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Semi-Annual Remedy Selection and Design Progress Report Plant Barry

Prepared for Alabama Power Company

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ABBREVIATIONS

ACM	Assessment of Corrective Measures
ADEM	Alabama Department of Environmental Management
Alabama Power	Alabama Power Company
CCR	coal combustion residuals
CEC	cation exchange capacity
CFR	Code of Federal Regulations
COI	constituent of interest
CSM	conceptual site model
EPA	U.S. Environmental Protection Agency
MNA	monitored natural attenuation
Site	Ash Pond at Barry
SEM	scanning electron microscopy
SSE	selective sequential extraction
SSL	statistically significant level
USGS	U.S. Geological Survey
XRD	X-ray diffraction
XRF	X-ray fluorescence

1 Introduction

In accordance with the U.S. Environmental Protection Agency's (EPA's) coal combustion residuals (CCR) Rule 40 Code of Federal Regulations (CFR) § 257.97(a), the Alabama Department of Environmental Management's (ADEM's) Admin. Code r. 335-13-15-.06(8)(a), and Part C of Administrative Order No. 18-094-GW, this *Semi-Annual Remedy Selection and Design Progress Report* has been prepared for the Ash Pond at Plant Barry (Site). Specifically, this report has been prepared to describe the progress made in evaluating the selected remedy and alternative remedies and designing a remedy plan in the second semi-annual period of 2020.

In June 2019, Alabama Power Company (Alabama Power) completed an Assessment of Corrective Measures (ACM; Anchor QEA 2019) to address the occurrence of arsenic and cobalt in groundwater at statistically significant levels (SSLs). In the ACM, the following remedies were considered feasible for corrective measures for groundwater:

- Monitored natural attenuation (MNA)
- Hydraulic containment (pump and treat)
- Permeable reactive barrier walls
- Vertical barrier walls
- Geochemical manipulation via injections (i.e., enhanced natural attenuation)

As required by the Administrative Order, MNA was proposed as the main groundwater corrective action remedy for the Site. Source control measures consisting of consolidation, dewatering, and capping of the ash (source) were already planned as part of pond closure.

Additional assessment work has been completed in 2020 to evaluate and demonstrate MNA and geochemical manipulation as corrective measures at the Site. Groundwater samples and solids (precipitates) were collected from select wells, and groundwater sampling results were used to perform geochemical modeling, which predicted attenuating species under Site geochemical conditions. Well solids were analyzed to determine attenuating phases for the constituents of interest (COI; arsenic and cobalt) at the Site. Solids analysis also provides insight into the stability of the attenuating mechanisms. The well solids were analyzed as follows:

- Elemental analysis by X-ray fluorescence (XRF) to determine the chemical composition of the matrix (e.g., iron compounds, aluminosilicates, and carbonates) and presence of COI
- X-ray diffraction (XRD) to determine crystalline mineral phases
- Scanning electron microscopy (SEM) and associated elemental analysis to confirm mineral phases and attenuating mechanisms
- Selective sequential extraction (SSE) to determine the association of COI with attenuating phases and the relative binding strength of attenuated COI, and to provide a sense of permanence

• Cation exchange capacity (CEC) and exchangeable COI concentrations for samples that contain clay minerals

In addition, concentration versus time and concentration versus distance graphs were created to help determine if attenuation is occurring with time and/or distance from the ash pond.

Any data obtained during on-site investigations or to evaluate corrective action alternatives will be included in the subsequent *Semi-Annual Groundwater Monitoring and Corrective Action Reports*.

2 Summary of Work Completed

Site investigations and preliminary design work have continued at the Site to support remedy selection and design. As discussed in the ACM (Anchor QEA 2019), completing a final long-term corrective action plan is often a multi-year process. Additional assessment work has been completed since June 2020, and laboratory work has been performed to support MNA and in situ geochemical manipulation as discussed in the ACM. MNA and geochemical manipulation are both geochemically based, such that site-specific geochemical data and analyses can be applied to both technologies.

Laboratory analysis of groundwater and precipitates (attenuating solids) was conducted to support MNA and geochemical manipulation. The major rationale for these investigations includes the following:

- Identifying attenuating mechanisms
- Gaining an understanding of the stability of the attenuating mechanisms
- Identifying potential geochemical manipulation approaches for COIs based on Site geochemical conditions and attenuation processes already occurring naturally

In the previous reporting period (January through June 2020), the following field and laboratory investigations were performed:

- Evaluated groundwater analytical data (primarily graphing) to look for evidence of natural attenuation occurring in space and time.
- Collected groundwater samples from background and impacted wells and performed a complete chemical analysis on the samples to enable groundwater geochemical modeling and the development of a geochemical conceptual site model (CSM).
- Performed geochemical modeling using the U.S. Geological Survey (USGS) computer program PHREEQC with the WATEQ4F thermodynamic database.
- Collected precipitate samples from the bottom of monitoring wells.
- Analyzed precipitate samples by XRF and XRD.

