided and the larger dilution flow associated with the Saline River would mitigate any issues from selenium directly at the point of discharge.

A preliminary engineering design and cost estimate were prepared for installing a pipeline from Alcoa's existing Outfall 009 to the Saline River. This conveyance could be achieved with a forced gravity system consisting of two 30-inch, high-density polyethylene (HDPE) SDR 26 pipes that would carry the design flow of 20 million gallons per day (MGD). The existing ponds above Outfall 009 would be used to equalize flows and control discharge rates to the Saline River so that water quality in the river could be maintained.

The length of the pipeline would be approximately 15,000 linear feet (approximately 3 miles) installed in close proximity to the path of Holly Creek. A 50-ft-wide right-of-way (ROW) would be obtained where the pipelines would be buried. The ROW would require clearing and grubbing of vegetation and trees before installation of the pipeline could begin. One road crossing would occur at Highway 35.

The project cost estimate as of May 15, 2009, is \$6.2 million. Material and labor rates should be reviewed when the project is issued for a more current cost estimate.

Project cost estimate assumes the use of native soils and the ability to keep excess excavated soils on or near the project site. This cost does not include leasing or purchasing of property for additional pipeline ROW.

The following table provides a summary of the expected costs that would be incurred with the installation of the pipeline.

Table 1. Estimated construction costs.

<b>Item</b>	<b>Description</b>	<b>Unit</b>	<b>Estimated Quantity</b>	<b>Unit Cost</b>	<b>Estimated Cost</b>
1	ROW Clearing	acre	18	\$2,500.00	\$45,000.00
2	Demo Existing Flume	lump	1	\$9,500.00	\$9,500.00
3	Pipe Material – 30 inch	L.F.	30,000	\$75.00	\$2,250,000.00
3a	Pipe miscellaneous materials	lump	1	\$150,000.00	\$150,000.00
3b	Pipe fusion labor	lump	1	\$240,000.00	\$240,000.00
4	Pipe installation labor	lump	1	\$300,000.00	\$300,000.00
5	Highway bore	L.F.	720	\$500.00	\$360,000.00
6	Equipment	lump	1	\$268,298.00	\$269,000.00
7	Instruments	lump	2	\$12,143.00	\$25,000.00
8	Electrical	lump	1	\$1,500.00	\$1,500.00
9	Permits	lump	1	\$100,000.00	\$100,000.00
8	Engineering	lump	1		\$648,000.00
<b>SUBTOTAL</b>					<b>\$4,970,000.00</b>
<b>CONTINGENCY TOTAL</b>					<b>\$6,220,000.00</b>

## **APPENDIX C**

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### **Engineering Evaluation Review – Source Control Options**

## **ENGINEERING EVALUATION REVIEW – SOURCE CONTROL OPTIONS**

### **1.0 BACKGROUND**

Leachate from the two closed bauxite residue disposal areas (BRDAs) has been determined to be the primary source of selenium on the Alcoa site. There are two BRDAs: one on the Alcoa site (Figure 1; all figures and tables provided at the end of the text) and one on the former Reynolds Metals Company (Reynolds) site (Figure 2). Leachate continuously flows from the BRDAs, but wet weather increases the leachate production. This is a year-round occurrence with wet weather providing increased flow. The feasibility of reducing or eliminating rainfall infiltration into the BRDA (in an effort to reduce the generation of leachate from the BRDAs, thus reducing selenium sources) has been assessed, and will continually be evaluated during the EIP.

Potential cover improvements include, but are not limited to, modifications to the soil cover to reduce/eliminate stormwater infiltration, use of liners, and modifications to the vegetative cover in efforts to increase stormwater runoff. Engineering analyses were used to develop the quantities and conditions needed to prepare preliminary cost estimates. The preliminary engineering analyses and cost estimates are based on existing contour data.

If both BRDAs were covered with a tent, leachate would continue to be generated for many years due to the hydraulic characteristics of the soil structure.

