



December 2020



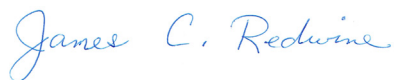
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# Semi-Annual Remedy Selection and Design Progress Report Plant Miller

Prepared for Alabama Power Company

December 2020

# Semi-Annual Remedy Selection and Design Progress Report Plant Miller



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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 Plant Miller
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. 18-098-GW, this *Semi-Annual Remedy Selection and Design Progress Report* has been prepared for the Ash Pond at Plant Miller (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, cobalt, and lithium 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)
- Geochemical manipulation via injections (i.e., enhanced natural attenuation)
- Permeation grouting

As required by the Administrative Order, MNA was proposed as the main 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, cobalt, and lithium) 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:

- Installing replacement downgradient monitoring wells, installing replacement horizontal delineation wells, and installing upgradient monitoring wells; and sampling monitoring 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, cobalt, and lithium, as summarized in Table 1. The attenuating mechanisms identified include sorption on or coprecipitation in iron oxides (arsenic and cobalt), precipitation of barium arsenate (arsenic), and cation exchange on clays (cobalt and lithium).

### 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, cobalt, and lithium 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.

No trends are apparent for the concentration versus distance graphs, though this could change as more data become available with continued monitoring. Figures 1 through 3 show that cobalt concentrations are decreasing with time in wells MR-AP-MW-2, MR-AP-MW-4, and MR-AP-MW-6, which provide evidence for natural attenuation. Because it is poorly chemically attenuated, but subject to physical attenuation (e.g., dispersion), plotting boron against the other COI provides insight into attenuation mechanisms for the other COI. Boron concentrations in MR-AP-MW-4 are remaining relatively stable, indicating that cobalt attenuation is not physical but rather chemical as described later in this section. Similar evidence from other wells is expected in the future as closure activities reduce the source of COI to groundwater.

### 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.

Some of the wells at Plant Miller did not yield sufficient quantities of solid samples (precipitates) for the entire testing protocol. Table 2 shows bulk chemistry (XRF), and Table 3 shows XRD analysis for available samples. The bulk chemistry identified elements associated with potentially attenuating phases (iron and calcium), and the XRD analysis identified minor muscovite-illite in both samples and calcite and zeolite in one sample, which are potentially attenuating minerals.

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 MR-AP-MW-4 are a mix of quartz and calcite, with smaller aluminum-rich and iron-rich grains. Some alteration with dissolution pitting and thin coatings of aluminum-rich material was observed. SEM results indicate that the solids collected from MR-AP-MW-3D are predominantly silica (quartz) interspersed with calcite, feldspar, and iron-rich grains. Very little alteration with dissolution pitting was observed in some grains, and thin coatings of aluminum, calcium, and iron-rich material was observed in others.

Based on the results from the XRF and XRD analyses and available sample volumes, 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 F4 and F5 fractions represent relatively stable (permanent) attenuating mechanisms, provided Site geochemical conditions do not change drastically.

Figure 4 shows the results of SSE for three samples from the Site. Interpretation by COI includes the following:

- Arsenic – A small amount of arsenic is detected in the soluble fraction (F1). Arsenic was not detected in fractions F2 to F5, but detection limits for these are elevated due to small sample mass available and therefore provide limited information. However, iron (which is commonly associated with arsenic attenuation) is present in the exchangeable (F2), reducible (F3), and oxidizable fractions (F4; Figure 5), which is consistent with the presence of poorly crystalline to crystalline iron oxide coatings.
- Cobalt – Depending upon the well, cobalt is distributed among the F2 (exchangeable), F3 (reducible), F4 (oxidizable), and F5 (residual) fractions. F2 is consistent with cobalt ion exchange on clays reported in the scientific literature, and F4 is consistent with cobalt association with iron oxides as also suggested by geochemical modeling results (stability of cobalt iron oxides).
- Lithium – Detected primarily in the F5 (residual) fraction, but detection limits are elevated due to limited available sample mass for SSE.

Two samples with suspected clay content were submitted for CEC testing. CEC was very high for these samples, specifically 1,910 and 6,100 milliequivalents per kilogram and mostly due to calcium (Table 4), which reflects clay mineralogy and possibly some dissolution of calcite. Exchangeable lithium was identified in solids from one of the wells.

## 2.2 Groundwater Geochemical Equilibrium Modeling

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

The Geochemist's Workbench software was used to construct Pourbaix (Eh-pH) diagrams for COI, iron, and manganese based on Site groundwater chemistry, and to assess the geochemical stability of phases potentially controlling COI concentrations under Site conditions (Figures 5 through 8). The blue shaded fields indicate conditions under which dissolved/mobile species are predicted to be more stable, while yellow fields indicate conditions where solid phases are stable. Eh-pH data from Site groundwater wells are also plotted to determine the most stable forms under Site conditions. The Pourbaix stability diagrams indicate the following:

- Iron concentrations appear to be controlled by amorphous iron oxides (Figure 5). Iron oxides are strong sorbents for many metals and metalloids including arsenic and cobalt.