The following investigations were begun in the previous reporting period but completed in the current reporting period:

- SEM to directly observe attenuating mineral phases
- SSE to determine association of COI with attenuating phases, determine relative strength of attenuation, and provide a sense of permanence
- CEC to assess ion exchange as an attenuation mechanism

The work performed since the completion of the June 2020 progress report includes the following:

- Sampling on-site and off-site delineation wells
- Completing SEM, SSE, and CEC testing on well solids samples

- Analyzing and synthesizing the laboratory data described above to develop a geochemical CSM and to evaluate MNA and geochemical manipulation
- Conceptualizing other corrective action options in the context of site-specific conditions, should MNA or geochemical manipulation not perform as expected

2.1 Preliminary Data Analysis

Results from existing groundwater data analysis, geochemical modeling, and well solids analyses provide evidence for attenuation mechanisms for arsenic and cobalt, as summarized in Table 1. The attenuating mechanisms identified include sorption-coprecipitation on iron oxides, cation exchange on clays, coprecipitation in carbonate minerals, and incorporation of arsenic in barium arsenate.

2.1.1 Concentration Versus Time and Concentration Versus Distance Graphs

Existing groundwater data were used to generate concentration versus time and concentration versus distance graphs to determine if attenuation is occurring over space and/or time and to assess natural attenuation occurrence and rates. Arsenic and cobalt were plotted on the y-axis. For the concentration versus distance graphs, the distance between the pond boundary and the monitoring well was plotted on the x-axis. For the concentration versus time plots, the time between sampling events (in days) was plotted on the x-axis. Because of the limited time span of the dataset and associated small number of samples through time for a given well, no meaningful trends in concentration versus time were noted. Concentration versus distance graphs were made for upgradient-downgradient well pairs along flowpaths. Specifically, graphs were made for wells BY-AP-MW-7 to BY-AP-MW-23H (which had both arsenic and cobalt SSLs) and wells BY-AP-MW-8 to BY-AP-MW-18H, BY-AP-MW-10 to BY-AP-MW-19H, and BY-AP-MW-12 to BY-AP-MW-20H (which had only arsenic SSLs). All four transects showed arsenic concentrations decreasing with distance away from the pond, indicating spatial attenuation (as shown in example Figure 1). Cobalt concentrations showed an increasing trend with distance from BY-AP-MW-7 to BY-AP-MW-23H, but decreasing trends are expected to occur after pond closure is complete.

2.1.2 Laboratory Analyses

Well solids (precipitates) were previously collected and were analyzed as follows:

- XRF to determine the chemical composition of the matrix (e.g., iron compounds) and presence of COI
- XRD to determine mineral phases
- SEM to directly observe attenuating phases
- SSE to determine association of COI with attenuating phases, determine relative strength of attenuation, and provide a sense of permanence

• CEC to assess ion exchange as a mechanism for attenuation

All samples with sufficient volume were analyzed by XRF. A select number of samples were chosen to be analyzed by XRD to determine predominant mineralogy. Samples for XRD analysis were selected by looking at a variety of data, including, but not limited to, XRF data, field parameters, sample location, chemical analysis, and recovered sample mass.

The XRF chemical analysis of the well solids (Table 2) showed relatively high concentrations of iron (an attenuating species) in well solids (precipitates) from seven wells. Figure 2 shows that a relationship exists between arsenic and iron. This suggests that iron compounds are attenuating arsenic, especially because most of the arsenic values are above those in precipitates from background wells.

XRD identified quartz as a major component of the well solids in all wells and minor feldspar. Goethite (an attenuating iron oxide) was identified in solids from one well from the Site and montmorillonite and zeolite from solids in five wells from the Site. Muscovite-illite was identified in one well. Montmorillonite and muscovite-illite are attenuating clay minerals, and zeolite is an attenuating clay-like mineral (Table 3).

SEM and associated elemental mapping were conducted on select samples to confirm mineral phases and attenuating mechanisms. SEM results indicate that the solids collected from BY-AP-MW-1 (Figure 3) are predominantly quartz interspersed with feldspar and iron-rich grains. Some alteration was observed, with dissolution pitting in some grains and thin coatings of aluminum, calcium, and iron material in others. Elemental mapping (Figure 3) indicates these secondary minerals contain iron and are likely coatings of amorphous iron oxides. The colors in Figure 3 are not natural but are added to show the relative abundance and distribution of the various elements analyzed. SEM results indicate that the solids collected from BY-AP-MW-2 (Figure 4) are predominantly freshly fractured quartz interspersed with small calcite, feldspar, and iron-rich grains. Alteration is minimal, with some very thin coatings of aluminum or iron material. Figure 4 shows secondary mineral growth on sand grains. These secondary minerals likely contain iron.