## 2.0 ALTERNATIVE VEGETATIVE COVER ON BRDAS (OPTION 1)

Alternative vegetative cover in the BRDAs has been investigated to improve evapotranspiration of rainfall. Improving evapotranspiration will reduce the amount of rainfall that infiltrates the soil cap and becomes leachate. Current grass cover on the BRDAs mainly consists of:

- Orchard grass,
- Fescue,
- Bermuda grass,
- Lovegrass,
- Crimson clover, and
- Hairy vetch.

The existing vegetation consists of both cool and warm season grasses and currently reduces the infiltration to a significant degree.

A part of the evaluation was to find vegetation that would provide more evapotranspiration (i.e., water loss from evaporation and transpiration through leaves) than the existing vegetative cover. Some of the plants evaluated include, but are not limited to:

- Cordgrass (*Spartina* sp.),
- Camphor-weed (*Pluchea camphorata*),
- Salt cedar (*Tamarix gallica*),
- Switch grass (*Panicum virgatum*),
- Willow (*Agonis* sp.),
- Cypress (*Cupressocyparis* sp.),
- Juniper (*Juniperus* sp.), and
- Black locust (*Robinia pseudoacacia*).



To some degree, these plants can tolerate a high alkalinity, high chlorides, and/or high moisture. However, few of the plants will tolerate soil pH values above 8.5 su and none of the plants will tolerate soil pH values that exceed 11.5 su. The pH of the residue is 11 to 13 su. While some plants will tolerate high soil pH values, and others will tolerate high salt concentrations or high moisture values, none have been found that will tolerate all three conditions simultaneously, which exist on the BRDAs.

The benefit provided by an alternate vegetative coverage is difficult to quantify. Alcoa, through its world-wide network of facilities, will continue to work on plant issues.

### **3.0 BRDA COVER IMPROVEMENTS (OPTION 2)**

Several options exist to cover the BRDAs with impervious caps. These liners or caps would be placed over the areas to reduce and/or eliminate stormwater infiltration.

The Alcoa BRDA is confined to one area of approximately 420 acres, while the Reynolds BRDA consists of 560 acres.

#### **3.1 High-Density Polyethylene Cap (Option 2.1)**

Covering the BRDAs with an impervious 40-mil textured high-density polyethylene (HDPE) cap was estimated to require the placement of the liner material over about 980 acres. After the placement of the liner, 18 inches of soil would be needed to cover the HDPE cap (14 inches of suitable soil materials with a 4-inch minimum of topsoil). The Reynolds site would require some cut and fill to provide a minimum of a 1% slope to improve drainage. Approximately 2.4 million cubic yards of material would be required to be moved to provide this slope. The cost has been estimated at \$58.3 million for installation of an HDPE cap on both the Alcoa and Reynolds BRDAs. A summary of this cost estimate is shown in Table 1.

#### **3.2 Geosynthetic Clay Liner Cap (Option 2.2)**

Another option would involve placing a geosynthetic clay liner (GCL) cap over the 950 acres. An 18-inch-thick layer of soil would cover the GCL cap – 14 inches of suitable soil materials with 4-inch minimum of topsoil. The Reynolds site would require some cut and fill to provide a minimum of a 1% slope to improve drainage. Approximate 2.4 million cubic yards of material would be required to be moved. The cost has been estimated at \$67.7 million for installation of a GCL cap. Table 2 provides the summary of this cost estimate.

#### **3.3 Clay Cap (Option 2.3)**

Another option is to install a thicker clay cap on the Alcoa BRDA site, which has an existing 8- to 10-inch clay cap. Some additional benefit could potentially be achieved with the additional layer of clay, particularly if a reasonably available clay source with lower permeability

could be found. The topsoil would be stripped, and then another 10 inches of compacted clay would be added to give a total 18-inch clay cap. Then 18 inches of suitable soil material with re-vegetation would cover the clay. The estimated cost of this option would be \$14.4 million for the Alcoa BRDA.