- Arsenic is predominantly in the +5 valence state, and concentrations may be controlled by a barium arsenate mineral phase (Figure 6) and/or adsorption on iron oxides (e.g., ferrihydrite; Figure 5).
- Cobalt concentrations are likely controlled by a cobalt-iron oxide mineral phase (Figure 7) and/or sorption on iron oxides.
- Lithium is often associated with manganese oxides. In Figure 8, this association is represented by the stability field of the mineral lithiophorite. The thermodynamic properties of lithiophorite and other lithium-bearing manganese oxides are not well known, and the stability field is approximate. Site groundwater conditions appear to be too reducing to stabilize lithium in manganese oxides.

Geochemical speciation-solubility calculations were also performed using PHREEQC with the WATEQ4F thermodynamic database (augmented with data for lithiophorite) to evaluate charge balance, calculate aqueous speciation, and determine the saturation state of groundwater samples with respect to possible mineral phases. 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 groundwater is close to equilibrium with amorphous iron oxide and supersaturated with more crystalline iron oxides (goethite, hematite, and magnetite). Barite (barium sulfate) is close to equilibrium in all samples, and a barium arsenate phase is also predicted to be supersaturated in groundwater samples with detectable arsenic. No lithium bearing mineral phases are close to saturation. Note that SSE results indicate lithium is bound primarily in the F5 (residual) fraction, and CEC data show exchangeable lithium was identified in solids from one of the wells. Groundwater samples appear to be supersaturated with respect to a cobalt-iron oxide phase.

In summary, geochemical modeling evaluations indicate the following:

- Arsenic concentrations are likely controlled by adsorption on iron oxides and possibly a barium arsenate phase.
- Cobalt concentrations are likely controlled by adsorption on and/or incorporation in iron oxides.
- No solubility controls were identified for lithium although limited laboratory data indicate lithium is present in cation exchange sites on clay minerals.

These mineral associations are well documented in the scientific literature as attenuation mechanisms for arsenic, cobalt, and lithium.

## 2.3 Geochemical Conceptual Site Model

The laboratory investigations described previously were integrated with geochemical modeling results to develop an initial geochemical CSM, including probable attenuating mechanisms for

arsenic, lithium, and molybdenum, and the relative permanence of those mechanisms. The initial CSM for the Site is as follows:

- Multiple lines of evidence for arsenic, cobalt, and lithium attenuation
- Moderately reducing, weakly acidic groundwater conditions
- Redox buffered by iron oxide equilibria
- Arsenic attenuation by sorption to iron oxides and possibly precipitation of barium arsenate
- Cobalt attenuation by adsorption on and co-precipitation with iron oxides
- Lithium attenuation by ion exchange on clay minerals

As supported by SSE results and the scientific literature, incorporation of arsenic and cobalt into iron minerals, arsenic into barium arsenate, and lithium on clay minerals 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 and/or rock 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 Miller 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

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**Table 1**  
**Lines of Evidence for Attenuation Mechanisms**

<b>Mechanism</b>	<b>Geochemical Modeling</b>	<b>XRF</b>	<b>XRD</b>	<b>SSE</b>	<b>CEC</b>
Sorption on iron oxides (arsenic, cobalt)	X	X			
Precipitation of barium arsenate	X				
Co-precipitation in iron oxides (cobalt)	X			X	
Cation exchange on clays (cobalt, lithium)			X	X	X

Notes:

CEC: cation exchange capacity

SSE: selective sequential extraction

XRD: X-ray diffraction

XRF: X-ray fluorescence

**Table 2**  
**Bulk Chemistry of Well Solids Samples by XRF**

Well ID	Arsenic	Cobalt	Iron	Manganese	Aluminum	Calcium	Magnesium	Potassium	Silicon
MR-AP-MW-3D	ND	ND	7,610	ND	6,580	22,300	ND	4,260	199,000
MR-AP-MW-4	11	ND	17,000	ND	9,400	126,000	ND	7,370	117,000

Notes:

Direct analysis of lithium is not possible with portable XRF due to X-ray physics limitations.

Units are in milligrams per kilogram

ND: below limit of detection

XRF: X-ray fluorescence

**Table 3**  
**Minerals Identified in Well Solids Samples by XRD<sup>1</sup>**

Well ID	Quartz	Albite	Muscovite-illite	Zeolite	Calcite
MR-AP-MW-3D	93.8	1.3	0.3	--	4.6
MR-AP-MW-4	36.1	--	3.9	0.3	59.6

Notes:

1: Estimated concentration (weight %) reported where available

XRD: X-ray diffraction

**Table 4**  
**Cation Exchange Capacity of Well Solids Samples**

Well ID	Aluminum	Boron	Calcium	Lithium	Magnesium	Potassium	Sodium	Sum
MR-AP-MW-3D	<0.036	<0.040	1,910	0.046 J	27	1.3	4.6	1,940
MR-AP-MW-4	1.78 J	<1.48	6,100	<1.73	97	8.2 J	14 J	6,200

Notes:

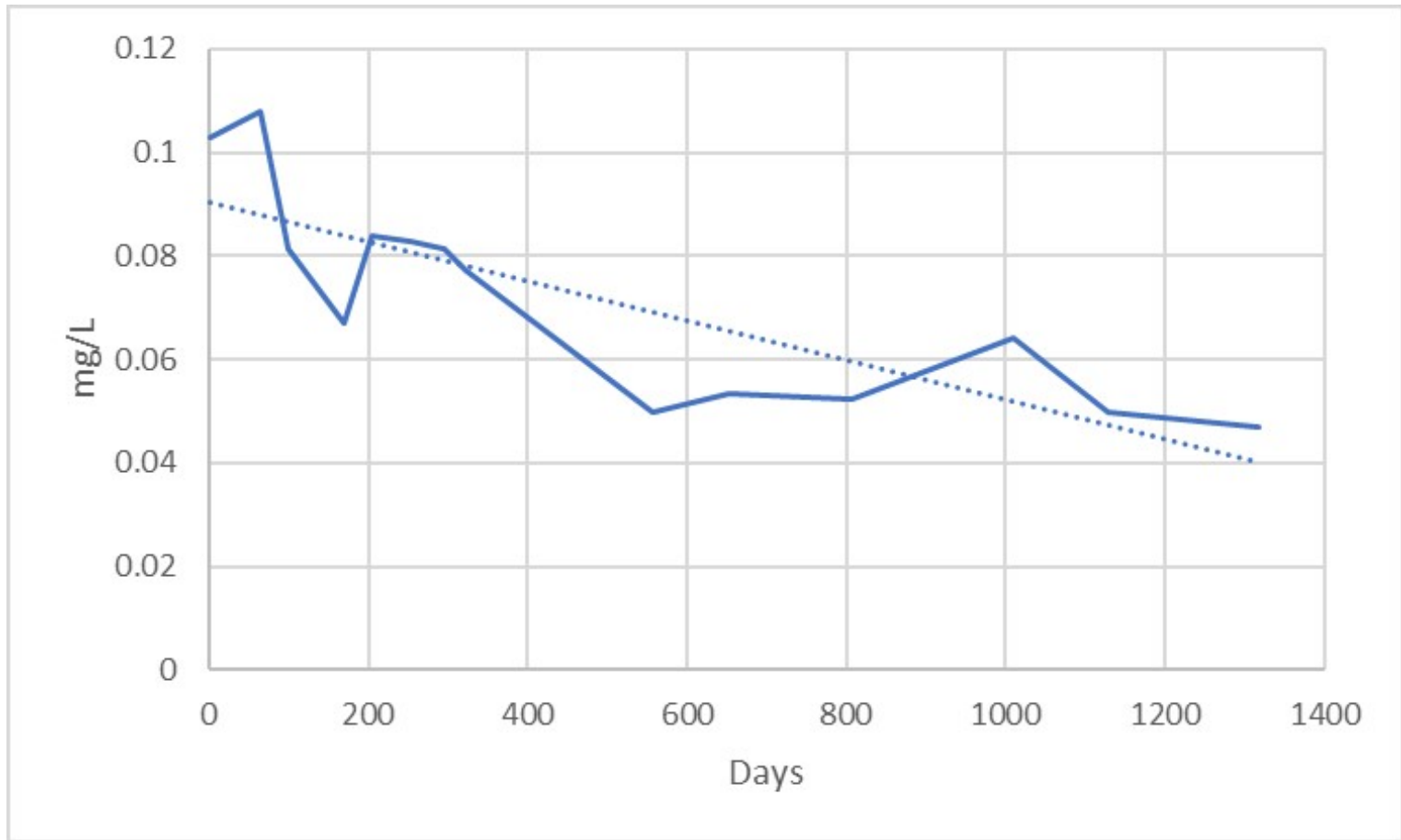
Units are in milliequivalents per kilogram

