

Pre- and Post-Remediation Characterization of Acid-Generating Fluvial Tailings Material⁶

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Abstract

The upper Arkansas River south of Leadville, Colorado, USA, contains deposits of fluvial tailings from historical mining operations in the Leadville area. These deposits are potential non-point sources of acid and metal contamination to surface- and groundwater systems. We are investigating a site that recently underwent *insitu* remediation treatment with lime, fertilizer, and compost. Pre- and post-remediation fluvial tailings material was collected from a variety of depths to examine changes in mineralogy, acid generation, and extractable nutrients. Results indicate sufficient nutrient availability in the post-remediation near-surface material, but pyrite and acid generation persist below the depth of lime and fertilizer addition. Mineralogical characterization performed using semi-quantitative X-ray diffraction and quantitative SEM-based micro-mineralogy (Mineral Liberation Analysis, MLA) reveal formation of gypsum, jarosite, and complex coatings surrounding mineral grains in post-remediation samples.

Key Words: acidic drainage, ARD, mineralogy, QXRD, mineral liberation analysis, MLA

Introduction

The Leadville mining district, located at an altitude of about 3000 m in the Colorado Rocky Mountains, USA, has been mined for silver, gold, lead, zinc, and copper (Tweto 1968; Emmons *et al.* 1927). Mine-waste material and tailings rich in pyrite and other sulfide minerals were dispersed around the town of Leadville and surrounding areas (see maps in Swayze *et al.* 2000), and much of the Leadville mining district was designated as part of the California Gulch Superfund Site by the U.S. Environmental Protection Agency (USEPA) (USEPA 2011). Tailings and mine-waste material from the historical mining activities have been deposited along the banks of an 18-km reach of the Arkansas River south of the town of Leadville. These fluvial tailings deposits generally are overbank and pointbar deposits consisting of fine-grained mixtures of tailings and other sediment. Material from the deposits is compositionally heterogeneous. Interaction between the deposits, water, and oxygen has resulted in pyrite weathering and acidic conditions in these deposits, and riparian habitat and water-quality conditions have been degraded. Contaminants of concern include copper, lead, silver, zinc, arsenic, antimony, barium, beryllium, cadmium, chromium, nickel, manganese, mercury, and thallium, with lead and arsenic being the main elements of concern for human health (USEPA 2005).

The upper Arkansas River has been the site of numerous research studies on impacts from historical mining practices. The U.S. Geological Survey (USGS) had been monitoring surface-water and shallow groundwater quality at several sites along the upper Arkansas River. Results from this monitoring effort indicate that groundwater quality beneath the fluvial tailings deposits has been degraded (decreased pH and elevated metal concentrations), and that water quality in the Arkansas River exhibits minimal impact from the deposits (Walton-Day *et al.* 2000).

In 1998 the USEPA initiated a soil amendment and revegetation demonstration project along the floodplain of the upper Arkansas River that included mixing the fluvial tailings material with biosolids, lime, fertilizer, and compost to reduce soil acidity and provide plant nutrients. The intent of the soil amendment endeavor was to treat the full depth of the fluvial tailings material to the extent practical. However, isolated areas contain untreated material due to heterogeneity of the depth profile. These efforts have resulted in revegetation of denuded areas, soil neutralization, reduced soil erosion, and re-establishment of riparian communities (Colorado NPS 2005; USEPA 2008).

Site Description

The study site (Site OA) is a fluvial tailings deposit located adjacent to the Arkansas River, Lake County, Colorado, USA (Figure 1). The site is approx 0.004 km². The deposit consists of fine-grained to sandy tailings and fluvial sediments deposited over sand and cobble alluvium. Pre-remediation, the deposit was largely devoid of vegetation, with sparse dead and live willows present along the borders of the deposit. Figure 2 shows the contrast between pre- and post-remediation profiles in trenches at Site OA.

Remediation at the site consisted of (1) lime amendment (sugar beet processing residual) applied at a rate of 182 dry tons calcium carbonate equivalence per 1000 tons soil, and (2) fertilizer (0-45-0; nitrogen-phosphorus-potassium or “NPK”) applied at a rate of 153 lbs per 1000 tons soil using a deep till rotary mixer (Jan Christner, URS Operating Services, Inc., written comm 11/4/11). Remediation depth was approx 40 cm at Site OA (see Figure 2). Soil amendments were added to the full depth of the tailings material when possible; however heterogeneity in the depth profile resulted in incomplete treatment in isolated areas. Cow manure compost was applied to the top 30 cm of the deposit (target 1.5% organic carbon) (Jan Christner, URS Operating Services, Inc., written comm 11/4/11).

