Supplementary Information for:

Synchrotron-based X-ray Studies on Subsurface Transformations of Lead, Zinc, and Cadmium in Mine Waste Materials

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This document includes 5 supplementary figures, and 7 supplementary tables. Terms, abbreviations, and symbols are the same as in the main text.
Supplementary Figures and Tables
Fig. S1. Micro Fe-XANES spectra for OC plus S-treated (C1S1) samples under short- (32-day), medium- (119-day), and long-term (252-day) submergence. In each spectrum, ‘d’ represents days of submergence and P1-P3 represent points selected on micro-XRF maps for Fe-XANES data collection. Solid lines represent normalized spectra and dotted lines represent best fits obtained using statistical analyses, principal component analysis (PCA), and linear combination fitting (LCF). Micro Fe-XANES linear combination fitting (LCF) results, for control OC plus S-treated (C1S1), show % components of Fe$^{2+}$ and Fe$^{3+}$ minerals formed.
Fig. S2. a) Micro S-XRF maps, showing the S point of interest (POI) under medium- (119-day) and long- (252-day) term submergence used to collect S-XANES spectra. In each map, the brightest color (white) represents the highest fluorescence signal or highest concentration of an element, whereas the darkest color represents the lowest fluorescence signal or lowest concentration of an element. Shading is relative across each map. S-fluorescence was collected at 2550 eV. b) Micro S-XANES spectra for control (C0S0) and OC plus S-treated (C1S1) samples under medium-term (119-day), and long-term (252-day) submergence. In each spectrum, ‘d’ represents days of submergence, and P1-Pn represent points selected on micro-XRF maps for S-XANES data collection. Solid lines represent a first-order derivative spectra and dotted lines represent best fits obtained using linear combination fitting (LCF). $\chi^2<1$ represents the goodness of fit.
Fig. S3. Micro Pb-XANES spectra for a) control (C0S0) and b) OC plus S-treated (C1S1) samples under short- (32-day), medium- (119-day), and long-term (252-day) submergence. In each spectrum, ‘d’ represents days of submergence and P1-P5 represent points selected on micro-XRF maps for XANES data collection. Solid lines represent normalized spectra, and dotted lines represent best fits obtained using principal component analysis (PCA) and linear combination fitting (LCF). Bulk Pb-XAFS spectra collected for c) control (C0S0), d) only S-treated (C0S1), e) only OC-treated (C1S0), and f) OC plus S-treated (C1S1) samples submerged for short- (32-day), medium- (119-day), and long-term (252-day) submergence. Solid lines represent $k^1$-weighted $\chi$-spectra and dotted lines represent best fits obtained using principal component analysis (PCA) and linear combination fitting (LCF). $\chi^2<1$ represents the goodness of fit.
**Fig. S4.** Micro Zn-XAFS spectra for a) control (C0S0) and b) OC plus S-treated (C1S1) samples under short- (32-day), medium- (119-day), and long-term (252-day) submergence. In each spectrum, 'd' represents days of submergence and P1-P5 represent points selected on micro-XRF maps for XAFS data collection. Bulk Zn-XAFS spectra collected for c) control (C0S0), d) only S-treated (C0S1), e) only OC-treated (C1S0), and f) OC plus S-treated (C1S1) samples submerged for short- (32-day), medium- (119-day), and long-term (252-day) submergence. Solid lines represent $k^1$-weighted $\chi$-spectra and dotted lines represent best fits obtained using principal component analysis (PCA) and linear combination fitting (LCF). $\chi^2<1$ represents the goodness of fit.
Fig. S5: Bulk Cd-XAFS linear combination fitting (LCF) results for control (C0S0), only S-treated (C0S1), only OC-treated (C1S0), and OC plus S-treated (C1S1) from long-term (252-day) submergence and control (C0S0), and OC and S added (C1S1) from medium-term (119-day) submergence. $\chi^2 < 1$ gives the goodness of fit.
### Table S1: Principle component analysis (PCA) results showing SPOIL values for Pb- and Zn- mineral standards used for micro Zn- and Pb-XAFS.