The Reynolds BRDA site has no existing clay cap, so it would require an 18-inch clay cap, and 18 inches of suitable soil material. An estimated cost of \$38.8 million is expected for the clay cap in this area.

The total cost of applying a clay cap to the BRDAs is \$53.2 million. Table 3 provides a summary of the cost estimate for this option. As previously stated, applying a clay cap to the BRDAs will not eliminate the formation of alkaline leachate.

## **4.0 REYNOLDS SITEWORK IMPROVEMENTS (OPTION 3)**

To improve stormwater drainage of the Reynolds BRDA, an option was evaluated to modify the site contours to provide a minimum of 2% slope off of the BRDA. If the site was to remain undisturbed, and fill material was to be hauled to the site, 7.3 million cubic yards of material would be required. Total cost is expected to exceed \$100 million for this option.

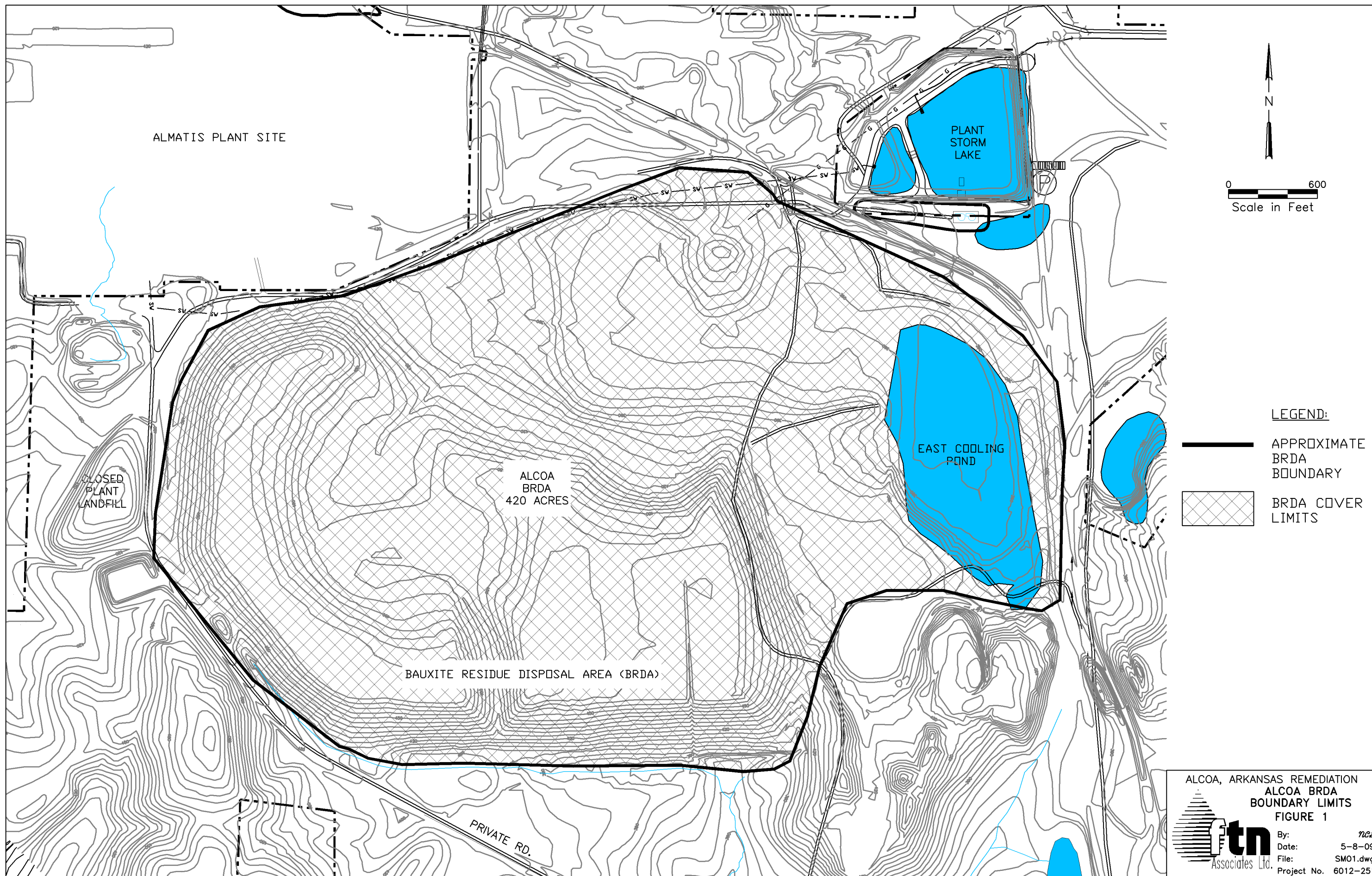
If the BRDA was to be reshaped with the existing BRDA material to achieve the 2% slope, most of the BRDA material could be moved away from Hurricane Creek by approximately 450 ft. The area would then be provided with an 18-inch clay cap and 18-inch topsoil cover. The estimated cost for the BRDA site work would be about \$49.5 million. Table 4 provides a summary of the cost estimate for this option.