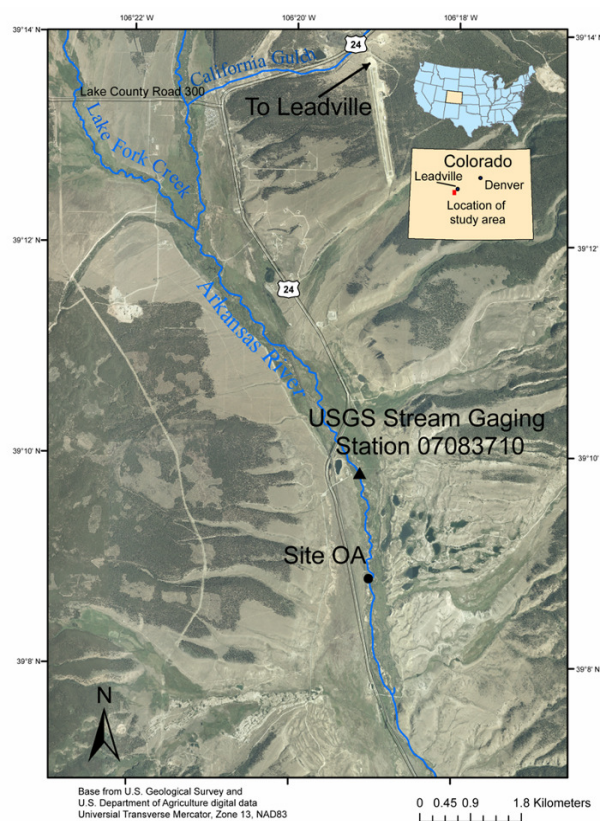


Figure 1. Location of Site OA and USGS stream gaging station 07083710, Lake County, Colorado. USGS stream gaging station 07081200 is on the Arkansas River approx 1 km upstream from the northern boundary of the map.

