

# FUNDAMENTAL PROCEDURES TO EVALUATE AND DESIGN INDUSTRIAL WASTE WATER METALS TREATMENT SYSTEMS, CASE STUDY DISCUSSIONS

Jay McCloskey<sup>1</sup>, Dr. Larry Twidwell<sup>2</sup>, Dr. Hsin-Hsinng Huang<sup>2</sup>, Lucas Goldstien<sup>3</sup>

<sup>1</sup>Center for Advanced Mineral and Metallurgical Processing, [jmccloskey@mtech.edu](mailto:jmccloskey@mtech.edu)

<sup>2</sup>Montana Tech of The University of Montana, Butte, Montana  
1300 West Park Street, Butte, Montana USA

<sup>3</sup>LFR an ARCADES Company, 1900 Powell Street, 12<sup>th</sup> Floor, Emeryville, California 94608-1827

## ABSTRACT

Methods and techniques to evaluate, design, and implement innovative hydrometallurgical systems for the reduction of dissolved arsenic, barium, selenium, thallium, and other constituents from industrial waste waters are discussed. Case studies utilizing geochemical modelling and matrix design testing to provide efficient methods to identify design parameters for precipitation processes to remove metals from an industrial wastewater are presented.

## INTRODUCTION

The use of geochemical modelling and matrix design testing provides efficient methods to identify design parameters for industrial wastewater treatment approaches. The case study presented in this paper is an example of the standard approach practiced by the Center for Advanced Mineral and Metallurgical Processing (CAMP) to identify appropriate treatment approaches along with optimization of design parameters.

Geochemical modeling for the project waters was performed using the software program STABCAL developed by H.H. Huang at Montana Tech of the University of Montana (Huang, 2008). The program allows the user to evaluate: relative compound solubilities as a function of pH, ion concentration, and solution potential (Eh); adsorption phenomena, potential/pH diagrams (Eh/pH); titration reactions and kinetics of compound formation. The STABCAL program can perform all of the mentioned calculations at any selected temperature from 25 to 200°C.

Design Expert software (StatEase Corporation Version 7.1.1) was utilized to design the test matrix and statistically evaluate the experimental results. Three Design Expert experimental matrices are presented involving the same project water. The design matrix (Minimum Run Resolution IV) allows the user to determine the influence of the variable factors on the measured response. Binary interaction effects are aliased but the main variable factors are cleanly determined. A Discussion of the influence of variable factors on the measured responses is presented along with the statistical validations of the selected models for each selected design space.

## CASE STUDY PROJECT WATER

The water used as a case study for this paper was from groundwater contaminated with solvents from historical dry cleaning operations, and will be referred to as the project water in this paper. The groundwater contains naturally occurring metals, specifically arsenic and barium that are the subject of this study. The flow rate for the proposed pump and treat system is estimated at 150 gallon per minute (gpm).

## TREATMENT OBJECTIVE

The objective for this project was to develop a viable treatment approach to reduce arsenic (As) and barium (Ba) from the project water. The goal was to reduce the As from 15.0 parts per billion (ppb) to less than 5.0 ppb and reduce Ba from 300 ppb to less than 100 ppb. As a secondary goal, the treatment process cannot increase iron (Fe) concentrations from their current levels of 100 ppb. CAMP performed laboratory treatability tests at their facility in Butte, Montana. Laboratory analytical tests were conducted at a state-certified analytical laboratory. Metals were analyzed using inductively coupled plasma mass spectrometry (ICP-MS) methodology.

## GEOCHEMISTRY DISCUSSION

An historical analysis of the project water is provided in Table 1. Prior to a discussion on selected technologies, a short review on aqueous geochemistry of both As and Ba is given below.

**Table 1. Project Water Analysis**

| PARAMETER              | RESULT | UNITS |
|------------------------|--------|-------|
| Total Dissolved Solids | 410    | mg/l  |
| pH                     | 8.1    | SU    |
| TEMP                   | 68     | F     |
| Specific Conductance   | 760    | umhos |
| Turbidity              | 0.1    | NTU   |
| Aluminum               | 100    | ug/L  |
| Ammonia-NH3            | 0.08   | mg/l  |
| Antimony               | 60     | ug/L  |
| Arsenic                | 15     | ug/l  |
| Barium                 | 300    | ug/l  |
| Beryllium              | 2      | ug/L  |
| Cadmium                | 5      | ug/L  |
| Calcium                | 100    | mg/l  |
| Chloride               | 54.2   | mg/l  |
| Chromium               | 10     | ug/L  |
| Chromium VI            | 2.88   | ug/l  |
| Copper                 | 2.0    | ug/l  |
| Cyanide                | 0.01   | mg/L  |
| Fluoride               | 0.1    | mg/L  |
| Hardness (CaCO3)       | 390    | mg/L  |
| Iron                   | 100    | ug/l  |
| Lead                   | 1.0    | ug/l  |
| Manganese              | 50     | ug/l  |
| Mercury                | 0.5    | ug/l  |
| Nickel                 | 20     | ug/L  |
| Nitrate as NO3         | 6.02   | mg/l  |
| Nitrite as NO2         | 0.500  | mg/l  |
| Nitrogen, Nitrite      | 0.05   | mg/L  |
| Phosphorous            | 2.2    | mg/L  |
| Selenium               | 5      | ug/L  |
| Silver                 | 5      | ug/L  |
| Sulfate                | 68     | mg/L  |
| Sulfate as S           | 26.5   | mg/l  |
| Sulfite                | 2      | mg/L  |
| Surfactants (MBAS)     | 0.1    | mg/L  |
| Thallium               | 5      | ug/L  |
| Zinc                   | 38     | ug/l  |

**Arsenic**

Arsenic is a naturally occurring element in the earth's crust, and is found throughout the environment. Arsenic is a redox-sensitive element. This means that arsenic may gain or lose electrons in redox reactions. As a result, arsenic may be present in a variety of redox states. Arsenate (As(V)) and arsenite (As(III)) are the two forms of arsenic commonly found in groundwater (Deutsch 1997). As(V) generally predominates under oxidizing conditions. As(III) predominates when conditions become sufficiently reducing. Under the pH conditions of most ground water, As(V) is present as the negatively charged oxyanions  $H_2AsO_4^-$  and  $HAsO_4^{2-}$ , whereas As(III) is present as the uncharged species  $H_3AsO_3^0$  (Deutsch 1997). The strength of adsorption and desorption reactions between these different arsenic species and solid-phase surfaces in aquifers varies, in part, because of these differences in charge. Differences in species charge affect the character of electrostatic interactions between species and surfaces.

The mobility of arsenic under oxidizing conditions is primarily affected by the adsorption of As(V) onto metal oxyhydroxide surfaces. If the applicable adsorption capacity of these surfaces is not surpassed, then arsenic movement will be strongly retarded because of the high affinity of these surfaces for As(V). Under reducing conditions, the dominant arsenic redox species will be As(III), which is not as strongly absorbed. Furthermore, the primary adsorbing solids may not be stable if the redox potential is sufficiently low. As a consequence, arsenic is expected to be much more mobile under moderately low reducing conditions. This mobility may be significantly reduced if arsenic sulfide minerals become saturated and precipitate.

