Physical Distribution and Chemical Speciation of Arsenic and Selenium in Coal Fly Ash

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Background

❖ Coal Fly Ash (CFA) is the waste product of burning coal in power plants. CFA is typically stored in ash ponds next to power plants as seen in Figure 1 below. The ash ponds are most often placed near waterways like rivers and creeks. In 2015 the EPA changed CFA disposal legislation to require ash ponds be lined.[1] This regulation has been slow to be followed and there are still 500 unlined ash ponds in the United States.[2] CFA is also not considered a hazardous material, and it is still categorized as a waste product similar to household trash.[1] This is problematic, because ash ponds could contaminate not only surface water but also surrounding ground water.

❖ Typically CFA is comprised of silicon, aluminum, iron, calcium, and carbon with other trace elements including arsenic, selenium, mercury, and chromium.[3] Even small amounts of these trace elements (ppm or ppb) can create health and environmental hazards.[3]

❖ The type of coal and where it comes from as well as burning methods and added air pollution control devices affect the concentration, physical distribution, and speciation of elements found in the ash.[4] These then lead to the leachability and thus mobility of arsenic and selenium into the environment.

❖ The speciation of arsenic and selenium also dictates its toxicity. For example arsenite (As(III)) is 5-10 times more toxic than arsenate (As(V)), because it is much more soluble.[5]