Based on the results from the XRF and XRD analyses and available sample volume, samples were selected for SSE. SSE targets a series of operationally defined mineral fractions. In SSE, samples are leached with increasingly aggressive solutions to determine the chemical associations and mechanisms of attenuation. Generally, COIs released in each successive step represent stronger sequestration and greater stability than the previous step. The fractions, from most to least environmentally available, are as follows:

- F1 Water soluble
- F2 Exchangeable (e.g., clay minerals)

- F3 Reducible (e.g., poorly crystalline metal oxides such as iron oxides)
- F4 Oxidizable (e.g., crystalline oxide and crystalline sulfide minerals)
- F5 Residual (e.g., silicate phases)

The F3, F4, and F5 fractions represent relatively stable (permanent) attenuating mechanisms, provided Site geochemical conditions do not change drastically.

Figure 5 shows the results of SSE for six samples from the Site. Interpretation by COI includes the following:

- Arsenic Bound primarily in the F2 (exchangeable), F3 (reducible), F4 (oxidizable), and F5 (residual) fractions. This is consistent with the identification of montmorillonite and zeolite (F2; clays), iron oxides (e.g., amorphous iron oxides, F3, and goethite, F4) from the other investigations, and barium arsenate (F3 and F4) predicted by geochemical modeling.
- Cobalt Bound primarily in the F4 (oxidizable) fraction and F5 (residual) fractions. Significant cobalt is also associated with the F1 (soluble) and F2 (exchangeable) fractions. This is consistent with the identification of montmorillonite and zeolite (F2) and goethite (F4) from the analysis of well solids, and possibly iron carbonate phases (F3; siderite) predicted by geochemical modeling.
- The F4 and F5 fractions indicate relatively stable (strong) attenuation mechanisms for arsenic and cobalt.

Select samples with suspected clay content were submitted for CEC testing. CEC was variable in the samples, ranging from 45 to 350 milliequivalents per kilogram (Table 4). This is consistent with clay mineralogy (calcium-rich montmorillonite) and supports evidence of cobalt attenuation by cation exchange on clays.

2.2 Geochemical Modeling

Geochemical equilibrium modeling was performed to help determine what phases may be controlling the dissolved concentrations, mobility and attenuation of arsenic and cobalt, as well as the behavior of other species (such as iron) that influence the behavior of arsenic and cobalt.

The Geochemist's Workbench software was used to plot Eh-pH data on Pourbaix stability diagrams to assess the geochemical stability of potentially controlling phases under site conditions. Figures 6 through 7, based on geochemical modeling and Site groundwater Eh-pH conditions, predict the attenuating species included below. In Figures 6 through 8, blue fields indicate dissolved/mobile species, and yellow fields indicate solid/attenuated species. The Pourbaix stability diagrams indicate the following associations and attenuating mechanisms, by COI:

• Iron oxides (e.g., ferrihydrite and/or goethite) and carbonates (siderite) are supersaturated or near equilibrium (Figure 6)

- Arsenic concentrations are likely controlled by sorption on iron oxides (e.g., ferrihydrite) and/or a barium arsenate mineral phase (Figure 7)
- Cobalt concentrations are likely controlled by co-precipitation in a cobalt-iron oxide mineral phase (Figure 8)

These mineral associations are well documented in the scientific literature for arsenic and cobalt.

Geochemical speciation-solubility calculations were performed using PHREEQC with the WATEQ4F thermodynamic database to evaluate charge balance, calculate aqueous speciation, and determine mineral saturation indices for the groundwater samples collected. Saturation index calculations can be useful in inferring potential solid phases present in an aquifer and controls on water chemistry and reactivity of an aqueous solution toward specific mineral phases. Geochemical modeling results indicate that iron oxides (e.g., goethite and ferrihydrite) and carbonates (siderite) are stable. Arsenic concentrations are likely controlled by sorption to iron oxides and a barium arsenate mineral phase is also predicted to be stable. Cobalt concentrations are likely controlled by sorption and/or coprecipitation with iron oxides.

2.3 Geochemical Conceptual Site Model

The investigations described previously and geochemical equilibrium modeling were used to develop an initial geochemical CSM, including probable attenuating mechanisms for arsenic and cobalt, and the relative permanence of those mechanisms. The initial CSM for the Site is as follows:

- Multiple lines of evidence for arsenic and cobalt attenuation
- Suboxic and acidic conditions in groundwater
- Redox appears to be buffered by iron oxide (+/- carbonate) equilibria
- Arsenic attenuation by adsorption to iron oxides and possibly by a predicted (but not observed) barium arsenate phase
- Cobalt attenuation by adsorption/co-precipitation in iron oxides and cation exchange on clay minerals
- Increased arsenic and cobalt sequestration over time; iron oxides age to more crystalline forms

As supported by SSE results and the scientific literature, incorporation of arsenic and cobalt into iron minerals and arsenic into barium arsenate are relatively stable attenuation mechanisms.