## **5.0 SUMMARY**

Different methods have been investigated for reducing infiltration into the BRDAs, thereby reducing production of the leachate. Given the amount of perched water already known to exist in the BRDAs, the exact timing of benefits to be achieved by reducing infiltration is difficult to quantify.

Cost estimates have been provided for the different infiltration control methods that were analyzed. In general, these cost estimates are significantly higher than other options that have been studied, such as water treatment methodologies or a pipeline to the Saline River.

Alcoa will continue to study, evaluate, and test methods to reduce leachate from the BRDAs throughout the EIP. Economically, since leachate is the highest cost item to treat on the site, Alcoa will continue these evaluations beyond the conclusion of the EIP.







**TABLE 1 - HDPE CAP (OPTION 2.1)**  
**ESTIMATE DETAIL WORKSHEET**

[illegible]

Subtotal	\$52,952,000
Contingency @ 15%	\$5,295,200
<b>Total</b>	<b>\$58,250,000</b>



**TABLE 2 - GCL CAP (OPTION 2.2)**  
**ESTIMATE DETAIL WORKSHEET**

[illegible]

Subtotal	\$61,558,000
Contingency @15%	\$6,155,800
<b>Total</b>	<b>\$67,710,000</b>

**TABLE 3 - CLAY CAPS AT ALCOA AND REYNOLDS BRDAS (OPTION 2.3)**  
ESTIMATE DETAIL WORKSHEET

AREA \_\_\_\_\_ Site Work \_\_\_\_\_ SH \_\_\_\_\_  
DATE \_\_\_\_\_ 30-Apr-09 \_\_\_\_\_ BY \_\_\_\_\_