❖ The elements As and Se can be found in different compounds with other elements which also dictate their leachability and mobility. For example, Si and Al are very stable and create glass formations which require an extremely strong acid to dissolve. If As or Se are associated with Si or Al as inclusions, their mobility will be limited unless there's extreme changes in redox or pH. If As and Se are associated with Na, these compounds are generally more soluble and mobile. If As or Se is found attached to Ca than As or Se could be soluble depending on what else is in the environment.
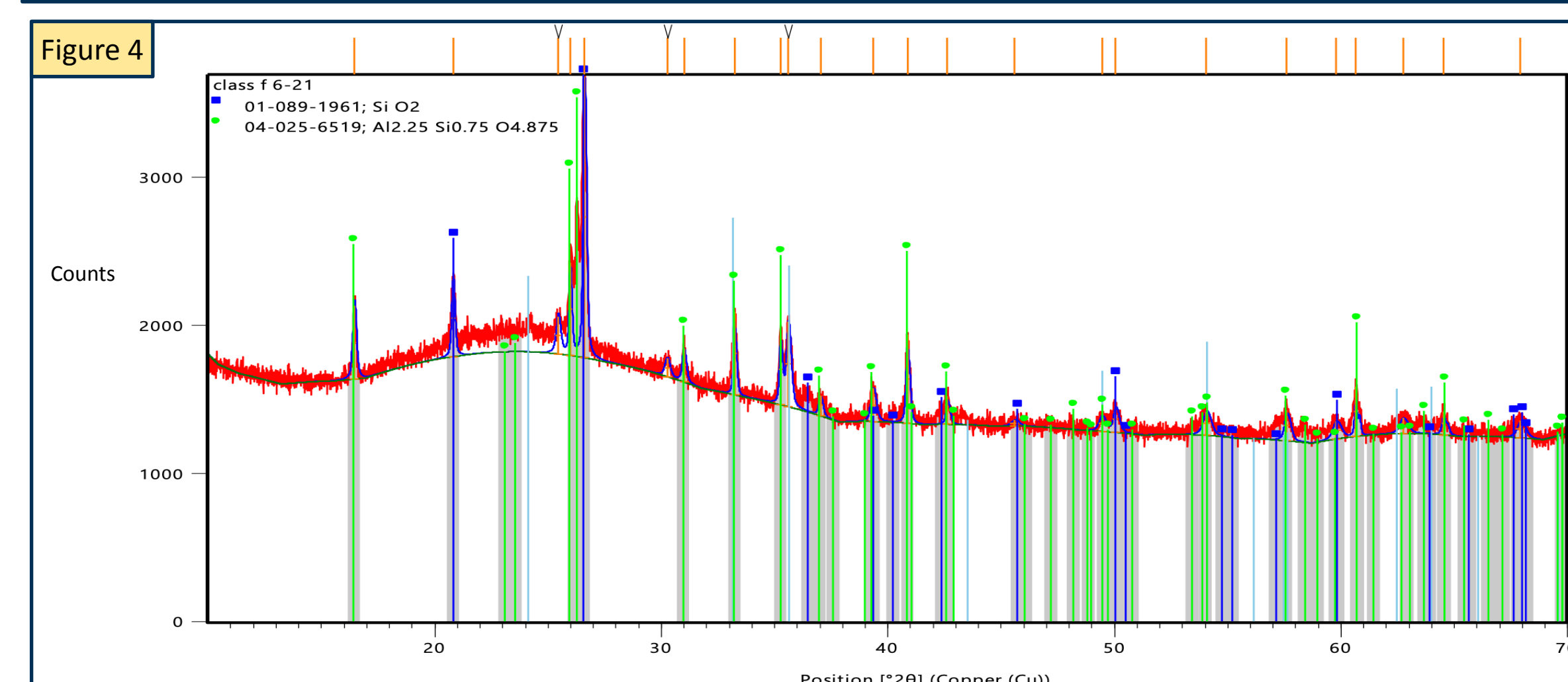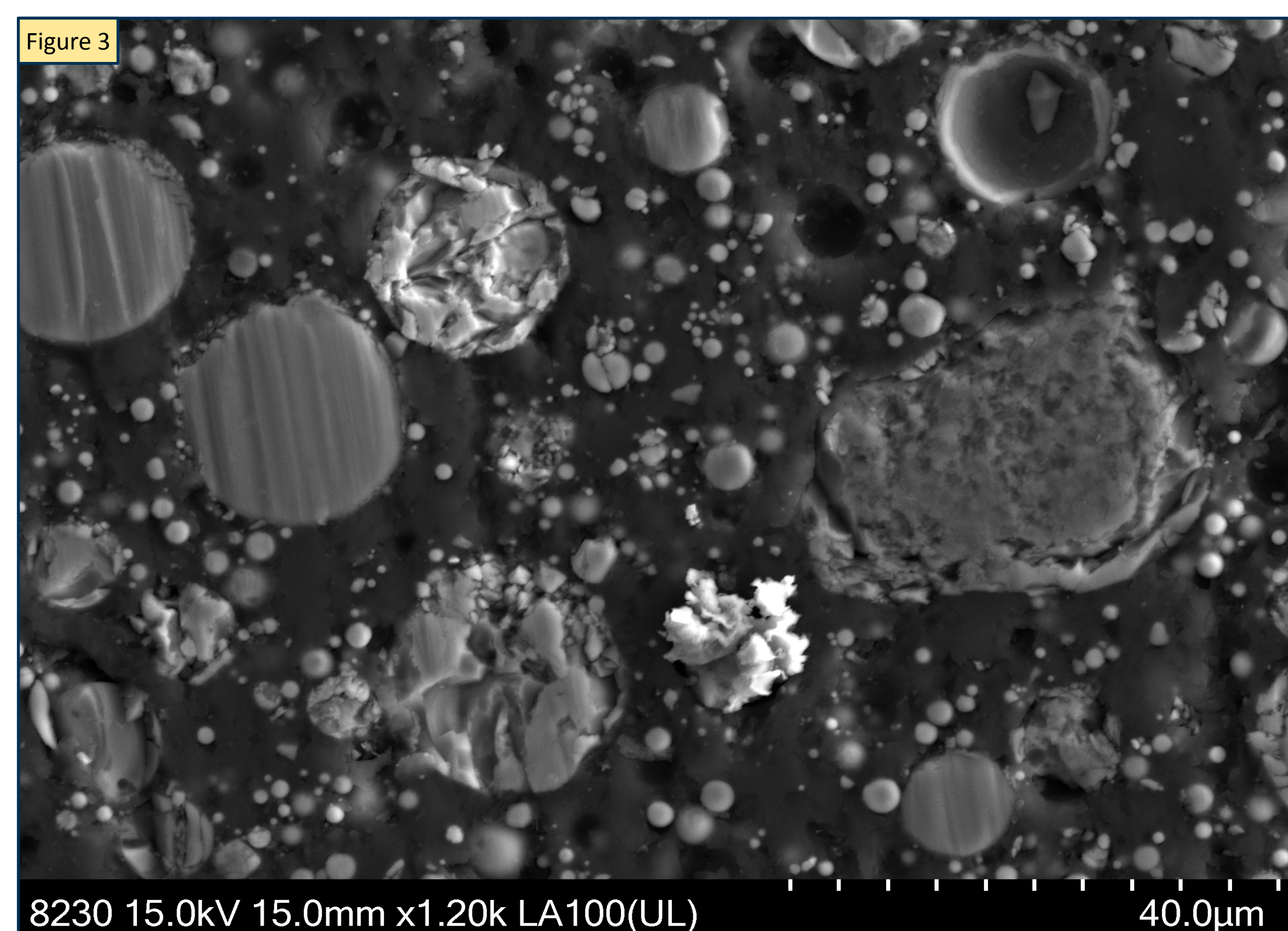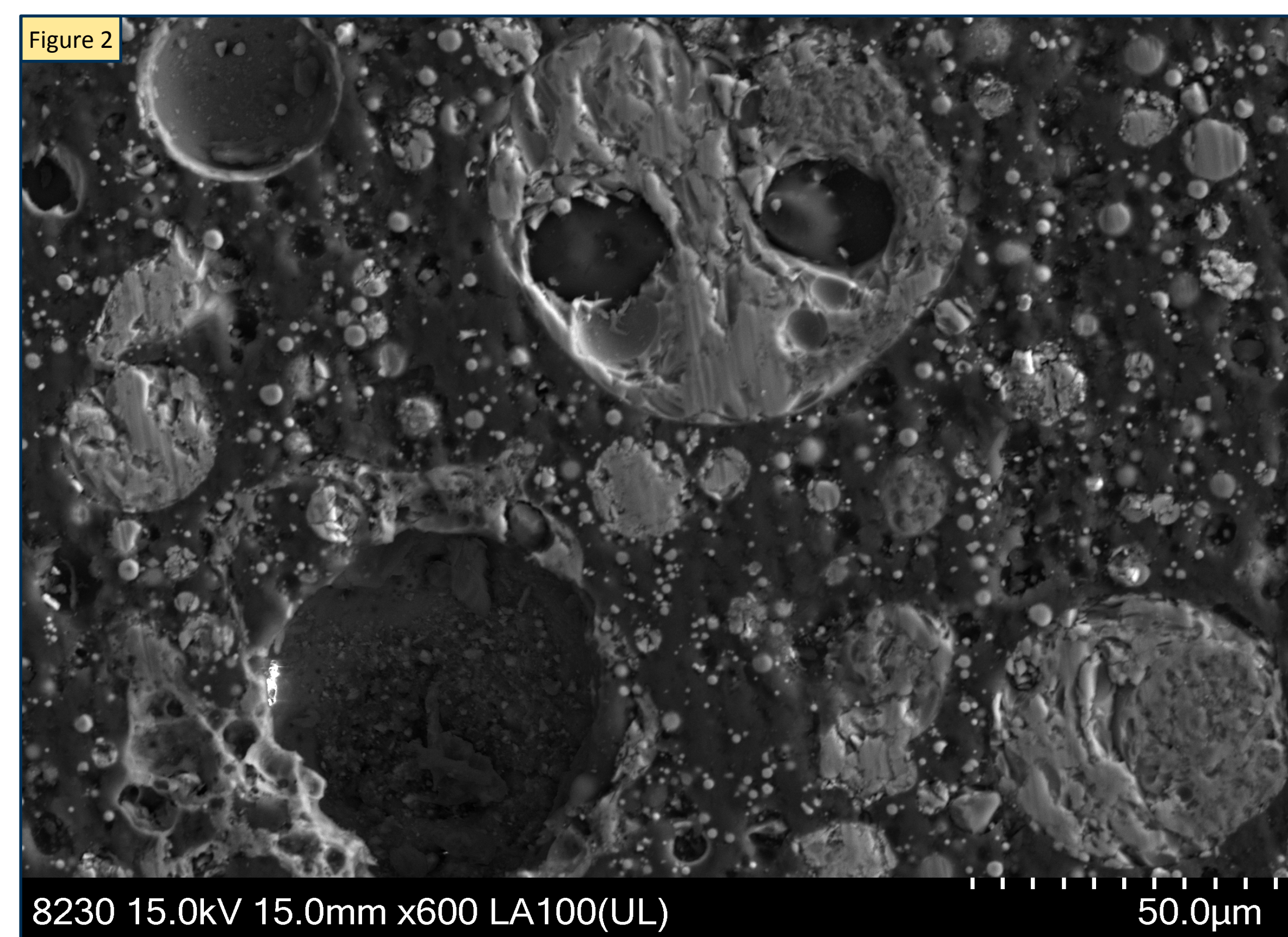