3 Planned Activities and Anticipated Schedule

The following conceptual-level feasibility study activities are planned for the next reporting period (January to June 2021) to evaluate MNA, geochemical manipulation, and possibly other corrective action technologies:

- Continue to compare site-specific corrective actions to the evaluation criteria in the CCR Rule, with emphasis on deficiencies that could eliminate a corrective action from further consideration
- Continue to determine how corrective actions could be integrated with pond closure, such as dewatering and associated water treatment systems
- Develop plans for additional Site investigations and associated laboratory work to determine MNA capacity, rates, and stability; and plans for laboratory treatability and/or field pilot tests to determine the effectiveness of geochemical manipulation as needed

Section 2 describes substantial evidence for the occurrence of natural attenuation at the Site. The EPA's four phases (or tiers) of MNA (EPA 2015) are as follows:

- Phase 1 Demonstrate area of impacts (plume) is stable or shrinking
- Phase 2 Determine mechanisms and rates of attenuation
- Phase 3 Determine system capacity and stability
- Phase 4 Design performance monitoring program and identify alternative remedies

The MNA work performed at the Site to date primarily supports Phase 2 (specifically mechanisms of attenuation), though some information has been collected that supports all four phases. To advance MNA at the Site, additional work needs to be performed with respect to rate, aquifer capacity, and stability (permanence) of MNA.

Though substantial evidence for natural attenuation exists for the Site, natural attenuation is expected to increase as source control measures are implemented (i.e., dewatering, consolidation, and capping). MNA will almost certainly be one component, if not the only component, of corrective action. MNA could be implemented immediately upon pond closure.

The longer-term schedule for developing a groundwater corrective action system at the Site is as follows:

- Collect additional soil samples and perform associated laboratory work to determine MNA capacity, rates, and stability (first and second quarters 2021)
- Perform laboratory treatability studies and implement field pilot tests as needed (second and third quarters 2021)
- Prepare a Remedy Selection Report (fourth quarter 2021)
- Develop a Corrective Action Groundwater Monitoring Program (fourth quarter 2021)

During the next reporting period, other potential remedies identified in the ACM will continue to be evaluated with respect to technical feasibility, ability to attain target standards, and ease of implementation. Based on the site-specific evaluation, additional studies may be implemented.

The schedule of activities above is considered typical and will be affected by the pond closure activities and schedule. For example, some of the activities could be performed sooner, to enable integration of corrective action with pond closure. Similarly, pond closure activities might delay implementation of some of the items above.

Pursuant to 40 CFR 257.97(a) and ADEM Admin. Code r. 335-13-15-.06(8)(a), semi-annual status progress reports will continue to be finalized in June and December until a final remedy plan is developed. Upon developing a final remedy plan, the Remedy Selection Report will be prepared describing the remedy plan and how it demonstrably meets the requirements of § 257.97 and r. 335-13-15-.06(8). Details regarding adaptive management triggers and criteria will be included in the Corrective Action Groundwater Monitoring Program.

Alabama Power will continue groundwater monitoring at the Site and will submit the next *Semi-Annual Remedy Selection and Design Progress Report* by June 12, 2021.

4 References

- Anchor QEA (Anchor QEA, LLC), 2019. *Assessment of Corrective Measures*. Plant Barry Ash Pond. Prepared for Alabama Power Company. June 2019.
- EPA (U.S. Environmental Protection Agency), 2015. Use of Monitored Natural Attenuation for Inorganic Contaminants in Groundwater at Superfund Sites. Office of Solid Waste and Emergency Response Directive 9283.1-36. August 2015.

Tables

Table 1

Lines of Evidence for Attenuation Mechanisms

Mechanism	Geochemical Modeling	XRD	SSE	CEC
Sorption-coprecipitation on iron oxides	Х	Х	Х	
Cation exchange on clays		Х	Х	Х
Coprecipitation in carbonates	Х	Х	Х	
Incorporation of arsenic in barium arsenate	Х		Х	

Notes:

CEC: cation exchange capacity

SSE: selective sequential extraction

XRD: X-ray diffraction

Table 2 Bulk Chemistry of Well Solids Samples by XRF

Well ID	Arsenic	Cobalt	Iron	Manganese	Aluminum	Calcium	Magnesium	Potassium	Silicon
BY-AP-MW-1	21	ND	25,600	ND	11,700	2,170	ND	6,530	302,000
BY-AP-MW-2	ND	ND	7,810	ND	7,020	2,010	ND	7,060	362,000
BY-AP-MW-3	ND	ND	11,200	ND	5,980	1,470	ND	4,610	283,000
BY-AP-MW-5	24	ND	6,540	ND	2,490	946	ND	1,160	263,000
BY-AP-MW-7	44	ND	49,800	ND	4,290	3,710	ND	3,760	223,000
BY-AP-MW-9	44	ND	33,000	ND	2,360	6,260	ND	2,450	46,500
BY-AP-MW-11	11	ND	10,200	ND	4,060	2,280	ND	4,840	237,000
BY-AP-MW-12	ND	ND	2,220	ND	1,810	1,340	ND	2,170	279,000
BY-AP-MW-13	ND	ND	2,650	ND	1,370	816	ND	2,890	253,000
BY-AP-MW-16	ND	ND	4,020	ND	4,340	1,920	ND	5,920	311,000

Notes:

Units are in milligrams per kilogram

ND: below limit of detection

XRF: X-ray fluorescence

Table 3

Minerals Identified in Well Solids Samples by XRD¹

Well ID	Quartz	Albite	Orthoclase	Muscovite-illite	Montmorillonite	Zeolite	Calcite	Geothite
BY-AP-MW-1	Х			х				
BY-AP-MW-2	98	1.9			0.1	0.19		
BY-AP-MW-5	99				0.17	0.41		
BY-AP-MW-7	Х							х
BY-AP-MW-11	90	9			0.13	0.59		
BY-AP-MW-13	100				0.14	0.33		
BY-AP-MW-16	97		1.1		0.17	0.33	1.8	

Notes:

1: Estimated concentration (weight %) reported where available

--: not detected

X: Positive identification, not quantified

XRD: X-ray diffraction

Table 4Cation Exchange Capacity of Well Solids Samples

Well ID	Aluminum	Boron	Calcium	Lithium	Magnesium	Potassium	Sodium	Sum
BY-AP-MW-1	0.037 J	<0.019	100	<0.019	7.4	0.73	5.4	114
BY-AP-MW-2	0.14 J	<0.10	29	<0.16	4.8	4.0	7.0	44.8
BY-AP-MW-11	0.010 J	<0.0063	84	0.069	4.0	1.6	1.9	91.6
BY-AP-MW-16	<0.013	<0.013	340	0.075	4.4	1.7	2.8	350

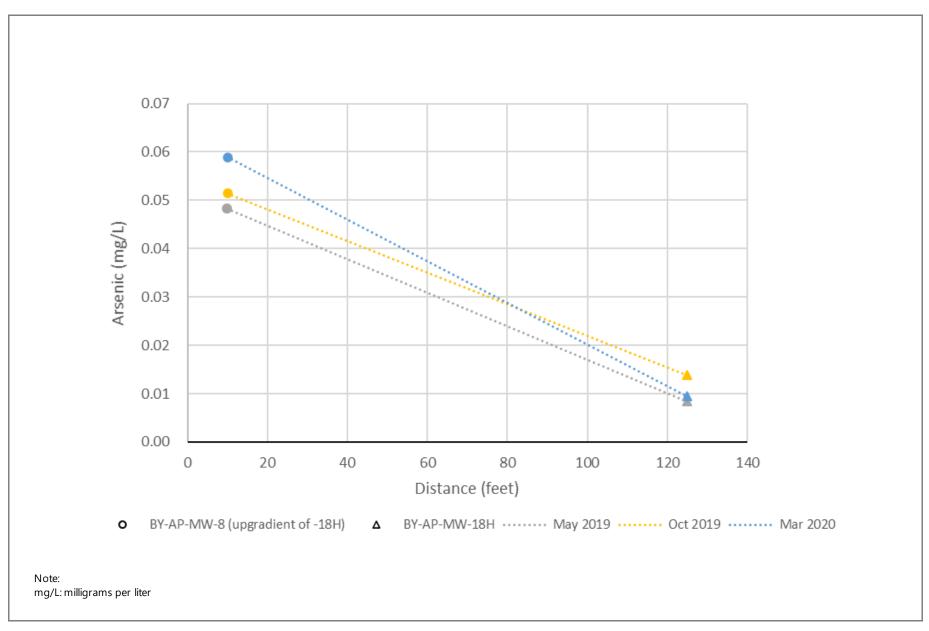
Notes:

Concentrations are in milliequivalents per kilogram.