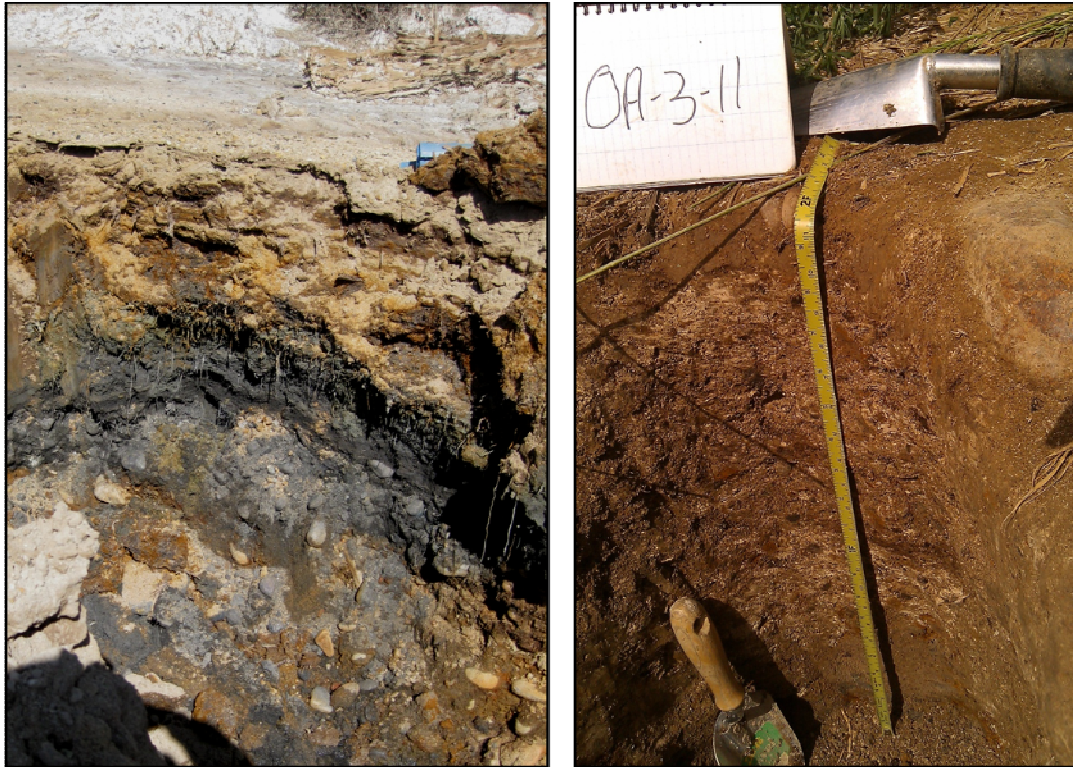


Figure 2. Trenches at Site OA. Left photograph shows pre-remediation conditions in April 2009. Scale from ground surface to bottom of trench/photograph is approx 1 m. Right photograph shows post-remediation conditions in August 2011, approx 26 months after remediation. Scale is in ft, which corresponds to approx 60 cm from top of trench to bottom. In the post-remediation photograph on the right, note the tailings material near the bottom of the trench; this indicates the depth of mixing during remediation. Note the homogeneous nature of the deposit from the surface to approx 40 cm depth on the right versus the heterogeneous nature in the pre-remediation photograph on the left. Also note surficial vegetation on the right versus no vegetation on the left.

Pre-remediation samples of the deposit were collected at different depths from a trench dug by a backhoe at the site in April 2009 (see Figure 2, left). At that time, cobbles were encountered at the base of the fluvial tailings deposit at approx 60 cm depth, and the water table was encountered just below one-meter depth. Remediation and amendment addition was completed in June 2009. The first set of post-remediation samples was collected in October 2009 using a 2 ¾-in bucket auger. At that time cobbles were encountered at 68 cm depth, and possible pyrite was visually identified between about 45 and 56 cm depth. The second set of post-remediation samples was collected in August 2011 from a hand-dug trench (see Figure 2, right). Due to site disturbance, samples collected from the three different sampling dates are not exactly co-located, but are within approximately 10 m of each other (based on GPS measurements).

Characterization Methods

Extractable nutrients were determined by the Soil, Water, and Plant Testing Laboratory at Colorado State University using methods described in Sparks (1996). Extractable nitrate-nitrogen ($\text{NO}_3\text{-N}$), phosphorus, and potassium were determined by extraction with 1 *M* ammonium bicarbonate and 0.005 *M* diethylenetriaminepentaacetic acid (AB-DTPA). From the AB-DTPA solution, $\text{NO}_3\text{-N}$ was determined by flow injection analysis (OI Analytical FS3000 flow injection analyzer) using cadmium reduction.

Phosphorus was determined using the molybdate-blue method by colorimetry, and potassium was analyzed by inductively coupled plasma-atomic emission spectrometry (ICP-AES) using a TJA Solutions IRIS Advantage Radial View ICP-AES.

Deionized water extractions were performed by carefully mixing and subsampling the sample, weighing out a 10.0 g subsample into a centrifuge tube, and adding 40.0 g deionized water. The subsamples were put on a shaker overnight (18 hrs), and then centrifuged at 3,000 rpm for 30 minutes at 25°C. The pH value was measured on an aliquot of the centrifuged extract.

Semi-quantitative X-ray diffraction analysis (QXRD) was performed at the USGS Analytical Laboratories in Denver, Colorado. A portion of each sample was finely ground, and the sample was combined with a 10% internal standard of titanium (IV) oxide powder and isopropyl alcohol, and was micronized for 3 min using a McCrone micronizing canister with corundum grinding elements. Sample mineralogy was determined using a Shimadzu XRD-6000 X-ray diffractometer equipped with a standard Cu-radiation tube and run with continuous 2 Theta/Theta scans. Raw XRD data acquired from the Shimadzu instrument were analyzed using Jade Search/Match software, Version 7.5, and mineral identities were selected from the ICDD, PDF-2, Release 2007 Minerals Database. Siroquant Analytical Software, Version 2.5, was used to calculate the individual wt % of sample constituents. Amorphous content was calculated as unidentified trace crystalline and non-crystalline remainder.

Mineral Liberation Analysis (MLA) was performed by JK Tech Pty Ltd. MLA is an automated scanning electron microscopy (SEM) based technique for the rapid acquisition and quantification of mineralogical information. The method uses electron-beam excitation combined with dual energy-dispersive X-ray spectroscopy (EDS) detectors that measure spectra at a count rate of approx 30,000 counts per second (cps), and quantitative mineralogy software. The analytical settings for this study were 20kV @ 38µA with approx 3000 counts/80-100ms. The range of counts per phase was 2500 to 3500.