LINE NO.	RESPONS.		DESCRIPTION	QTY. EST.	UOM	UNIT COST	TOTALS	BASIS (attach support)
	COMPANY	INDIV.						
1	FTN	NCS	Stripping Topsoil	420	Acre	\$2,500.00	\$1,050,000	
2	FTN	NCS	Subgrade Preparation	420	Acre	\$2,000.00	\$840,000	
3	FTN	NCS	Clay - 10" compacted	559,000	CY	\$14.00	\$7,826,000	
4	FTN	NCS	Erosion Control	1	LS	\$300,000.00	\$300,000	
5	FTN	NCS	Replacement of Topsoil	420	Acre	\$2,000.00	\$840,000	
6	FTN	NCS	Seeding and Mulching	420	Acre	\$3,000.00	\$1,260,000	
7	FTN	NCS	Engineering	1	LS	\$970,000.00	\$970,000	
<b>Subtotal</b>							\$13,086,000	
<b>Contingency @15%</b>							\$1,308,600	
<b>Total (Alcoa)</b>							<b>\$14,390,000</b>	
8	FTN	NCS	Subgrade Preparation	580	Acre	\$2,000.00	\$1,160,000	
9	FTN	NCS	Clay - 18" compacted	1,403,590	CY	\$14.00	\$19,650,260	
10	FTN	NCS	Erosion Control	1	LS	\$300,000.00	\$300,000	
11	FTN	NCS	Topsoil - 18"	1,403,590	CY	\$7.00	\$9,825,130	Assuming Topsoil borrow pit on Alcoa property
12	FTN	NCS	Seeding and Mulching	580	Acre	\$3,000.00	\$1,740,000	
13	FTN	NCS	Engineering	1	LS	\$2,620,000.00	\$2,620,000	
<b>Subtotal</b>							\$36,295,000	
<b>Contingency @ 15%</b>							\$3,529,500	
<b>Total (Reynolds)</b>							<b>\$38,820,000</b>	
<b>Total (Alcoa and Reynolds)</b>							<b>\$53,210,000</b>	

**TABLE 4 - CLAY CAP AT RMC BRDA WITH 2% SITE GRADING (OPTION 3)**  
**ESTIMATE DETAIL WORKSHEET**

AREA	Site Work	SH
DATE	30-Apr-09	BY

[illegible]

Subtotal	\$52,020,000
Contingency @15%	\$5,202,000
<b>Total</b>	<b>\$57,220,000</b>

## **APPENDIX D**

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**Cross-Reference of Regulation No. 2, Appendix B, with the EIP**

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## APPENDIX D

### CROSS-REFERENCE OF REGULATION NO. 2 APPENDIX B WITH EIP

Section 3 of Appendix B in Regulation No. 2 discusses the procedures for approval of environmental projects. A petitioner seeking approval of a change in water quality criteria to accommodate a long-term environmental improvement project shall file a Notice of Intent with the Arkansas Department of Environmental Quality.

Below is a list of items that must be included in the Notice of Intent and the section of the EIP that corresponds to each of these items.

<b>Appendix B Requirement</b>	<b>EIP Section</b>
1. A description of the waterbody or stream segment affected by the project;	2.0
2. The existing ambient water quality for the use of criteria at issue;	3.0
3. The affected water quality standard;	4.0
4. The modifications sought;	5.1
5. The proposed remediation activities;	6.0
6. A proposed Remediation Plan, which shall contain:	6.0
A. A description of the existing conditions, including identification of the conditions limiting the attainment of the water quality standards;	6.1.1
B. A description of the proposed water quality standard modification, both during and post-project;	6.1.2
C. A description of the proposed remediation plan; and	6.1.3
D. The anticipated collateral effects, if any, of the Remediation Plan.	6.1.4
7. A schedule for implementing the Remediation Plan that ensures that the post-project water quality standards are met as soon as reasonably practicable.	9.0

## **APPENDIX E**

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### **Saline River Biomonitoring Survey Plan for Selenium Exposure in Birds and Mussels**

# **SALINE RIVER BIOMONITORING SURVEY PLAN FOR SELENIUM EXPOSURE IN BIRDS AND MUSSELS**

**AUGUST 4, 2010**

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SALINE RIVER BIOMONITORING  
SURVEY PLAN FOR SELENIUM  
EXPOSURE IN BIRDS AND MUSSELS

Prepared for

Alcoa, Inc.  
1401 Bauxite Cutoff Rd.  
Bauxite, Arkansas 72011

Prepared by

FTN Associates, Ltd.  
3 Innwood Circle Suite 220  
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FTN No. 6012-251.E

August 4, 2010



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## 1.0 INTRODUCTION

Through its routine monitoring the Arkansas Department of Environmental Quality (ADEQ) has documented that water column selenium (Se) concentrations in the Saline River downstream of its confluence with Holly Creek meet the state and national water quality criterion of 5 µg/L. In addition, Alcoa's studies demonstrate that no bioaccumulation of Se is occurring in the tissues of fish collected from the Saline River both upstream and downstream of the mouth of Holly Creek. Although this information suggests that little, if any, Se bioaccumulation is occurring in the Saline River in the vicinity of Holly Creek, the US Fish and Wildlife Service (USFWS) has expressed concerns of possible increased body burdens of selenium (Se) in populations of freshwater mussels and birds in the Saline River due to Se input from Holly Creek.