<: Indicates the compound was analyzed for but not detected

J: Detected but result is below the method reporting limit

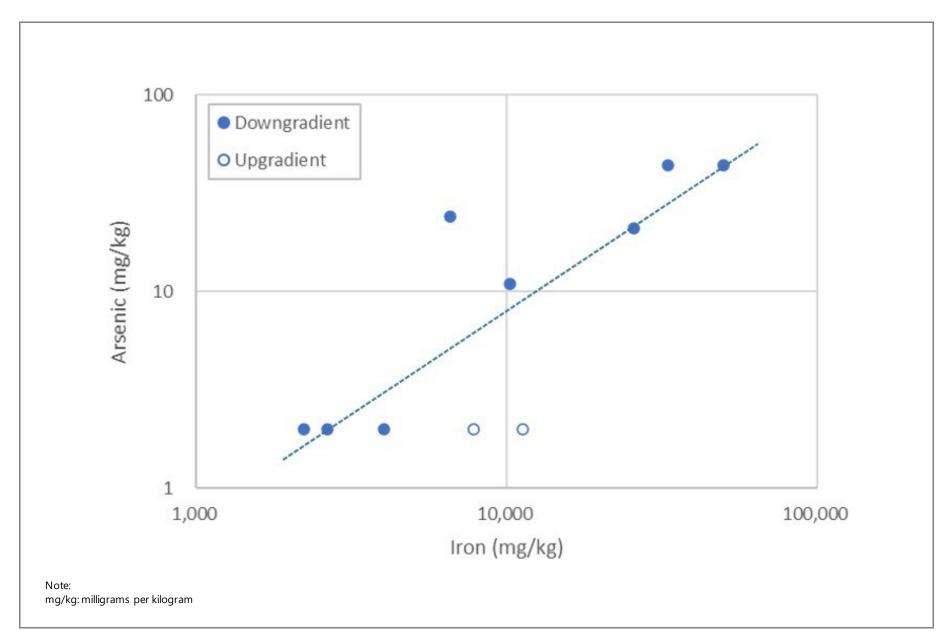
Figures



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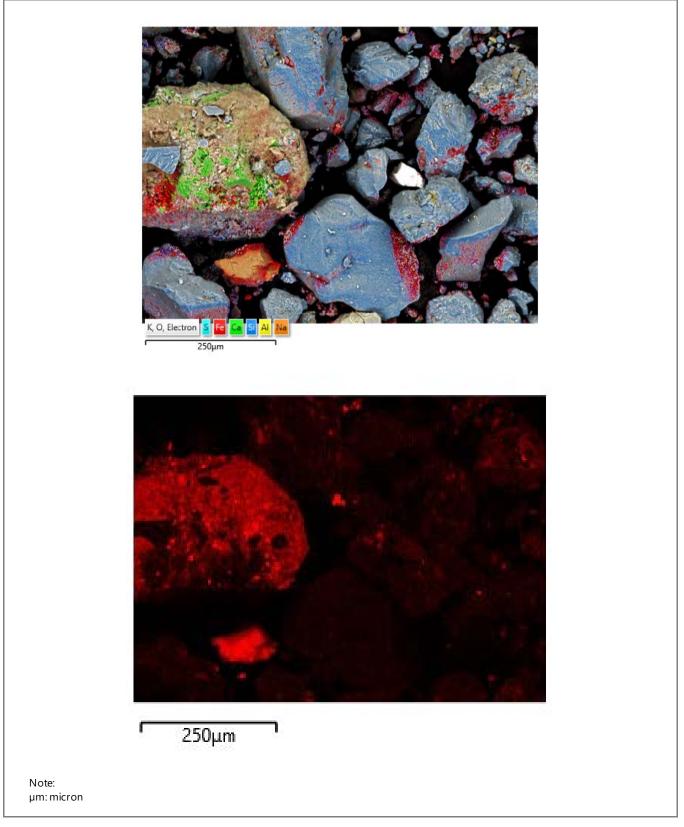
Figure 1 Arsenic Concentration Versus Distance: BY-AP-MW-8 to BY-AP-MW-18H



