Environmental geochemistry of St. Anthony Mine uranium ores

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ENVIROMENTAL GEOCHEMISTRY OF ST. ANTHONY MINE URANIUM ORES

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ABSTRACT—The St. Anthony Mine, in the Laguna mining subdistrict of the Grants uranium district, is slated for remediation. Its “Large Pit” has been accumulating uraniferous runoff and infiltrated groundwater since active mining ended in 1979. The site’s responsible party, United Nuclear Corporation, has successfully petitioned for alternative abatement standards of regulated parameters, including uranium, as a result of geochemical modeling (using uranophane) and environmental impact assessments, which predicted unavoidably high levels of dissolved uranium post-reclamation. This study examined the geochemistry and leachability of ore samples to evaluate the potential for uranium, vanadium and arsenic release into groundwater under industrial leaching and post-closure conditions. The uranium ore of St. Anthony Mine is characterized by uraniferous organic matter — where uranium is part of an amorphous, organic-carbon rich matrix, which permeates the sandstone, and a minor secondary, oxidized mineral component. This study did not identify the mineral uranophane. Batch leaching tests showed that significant uranium, vanadium and arsenic are released under oxidizing, alkaline conditions. Groundwater leaching experiments showed appreciable release of uranium and vanadium, but not arsenic. Higher levels of organic carbon in ore material slows leaching rates.

INTRODUCTION

Although active mining at the St. Anthony Mine (Fig. 1) ceased in 1979 (Wilton, 2017), it is still awaiting remediation. Uranium concentrations in groundwater are high enough that an alternative abatement standard has been set for the site: 12.4 mg/L, 400 times the drinking water limit (U.S. Environmental Protection Agency, 2001). As the location is naturally host to large ore bodies permeated by groundwater, it is technically infeasible to lower uranium concentrations to the regulatory limits. The reclamation plan for St. Anthony includes partially backfilling the mine’s “Large Pit” to mitigate issues of it acting as a hydraulic sink. Groundwater, discharging into the pit and pooling at the bottom, is highly contaminated with uranium due to evapo-concentration and weathering of exposed ores in pit walls (State of New Mexico, 2017). However, once the pit is filled and a pre-mining hydraulic gradient is reestablished, through-flowing groundwater may slowly carry dissolved uranium away from it. Despite this possibility, the host member where contamination is confined, the Jackpile Sandstone, is not currently and is unlikely to ever be used as a drinking water source (State of New Mexico, 2017).

The tabular uranium ore bodies of northwestern New Mexico, including those at the St. Anthony mine, formed at the focus of a 400,000 km² watershed encompassing the San Juan Basin. The paleo-hydrologic regime was such that saline, regional groundwater discharged into topographic depressions and mixed with fresher local waters laden with humic acids. Humic acids scavenged dissolved uranium and flocculated as humates, thus fixing uranium within a jellylike mass of organic matter that permeated the Jackpile Sandstone (Sanford, 1994). These deposits sustained several mines in the area, known
collectively as the Cebolleta project (Wilton, 2017), which yielded 3.8 million lbs of U₃O₈ by 1981. Of this, St. Anthony produced some 1.6 million lbs. Despite the large amounts of uranium extracted, extensive mineralogical characterization was not performed on ore material beyond the identification of tetravalent uranium minerals uraninite (UO₂) and coffinite (USiO₄), “organo-uranium complexes”, and “unidentified, oxidized uranium complexes” (Wilton, 2017).