<: Indicates the compound was analyzed for but not detected

J: Detected but result is below the method reporting limit

## Figures

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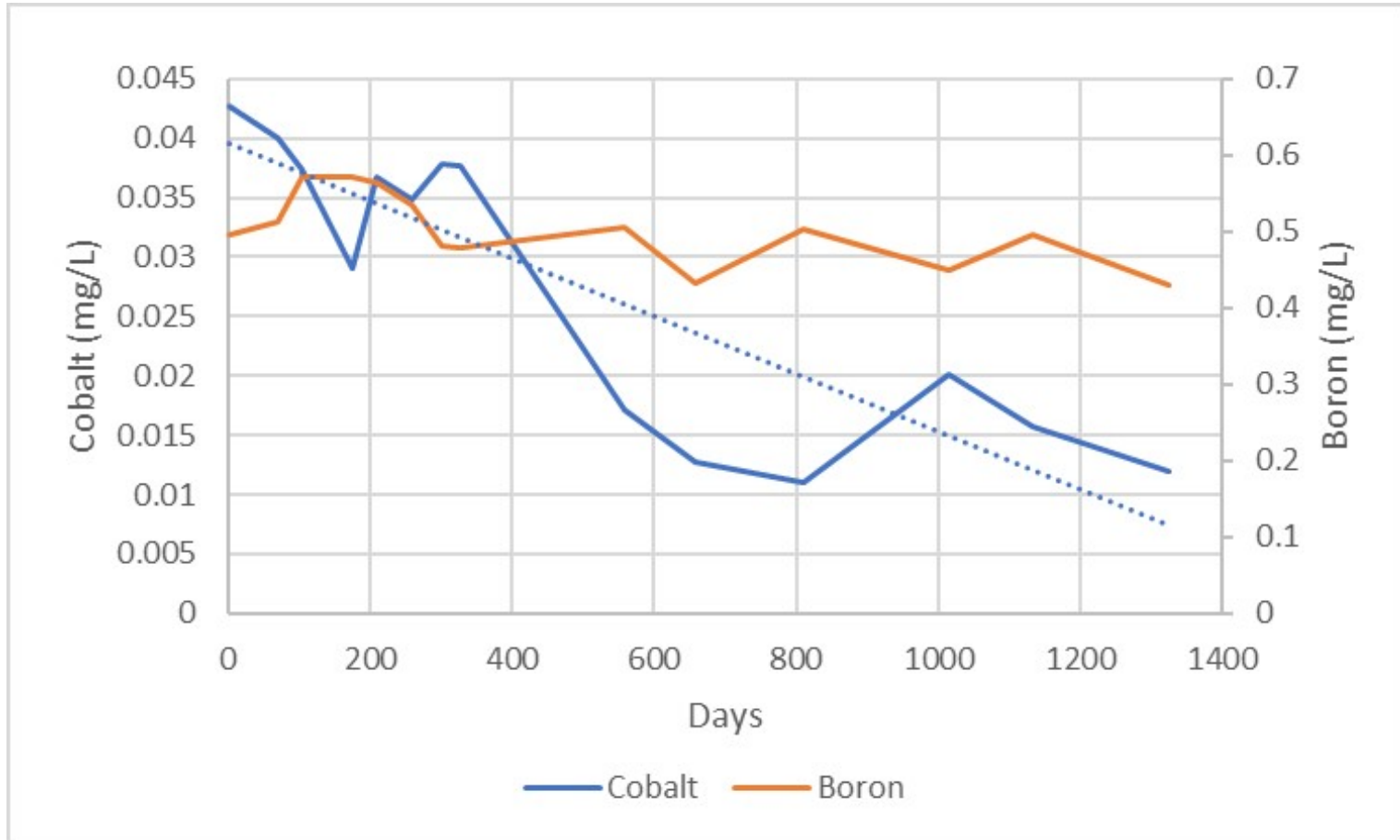


Note:  
mg/L: milligrams per liter

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**Figure 1**  
**Cobalt Concentration Versus Time in MR-AP-MW-2**  
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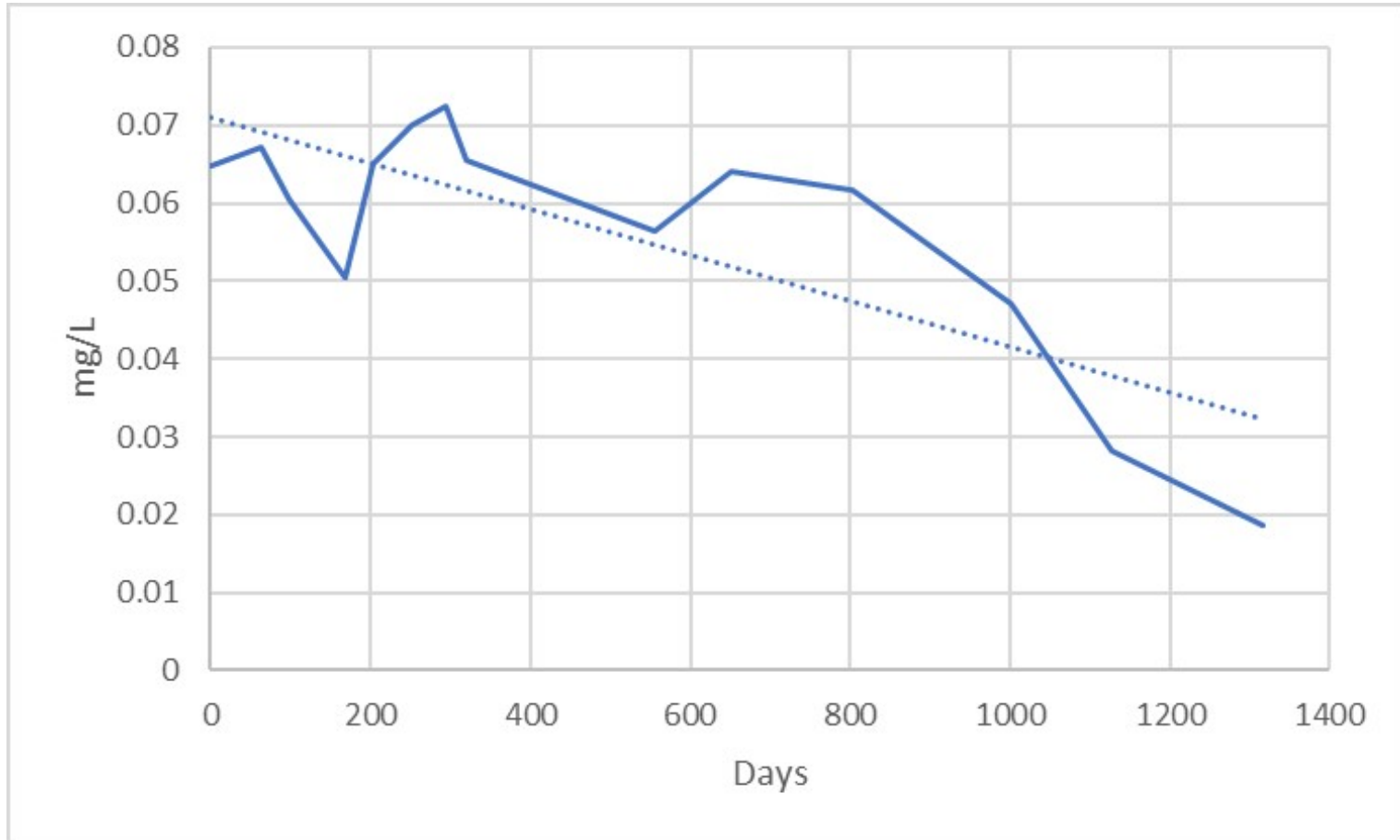