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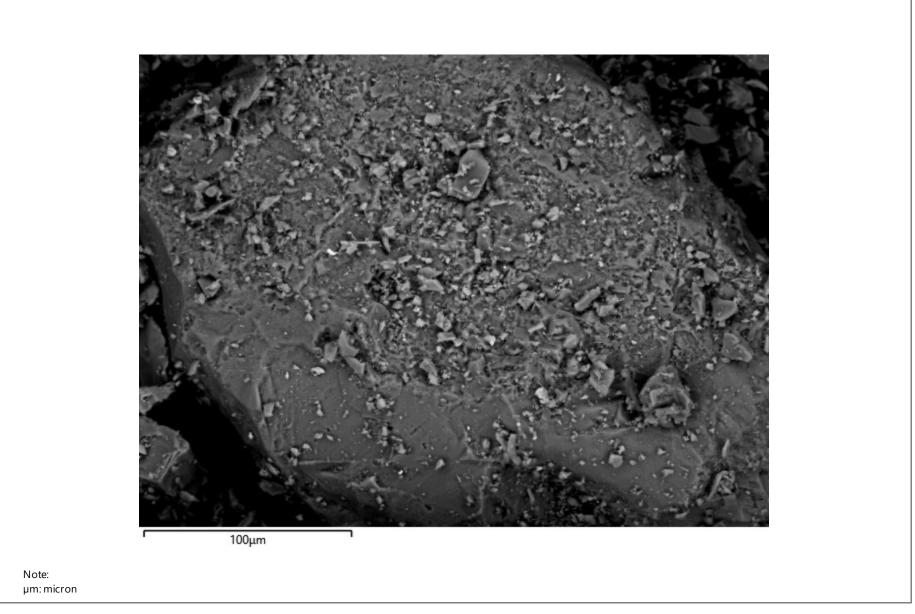
Figure 2 Bulk Chemistry Relationship Between Arsenic and Iron



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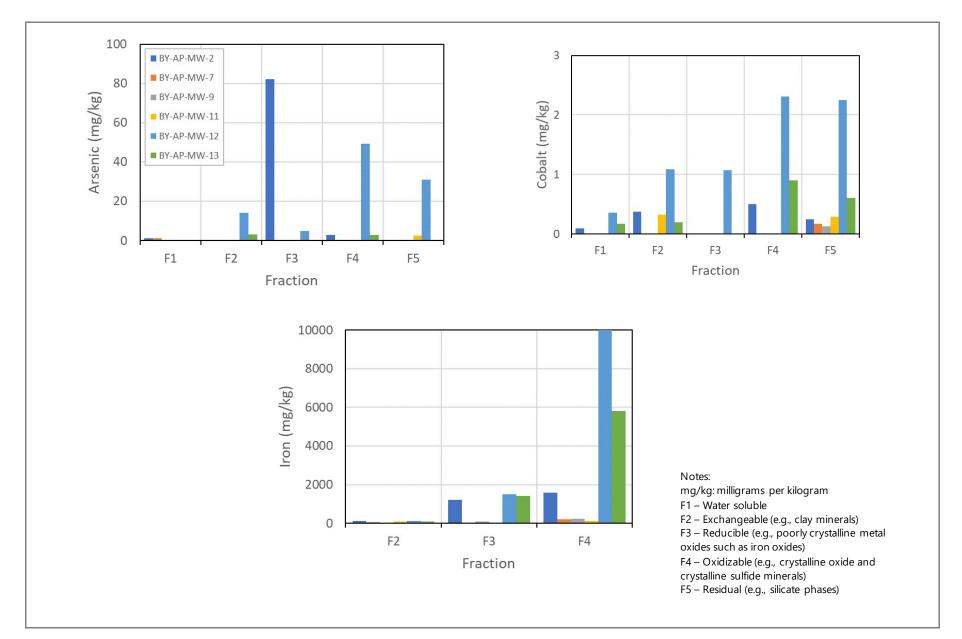
Figure 3 SEM Results for BY-AP-MW-1



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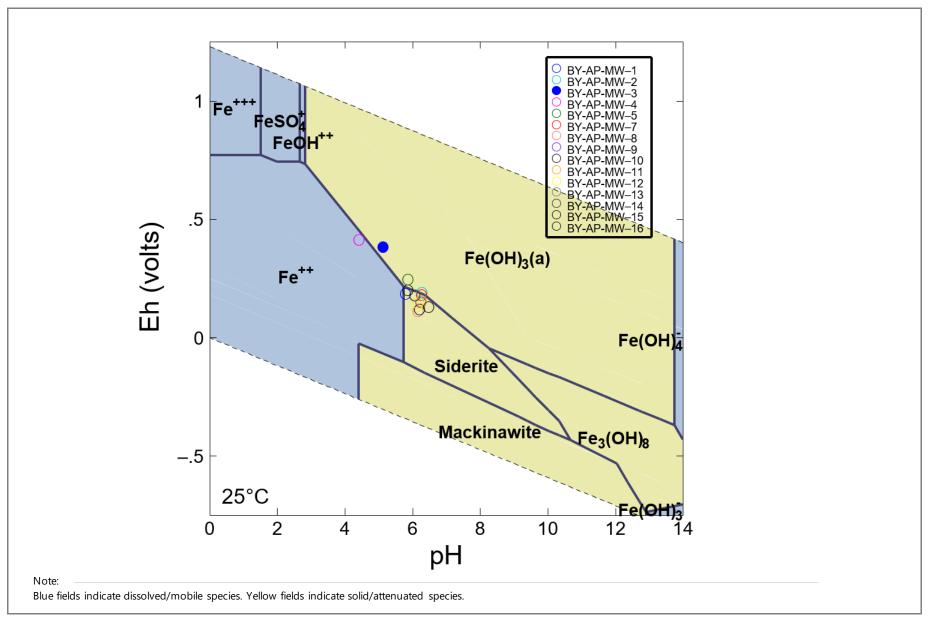
Figure 4 SEM Results for BY-AP-MW-2