Figure 1: Plant Scherer and Ash Pond
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Methods

My research was conducted using CFA samples from the National Institute of Standards and Technology (NIST). Two samples were sent as standards with supporting documentation of their elemental composition. The samples come from coal burning power plants across the United States with different coal sources as well as burning methods. The feed coals were mostly bituminous with some sub-bituminous. The samples underwent two different extraction procedures to determine the chemical speciation and concentration of arsenic and selenium. EPA TCLP Method 1311 and sequential extraction were performed. The samples were then acidified and prepared for ICP-MS assessment. The Malvern PANalytical Materials Research Diffractometer for XRD was used to evaluate the phase ID and concentration. The Class F CFA standard from the NIST was used for XRD analysis. A High Resolution Scanning Electron Microscope was used to obtain SEM-EDX/EDS imagery. The SEM-EDX/EDS images were processed through the software AZtec for locating arsenic and selenium clusters within CFA cenospheres. The slides that were imaged are carbon coated and were created by the National Petrographic Service after being sent the CFA samples. A model compound method was developed using As_2O_3, As_2O_5, $HAsNa_2O_4 \bullet 7H_2O$, and $Ca_3(AsO_4)_2$. The compounds were chosen based on their likelihood to be found in CFA samples based on previous results. The model compounds were added to a 0.1 M NaCl solution and then leached at a range of pH values, using HNO_3 and NaOH until the desired pH was achieved. The solutions were then placed in the shaker for 10 hours. The pH was measured at different time points and 1 mL aliquots were taken to observe when the arsenic in the compounds is more mobile. The solutions will be later analyzed with ICP-MS on the VG Plasma Quad-3.

Results

8230 15.0kV 15.0mm x600 LA100(UL)   50.0µm

8230 15.0kV 15.0mm x1.20k LA100(UL)   40.0µm

Model Compounds at pH 1

Model Compounds at pH 4

Model Compounds at pH 6

Figures 2 and 3 show SEM-EDX/EDS Imagery. In Figure 2 the face shape was used as a reference point when determining location on the slide. Figure 3 shows a white coral like structure that contained the most found Arsenic at 3%.
Figure 4 displays the results from analyzing Class F through XRD techniques. The associated software was able to positively ID several peaks in the sample.
Figures 5-7 show the changes in pH over time for the model compound method. The purple dashed lines represent the addition of HNO_3 to achieve the desired pH. Aliquots were taken at the 2,4,6, 8, and 10 hr marks for further testing. As_2O_3, As_2O_5, and $HAsNa_2O_4 \bullet 7H_2O$ did not require additional acid or base added once they initially reached the desired pH with the exception of As_2O_5 at the 8 hour mark at pH 4.
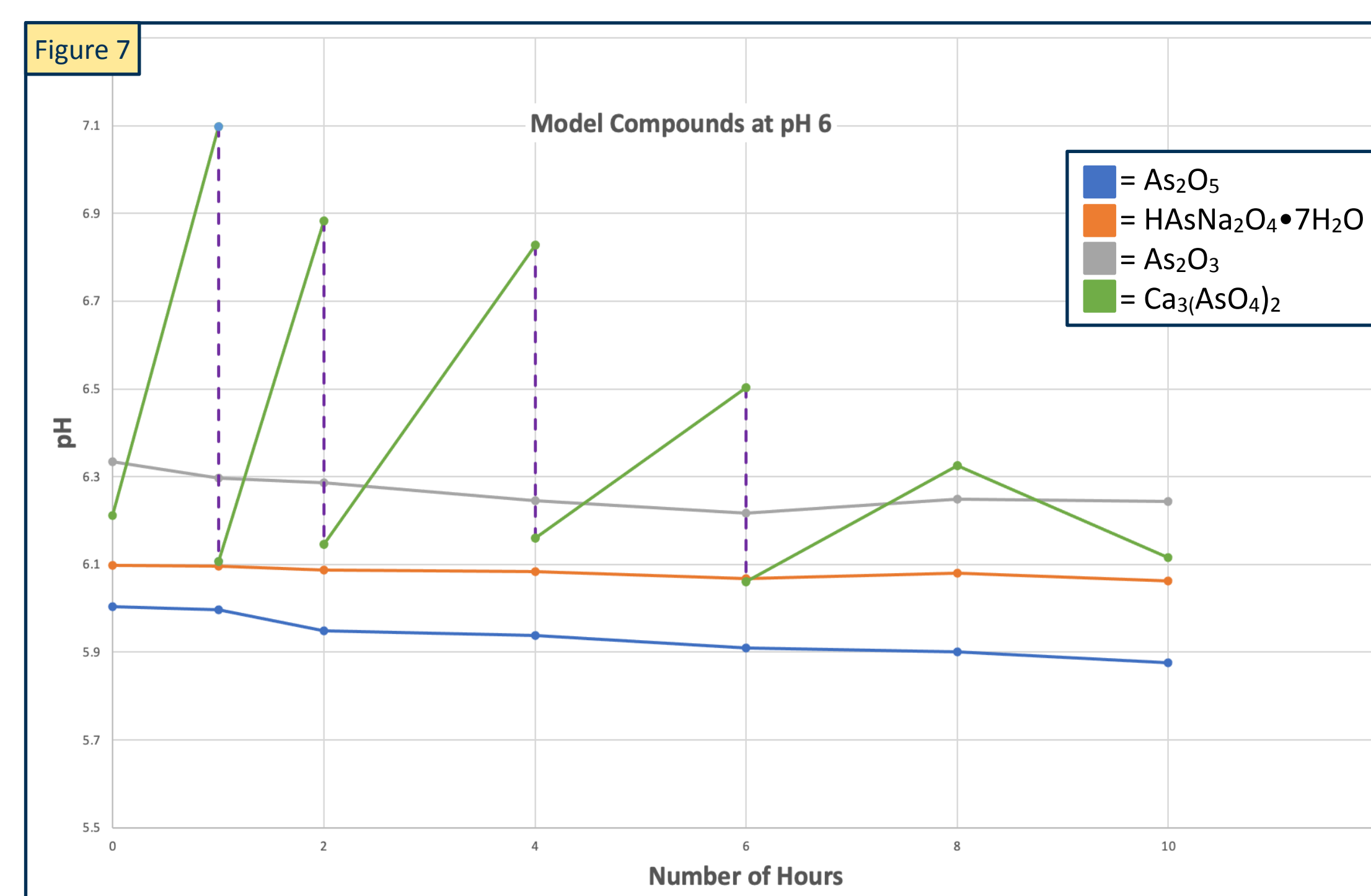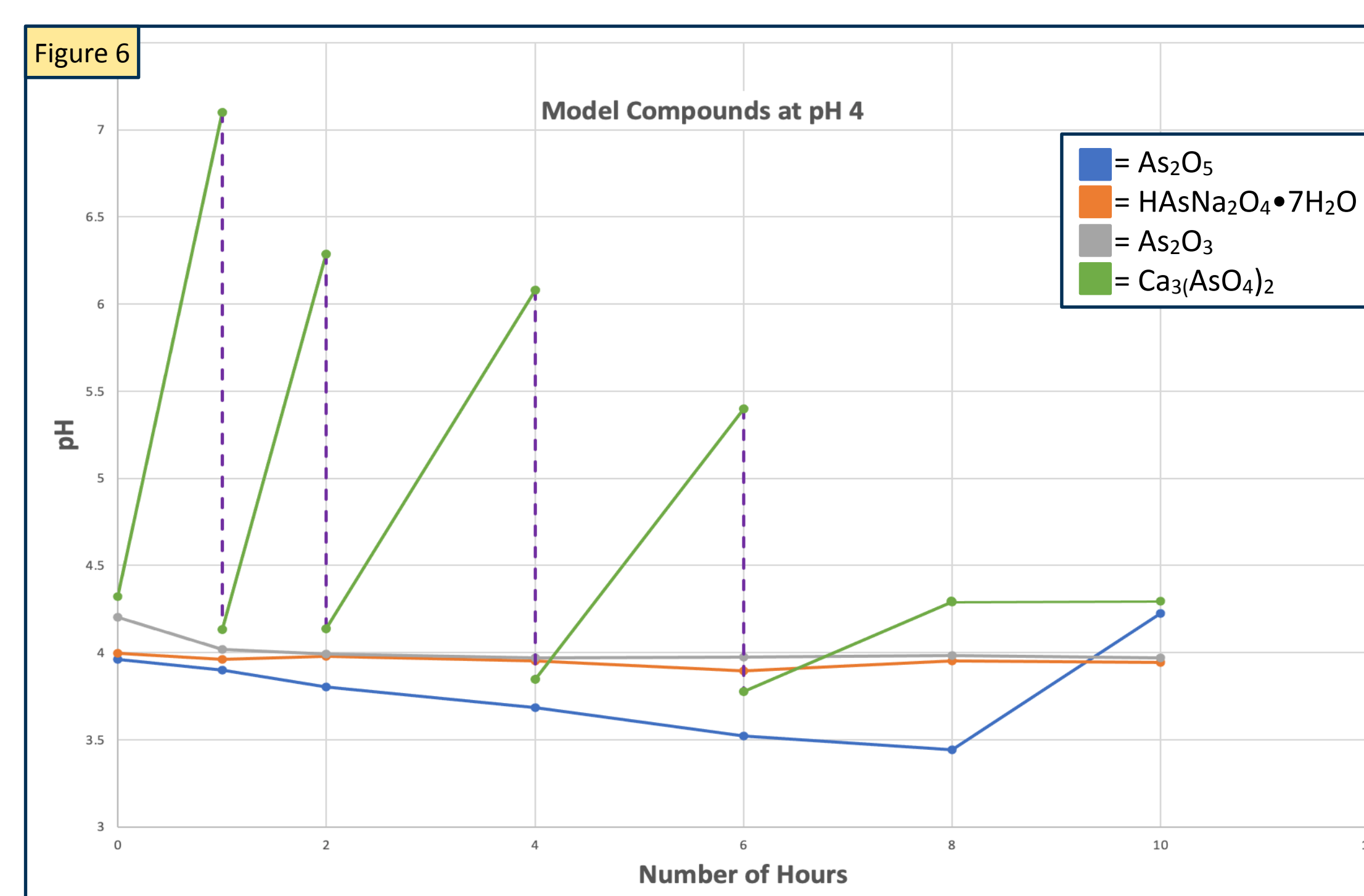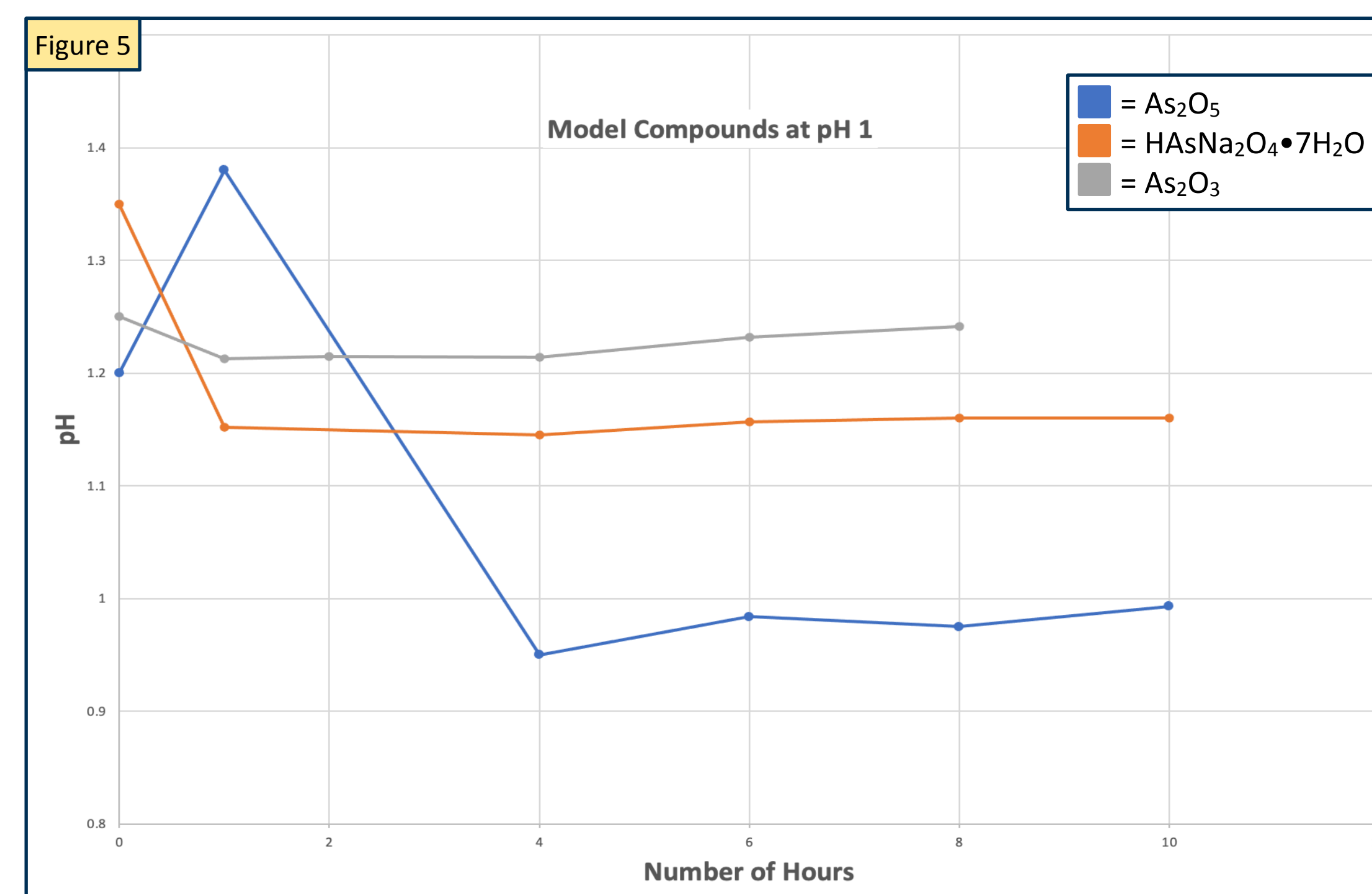
Future Works