Results and Discussion

Pre- and post-remediation extractable nutrient (nitrate-nitrogen, phosphorus, and potassium) concentrations in the fluvial tailings material are given in Figure 3. The extraction used is an availability index and, as such, does not measure the total amount in the samples. Pre-remediation concentrations are low and post-remediation (October 2009) concentrations reflect the fertilizer and compost amendments added during the remediation process. Post-remediation fluvial tailings samples have good availability of extractable nutrients suitable for plant growth. According to Self (2010), available phosphorus greater than 15 ppm and available potassium greater than 180 ppm indicates very high availability of extractable nutrients.

Figure 4 shows pH values of deionized-water leachates of the fluvial tailings material. Pre-remediation samples generated low-pH leachate values (pH 2.5-3) near the surface of the deposit and leachates became circumneutral at approx 40 cm below the surface. Post-remediation samples collected shortly after remediation (October 2009) yielded leachate pH values near 8, and circumneutral pH values at approx 70 cm below the surface. Post-remediation samples collected about 26 months after remediation (August 2011) yielded leachate pH values near 8 down to about 40 cm, and acidic pH values (pH 3-4) below about 40 cm (the approximate treatment depth). This depth of acid generation corresponds to the depth of tailings material noted beneath the remediated material in the post-remediation photograph in Figure 2. These results suggest that the August 2011 post-remediation samples intersected an area where the fluvial tailings material was not treated to full depth.

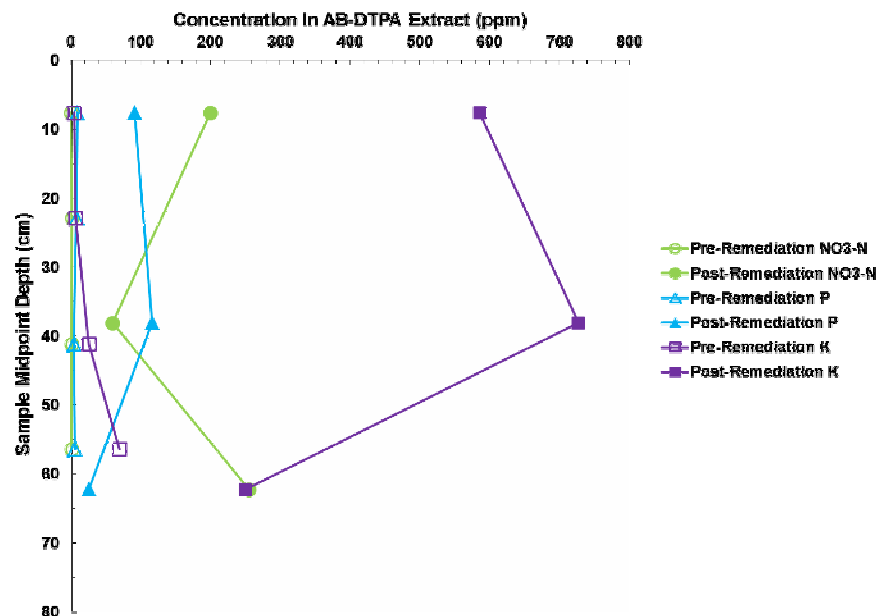


Figure 3. Extractable nutrients in fluvial tailings samples collected in April 2009 (pre-remediation) and October 2009 (post-remediation) at Site OA along the upper Arkansas River, Colorado. The extractant used was ammonium bicarbonate-diethylenetriaminepentaacetic acid (AB-DTPA).