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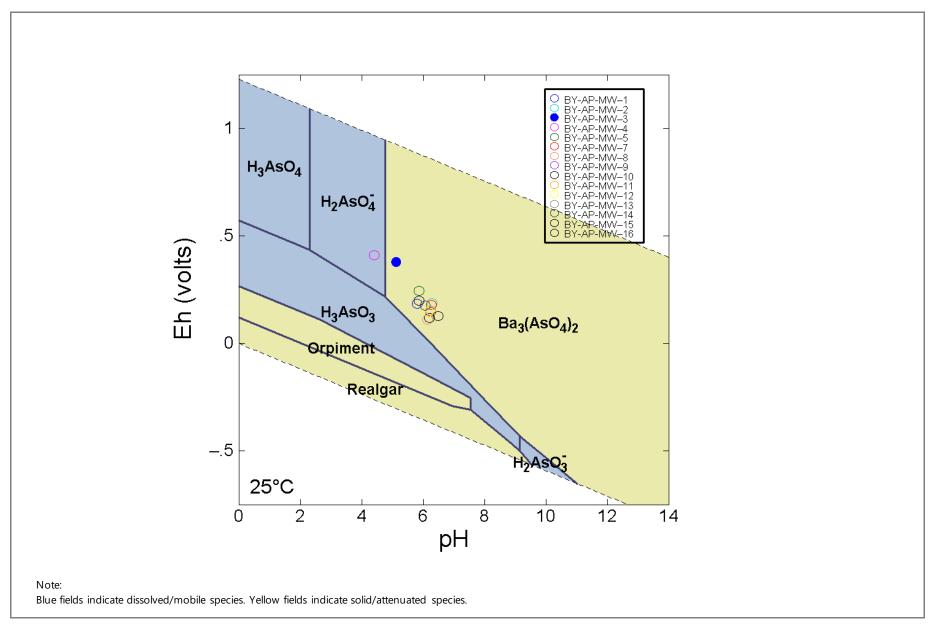
Figure 5 SSE Results for Well Solids



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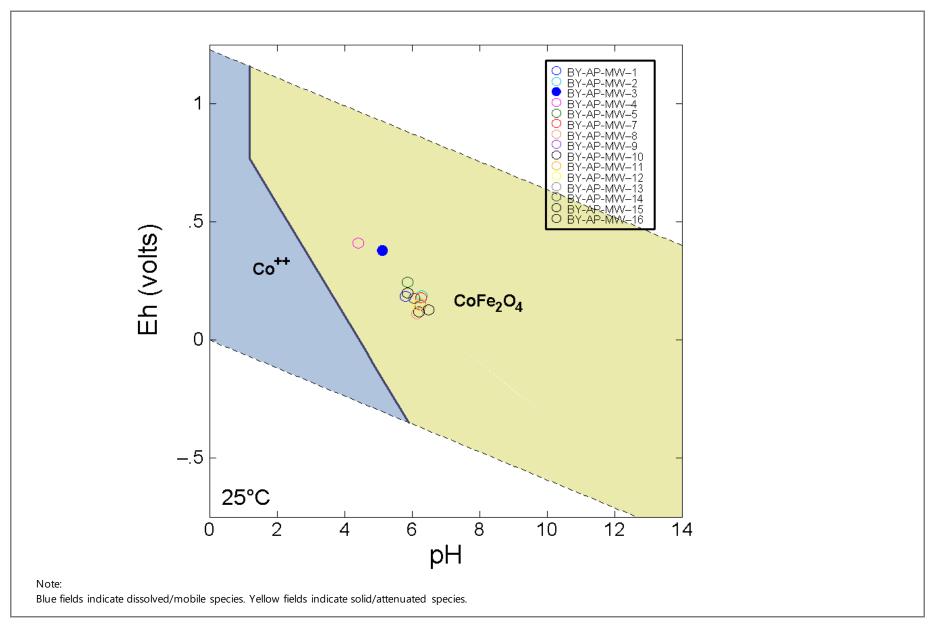
Figure 6 Eh-pH Stability Diagram for Dissolved and Solid Iron Phases



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Figure 7 Eh-pH Stability Diagram for Dissolved and Solid Arsenic Phases



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Figure 8 Eh-pH Stability Diagram for Dissolved and Solid Cobalt Phases