Note:  
mg/L: milligrams per liter

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**Figure 2**  
**Cobalt and Boron Concentration Versus Time in MR-AP-MW-4**  
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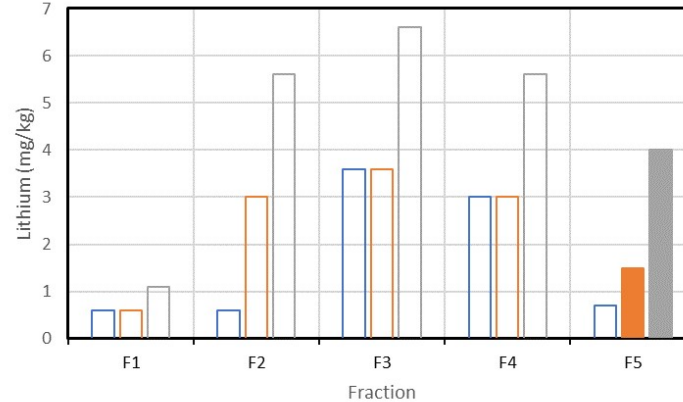
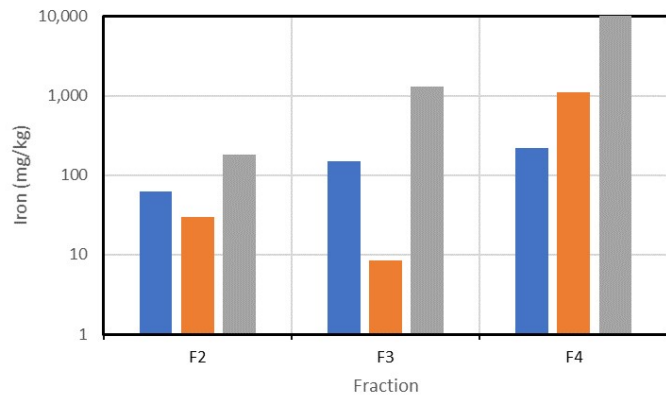
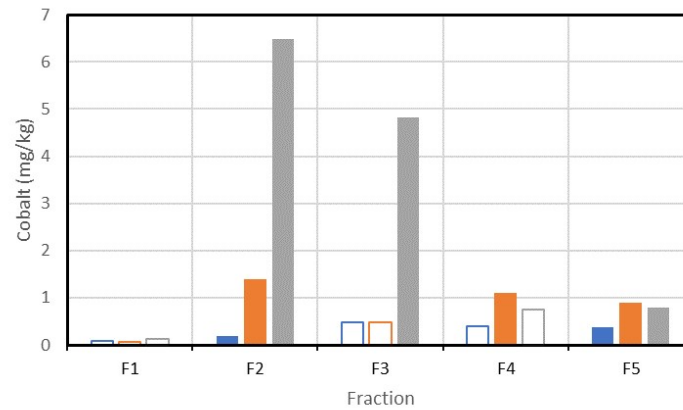
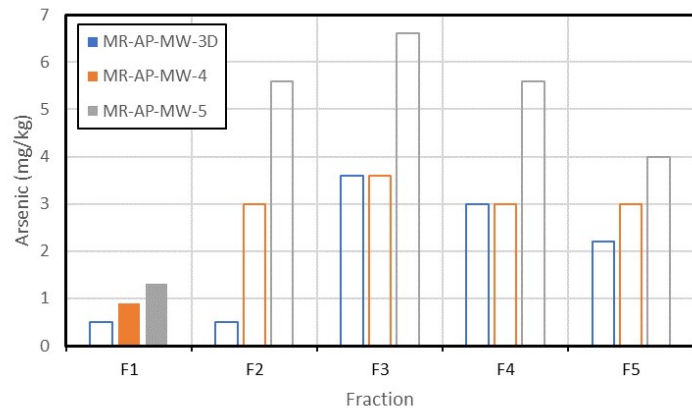
Note:  
mg/L: milligrams per liter