In a March 10, 2010 letter to Nicholas Willis of ADEQ, Mark Sattleburg, USFWS Field Supervisor, noted that the federally endangered Arkansas fatmucket mussel (*Lampsilis powelli*) and 5 mussel species of state conservation concern (western fanshell – *Cyprogenia aberti*; flutedshell – *Lasmigona costata*; black sandshell – *Ligumia recta*; Ouachita kidneyshell – *Ptychobranhus occidentalis*; little spectaclecase – *Villosa lienosa*) are known to occur within 1 mile downstream of the confluence of Holly Creek with the Saline River. The March 10 letter recommended:

1. Conducting observations of birds to determine if birds such as wood ducks, egrets or herons were foraging regularly in Holly Creek, and
2. Sampling and analysis of mussel tissues to evaluate whether bioaccumulation of Se could potentially be occurring in the federally endangered Arkansas fatmucket mussel (*Lampsilis powelli*).

In its recommendation for additional data from mussels, USFWS acknowledges that there is no tissue-based criterion or benchmark concentration that can be used to evaluate whether or not adverse effects are occurring in the mussels. In subsequent conversations, USFWS also acknowledged that there was no basis for interpreting any upstream vs. downstream differences in tissue concentrations that might be observed. Discussions with USFWS have also indicated:

1. Absence of an increase in tissue concentrations in the Saline River downstream of the mouth of Holly Creek would essentially close the issue,
2. Only a “large” downstream increase in tissue concentration would be potential cause for concern, and
3. Only the presence of nesting aquatic or piscivorous birds is of concern in the vicinity of Holly Creek.

In accordance with USFWS recommendations, Alcoa has developed the monitoring plan provided herein. The purpose of this plan is to:

1. Use surrogate mussel species to evaluate potential Se body burdens in populations of federally endangered mussel species and mussel species of state conservation concern, and
2. Observe and document aquatic and piscivorous bird use and activity in Holly Creek habitats to evaluate the potential for Se exposure of aquatic and piscivorous birds using those habitats.

## **2.0 BIOMONITORING APPROACH**

### **2.1 Mussels**

The objective of the mussel sampling is to obtain measurements of individual Se body burdens in the Saline River upstream and downstream of the mouth of Holly Creek. Sampling will not target freshwater mussels that are federally endangered or species of concern. Rather, other common mussel species found in the Saline River reached upstream and downstream of the Holly Creek confluence will be used as surrogates. No fish will be collected.

Alcoa will collect mussels from accessible habitats in Saline River upstream and downstream of the Holly Creek confluence and analytically determine the soft tissue concentration of Se in each one collected, excluding federally endangered species and species of state concern. The mussels collected will be identified to species and sized. The study will not attempt to generate data to compare upstream and downstream Se concentrations within species or size classes. Rather, the intent is to pool individual concentrations irrespective of species and size to allow upstream vs. downstream comparisons. This approach will avoid impacting the mussel populations that require protection.

### **2.2 Birds**

The objective of bird monitoring will be to develop a list of aquatic and/or piscivorous bird species that use Holly Creek habitats including how the habitats are used (e.g. feeding, resting, breeding) and a rough indication of their numbers. This information will provide the basis to evaluate the potential exposure of bird populations to dietary Se.