Unfortunately I caught covid before my research could be completed. The model compound aliquots should be tested with ICP-MS methods to determine the concentration and mobility of As and Se as the pH changes and the original compound concentration decreases. I was also unable run the solutions obtained from the sequential extraction and TCLP Method 1311, so these should also be analyzed using ICP-MS testing. They solutions were not acidified so that my mentor can analyze them at her discretion at a later date. The model compound method should include more pH values in the future, specifically pH 2, 7, and 8. pH 7 and 8 will give a more realistic view into the interactions of arsenic compounds with surface and ground water. I was unable to include selenium compounds due to chemical availability, so similar selenium compounds should be included in a similar model compound method in the future. The surface water, ground water, and soil should be tested near the remaining unlined ash ponds. Current or relatively recent water quality data near these sites was not obtainable from USGS. Remembering the Kingston coal ash spill, more rigorous and immediate action is needed to protect our waterways from the hazards of coal ash and its trace elements.

Discussion/Conclusions

- When looking at the SEM-EDX/EDS imagery and analyzing it through AZtec, the brightest locations under high magnification were targeted. The brightest locations produced the highest concentrations of not only arsenic, but also calcium. This lead to following the calcium when mapping and performing spot sequencing in Aztec. In Figure 3, the white coral spot is shown in the bottom center. Of all the locations on the different images taken, this location produced the most Arsenic by atomic percent at 3%. The location also contained a high amount of calcium (over 40% by atomic percent), with more calcium than silicon. Locations that were higher in magnesium (over 4%) and silicon (at least over 35%) trended higher in selenium, however, over 2% selenium was not achieved.

- The XRD analysis was able to confirm the composition of the Class F CFA sample. Silicon dioxide was primarily found as well as aluminum. Silicon and aluminum are very stable and create glass formations, which require an extremely strong acid to dissolve. If arsenic or selenium are associated with silicon or aluminum as inclusions, then their mobility will be limited unless there are extreme changes in redox reactions or pH.

- In Figures 4-6, the model compounds As_2O_3, As_2O_5, $HAsNa_2O_4 \bullet 7H_2O$, $Ca_3(AsO_4)_2$ had HNO_3 and NaOH added to them until the desired pH was reached. While As_2O_3, As_2O_5, and $HAsNa_2O_4 \bullet 7H_2O$ all followed similar trend lines once the desired pH was reached, $Ca_3(AsO_4)_2$ did not follow the same behavior. When lowered to the desired pH, the $Ca_3(AsO_4)_2$ solutions gravitated towards the 6-7 pH range when tested again at the next time interval. The solutions also created a white bubbly precipitate when NaOH was added, which slowly solidified more to resemble table salt. This precipitate could have occurred because of the following reactions:

(1) $Ca_3(AsO_4)_2 + 6NaCl \longrightarrow 3CaCl_2 + 2Na_3(AsO_4)$
(2) $CaCl_2 + Na_3(AsO_4) + 2NaOH \longrightarrow Na_3(AsO_4) + Ca(OH)_2 + 2NaCl$

$Ca(OH)_2$ can be slightly insoluble in water and could have created the precipitate. Further analysis will need to be done for confirmation of $Ca(OH)_2$ as a product. There seemed to be less of a dramatic increase of pH towards the 6 to 10 hour marks. This could be due to the fact that the original compound concentration decreased with each aliquot removed.

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