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**Figure 3**  
**Cobalt Concentration Versus Time in MR-AP-MW-6**  
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**Notes:**

Non-detect results shown as unfilled bars plotted at detection limit.

mg/kg: milligrams per kilogram

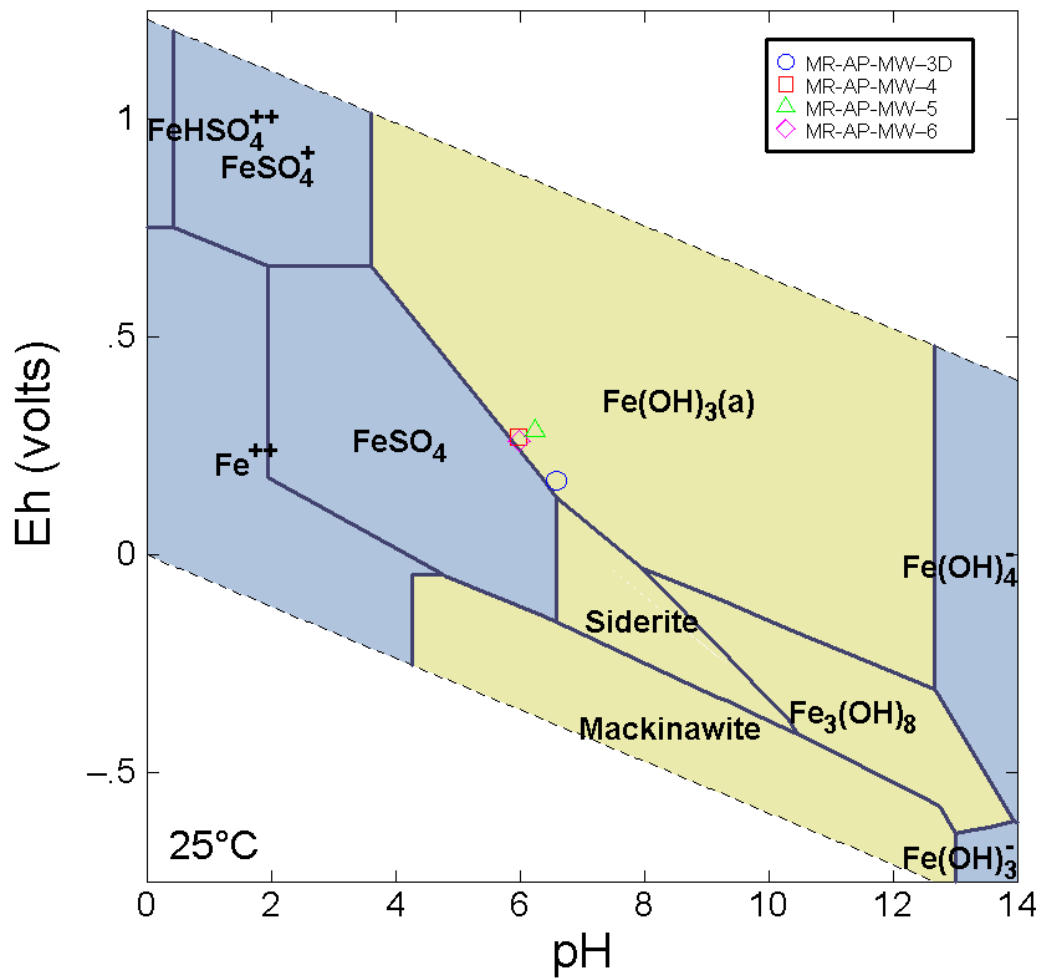
F1 – Water soluble

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)

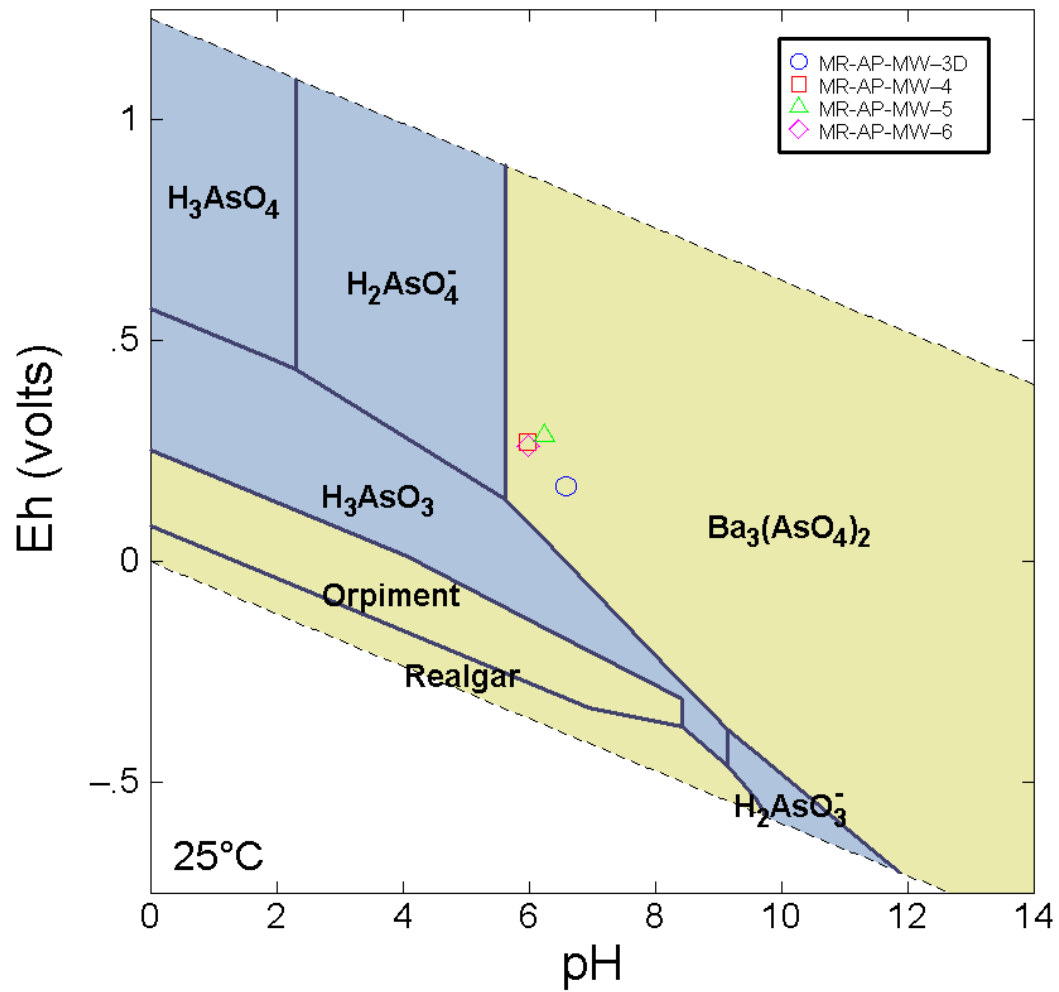


Note:  
Blue fields indicate dissolved/mobile species. Yellow fields indicate solid/attenuated species.

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**Figure 5**  
**Eh-pH Stability Diagram for Dissolved and Solid Iron Phases**  
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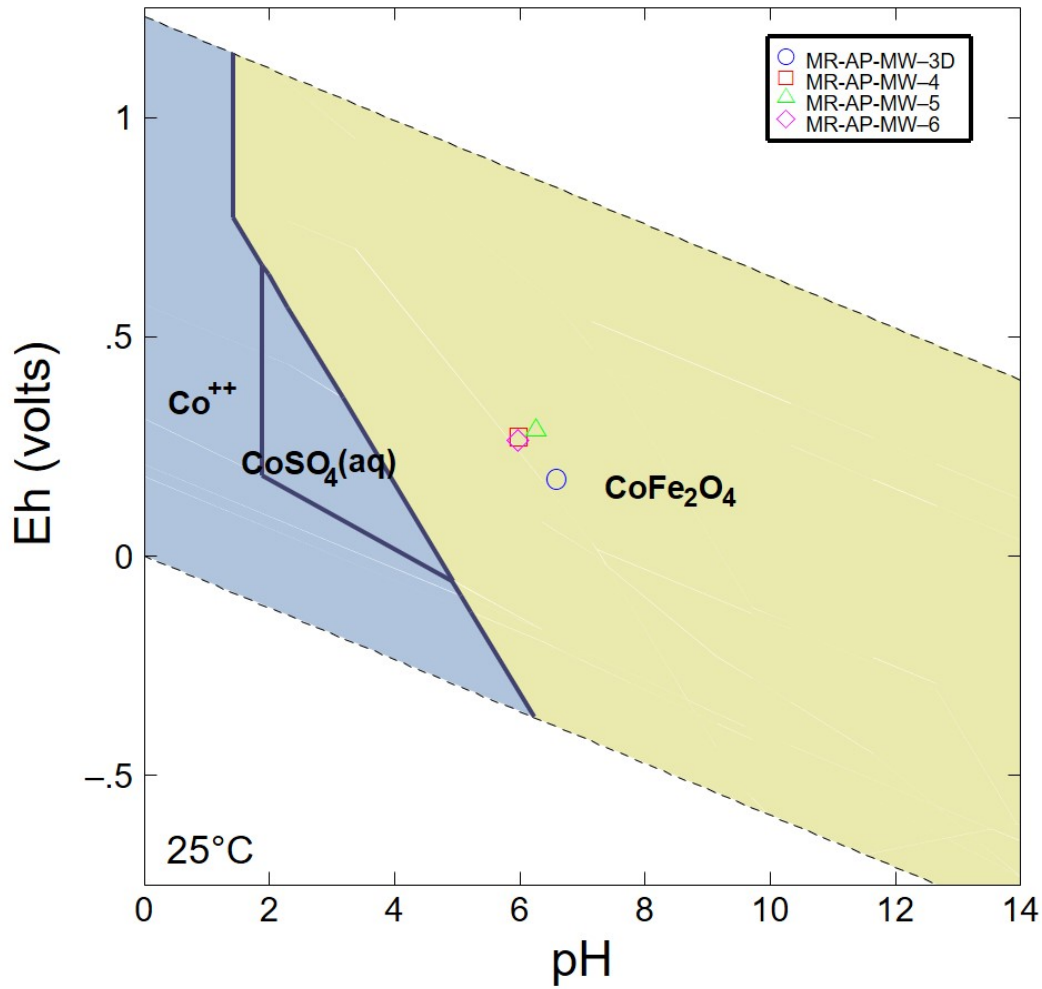


Note:  
Blue fields indicate dissolved/mobile species. Yellow fields indicate solid/attenuated species.

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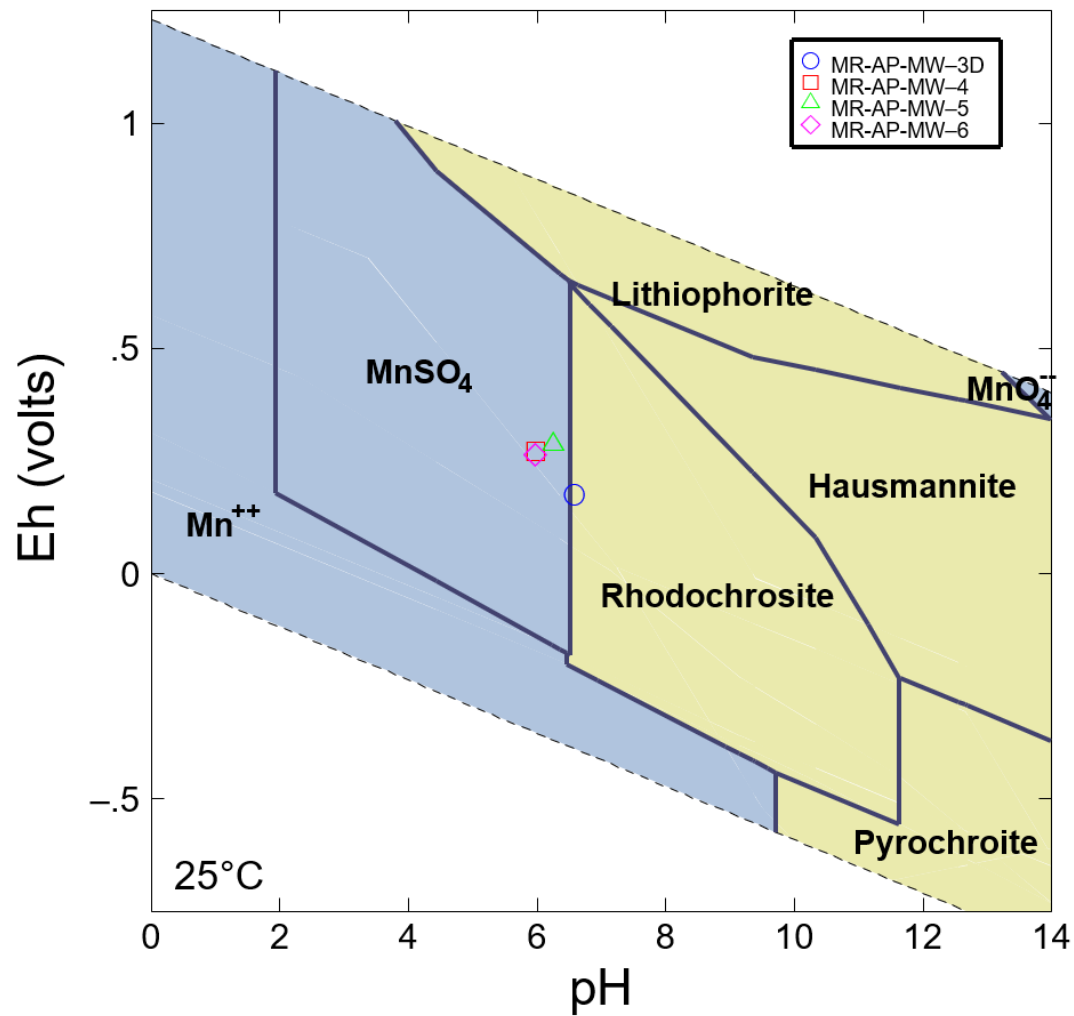


Note:  
Blue fields indicate dissolved/mobile species. Yellow fields indicate solid/attenuated species.

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**Figure 7**  
**Eh-pH Stability Diagram for Dissolved and Solid Cobalt Phases**  
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Note:  
 Blue fields indicate dissolved/mobile species. Yellow fields indicate solid/attenuated species.

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