Geochemical modeling of the Project Water was performed using the software program STABCAL and the Eh/pH diagram is shown in Figure 1 for the Lincoln Center Site groundwater iron/arsenic/barium/sulfur/water system. The shaded areas show conditions where iron solid compounds form and illustrate that the adsorption of arsenic onto these solids should occur when conditions are within these regions.

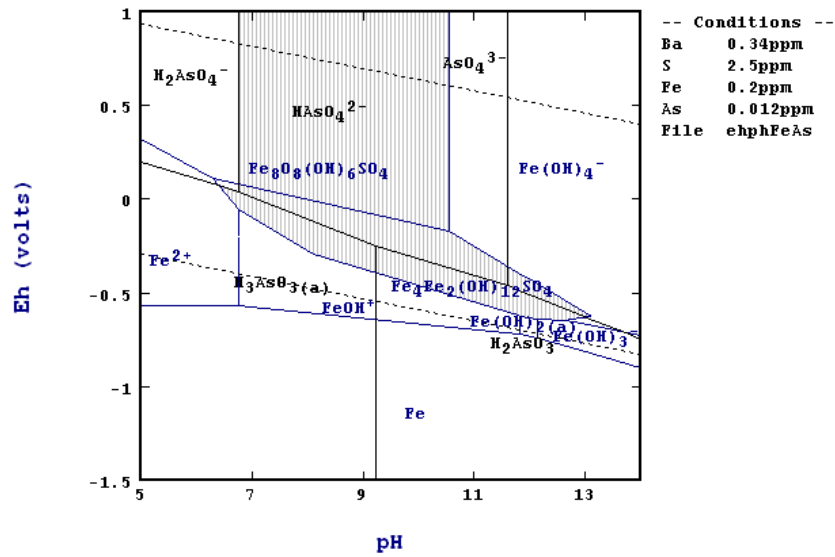


Figure 1. Eh/pH diagram for the Fe/As/Ba/S water system. The conditions for the formation of iron solid compounds are shown as shaded regions. (Diagram constructed using STABCAL, Huang 2008).

### Barium

Barium is a metallic element that is chemically similar to calcium and strontium, but more reactive. The most common naturally occurring minerals are the very insoluble barium sulfate,  $\text{BaSO}_4$  (barite), and barium carbonate,  $\text{BaCO}_3$  (Witherite). Barium is not found in nature in its elemental pure form due to its reactivity with air. Figure 2 is a distribution diagram (produced using STABCAL, Huang 2008) that illustrates barium should be removed by adsorption beginning at pH levels above approximately 8 (best at 10). The barium is removed not by compound precipitation but by surface phase adsorption. The removal of barium by iron hydroxide adsorption optimization of the doping done for barium removal has not been previously studied. This is the first study of which we have knowledge where the removal of barium at relatively low concentrations (less than 500 ppb) was studied by adsorption processes.

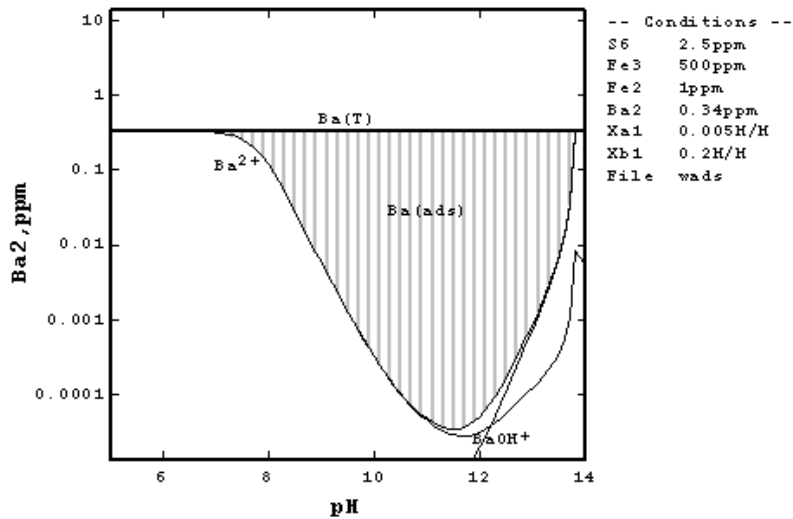


Figure 2. Distribution Model for the Fe/As/Ba/S water system. (Diagram constructed using STABCAL, Huang 2008).

## TECHNOLOGY DISCUSSIONS

Three technologies were selected for evaluation. These technologies were selected based on the geochemical modeling information, CAMP's experience working with similar water, and potential capabilities of each of the selected technologies for removing arsenic and barium from the project water. These technologies are:

1. **Reductive precipitation**, sometimes referred to as iron cementation, followed by ferric or ferrous hydroxide adsorption,
2. **Ferrous Hydroxide precipitation** and dissolved specie adsorption process, and
3. **Ferric Hydroxide precipitation** and dissolved specie adsorption process.

These technologies fall under the category of Precipitation Processes, specifically, coagulation assisted filtration. As such, waste generated by these technologies includes: backwash water and sludge. This study does not assess the mass or quality of sludge that would be generated. A brief discussion for each technology is provided below. Additional information on each technology is discussed in the Testing and Results section.

### Reductive Precipitation

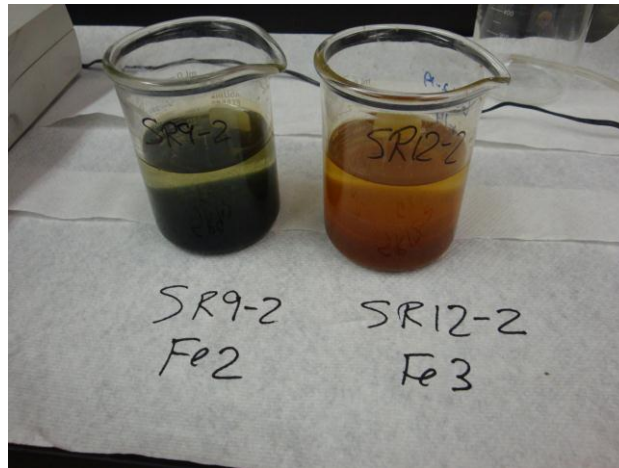
Arsenic occurs in solution as oxyanions (discussed above). These oxyanions can be reduced by electrochemical reactions. Metals can be used as the reductant. Any metal that has a reduction potential that is less noble than the impurity reduction potential will thermodynamically reduce the impurity specie, e.g., those metals that will reduce arsenic oxyanions include iron, zinc, aluminum, and magnesium. The presence of elemental iron in a slurry reactor or column reactor provides an operating potential sufficiently reducing to remove arsenic oxyanions as elemental arsenic. In the reductive precipitation tests, a stirred reactor with 100 grams of iron powder per liter of process solution is maintained. In a continuous system, the iron powder is replaced as it is used in the iron surface electrochemical reaction and goes into solution. One of the advantages of the reductive cementation technology is that it will remove both arsenate and arsenite species to less than the The Maximum Contaminant Level (MCL) which is the maximum concentration of a chemical that is allowed in public drinking water systems. The MCL is established by the U.S. Environmental Protection Agency (EPA)(Kamrin, 1997). It will also remove other oxyanions, such as antimony and selenium, and associated cationic metal species, e.g. mercury, copper, and nickel. Unlike adsorption processes, the removal efficiency is unaffected by the presence of sulfate. The limitations of this technology is that the water pH must be less than 7, preferably about pH 5.5 and as the electrochemical reactions occur iron is added to the solution phase and must be removed in a subsequent precipitation stage. Either calcium hydroxide (caustic) or sodium hydroxide (lime) can be used to raise the solution pH in the precipitation stage. The reductive cementation approach will not remove barium. However, the barium will be removed via adsorption in the subsequent precipitation stage.