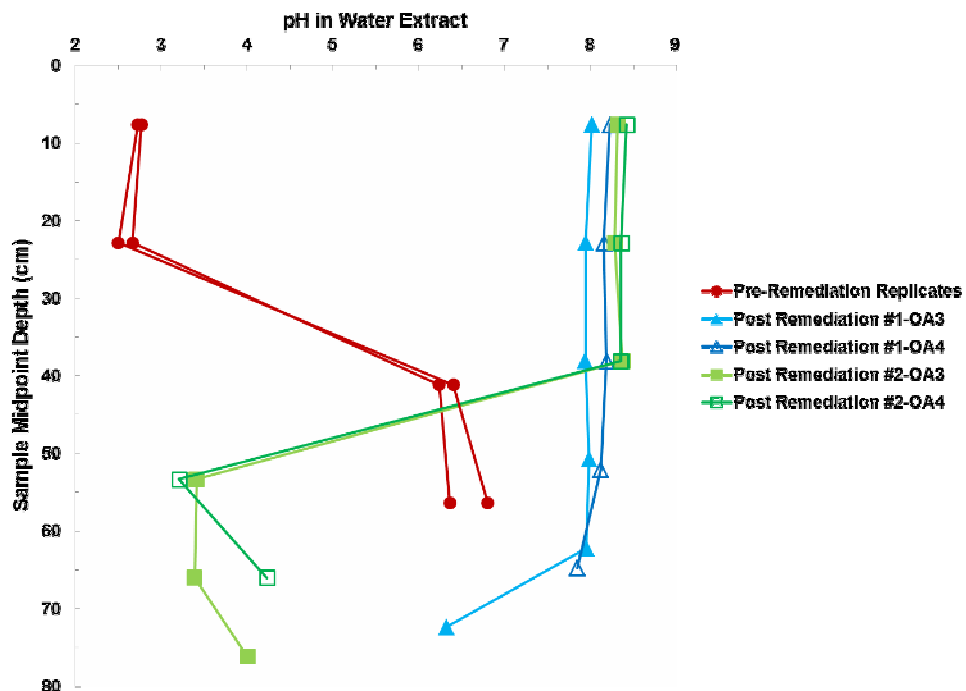


Figure 4. Water-extraction pH values for fluvial tailings samples collected in April 2009 (pre-remediation), October 2009 (post-remediation #1), and August 2011 (post-remediation #2) at Site OA along the upper Arkansas River, Colorado. OA3 and OA4 are adjacent sampling locations at Site OA. Samples from depths greater than about 70 cm are within the alluvium beneath the fluvial tailings deposit.

Semi-quantitative mineralogy by X-ray diffraction (QXRD) reveals the presence of pyrite at depths below the treatment depth of about 40 cm in the August 2011 post-remediation profile (Figure 5). These data also show a lack of calcite and presence of jarosite at about the same depth (Figure 5). This depth corresponds to the depth of acid generation in extracts from post-remediation samples collected in August 2011 (Figure 4). There is a significant amount (about 35%) of X-ray amorphous material in the upper 40 cm of the deposit, which decreases to about 20% in the lower portion of the deposit (Figure 5). This amorphous material likely is iron oxyhydroxysulfates and other fine-grained weathering products. Gypsum steadily increases with depth in the upper 40 cm of the deposit, and then steadily decreases with depth below 40 cm (Figure 5). Samples collected from depths greater than about 70 cm are mixtures of the fluvial tailings deposit with alluvial material beneath the fluvial tailings deposit, and the profiles in Figure 5 show a sharp decrease in pyrite and jarosite abundance below this depth.

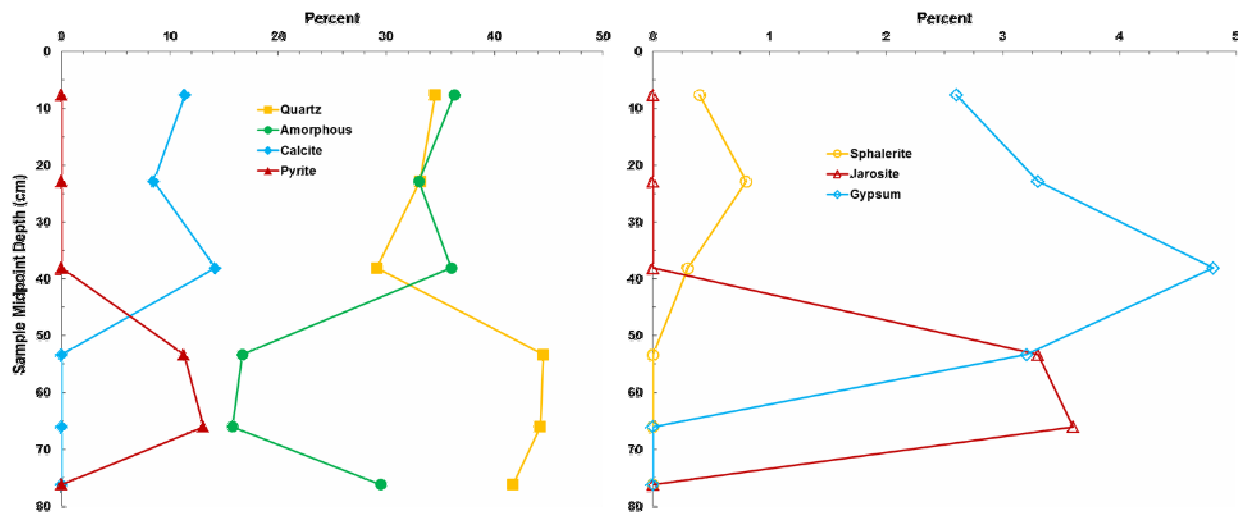


Figure 5. Semi-quantitative X-ray diffraction (QXRD) mineralogy results for selected constituents in post-remediation fluvial tailings samples collected in August 2011 (approx 26 months after remediation) at Site OA along the upper Arkansas River, Colorado. The deposit overlies sand and cobble alluvium, and the deepest sample reflects mixing of the fluvial tailings deposit with the alluvium.