Evaluation of Se risk to aquatic and/or piscivorous birds (herons, egrets, kingfishers, etc.) is, in theory, possible because tissue-based effects thresholds are available for bird eggs. However, locating and accessing sufficient numbers of aquatic bird eggs for Se analysis is problematic (due to the difficulty in locating and accessing aquatic bird nests<sup>1</sup>) unless a nearby breeding rookery can be located that includes species that also use Holly Creek or Saline River

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<sup>1</sup> Many aquatic/piscivorous birds nest in solitary secluded locations (e.g. grebes, night herons, kingfishers) or in small groups in tall trees (e.g. great blue herons).

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habitats. Therefore no bird eggs will be collected for this study unless a nearby nesting concentration containing the appropriate species can be located<sup>2</sup>. Because of these restrictions, the monitoring strategy for birds will be to evaluate the potential for Se exposure by observing aquatic bird use of marsh, backwater and channel habitats of Holly Creek. Observers will conduct surveys from fixed stations or transects and observe and record aquatic bird activity (resting, feeding) in Holly Creek habitats.

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<sup>2</sup> For example, cattle egret breeding colonies are likely to exist nearby, but these birds typically forage in pastures rather than in the type of marsh, backwater and channel habitats found Holly Creek. Therefore, eggs from nearby cattle egret colonies will not be collected unless cattle egrets are observed foraging in Holly Creek habitats or if other species of egrets or herons that use Holly Creek are also found in the egret colonies.

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## **3.0 SAMPLING/SURVEY METHODS**

### **3.1 Mussels**

Field and laboratory methods will be based on the Environmental Protection Agency's (EPA) guidance for assessing chemical contamination in fish (EPA 1996). Mussel sampling will be conducted on a single occasion in July or August during a period of low flow and high water clarity. The stream bottom in pool, riffle and run habitats will be searched by snorkeling and with viewing buckets. Sampling will target only freshwater mussels (no fish) that are not federally endangered or species of concern. If federally endangered or species of concern are captured they will be released at the point of capture after recording their numbers, sampling location, identity and size (valve length). Upon identification in the field, mussels to be used for tissue analysis will be placed on ice in sealable plastic bags containing appropriate labels (species, date of collection, sampling location) and shipped to FTN Associates, Ltd. (FTN) for further processing.

### **3.2 Birds**

Using maps, aerial photos and knowledge of the area, transects and observation stations will be established in representative habitats in Holly Creek. It is anticipated that 2 transects and 2 observation stations will provide sufficient coverage of the habitats present in Holly Creek. Observations will be made by 2 persons each equipped with binoculars and a spotting scope who will each work 1 transect and 1 station each. Observations will be made on 3 days at approximately weekly intervals in the late spring or early summer and on 3 days at approximately weekly intervals in the late summer or early fall.

Each observation day will consist of a 2 hour session beginning 0.5 hour before sunrise and a 2 hour session beginning approximately 1.5 hours before sunset. Observers will divide their observation time between the station and the transect in proportions yet to be determined. During their observation time the observers will identify and record the presence of any aquatic or piscivorous birds observed. They will also note the behavioral patterns of the birds as they concern feeding, nesting, courtship, resting, roosting, etc. Expected species include great blue

heron, great egret, little blue heron, green heron, yellow crowned night heron, white crowned night heron, pie billed grebe, bittern, double crested cormorant, anhinga, bald eagle, osprey, wood duck, bluewing teal, American coot, and belted kingfisher. Presence and behavior of non-aquatic non-piscivorous birds such as sparrows, warblers, vireos, buntings, crows, raptors (except as noted above) will not be noted.

Observation data will be entered into an Excel spreadsheet that will contain entries for each species observed indicating date, observer, location, approximate time species was present, and activities (feeding, resting, etc.)