### Ferrous Hydroxide Process

In the Ferrous Hydroxide Process, ferrous sulfate is added to the solution in predetermined amounts. The pH of the solution is then adjusted to approximately 10 or greater using either caustic or lime to form a ferrous hydroxide (green rust) precipitate which is a good adsorber for arsenic and barium. (McCloskey and Twidwell) have demonstrated that Green Rust is an effective adsorbent for arsenic oxyanions (both arsenite and arsenate) over the pH range 9-11 at solution potentials shown in the shaded stability region in Figure 1. Green Rust is a mixed valence ferric/ferrous hydroxysulfate solid  $[(Fe^{2+})_4(Fe^{3+})_2(OH)_{12}SO_4]$ .

### Ferric Hydroxide Process

In the Ferrous Hydroxide Process, ferric sulfate or ferric chloride is added to the solution in predetermined amounts. The pH of the solution is then adjusted to 6.5 or greater using either caustic or lime to form a ferric hydroxide precipitate that can be a good adsorber for arsenic and barium. Figure 3 is a photo of the ferrous (left/green) and ferric (right/red) hydroxide test solutions.



**Figure 3. Photo of both the ferrous (left) and ferric (right) hydroxide test solutions.**

### EXPERIMENTAL TEST MATRIX DEVELOPMENT

Three Design Expert Test Matrices were followed:

1. The first test matrix was designed to evaluate reductive precipitation in combination with utilizing the ferrous iron in solution resulting from the iron powder and solution chemistry followed by ferrous hydroxide and ferric hydroxide (with additional of peroxide) precipitation tests.
2. The second test matrix was designed to evaluate straight reductive precipitation tests.
3. The third test matrix was designed for ferrous hydroxide and ferric hydroxide tests utilizing the reagents ferrous sulfate and ferric sulfate respectively.

The data collected were evaluated using Design Expert software (StatEase Corporation Version 7.1.1). Each test matrix was set up to evaluate influence of variable factors on the measured responses as a function of As, Ba, and Fe concentrations. When appropriate, a maximum and minimum variable level was determined and in some matrix sets a mean level as used.

### TESTING AND RESULTS

The three Design Expert experimental matrices are presented in the order discussed above in Tables 2-4. Each table outlines the required test conditions and the experimental results. Due to restrictions on paper length requirements, the statistical validation of the selected models for each selected design space is not provided in this paper.

**Table 2. Design Expert Matrix 1 and Measured Responses for Reductive Precipitation Tests Followed by Either Ferrous Hydroxide or Ferric Hydroxide.**

| Standard Run No. | Factors (Variables) |                       |                     |                        | Responses, µg/L |              |              |
|------------------|---------------------|-----------------------|---------------------|------------------------|-----------------|--------------|--------------|
|                  | A:pH                | B:Reduction Time, hrs | C:Type of Adsorbent | D:Adsorption Time, hrs | [As]            | [Ba]         | [Fe]         |
| LFR-SR1-21709-2  | 5                   | 1                     | Fe2                 | 1                      | <b>3.65</b>     | <b>16.88</b> | 106.81       |
| LFR-SR2-21809-2  | 7                   | 1                     | Fe2                 | 2                      | <b>3.37</b>     | <b>11.07</b> | <b>80.08</b> |
| LFR-SR3-21709-2  | 5                   | 2                     | Fe2                 | 2                      | <b>3.69</b>     | <b>63.00</b> | 154.41       |
| LFR-SR4-21909-2  | 7                   | 2                     | Fe2                 | 1                      | <b>2.48</b>     | <b>12.20</b> | 204.43       |
| LFR-SR5-21709-2  | 5                   | 1                     | Fe3                 | 2                      | <b>3.75</b>     | <b>20.04</b> | 255.98       |
| LFR-SR6-21809-2  | 7                   | 1                     | Fe3                 | 1                      | <b>3.37</b>     | <b>11.99</b> | <b>37.52</b> |
| LFR-SR7-21709-2  | 5                   | 2                     | Fe3                 | 1                      | <b>2.54</b>     | <b>8.81</b>  | 339.42       |
| LFR-SR8-21909-2  | 7                   | 2                     | Fe3                 | 2                      | <b>2.45</b>     | <b>15.20</b> | 204.40       |
| LFR-SR9-21909-2  | 6                   | 1.5                   | Fe2                 | 1.5                    | <b>2.48</b>     | <b>62.78</b> | <b>29.39</b> |
| LFR-SR10-22009-2 | 6                   | 1.5                   | Fe3                 | 1.5                    | <b>2.46</b>     | <b>22.29</b> | <b>26.34</b> |
| LFR-SR11-22009-2 | 6                   | 1.5                   | Fe2                 | 1.5                    | <b>1.47</b>     | <b>70.53</b> | <b>62.00</b> |
| LFR-SR12-22009-2 | 6                   | 1.5                   | Fe3                 | 1.5                    | <b>2.49</b>     | <b>10.59</b> | <b>76.96</b> |

Note - achieved project goal concentrations; Detection Limit (DL) concentrations taken as data point values for Design Expert evaluations