Mineral Liberation Analysis (MLA) was performed on three pre-remediation and three post-remediation (August 2011) fluvial tailings samples from various depths. Figure 6 illustrates the microscopic-scale complexity of the texture and mineralogy of the fluvial tailings material. General findings of the MLA indicate that mineralogical differences between pre- and post-remediation samples largely is reflected in changes in carbonate and sulfate abundances, and that post-remediation samples contain more gypsum (increase of 50x) and somewhat more goethite. This is in agreement with the QXRD data previously discussed. Various types of grain coatings were identified by MLA. These coatings contain combinations of hydrous iron oxides and iron oxyhydroxysulfates mixed with various trace metals and clay minerals. MLA also identified a carbonate coating and a zinc-cadmium-sulfate coating. MLA identified organic phases (cellulose remnants of plants and roots) that appear to provide a residence phase for various metals, especially zinc, cadmium, and lead. The coatings and organic/metal phases identified by MLA likely are the main constituents in the “amorphous” phase identified by QXRD.

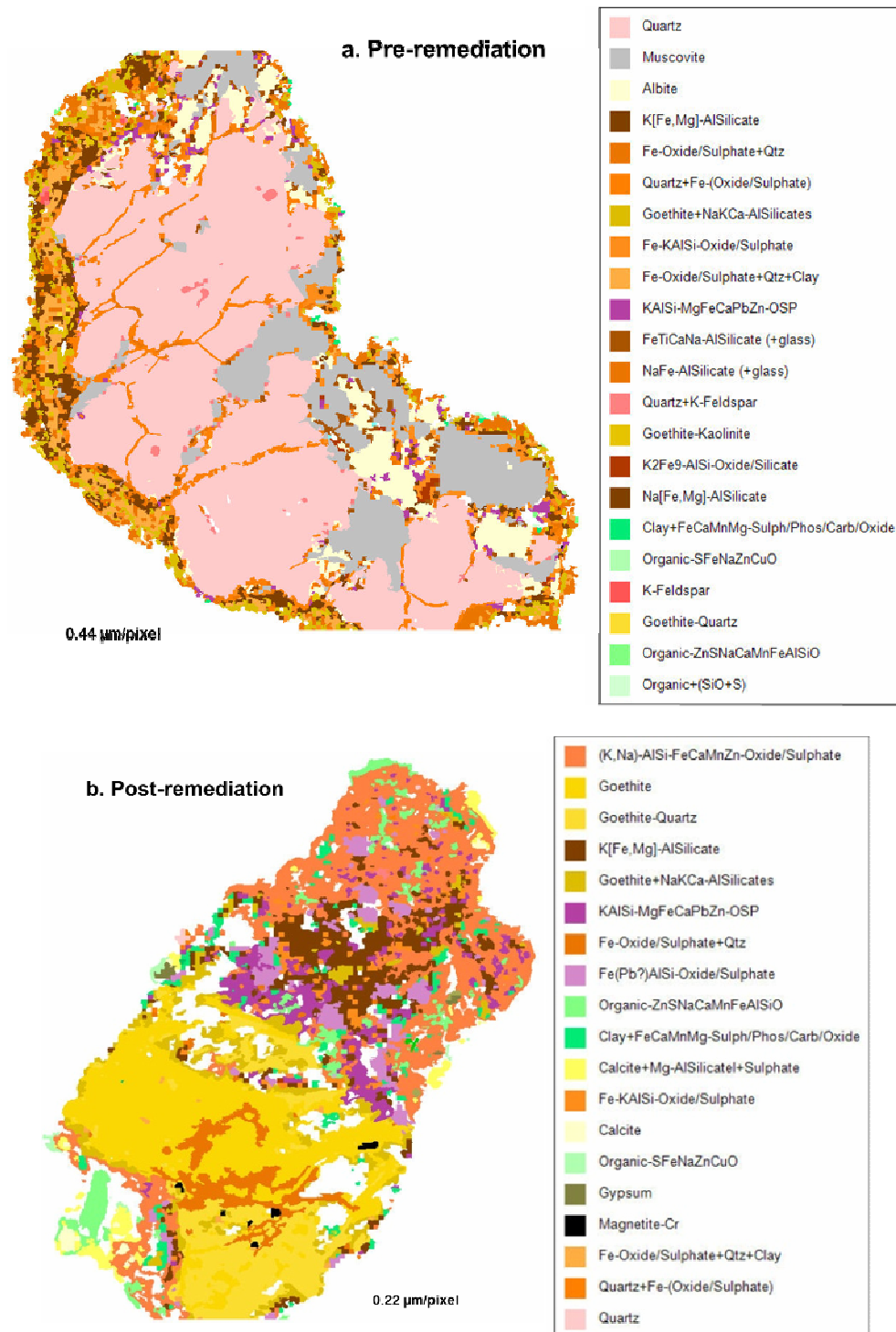
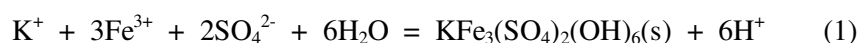