## **4.0 LABORATORY METHODS**

### **4.1 Mussel Sample Processing**

This section provides procedures for preparing mussel soft tissue to be analyzed for Se. Intact mussels will be delivered to the FTN office for processing in a clean and controlled environment. Upon arrival at FTN, mussels will be killed by freezing and will be stored frozen until processing for delivery to the laboratory. Laboratory analysis will be conducted by American Interplex Corporation (AIC; 8600 Kanis Road, Little Rock, 72204) which is certified by ADEQ. Sample processing will be conducted within 7 days of sample collection. Any notes of the sample condition will be made after the thawing process. Mussel processing procedures and measurements will be documented on the Sample Processing Record for Mussel Contamination (Attachment 1). Procedures for processing samples for analysis are as follows:

#### **4.1.1 Sample Inspection**

Before shipment to AIC, mussel specimens will be thawed and the soft tissues excised. Individual samples received for processing will be carefully unwrapped and inspected to ensure that they have not been compromised in any way. Any specimen deemed unsuitable by the biologist will be rejected for processing.

#### **4.1.2 Weigh Individual Intact Mussels**

Wet weights will be determined for each mussel specimen. Balances will be calibrated at the beginning and end of each weighing session or after every 20 weighings.

#### **4.1.3 Describe Morphological Abnormalities**

Any gross morphological abnormalities will be noted and documented for each specimen.

#### **4.1.4 Resection**

Resection will be conducted under the supervision of a fisheries biologist. After thawing, a sharp clean filet knife will be inserted between the valves to cut the adductor muscle. Talc or



dust free gloves will be used. Precautions will be taken to minimize contamination of samples. Samples will be processed on a glass or PTFE cutting board. Stainless steel utensils will be used to cut as much soft tissue, including adductor muscle, from the inside of the valves as possible.

#### **4.1.5 Weigh Tissue**

The tissue portions from each individual specimen will be weighed individually to the nearest 0.1 gram and their weights recorded.

#### **4.1.6 Package and Ship Fillets**

Tissue from each individual specimen will be placed in a sealable plastic bag and labeled with a sample identification number, the sample type, the weight (g), and the date of resection. Samples will be stored and delivered frozen to AIC.

### **4.2 Se Analysis**

AIC will homogenize and digest samples (acid/microwave digestion) per EPA Method 3051. Digested samples will be analyzed by Inductively Coupled Plasma (ICP) per EPA 6010. Results will be reported on a dry weight basis. Table 4.1 summarizes the method detection limit, quantification limits of the laboratory, and other quality control information relevant to the analysis. The method detection limit is adequate for the purposes of the project.

Table 4.1. EPA Method 6010 quality control acceptance criteria.

<b>Test</b>	<b>Acceptable Criteria</b>
Method Detection Limit (MDL)	0.2 to 5 µg/g
Minimum Quantitation Level (MQL)	2 µg /g
MS/MSD Recovery	70-130%
MS/MSD Precision	<20% RPD
Method Blank	<0.1x sample whichever is greater

### **4.3 Data Validation**

Original analytical data will be sent to and housed at FTN's office in Little Rock, Arkansas. A copy of the analytical data and the associated QA/QC data will be sent to Alcoa. FTN will review the analytical results and the QA data for adherence to the QAPP and for identification of possible flagged data. Data will not be used or reported until appropriate data validation/verification has been completed.

## **5.0 REPORTING**

A data summary table with appended laboratory reports will be provided to ADEQ and USFWS.

## **6.0 REFERENCES**

EPA. 1995. Guidance for assessing chemical contaminant data for use in fish advisories, Vol. 1: Fish sampling and analysis. United States Environmental Protection Agency, Office of Water, EPA 823-R-95-007, September 1995.

# **ATTACHMENT 1**

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Mussel Tissue Lab Processing Documentation Form

Sample ID No. \_\_\_\_\_

Log No. \_\_\_\_\_

Sample ID No. \_\_\_\_\_

Log No. \_\_\_\_\_

Sample ID No. \_\_\_\_\_

Log No. \_\_\_\_\_

Sample ID No. \_\_\_\_\_

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