**Table 3. Design Expert Matrix 2 and Measured Responses for Reductive Precipitation.**

| Standard Run No. | Factors (Variables) |                       |                     |                        | Responses, µg/L |              |         |
|------------------|---------------------|-----------------------|---------------------|------------------------|-----------------|--------------|---------|
|                  | A:pH                | B:Reduction Time, hrs | C:Type of Adsorbent | D:Adsorption Time, hrs | [As]            | [Ba]         | [Fe]    |
| LFR-SR1-21709-1  | 5                   | 1                     | Fe2                 | 1                      | 8.98            | 276.13       | 698290  |
| LFR-SR2-21809-1  | 7                   | 1                     | Fe2                 | 2                      | <b>3.08</b>     | 163.18       | 84108   |
| LFR-SR3-21709-1  | 5                   | 2                     | Fe2                 | 2                      | 9.65            | 283.99       | 1305889 |
| LFR-SR4-21909-1  | 7                   | 2                     | Fe2                 | 1                      | <b>1.45</b>     | <b>45.56</b> | 3036    |
| LFR-SR5-21709-1  | 5                   | 1                     | Fe3                 | 2                      | 5.92            | 286.72       | 708870  |
| LFR-SR6-21809-1  | 7                   | 1                     | Fe3                 | 1                      | <b>2.98</b>     | 153.05       | 81067   |
| LFR-SR7-21709-1  | 5                   | 2                     | Fe3                 | 1                      | 8.89            | 305.76       | 1305889 |
| LFR-SR8-21909-1  | 7                   | 2                     | Fe3                 | 2                      | <b>1.46</b>     | <b>43.54</b> | 2631.56 |
| LFR-SR9-21909-1  | 6                   | 1.5                   | Fe2                 | 1.5                    | <b>1.45</b>     | 152.81       | 637393  |
| LFR-SR10-22009-1 | 6                   | 1.5                   | Fe3                 | 1.5                    | <b>1.41</b>     | 301.72       | 425160  |
| LFR-SR11-22009-1 | 6                   | 1.5                   | Fe2                 | 1.5                    | 5.09            | 270.66       | 414790  |
| LFR-SR12-22009-1 | 6                   | 1.5                   | Fe3                 | 1.5                    | 5.91            | 264.10       | 596923  |

Note- achieved project goal concentrations; DL concentrations taken as data point values for Design Expert evaluations

**Table 4. Design Expert Matrix 3 and Masured Responses for Species Removal by Adsorption on Ferrous and Ferric Hydroxide**

| Standard Run No. | Factors (Variables) |              |                     |                   | Responses, (µg/L) |              |              |
|------------------|---------------------|--------------|---------------------|-------------------|-------------------|--------------|--------------|
|                  | A:pH                | B: Time, hrs | C:Type of Adsorbent | D:Amount Fe, mg/L | [As]              | [Ba]         | [Fe]         |
| SR1-21709-1      | 10                  | 2            | Fe2                 | 800               | 15.23             | <b>4.09</b>  | <b>5.19</b>  |
| SR2-21809-1      | 8                   | 1            | Fe2                 | 800               | <b>1.46</b>       | <b>32.70</b> | <b>34.43</b> |
| SR3-21709-1      | 8                   | 2            | Fe3                 | 800               | <b>1.45</b>       | <b>25.28</b> | <b>26.57</b> |
| SR4-21909-1      | 8                   | 2            | Fe3                 | 400               | <b>1.45</b>       | <b>45.62</b> | <b>47.26</b> |
| SR5-21709-1      | 10                  | 1            | Fe3                 | 800               | <b>1.45</b>       | <b>8.00</b>  | <b>9.11</b>  |
| SR6-21809-1      | 8                   | 1            | Fe3                 | 400               | <b>1.46</b>       | <b>47.65</b> | <b>49.32</b> |
| SR7-21709-1      | 10                  | 2            | Fe3                 | 400               | <b>1.56</b>       | <b>6.47</b>  | <b>7.54</b>  |
| SR8-21909-1      | 10                  | 1            | Fe2                 | 400               | 5.58              | <b>5.27</b>  | <b>6.36</b>  |
| SR9-21909-1      | 10                  | 1            | Fe2                 | 800               | 26.22             | <b>3.77</b>  | <b>4.84</b>  |
| SR10-22009-1     | 8                   | 2            | Fe2                 | 400               | <b>1.45</b>       | <b>36.22</b> | <b>37.45</b> |

Note- achieved project goal concentrations; DL concentrations taken as data point values for Design Expert evaluations

**INFLUENCE OF VARIABLE FACTORS ON THE MEASURED RESPONSES**

**Reductive Precipitation - Ferrous Hydroxide or Ferric Hydroxide Precipitation (Experimental Data in Table 2)**

**Design Expert Evaluation of Results**

**Arsenic**

A statistically valid model for arsenic removal is not applicable. The process is so effective that any combination of the variables investigated in this study result in a final arsenic concentration of (<5 µg/L).

**Barium**

A statistically valid model that describes the design space for the removal of barium shows that the most important variable is pH. Reduction time was shown not to be important as expected because the reductive precipitation (cementation) process is known to be ineffective for removing barium. The influence of pH, reduction time, and adsorption time is presented in the cubic display in Figure 4 (Left for Fe2 treatment and Right for Fe3 treatment). Note the comments presented in the caption. 3-Dimensional plots are presented in Figure 5. Briefly, the conclusion is that all combinations of conditions, regardless of whether cementation is followed by ferrous or ferric hydroxide adsorption, meet the project goal for barium (<100 µg/L).

**Iron**

A statistically valid model that describes the design space for the removal of iron shows that the most important variables are pH and reduction time. Short reduction times are desired so less iron enters the solution and higher pH is desired so that more ferrous or ferric hydroxides remove iron from solution by precipitation. Cubic displays are

presented in Figure 6 (Left for Fe<sub>2</sub> treatment and Right for Fe<sub>3</sub> treatment). 3-Dimensional plots are presented in Figure 7. Briefly, the conclusion is that only 50% met the <100 µg/L project goal for most combinations of conditions, regardless of whether cementation is followed by ferrous or ferric hydroxide adsorption, meet the project goal for iron (<100 µg/L).

### Cubic Visualizations for Final Barium Concentration

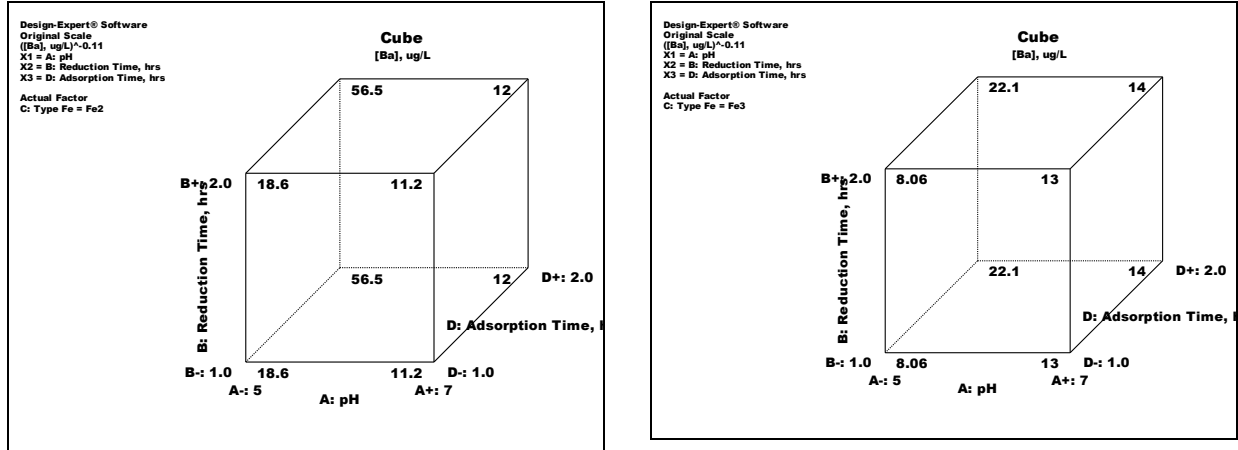


Figure 4. Cubic representation of the influence of variables on the final barium concentration (Left: ferrous hydroxide (Fe<sub>2</sub>) adsorbent, Right: ferric hydroxide (Fe<sub>3</sub>)). Reduction Time and Adsorption Time are unimportant, the pH is important. Most combinations of Fe<sub>2</sub> conditions result in barium concentrations <50 µg/L while most combinations of Fe<sub>3</sub> conditions result in barium concentrations <25 µg/L. Therefore, the formation of ferric hydroxide (called ferrihydrite and schwertmannite) is more effective for removing barium than ferrous hydroxide adsorption.