Figure 6. Mineral Liberation Analysis (MLA) false-colored image and mineralogical results for (a) a typical near-surface particle in pre-remediation fluvial tailings material collected in April 2009, and (b) a typical near-surface particle in post-remediation fluvial tailings material collected in August 2011, both at Site OA along the upper Arkansas River, Colorado. The list of minerals is in order of modal mineral abundance, and the elements in mixed-element phases are listed in order of abundance.

The August 2011 water-extract pH data, QXRD data, and MLA data all are consistent with the scenario of acid generation due to pyrite oxidation at depths below the treatment depth of about 40 cm in the fluvial tailings deposit at Site OA. The water extract data show that the extract pH changes from pH 8 to pH 3 between 40 and 50 cm depth. This trend deviates from the October 2009 post-remediation samples, which did not exhibit acidic extract pH values at depth. It appears that a zone of active pyrite oxidation exists at the base of the fluvial tailings deposit below a depth of about 40 cm for post-remediation samples collected in August 2011. Both the QXRD and the MLA data document the presence of pyrite at depths below 40 cm to the base of the deposit (about 70 cm), and the QXRD data show a lack of calcite at depths below 40 cm. The QXRD data also show jarosite at depths below 40 cm. The presence of jarosite is indicative of acid-sulfate weathering with pH values ranging from 1 to 3. Precipitation of potassium jarosite can be expressed as:



Jarosite formation requires a source of K^+ , which could be provided by the weathering of mica and by the amendments, and a source of Fe^{3+} and low-pH conditions, both of which could be provided by pyrite weathering. Formation of potassium jarosite in the August 2011 post-remediation sample at depths below about 40 cm corresponds with low-pH conditions (Figure 4) and the decrease in extractable potassium shown in Figure 3.

The top 40 cm of Site OA underwent remediation using a deep till rotary mixer to combine the pyrite-rich fluvial tailings material with lime, fertilizer, and compost. This remediation led to the co-existence and weathering of pyrite and lime in the top 40 cm of the deposit. These weathering reactions resulted in the formation of gypsum, which can be expressed as:



The QXRD data show the presence of gypsum in the top 40 cm, and steadily decreasing gypsum abundance below 40 cm. Gypsum precipitation is not directly dependent on pH conditions, but does require a source of Ca^{2+} and SO_4^{2-} . The steady decrease in gypsum below 40 cm reflects the decreasing source of calcium from the lime amendment.

The existence of an active zone of pyrite oxidation below about 40 cm in post-remediation samples from August 2011 likely indicates incomplete treatment to the full depth of the fluvial tailings deposit at this location. This occurrence of incomplete treatment to the full depth of the deposit is not indicative of the situation throughout the treatment area. For example, a nearby site had pre-remediation water-extract pH values ranging between 3 and 6 from the surface to 80 cm depth and post-remediation values ranging between 6 and 8 for samples collected both in October 2009 and August 2011. Because pyrite oxidation requires a source of oxygen and water, a possible mechanism to provide oxygen and water involves the fluctuating water table beneath the fluvial tailings deposit (Walton-Day *et al.* 2000). Previous shallow groundwater-level measurements below fluvial tailings deposits at two sites located near the study area indicate that the seasonal maximum of the water level relates to streamflow and is greater in years of greater runoff as recorded at the Arkansas River near Leadville (USGS stream-gaging station 07081200) (USGS, unpublished data). Figure 7 gives the streamflow for water years 2008 to 2011 at two gaging stations near Site OA (see Figure 1 for locations). The streamflow data show that the 2011 runoff was significantly above average. It is likely that the water table beneath Site OA rose high enough to provide the necessary oxygen and water to fuel active pyrite oxidation in a zone near the base of the deposit. In addition, water can be retained by capillary forces in fine-grained material and in hydrated mineral phases.