<table>
<thead>
<tr>
<th>Zinc minerals</th>
<th>SPOIL value</th>
<th>Lead minerals</th>
<th>SPOIL value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrihydrite_Zinc</td>
<td>2.63†</td>
<td>Anglesite</td>
<td>3.71†</td>
</tr>
<tr>
<td>Franklinite</td>
<td>2.66†</td>
<td>Cerussite</td>
<td>3.83†</td>
</tr>
<tr>
<td>Gahnite</td>
<td>5.64</td>
<td>Galena</td>
<td>1.89†</td>
</tr>
<tr>
<td>Hemimorphite</td>
<td>2.23†</td>
<td>Hydrocerussite</td>
<td>1.9†</td>
</tr>
<tr>
<td>Hopeite</td>
<td>2.19†</td>
<td>Hydroxypyromorphite</td>
<td>2.76†</td>
</tr>
<tr>
<td>Hydrozincite</td>
<td>5.63</td>
<td>Leadillite</td>
<td>1.98†</td>
</tr>
<tr>
<td>Scholzite</td>
<td>3.11†</td>
<td>Magnetoplumbite</td>
<td>3.45†</td>
</tr>
<tr>
<td>Smithsonite</td>
<td>2.73</td>
<td>Lead oxide</td>
<td>4.4</td>
</tr>
<tr>
<td>Willemite</td>
<td>2.03†</td>
<td>Lead phosphate</td>
<td>2.29†</td>
</tr>
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<td>Zincite</td>
<td>3.0†</td>
<td>Plumboferrite</td>
<td>2.31†</td>
</tr>
<tr>
<td>ZnAI_LDH</td>
<td>3.56†</td>
<td>Plumbogummite</td>
<td>3.85†</td>
</tr>
<tr>
<td>Zinc hydroxide</td>
<td>3.68†</td>
<td>Plumbosjarosite</td>
<td>4.76</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>2.73†</td>
<td>Pyromorphite</td>
<td>5.81</td>
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<tr>
<td>Zinc sulfate</td>
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<td>Lead hindsalite</td>
<td>3.21</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>2.07†</td>
<td>Lead chloride</td>
<td>3.53</td>
</tr>
<tr>
<td>Zinc_calcite</td>
<td>5.46</td>
<td>Platternite</td>
<td>3.98</td>
</tr>
<tr>
<td>Zinc silicate</td>
<td>20.5</td>
<td>Lead_humic acids</td>
<td>3.73†</td>
</tr>
<tr>
<td>Zn_Birnessite</td>
<td>4.23</td>
<td>Plumbonacrite</td>
<td>4.13</td>
</tr>
<tr>
<td>Zinc_humic acids</td>
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<td>Lead_fulvic acids</td>
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<td></td>
<td></td>
<td>Lead_ferrihydrite</td>
<td>3.99</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lead_birnessite</td>
<td>4.16</td>
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Mineral standards below SPOIL value <4 were selected. † on the value indicates standards used to run linear combination fittings for micro- Zn- and Pb-XAS.
Table S2: Principle component analysis (PCA) results showing SPOIL values for Zn-, Pb-, and Cd-mineral standards used for bulk Zn-, Pb-, and Cd-XAFS.

<table>
<thead>
<tr>
<th>Zinc minerals</th>
<th>SPOIL value</th>
<th>Lead minerals</th>
<th>SPOIL value</th>
<th>Cadmium compounds and minerals</th>
<th>SPOIL value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferricydrite_Zn</td>
<td>3.71\textsuperscript{f}</td>
<td>Anglesite</td>
<td>7.19</td>
<td>Cadmium acetate</td>
<td>1.08\textsuperscript{f}</td>
</tr>
<tr>
<td>Franklinite</td>
<td>9.87</td>
<td>Cerussite</td>
<td>0.97\textsuperscript{f}</td>
<td>Cadmium citrate</td>
<td>9.35</td>
</tr>
<tr>
<td>Gahnite</td>
<td>9.49</td>
<td>Galena</td>
<td>2.54\textsuperscript{f}</td>
<td>Cadmium cystein</td>
<td>1.96\textsuperscript{f}</td>
</tr>
<tr>
<td>Hemimorphite</td>
<td>1.57\textsuperscript{f}</td>
<td>Hydrocerussite</td>
<td>3.53\textsuperscript{f}</td>
<td>Cadmium EDTA</td>
<td>1.87\textsuperscript{f}</td>
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<tr>
<td>Hopeite</td>
<td>6.38</td>
<td>Hydroxypropyromorphite</td>
<td>7.29</td>
<td>Cadmium_ferricydrite</td>
<td>7.39</td>
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<td>Hydrozincite</td>
<td>2.74\textsuperscript{f}</td>
<td>Leadhillite</td>
<td>3.75\textsuperscript{f}</td>
<td>Cadmium_gibbsite</td>
<td>1.77\textsuperscript{f}</td>
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<td>Scholzite</td>
<td>5.23</td>
<td>Magnetoplumbite</td>
<td>2.51\textsuperscript{f}</td>
<td>Cadmium_humic_acid</td>
<td>1.68\textsuperscript{f}</td>
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<tr>
<td>Smithsonite</td>
<td>2.62\textsuperscript{f}</td>
<td>Lead oxide</td>
<td>1.63\textsuperscript{f}</td>
<td>Cadmium oxide</td>
<td>6.57</td>
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<td>Lead phosphate</td>
<td>4.7</td>
<td>Cadmium_phosphate</td>
<td>1.14\textsuperscript{f}</td>
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<td>Zincite</td>
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<td>Plumboferrite</td>
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<td>Cadmium_bismuthite</td>
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<td>ZnAl_LDH</td>
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<td>Plumbogummite</td>
<td>4.21</td>
<td>Cadmium_sulfate</td>
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<td>Plumbojarosite</td>
<td>7.68</td>
<td>Cadmium_carbonate</td>
<td>1.91\textsuperscript{f}</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>2.31\textsuperscript{f}</td>
<td>Pyromorphite</td>
<td>6.15</td>
<td>Cadmium_chloride</td>
<td>9.35</td>
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<td>Zinc sulfate</td>
<td>1.97\textsuperscript{f}</td>
<td>Lead_hindsalite</td>
<td>8.01</td>
<td>Cadmium_sulfide</td>
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<tr>
<td>Zinc silicate</td>
<td>5.27</td>
<td>Lead chloride</td>
<td>12.11</td>
<td>Cadmium_hydrate</td>
<td>2.91</td>
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<tr>
<td>Zn_{calcite}</td>
<td>5.46</td>
<td>Platternite</td>
<td>5.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>20.5</td>
<td>Lead_humic_acids</td>
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<td>Zn_{bismesitete}</td>
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<td>Plumbonacrite</td>
<td>5.45</td>
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<td></td>
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<tr>
<td>Zinc_{humic acids}</td>
<td>4.89</td>
<td>Lead_{dulvic acids}</td>
<td>4.10</td>
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<tr>
<td></td>
<td></td>
<td>Lead_{ferricydrite}</td>
<td>3.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lead_{bismesitete}</td>
<td>4.23</td>
<td></td>
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</tr>
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</table>

Mineral standards below SPOIL value <4 were selected. \textsuperscript{f} on the value indicates standards used to run linear combination fittings for bulk Zn-, Pb-, and Cd-XAFS.
<table>
<thead>
<tr>
<th>Element POI</th>
<th>µ-XRD</th>
<th>µ-XANES</th>
<th>Bulk XAFS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb_P1</td>
<td>Quartz, Massicot (PbO)</td>
<td>Hydroxypyromorphite, Hydrocerussite, Galena, PbO</td>
<td>Pyromorphite, Anglesite, hydrocerussite</td>
</tr>
<tr>
<td></td>
<td>Quartz, Neotocitc (Mn, Fe silicate), Despujolite (Ca, Mn sulfate)</td>
<td>Hydroxypyromorphite, Hydrocerussite, Galena, PbO</td>
<td></td>
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<tr>
<td>Pb_P2</td>
<td>Quartz, Calcite, Cerussite (Pb carbonate), Coronadite (Pb, Mn oxide), Pb/Zr oxide</td>
<td>Hydroxypyromorphite, leadhillite, Galena, Plumboferrite</td>
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</tr>
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<td>Pb_P3</td>
<td>Quartz, Calcite, Neotocitc (Mn, Fe silicate), Despujolite (Ca, Mn sulfate)</td>
<td>Hydroxypyromorphite, Hydrocerussite, Galena, PbO</td>
<td></td>
</tr>
<tr>
<td>Zn_P1</td>
<td>Quartz, Calcite, Nepouite (Ni silicate)</td>
<td>Willemite, Hopeite, Scholzite</td>
<td>Zn silicate, Smithsonite, Zn hydroxide</td>
</tr>
<tr>
<td></td>
<td>Quartz, Calcite, Hemimorphite (Zn silicate), Zn Phosphate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn_P2</td>
<td>Oxide</td>
<td>Willemite, Hopeite, Scholzite</td>
<td></td>
</tr>
<tr>
<td>Zn_P3</td>
<td>Quartz, Hemimorphite</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd_P1</td>
<td>Quartz, Calcite, Spurrite (Ca₅(SiO₄)₂(CO₃))</td>
<td>no data</td>
<td>Cd carbonate, Cd sulfate, Cd-hydroxides, Cd_HA</td>
</tr>
<tr>
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<td></td>
</tr>
<tr>
<td>Fe_P1</td>
<td>Quartz, Fe/Mn OOH, Cerussite</td>
<td>no data</td>
<td>no data</td>
</tr>
<tr>
<td>Fe_P2</td>
<td>Quartz, Neotocitc (Fe/Mn/Mg Oxide)</td>
<td>no data</td>
<td></td>
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</tbody>
</table>

†Cd_HA: Cd sorbed on humic acid
**Table S4:** Micro S-XANES linear combination fitting results showing % components of different sulfate, sulfite, and sulfide formed in control (C0S0), and OC and S-treated (C1S1) under medium- (119-day), and long-term (252-day) submergence.

<table>
<thead>
<tr>
<th>Treatments</th>
<th>Sulfide</th>
<th>Sulfate</th>
<th>Sulfite</th>
<th>$\chi^2$</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>C0S0 119-day P1</td>
<td>7%</td>
<td>93%</td>
<td>−</td>
<td>0.54</td>
<td>0.06</td>
</tr>
<tr>
<td>C0S0 119-day P3</td>
<td>20%</td>
<td>80%</td>
<td>−</td>
<td>0.43</td>
<td>0.05</td>
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<tr>
<td>C0S0 119-day P4</td>
<td>4%</td>
<td>96%</td>
<td>−</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>C0S0 119-day P5</td>
<td>19%</td>
<td>81%</td>
<td>−</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>C0S0 119-day P6</td>
<td>17%</td>
<td>81%</td>
<td>−</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>C0S0 119-day P7</td>
<td>17%</td>
<td>81%</td>
<td>−</td>
<td>0.02</td>
<td>0.04</td>
</tr>
<tr>
<td>C0S0 119-day P8</td>
<td>−</td>
<td>100%</td>
<td>−</td>
<td>0.56</td>
<td>0.02</td>
</tr>
<tr>
<td>C0S0 119-day P9</td>
<td>16%</td>
<td>84%</td>
<td>−</td>
<td>1.23</td>
<td>0.02</td>
</tr>
<tr>
<td>C0S0 119-day P10</td>
<td>−</td>
<td>100%</td>
<td>−</td>
<td>1.25</td>
<td>0.03</td>
</tr>
<tr>
<td>C0S0 119-day P11</td>
<td>−</td>
<td>100%</td>
<td>−</td>
<td>1.24</td>
<td>0.02</td>
</tr>
<tr>
<td>C0S0 119-day P12</td>
<td>−</td>
<td>100%</td>
<td>−</td>
<td>0.47</td>
<td>0.02</td>
</tr>
<tr>
<td>C0S0 252-day P2</td>
<td>−</td>
<td>93%</td>
<td>7%</td>
<td>0.35</td>
<td>0.02</td>
</tr>
<tr>
<td>C0S0 252-day P4</td>
<td>22%</td>
<td>78%</td>
<td>−</td>
<td>2.56</td>
<td>0.04</td>
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<tr>
<td>C0S0 252-day P6</td>
<td>10%</td>
<td>90%</td>
<td>−</td>
<td>1.79</td>
<td>0.02</td>
</tr>
<tr>
<td>C0S0 252-day P7</td>
<td>−</td>
<td>100%</td>
<td>−</td>
<td>1.11</td>
<td>0.03</td>
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<tr>
<td>C0S0 252-day P8</td>
<td>−</td>
<td>100%</td>
<td>−</td>
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<tr>
<td>C0S0 252-day P9</td>
<td>36%</td>
<td>64%</td>
<td>−</td>
<td>0.78</td>
<td>0.02</td>
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<tr>
<td>C0S0 252-day P10</td>
<td>32%</td>
<td>68%</td>
<td>−</td>
<td>0.66</td>
<td>0.02</td>
</tr>
<tr>
<td>C1S1 119-day P1</td>
<td>18%</td>
<td>68%</td>
<td>14%</td>
<td>1.29</td>
<td>0.07</td>
</tr>
<tr>
<td>C1S1 119-day P2</td>
<td>52%</td>
<td>48%</td>
<td>−</td>
<td>1.59</td>
<td>0.10</td>
</tr>
<tr>
<td>C1S1 119-day P3</td>
<td>49%</td>
<td>39%</td>
<td>12%</td>
<td>1.28</td>
<td>0.08</td>
</tr>
<tr>
<td>C1S1 119-day P4</td>
<td>45%</td>
<td>55%</td>
<td>−</td>
<td>1.84</td>
<td>0.15</td>
</tr>
<tr>
<td>C1S1 119-day P5</td>
<td>29%</td>
<td>62%</td>
<td>9%</td>
<td>1.93</td>
<td>0.15</td>
</tr>
<tr>
<td>C1S1 119-day P6</td>
<td>43%</td>
<td>57%</td>
<td>−</td>
<td>2.09</td>
<td>0.08</td>
</tr>
<tr>
<td>C1S1 119-day P7</td>
<td>44%</td>
<td>56%</td>
<td>−</td>
<td>1.99</td>
<td>0.21</td>
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<tr>
<td>Near C1S1 119-day P8</td>
<td>45%</td>
<td>43%</td>
<td>12%</td>
<td>0.88</td>
<td>0.07</td>
</tr>
<tr>
<td>C1S1 119-day P9</td>
<td>57%</td>
<td>43%</td>
<td>−</td>
<td>1.26</td>
<td>0.09</td>
</tr>
<tr>
<td>C1S1 119-day P10</td>
<td>63%</td>
<td>37%</td>
<td>−</td>
<td>1.56</td>
<td>0.14</td>
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<tr>
<td>C1S1 119-day P11</td>
<td>58%</td>
<td>42%</td>
<td>−</td>
<td>1.40</td>
<td>0.11</td>
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<tr>
<td>C1S1 252-day P2</td>
<td>56%</td>
<td>44%</td>
<td>−</td>
<td>1.35</td>
<td>0.08</td>
</tr>
<tr>
<td>C1S1 252-day P4</td>
<td>53%</td>
<td>47%</td>
<td>−</td>
<td>1.40</td>
<td>0.06</td>
</tr>
<tr>
<td>C1S1 252-day P5</td>
<td>42%</td>
<td>58%</td>
<td>−</td>
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<tr>
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<td>18%</td>
<td>8%</td>
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<td>0.16</td>
</tr>
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<td>73%</td>
<td>27%</td>
<td>−</td>
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<td>0.14</td>
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<td>26%</td>
<td>13%</td>
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</tr>
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<td>37%</td>
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<td>61%</td>
<td>−</td>
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<td>0.04</td>
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P1-Pn represent point of interests (POI) on the µ-XRF maps (Fig. S2a), where S-XANES spectra were collected. *The phase identified as less than 10% may not be significant due to error associated with smaller estimations.
control (C0S0) under short- (32-day), medium- (119-day), and long-term (252-day) submergence.

<table>
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<tr>
<th>Treatments over time</th>
<th>Galena</th>
<th>Cerussite</th>
<th>PbO</th>
<th>Hydroxy pyromorphite</th>
<th>Plumbo ferrite</th>
<th>Plumbogummite</th>
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<th>R-factor</th>
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<td>-</td>
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<td>0.0010</td>
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<td>0.0010</td>
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<td>59%</td>
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<td>21%</td>
<td>5%⁵</td>
<td>7%³</td>
<td>7%³</td>
<td>-</td>
<td>107%</td>
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<td>0.0003</td>
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<td>23%</td>
<td>8%³</td>
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<td>16%</td>
<td>39%</td>
<td>29%</td>
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<td>0.0002</td>
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<td>21%</td>
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<td>7%³</td>
<td>7%³</td>
<td>-</td>
<td>99%</td>
<td>0.02</td>
<td>0.0004</td>
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</table>

P1-Pn represents points of interest (POI) on the µ-XRF maps (Fig. 1). †indicates the POIs where XAS data collected were not usable.

Total % components greater or lesser than 100 are indicated. *The phase identified as less than 10% may not be significant due to error associated with smaller estimations.
<table>
<thead>
<tr>
<th>Treatments over time</th>
<th>Sphalerite</th>
<th>Franklinit</th>
<th>Hemimorphite</th>
<th>Zn(OH)$_2$</th>
<th>Willemite</th>
<th>Smithsonite</th>
<th>Ferrihydrite</th>
<th>ZnAl-LDH</th>
<th>ZnSO$_4$</th>
<th>Total</th>
<th>$\chi^2$</th>
<th>R-factor</th>
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<td>–</td>
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<td>36%</td>
<td>3.40</td>
<td>0.49</td>
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<td>–</td>
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<td>–</td>
<td>–</td>
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<td>–</td>
<td>–</td>
<td>–</td>
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<td>–</td>
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<td>–</td>
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<td>67%</td>
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<td>38%</td>
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<td>–</td>
<td>–</td>
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<td>5%$^\dagger$</td>
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<td>–</td>
<td>–</td>
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P1-Pn represent points of interest (POI) on the µ-XRF maps (Fig. 3). $^\dagger$ indicates the POI where XAS data collected were not usable.

Total % components greater or lesser than 100 are indicated. $^\dagger$ The phase identified as less than 10% may not be significant due to error associated with smaller estimations.
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<th>formula</th>
<th>Cadmium compounds and minerals</th>
<th>formula</th>
<th>Iron minerals</th>
<th>formula</th>
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<td>PbSO₄</td>
<td>Cadmium acetate</td>
<td>Cd(CH₃CO₂)₂</td>
<td>Magnetite</td>
<td>Fe₃O₄</td>
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<tr>
<td>Cerussite</td>
<td>Pb(CO₃)</td>
<td>Cadmium citrate</td>
<td>C₁₂H₁₀Cd₂O₁₄</td>
<td>Pyrite</td>
<td>FeS₂</td>
</tr>
<tr>
<td>Galena</td>
<td>PbS</td>
<td>Cadmium cystein</td>
<td>C₃H₇CdNO₃S</td>
<td>Green rust</td>
<td>Fe⁴⁺Fe³⁺(OH)₁₂[CO₃]·3H₂O</td>
</tr>
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<td>Hydrocerussite</td>
<td>Pb₃(CO₃)₂(OH)₂</td>
<td>Cadmium EDTA</td>
<td>Cd₁₆H₁₆N₅O₈</td>
<td>Magnetite</td>
<td>Fe²⁺Fe³⁺O₄</td>
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<tr>
<td>Hydroxypyromorphite</td>
<td>Pb₃(PO₄)₃OH</td>
<td>Cadmium ferrihydrite</td>
<td>Fe₂O₃·0.5(H₂O)·Cd</td>
<td>Goethite</td>
<td>(FeO(OH))</td>
</tr>
<tr>
<td>Leadhillite</td>
<td>Pb₄(CO₃)₂(SO₄)(OH)₂</td>
<td>Cadmium_gibbsite</td>
<td>Cd₁₂Al(OH)₃</td>
<td>Vivianite</td>
<td>Fe⁵⁺(PO₄)₂·8H₂O</td>
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<tr>
<td>Magnetoplumbite</td>
<td>(Pb,Mn)(Fe,Mn)₁₂O₁₉</td>
<td>Cadmium_humic acid</td>
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<td>Siderite</td>
<td>FeCO₃</td>
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<td>PbO</td>
<td>Cadmium oxide</td>
<td>CdO</td>
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<tr>
<td>Lead phosphate</td>
<td>Pb₃(PO₄)₂</td>
<td>Cadmium phosphate</td>
<td>Cd₃(PO₄)₂</td>
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<tr>
<td>Plumboferrite</td>
<td>PbFe₄O₇</td>
<td>Cadmium_birnessite</td>
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<tr>
<td>Plumbogummite</td>
<td>Pb₃Al₆(PO₄)₃(OH)₅·3H₂O</td>
<td>Cadmium sulfate</td>
<td>CdSO₄</td>
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<tr>
<td>Plumbojarosite</td>
<td>Pb₆Fe₆(SO₄)₄(OH)₁₂</td>
<td>Cadmium carbonate</td>
<td>CdCO₃</td>
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<td>Pyromorphite</td>
<td>Pb₃(PO₄)₃Cl</td>
<td>Cadmium chloride</td>
<td>CdCl₂</td>
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<tr>
<td>Lead hindsalite</td>
<td>Pb₃Al₃(PO₄)SO₄(OH)₆</td>
<td>Cadmium sulfide</td>
<td>CdS</td>
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<tr>
<td>Lead chloride</td>
<td>PbCl₂</td>
<td>Cadmium hydroxide</td>
<td>Cd(OH)₂</td>
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<td>Platternite</td>
<td>PbO₂</td>
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<td>Lead_humic acids</td>
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<td>Plumbonacrite</td>
<td>Pb₁₀(CO₃)₆O(OH)₆</td>
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Additional details of micro-XRF and micro-XAS data collection, and analysis of treated mine waste samples

Micro x-ray fluorescence (μ-XRF) and micro x-ray absorption spectroscopy (μ-XAS) for Pb, Zn, and Fe were conducted at sectors 13-BM-D, 13-ID-E, and 20-ID-B at the Advanced Photon Source, Argonne National Laboratory. The 13-BM-D beamline has a Si (111) double-crystal monochromator and energy range from 4.5 KeV to 70 KeV. It has Canberra 16-element Ge detectors. The 13-ID-E beamline uses a 3.6-cm period undulator source and double-crystal monochromator (DCM) with tunable energy from 2.4 KeV to 27.5 KeV. This beamline uses Kirkpatrick-Baez mirrors to focus the x-ray beam to 2 μm x 2 μm with a greater x-ray flux, and measures X-ray fluorescence spectra using a four-element, silicon-drift diode array detector. For flux information, refer to http://www.aps.anl.gov/Beamlines/Directory/showbeamline.php?beamline_id=62, and for details on the 20-ID-B microprobe, refer to Heald et al. (2007).

As XAS data were collected in the fluorescence mode, the angle of the incident x-ray beam was ~45° with respect to the sample surface. Elemental maps were generated with an incident x-ray energy of 13.5 KeV at ambient temperature for Pb, Zn, and Fe over an area varying from 200 μm x 200 μm to 500 μm x 500 μm, with two μm steps. Using XRF maps, five points of interest (POI) (high relative concentrations) for Pb and Zn, and three POI for Fe, were identified and used for more detailed spectroscopic investigations. For S, about 750 μm x 750 μm maps with 2-μm step size were collected at an energy of 2.55 KeV. Micro-XAFS spectra were collected from 100 eV below the absorption edge to 300 eV beyond the absorption edge, with increments varying from 0.05 to 10 eV. Four to five successful scans at each selected POI at the Pb LIII-edge and Zn K-edge, three scans at the Fe K-edge, and one scan at the S K-edge were collected.
Because of beam-induced S oxidation, only one scan per spot was collected. The samples for S-mapping and XANES data collection, the detector was set up in a He filled bag to minimize oxidation due to atmospheric oxygen. Due to a high level of background noise (a common issue in μ-scale XAFS related to a very small amount of sample being exposed to x-rays), only the XANES region of Pb was used for Pb data analysis (-30 eV to +50 eV). We were able to collect usable XAFS data for Zn, and the XAFS region (2 to 9 Å⁻¹ in k-space) was used for Zn data analysis. During processing, replicated spectra were aligned and merged, and the background was removed then normalized. A minimal smoothing (< four iterations) was done using Athena 0.8.056 software by applying a four-point smoothing algorithm while comparing carefully with unsmoothed spectra. Data were then converted to k space (k is photoelectron wavenumber). Pb, Zn, Fe, and S-XAS processed spectra were analyzed in a two-step process using Labview software (ALS beamline 10.3.2, Lawrence-Berkeley National Laboratory, Berkeley, CA) for principal component analysis (PCA), and the IFEFFIT software package for linear combination fitting (LCF) (Ravel, and Newville, 2005). Standards used for Pb, Zn, Cd, Fe, and S-XAS LCF, along with SPOIL values, are provided in supplementary information (Table S3, S4). LCF fittings, with the lowest $\chi^2$ and R-factor close to 1, were considered the most likely set of components in our experimental spectra and were used for data interpretation.