The contamination issues at St. Anthony arise from the mobility of uranium in an oxidizing environment. Once weathered from ores, its hexavalent form ($U^{VI}$) has a strong affinity for any organic acid or oxyanion it may encounter in groundwater, and uranyl ($UO_2^{2+}$) -carbonate, -sulfate, and -phosphate complexes may carry uranium long distances through an aquifer before precipitating out of solution. Uranyl carbonates are the most common groundwater species, encountered in carbonate-enriched systems at higher pH levels. Uranium carbonate minerals (e.g., cejkaite, Na₄(UO₂)(CO₃)₃) form in response to evaporation or increased carbon dioxide concentration. Uranyl sulfate complexes are present in waters at lower pH levels and will form minerals such as zippeite ($K_4(UO_2)_x(SO_4)O_x(OH)*3H_2O$) if groundwater evaporates (Hazen et al., 2009). Phosphate will complex with uranium where there are insufficient carbonate species (Cumberland et al., 2016). Uranil phosphate minerals form under highly oxidizing conditions (e.g., autunite (UO₂)(PO₄)•11H₂O). Uranyl ions can also precipitate with vanadium to form relatively insoluble minerals such as tyuyamunite (Ca(UO₂)(V₂O₈)•9H₂O; Hazen et al., 2009). Cezakaite, zippeite, and uranium vanadates may be encountered as efflorescent growths on pit walls at St. Anthony (Caldwell, 2018).

The site’s responsible party, United Nuclear Corporation, used the uranyl silicate mineral uranophane (Ca(UO₂)₂(SiO₃OH)•5H₂O) and silica saturation in a geochemical model to predict post-closure uranium levels (State of New Mexico, 2017). The alternative standard of 12.4 mg/L is the upper limit of uranium concentration of their model, Uranophane is one of the most common oxidized uranium minerals (Hazen et al., 2009) and was likely a convenient proxy for the more than two hundred $U^{VI}$ minerals that may form under oxidizing, circumneutral conditions (Bowell et al., 2011).

Uranium poses great risk to human health (Hund et al., 2015), but its dissolution may also be associated with that of other toxic metals such as arsenic (Bowell et al., 2011), as well as vanadium. Arsenic may be present in Jackpile Sandstone ores within pyrite (Moench and Schlee, 1967), or as a component of organic matter (Liu et al., 2011). The availability of potentially harmful aqueous species and the extent to which groundwater may be impacted is controlled by the deposit mineralogy and water chemistry. This study characterized ore samples from the St. Anthony Mine to determine the ore’s potential to release heavy metals into the environment when exposed to an industry standard alkaline lixiviant, as might be used in in-situ recovery efforts (Vogt et al., 1982), and native groundwater. This work is part of a broader study examining the leachability of ores found in the Grants uranium district.

**METHODS**

Two samples (SA2, SA4) were taken from an exposed ore face in the St. Anthony Mine (Fig. 2). Polished thin sections were made from epoxy-impregnated billets and were examined with an electron probe microanalyzer (EPMA) at the University of New Mexico’s Institute of Meteoritics. Bulk geochemical analyses for metals, carbon and sulfur forms were performed by ALS Ltd. Geochemistry Lab (Vancouver, Canada) on ground subsamples. Batch-leaching experiments on disaggregated ores (500–74 µm size fractions) were carried out to determine potential metal loading under active mining and post-closure conditions, represented by a calculated pseudo-first-order rate constant (k), defined as follows:

$$k = 1/t (\ln C_o - \ln C),$$

where t: time (48 hours), $C_o$: initial concentration of the metal in the ore; $C$: post-leaching metal concentration.

Briefly, disaggregated ore replicates were exposed to an alkaline lixiviant solution (1.98g/L H₂O₂ + 2g/L NaHCO₃, pH 8.2) and unaugmented groundwater (SA4 ore only) sourced from a Westwater Canyon Formation aquifer (pH 7.4). Leach-
ate was analyzed via inductively coupled plasma mass spectrometry (ICP-MS) for metals. Uncertainty values for analytical methods are listed in Appendix 1.

RESULTS
Ore Characterization

St. Anthony ores are arkosic, low-porosity (<4%) sandstones that have been enriched by an amorphous and nonstoichiometric uranium phase (Fig. 3A) associated with organic carbon. The samples are relatively high in bulk arsenic, uranium and vanadium (Table 1). Though the samples were collected from the same ore pocket, sample SA4 has higher levels of carbon and sulfur forms, arsenic, phosphorus and uranium. Sample SA2 contains more vanadium.

Figures 3 and 4 show examples of the major uranium phases encountered in both SA2 and SA4. Through high-resolution EPMA mapping, it is evident that organic matter is multiphase (Fig. 3). The organic matter is characterized by successions of barren and uraniferous types fixed in the sandstone. Figure 3 shows the association of barren and uraniferous organic matter. Figure 4 shows a region where the sandstone matrix is barren organic matter. EPMA point analyses (Table 2) show that the uraniferous organic matter is non-mineral (containing 10.80% carbon and 15.53% uranium). A secondary uranium-phosphorus phase also occurs, filling fractures (Fig. 3) and pores (Fig. 4). It is much higher in uranium (59.62%).

Leaching Behavior

Table 3 lists the reaction rate constants and metals leached for each experimental replicate. The leaching kinetics of the St. Anthony ores imply metal loading under both alkaline lixiviant and groundwater leaching conditions, although arsenic does not enter solution in appreciable amounts when exposed to groundwater. Metal solubility (inferred from k values) is, expectedly, an order of magnitude lower under groundwater leaching conditions. After 48 hours, approximately 11% of SA4’s total uranium is leached when exposed to an oxidizing alkaline lixiviant, whereas, only 3% is released into groundwater. Sample SA4 contains approximately two times more uranium than SA2 (Table 1), yet it released, on average, about 15% less uranium than SA2 into the alkaline solution. Conversely, SA4 released 30% more vanadium than SA2 under alkaline leaching conditions, although SA2 contains 25% more vanadium. SA4, which has 2.4 times more arsenic than SA2, released 2.8 times more arsenic into the alkaline solution. In terms of reaction rates (Table 3), SA2 leached uranium 1.6 times faster, vanadium 1.7 times slower, and arsenic at similar rates compared to SA4.

DISCUSSION

The processes that emplaced the tabular ore bodies at St. Anthony fixed uranium with organic matter, reflected by the predominant phase identified by this study: amorphous, nonstoichiometric, and intimately associated with organic carbon (Fig. 3). The organic matter is multi-phase: one characterized by higher potassium and uranium, the other devoid of the two elements. The latter “barren” organic matter is seen as large blebs in the upper half of Figure 3 images and as the matrix of Figure 4.
TABLE 1. Bulk geochemistry of St. Anthony ores.

<table>
<thead>
<tr>
<th></th>
<th>SA2</th>
<th>SA4</th>
</tr>
</thead>
<tbody>
<tr>
<td>C (%)</td>
<td>2.89</td>
<td>6.95</td>
</tr>
<tr>
<td>Organic C (%)</td>
<td>2.14</td>
<td>3.5</td>
</tr>
<tr>
<td>Carbonate C (%)</td>
<td>0.83</td>
<td>1.96</td>
</tr>
<tr>
<td>S (%)</td>
<td>0.24</td>
<td>0.33</td>
</tr>
<tr>
<td>Sulfide S (%)</td>
<td>0.12</td>
<td>0.15</td>
</tr>
<tr>
<td>Sulfate S (%)</td>
<td>0.12</td>
<td>0.18</td>
</tr>
<tr>
<td>As (ppm)</td>
<td>30.5</td>
<td>74</td>
</tr>
<tr>
<td>P (ppm)</td>
<td>300</td>
<td>660</td>
</tr>
<tr>
<td>U (%)</td>
<td>0.52</td>
<td>1.02</td>
</tr>
<tr>
<td>V (ppm)</td>
<td>2610</td>
<td>1960</td>
</tr>
</tbody>
</table>

A minor uranium-phosphorus phase component was also identified in the samples, as seen in elevated uranium and phosphorus areas in backscatter images (Figs. 3, 4). It fills pore space (Fig. 4) and cracks in feldspar grains (Fig. 3). Based on its texture and distribution, it is deduced to be a secondary mineral, an alteration product of the “primary” carbonaceous ore. This phase was identified as the mineral meta-autunite, Ca(UO2)(PO4)2•2-6(H2O), which contains 54.21–59.06% uranium. EPMA point analysis in SA4 (Table 2, point 2) shows a uranium weight percent in this range. Though point analyses for phosphorus were not performed, it is strongly congruent with uranium in the element map (Fig. 3B). Meta-autunite contains 7.05–7.36% phosphorus, which would bring the total weight percent shown for SA4 in Table 2 (90.97%) to close to 100% (~98%).

Previous work characterizing the hexavalent uranium minerals on the pit wall faces at St. Anthony (Caldwell, 2018) identified uranyl carbonates, sulfates, phosphates and vanadates via X-ray powder diffraction analysis. Uranophane, though used in the site’s post-closure model, was not a component of the examined St. Anthony ores, in this or Caldwell’s (2018) study. It appears that hexavalent uranium minerals are, volumetrically, a minor component of the site’s uraniferous material. Therefore, the leaching kinetics and attendant environmental impact of St. Anthony’s wastes and ores will be controlled by the major reservoir of uranium: uraniferous organic matter. This is a phase that does not have well-constrained leachability or thermodynamic data. Furthermore, uraniferous organic matter may have undergone significant reworking and radiation damage since it

TABLE 2. EPMA point analyses of elemental weight percent for labelled points in Figures 3 and 4. LOD: Limit of detection.

<table>
<thead>
<tr>
<th>Point</th>
<th>Sample</th>
<th>C</th>
<th>Si</th>
<th>S</th>
<th>Pb</th>
<th>U</th>
<th>K</th>
<th>Ca</th>
<th>As</th>
<th>Al</th>
<th>Ti</th>
<th>V</th>
<th>Fe</th>
<th>O</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SA2</td>
<td>10.8</td>
<td>3.68</td>
<td>0.44</td>
<td>0.09</td>
<td>15.53</td>
<td>0.64</td>
<td>0.33</td>
<td>&lt;LOD</td>
<td>23.83</td>
<td>0.02</td>
<td>0.1</td>
<td>0.98</td>
<td>30.56</td>
<td>87</td>
</tr>
<tr>
<td>2</td>
<td>SA4</td>
<td>2.33</td>
<td>0.04</td>
<td>0.01</td>
<td>&lt;LOD</td>
<td>59.62</td>
<td>0.21</td>
<td>3.55</td>
<td>0.07</td>
<td>&lt;LOD</td>
<td>0.03</td>
<td>&lt;LOD</td>
<td>&lt;LOD</td>
<td>25.1</td>
<td>90.97</td>
</tr>
</tbody>
</table>

FIGURE 4. Backscattered electron image (A) and corresponding element map (B) of a zone in sample SA4, hosting crystals of a uranium-phosphorus (U-P) phase, likely meta-autunite. Note this phase is surrounded by barren organic matter (OM). Warmer colors in B indicate a higher associated intensity of an element.
was precipitated (Hansley and Spirakis, 1992).

Batch tests, which provide an excess of leachate, are used to approximate the ultimate recovery of a particular element (Vogt et al., 1982). The leaching data reported here (Table 3) show that milled ores, characterized by uraniferous organic matter, readily release uranium, vanadium and arsenic under alkaline leaching conditions, and also release uranium and vanadium when exposed to ambient groundwater. However, in material that is in-place or left piled on the surface as whole rock, barren organic matter may armor uraniferous clots from dissolution, whether as a physical barrier to flow or by maintaining locally reducing conditions. Dissolved uranium could be re-mineralized by organic material into a more refractory form, thus preventing its future dissolution into oxidized waters. For example, mobile uranium may be reduced and fixed as coffinite by organic material (Deditius et al., 2008) or, provided there is enough vanadium and calcium present (e.g., a vanadiferous lignite and calcic groundwaters), as tyuyamunite (Stewart et al., 1999). The former process has been found by Deditius et al. (2008) to have occurred continuously over the last 30 million years in deposits associated with the Mount Taylor Mine, which is on the northwest side of Mount Taylor.

The biggest difference between SA2 and SA4 lies in their carbon, uranium and phosphorus contents—SA4 contains two times more of each component than SA2. On average, sample SA4 released less of its total uranium, and at a slower rate, than SA2 did under alkaline leaching conditions. It is feasible that the higher organic content of SA4 inhibited uranium dissolution, whether by maintaining reducing micro-environments, or by consuming the oxidant (H₂O₂). It could be hypothesized that under the highly oxidizing alkaline leach conditions, uranium-phosphate minerals/mineraloids may have precipitated out of solution after uranium and phosphorus were dissolved from SA4. However, given that the leaching solution was extremely high in carbonate (2g/L NaHCO₃), carbonate would have out-competed phosphate to complex with uranium.

Sample SA4 released more vanadium into solution than SA2 did, despite having a lower whole-rock percentage of this element. Vanadium in these systems may be associated with organic matter, vanadium-micas (roscoelite), and vanadiferous clays (Spirakis, 1996). It is therefore possible that more vanadium was in a soluble form (e.g., sorbed to clays) in SA4 than in SA2. Arsenic release from the samples was proportional to their bulk concentrations, implying a similar mineral reservoir within these samples.

The Jackpile Sandstone has been so thoroughly impregnated by organic matter, uraniferous or otherwise, that the original porosity has been much reduced, meaning significant fluid flow through the remaining ore zones is limited. Upon burial, there will no longer be evaporation-induced concentration of uranium in an open pit or aerial exposure of ores at the pit walls. Uranium dissolution may be slowed.

**CONCLUSIONS**

The major reservoir of uranium within St. Anthony ores is associated with organic matter. Post-closure interactions between ore material and oxidized groundwater may release uranium and vanadium, but not arsenic. A highly oxidizing alkaline leaching agent could be used to extract uranium, but the leachate could also contain significant amounts of vanadium and arsenic. Future work should take the complex organic hosts of uranium into consideration to better evaluate if uranophane is an appropriate modeling parameter for St. Anthony Mine. Future groundwater quality trends, once the Large Pit has been backfilled, will be of great scientific interest, not least to see if they match the modeled predictions (which informed the alternative abatement standards). St. Anthony’s long-awaited reclamation is one step of many needed to address the legacy of uranium mining in the state of New Mexico.

**ACKNOWLEDGMENTS**

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**REFERENCES**


**TABLE 3. Reaction rates and proportions of metals leached from ore samples under alkaline lixiviant and groundwater leaching experimental conditions. -r: Experimental replicate, k: reaction rate constant.**

<table>
<thead>
<tr>
<th></th>
<th>k (hr⁻¹) × 10⁻³</th>
<th>% Leached</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alkaline Leaching</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA2</td>
<td>2.6</td>
<td>0.4</td>
</tr>
<tr>
<td>SA2-r</td>
<td>2.4</td>
<td>0.3</td>
</tr>
<tr>
<td>SA4</td>
<td>1.5</td>
<td>0.6</td>
</tr>
<tr>
<td>SA4-r</td>
<td>1.6</td>
<td>0.6</td>
</tr>
<tr>
<td><strong>Groundwater Leaching</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SA4</td>
<td>0.7</td>
<td>0.005</td>
</tr>
<tr>
<td>SA4-r</td>
<td>0.6</td>
<td>0.004</td>
</tr>
</tbody>
</table>


Appendices can be found at http://nmgs.nmt.edu/repository/index.cfml?rid=2020003