### 3-D Visualizations for Final Barium Concentration

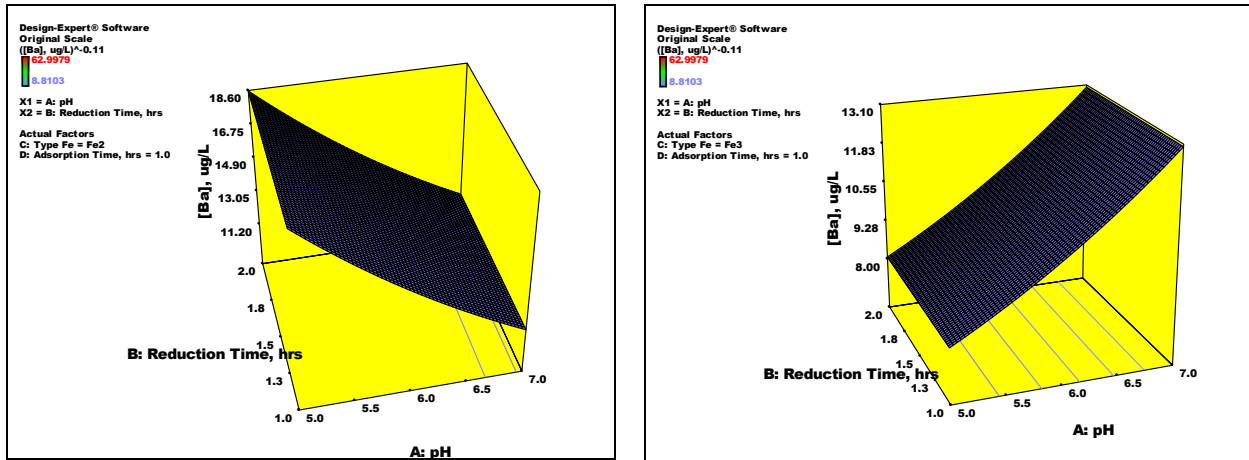


Figure 5. 3-D representation of the influence of variables on the final barium concentration (Left for the ferrous hydroxide (Fe<sub>2</sub>) adsorbent, Right for ferric hydroxide (Fe<sub>3</sub>) adsorbent). For Fe<sub>2</sub> the higher pH level is desirable, while for Fe<sub>3</sub> the lower pH level is desirable.

### Cubic Visualizations for Final Iron Concentration

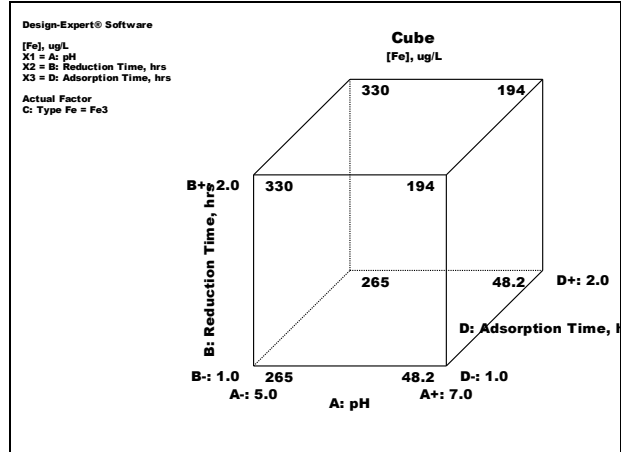
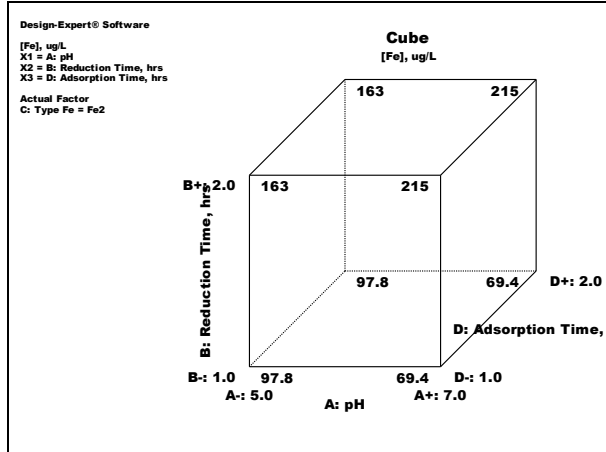


Figure 6. Cubic representation of the influence of variables on the final iron concentration (Left for ferrous hydroxide (Fe<sub>2</sub>) precipitation, Right for ferric hydroxide (Fe<sub>3</sub>) precipitation). For Fe<sub>2</sub> precipitation: Reduction Time and pH are important. In general, most combinations of conditions result in iron concentrations less than the project goal of <100 µg/L. For Fe<sub>3</sub> precipitation: Reduction Time and pH are important; Adsorption Time is unimportant

### 3-D Visualizations for Final Iron Concentration

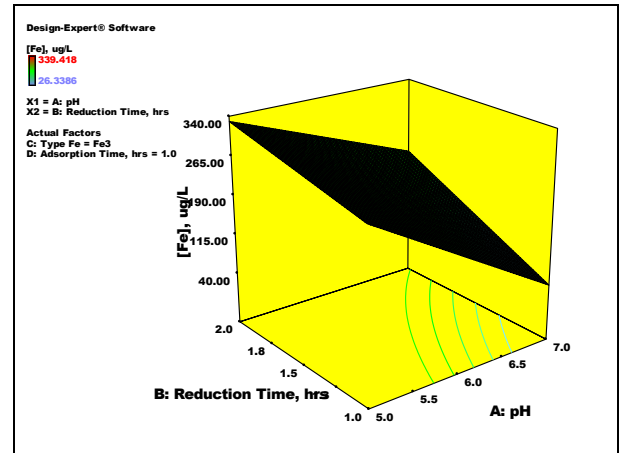
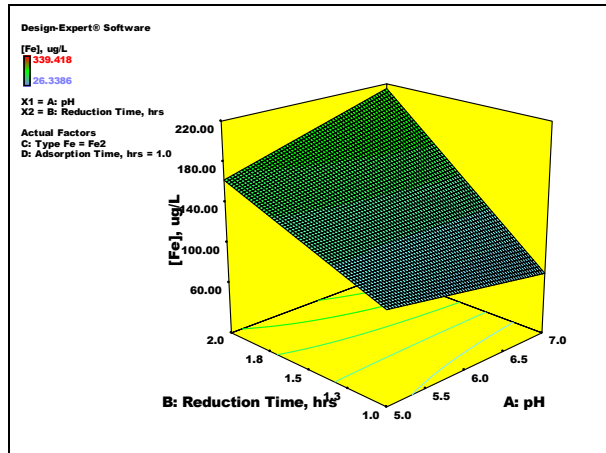


Figure 7. 3-D representation of the influence of variables on the final iron concentration (Left for ferrous hydroxide (Fe<sub>2</sub>) precipitation, Right for ferric hydroxide (Fe<sub>3</sub>) precipitation).



## **Reductive Precipitation (Experimental Data in Table 3)**

### **Design Expert Evaluation of Results**

#### ***Arsenic, Barium, Iron***

The use of reductive precipitation without further subsequent treatment is deemed not appropriate for the present application. The removal of arsenic is excellent; however, this treatment is ineffective for removing barium and the iron content of the solution is greater than the project goal concentrations of 100 µg/L. Therefore, a statistical evaluation will not be further discussed in this report.

## **Ferrous Hydroxide and Ferric Hydroxide (Experimental Data in Table 4)**

### **Design Expert Evaluation of Results**

#### ***Arsenic***

A statistically valid model that describes the design space for the removal of arsenic was developed. The adsorption technique is very effective as demonstrated by the data presented in Table 4. The influence of amount of iron added to the system, the time allowed for adsorption to occur and pH on arsenic removal are presented in Figure 8 as cubic representations and in Figure 9 as 3-dimensional representations. Note the comments on the Figure captions. Briefly, the conclusion is that both ferrous hydroxide and ferric hydroxide adsorption is effective for removing arsenic. However, the use of ferrous hydroxide requires lower pH values, whereas the use of ferric hydroxide lowers the arsenic concentration to <2 µg/L for all combinations of conditions in the selected design space.

#### ***Barium***

A statistically valid model that describes the design space for the removal of barium was developed. The adsorption technique is very effective for removing barium as demonstrated by the data presented in Table 4. The influence of amount of iron added to the system, the time allowed for adsorption to occur and pH are presented in Figure 10 as cubic representations and in Figure 11 as 3-dimensional representations. Note the comments on the Figure captions. The conclusion is that both ferrous hydroxide and ferric hydroxide adsorbents are equally effective for removing barium. Higher pH levels are favored. The project goal for barium is achieved by all combinations of conditions in the selected design space.

#### ***Iron***

A statistically valid model that describes the design space for the removal of iron was developed. The hydroxide precipitation technique is very effective for removing iron as demonstrated by the data presented in Table 4. The influence of amount of iron added to the system, the time allowed for adsorption to occur and pH are presented in Figure 12 for (Fe<sub>2</sub>) and (Fe<sub>3</sub>) as cubic representations and in Figure 13 as 3-dimensional representations. The conclusion is that both ferrous hydroxide and ferric hydroxide precipitation are equally effective for removing iron. Higher pH levels are favored. The project goal for iron (100 µg/L) is achieved by all combination of conditions in the selected design space.

### Cubic Visualizations for Final Arsenic Concentration

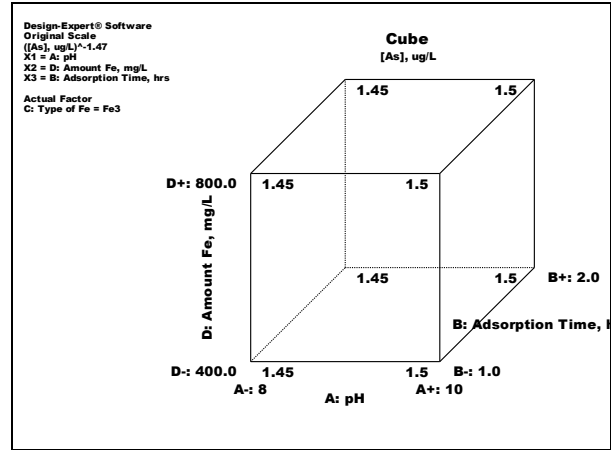
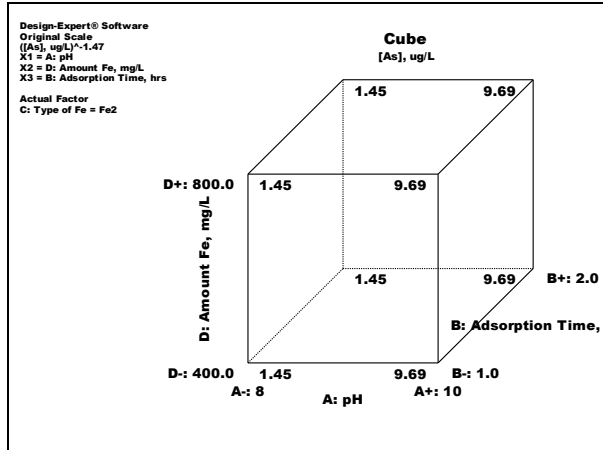


Figure 8. Cubic representation of the effect of three variables (Left for the Fe<sub>2</sub> hydroxide adsorbent, Right for Fe<sub>3</sub> hydroxide adsorbent) on the final concentration of arsenic in the solution phase. Note that arsenic adsorption on ferric hydroxide is more effective than on ferrous hydroxide at high pH levels (compare with Figure 6). The adsorption of arsenic via ferric hydroxide is independent of pH, whereas, lower pH levels are better for adsorption on ferrous hydroxide.

### 3-D Visualizations for Final arsenic Concentration

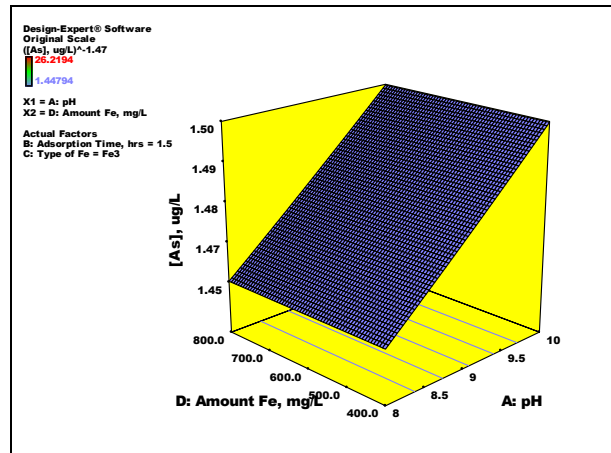
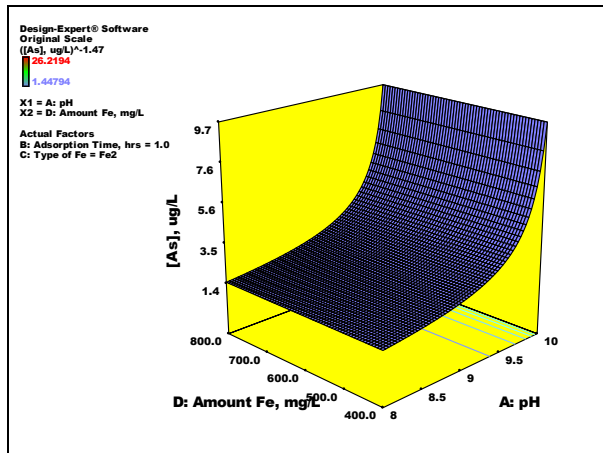


Figure 9. 3-D representation of the effect of two variables (Left for Fe<sub>2</sub> hydroxide adsorbent, Right for Fe<sub>3</sub> hydroxide adsorbent) on the final concentration of arsenic in the solution phase. For Fe<sub>2</sub> the arsenic adsorption is independent on adsorption time and amount of iron initially present. For Fe<sub>3</sub> the adsorption of arsenic is independent of the amount of iron initially present and adsorption time.

### Cubic Visualizations for Final Barium Concentration

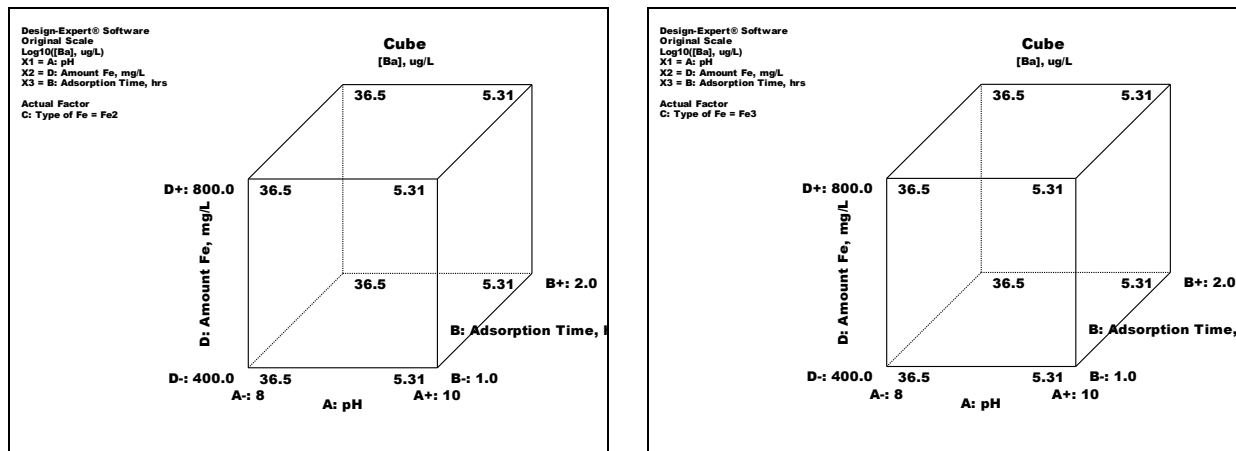


Figure 10. Cubic representation of the effect of three variables (Left for Fe<sub>2</sub> hydroxide adsorbent and Right for Fe<sub>3</sub> hydroxide adsorbent) on the final concentration of barium in the solution phase. The only variable of importance is pH; higher pH is favored. There was no difference in the final barium concentration for the ferrous or ferric hydroxide adsorbent solids. The type of adsorbent is unimportant (compare Figure 8).

### 3-D Visualizations for Final Barium Concentration

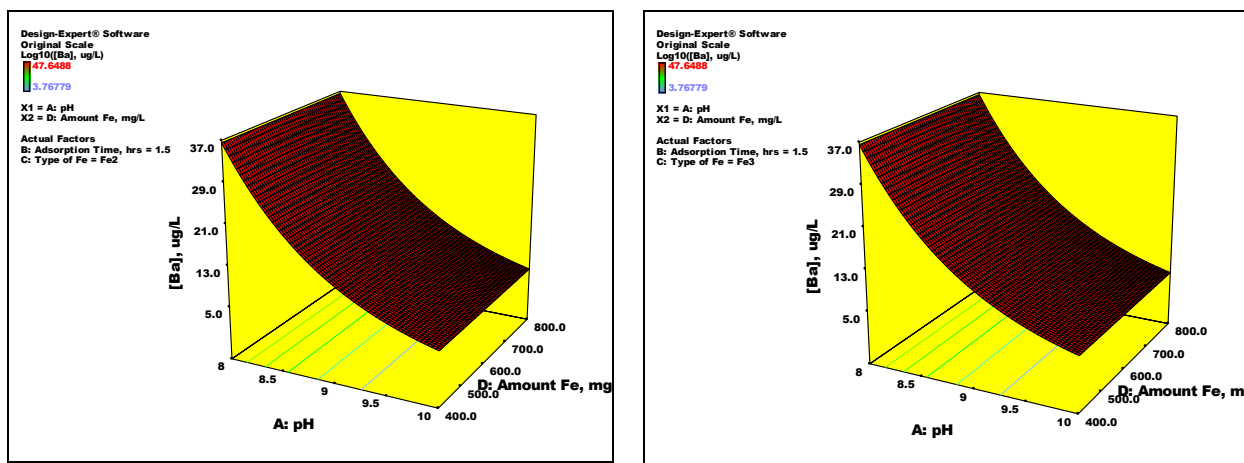


Figure 11. 3-D representation of the effect of two variables (Left for Fe<sub>2</sub> hydroxide adsorbent, Right for Fe<sub>3</sub> hydroxide adsorbent) on the final concentration of barium in the solution phase. The removal of barium was independent on adsorption time and amount of iron initially present.

### Cubic Visualizations for Final Iron Concentration

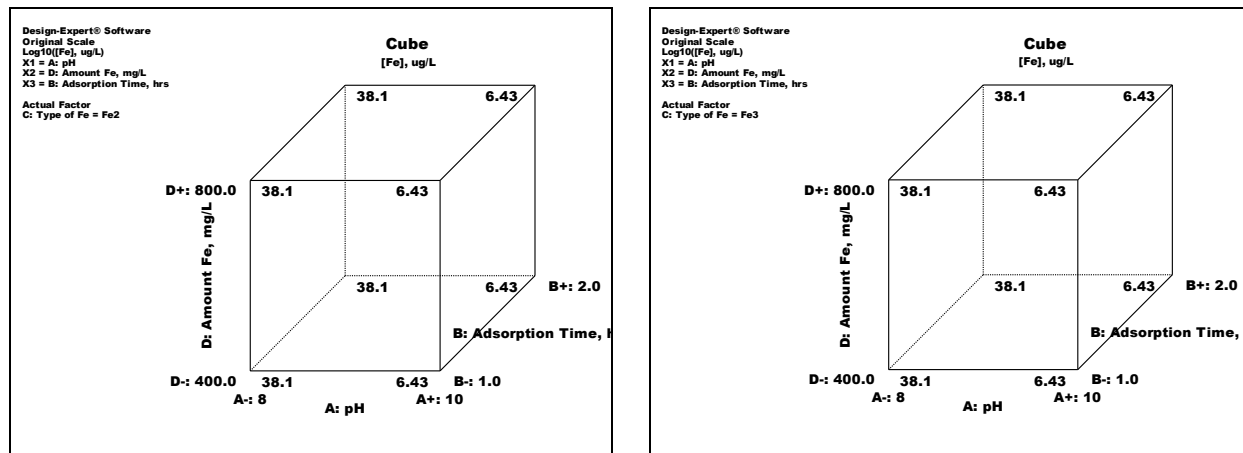


Figure 12. Cubic representation of the effect of three variables (for Fe<sub>2</sub> hydroxide adsorbent) on the final concentration of iron in the solution phase. For Fe<sub>2</sub>, the only variable of importance is pH; higher pH is favored. The type of adsorbent is unimportant (compare Figure 10). For Fe<sub>3</sub>, the only variable of importance is higher pH. There was no difference in the final iron concentration for the ferrous or ferric hydroxide adsorbent solids.

### 3-D Visualizations for Final Iron Concentration

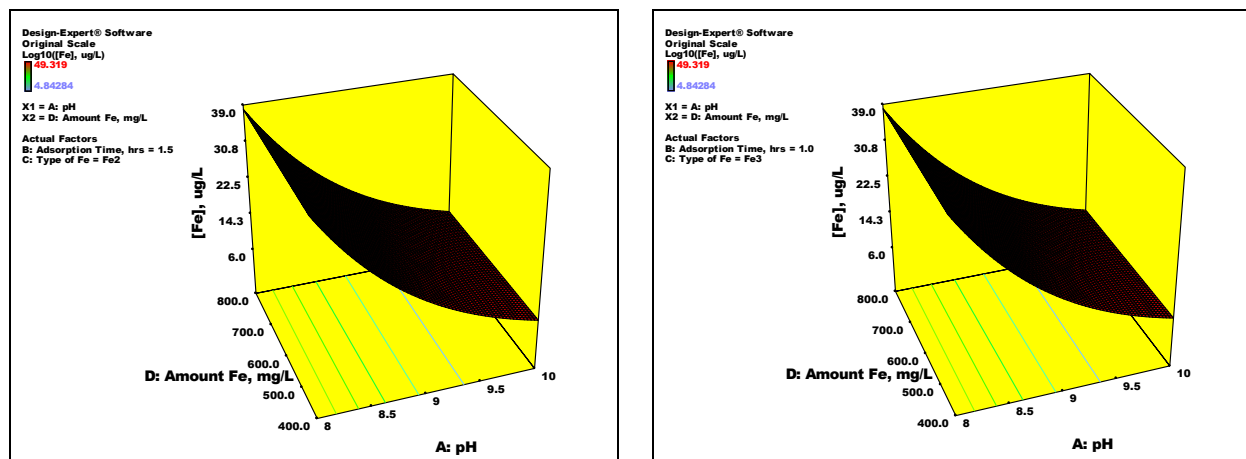


Figure 13. 3-D representation of the effect of two variables (Left for Fe<sub>2</sub> hydroxide adsorbent, Right for Fe<sub>3</sub> hydroxide adsorbent) on the final concentration of iron in the solution phase. For both Fe<sub>2</sub> and Fe<sub>3</sub> hydroxide adsorbent, the removal of iron depends only on the solution pH.

## SUMMARY AND CONCLUSIONS

The objective of the proposed scope of work was to perform fundamental chemistry evaluations and preliminary bench-scale tests on the Project Water to determine both As and Ba removal capabilities of selected treatment approaches that were capable of reducing the As from 15.0 µg/L to less than 5.0 ppb and reducing Ba from 300 µg/L to less than 100 µg/L. The three technologies that were evaluated were iron cementation (reductive precipitation), ferrous hydroxide, and ferric hydroxide. All three approaches were effective at reducing arsenic to below 5.0 µg/L. The data indicates that barium can be reduced to below 100 µg/L utilizing both ferrous and ferric hydroxide treatment approaches. Both barium and iron removal are a function of solution pH.

### Reductive Precipitation

The iron cementation process resulted in removal of arsenic to less than the ICP-AES detection limit of 0.4µg/L. This was true for most of the conditions investigated in the studied Experimental Design Matrix. Some of the matrix experiments, where the recovered solution after cementation, was treated at higher pH levels (forming green rust from the ferrous in solution) resulted in a significant decrease in the barium concentration (<100 µg/L limit).

Advantages:

- Project Goals achieved ([As]<5 µg/L, [Ba] <100 µg/L , [Fe] <100 µg/L) using cementation followed by either ferrous hydroxide adsorption or ferric hydroxide adsorption. In fact, conditions can be specified that result in significantly lower concentrations than those required by the Project Goals.
- Only minor amounts of sulfate added to system because elemental iron is source of iron for the hydroxide precipitations.

Limitations:

- Two pH adjustment unit operations required, i.e. cementation followed by hydroxide adsorption as follows:
  - Unit 1: pH must be lowered to 5-6
  - Unit 2: pH must be subsequently raised to about 10
- Hydroxide sludge is produced.
  - Further work needs to be performed to determine amount of sludge that would be produced.

### Ferrous Hydroxide or Ferric Hydroxide Precipitation

Both the ferrous and ferric hydroxide treatment approaches were successful at reducing the arsenic and barium in solution to below the discharge limits of 5.0 µg/L and 100 µg/L respectively. The solution pH was determined critical for the successful removal of barium.

Advantages:

- Project Goals achieved ([As] < 5 µg/L, [Ba] <100 µg/L, [Fe] <100 µg/L) using cementation followed by either ferrous hydroxide adsorption or ferric hydroxide adsorption. In fact, conditions can be specified that result in significantly lower concentrations than those required by the Project Goals.
- Treatment system is a relatively simple two-step process, i.e. doping with either ferrous or ferric salt followed by solid/liquid separation
- Only one pH adjustment step is required.

Limitations:

- Sulfate is added to system by the addition of iron sulfate salts; sulfate discharge limitations warrant further consideration.
- Hydroxide sludge is produced:
  - Further work needs to be performed to determine amount of sludge that would be produced
  - Further work needs to be performed to determine if recycle of initial hydroxide could significantly reduce amount of sludge, i.e. since the amount of removal of arsenic and barium should not saturate the hydroxide could the hydroxide be recycled to reduce the initial amount of iron sulfate required.

## REFERENCES

- Deutsch, W.J. 1997, Groundwater geochemistry, fundamentals and applications to contaminations, Lewis Publishers, 221 pp.
- Huang, H.H., 2000. STABCAL. Montana Tech of the University of Montana, Metallurgical and Materials Engineering Department, Butte, Montana ([huang@mtech.edu](mailto:huang@mtech.edu)).
- Kamrin, M., 1997, ExtorNet FAQ, MCLs and MCLGs, Michigan State University.
- Twidwell, L.G., J. McCloskey, M. Gale-Lee, 2002. Removal of Hazardous Constituents from Wastewater, In: *Proceedings Mineral Processing Plant Design, Control and Practice*, Vol. 2, Eds. A.L. Mular, D.N. Halbe, D.J. Baratt, Vancouver, Canada, SME , Littleton, CO., pp 1847-65.