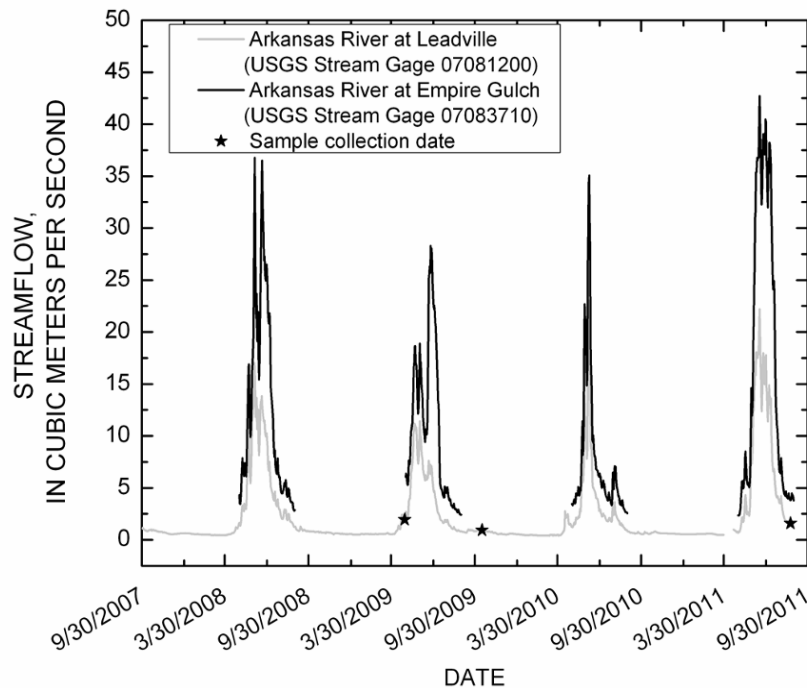


Figure 7. Streamflow in m^3/s for the Arkansas River at Leadville (USGS gaging station 07081200) and the Arkansas River at Empire Gulch (USGS gaging station 07083710; see Figure 1 for location) for water years 2008 to 2011. Data for October 2010 through August 2011 are provisional. Data retrieved from http://waterdata.usgs.gov/nwis/dv?referred_module=sw&site_no=07083710 http://waterdata.usgs.gov/nwis/dv?referred_module=sw&site_no=07081200 (viewed 7 November 2011).

Recharge from water entering the unsaturated zone at the surface of the deposit also would be expected to be greater during years of greater runoff. An outcome of recharge from the surface would be to dissolve and transport constituents from the amendments deeper into the deposit. Surface recharge also would provide oxygen and water for pyrite oxidation. As previously discussed, gypsum is a likely secondary product from pyrite oxidation in the presence of a calcium source. While the calcium carbonate soil amendment is relatively insoluble, gypsum is a soluble mineral and would be expected to be absent (dissolved) where significant recharge is occurring. Gypsum exhibits a maximum abundance at about 40 cm depth (Figure 5), the bottom of the treatment profile, indicating that it is likely that surface-recharge water did not infiltrate below a depth of about 40 cm.

In summary, efforts to remediate a pyrite-rich fluvial tailings deposit at Site OA adjacent to the Arkansas River has resulted in revegetation of denuded areas, soil neutralization, reduced soil erosion, and re-establishment of riparian communities. However, post-remediation samples collected in August 2011 indicate the presence of an acidic zone of active pyrite oxidation extending from about 40 cm depth to the base of the fluvial tailings in an area where the tailings material was not treated to the full depth. This zone of active pyrite oxidation may be enhanced by fluctuating groundwater levels beneath the deposit. Continued monitoring at this site would determine if the zone of active pyrite oxidation persists and migrates over time, and identifying changes in pH and mineralogy (e.g., presence of jarosite) could indicate if the acidic zone beneath the treated tailings is expanding or contracting.

Acknowledgements

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Acronyms

MLA	Mineral liberation analysis
NPK	Nitrogen-phosphorus-potassium
NPS	Nonpoint source
QXRD	Semi-quantitative X-ray diffraction
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey