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Limestone Gravel Cover System to Immobilize Sr-90 in the Vadose Zone: Materials and Lysimeter Deployment

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Executive Summary

This project investigates the relative migration of Sr-90 between control and limestone-applied cores to demonstrate that carbonate ions from surface applied limestone gravel can both reach and immobilize vadose zone contaminants. Sr-90 is a prime candidate for in situ immobilization with the application of the limestone cover. $SrCO_3$ has a low solubility and retention in the vadose zone leads to drastically lower groundwater concentrations as the isotope decays. To study the effect of carbonate from limestone gravel on Sr-90 immobilization, the Radionuclide Field Lysimeters (RadFLEx) at SRNL were utilized. This mid-project update documents the selection of cover materials and deployment of soil cores to the RadFLEx. Cores were prepared with soils representing the Savannah River Site, Hanford, and Sellafield. Each was spiked with strontium-90 and topped with a selected limestone amendment or a washed granite gravel. This report documents the screening of the amendments and the preparation and deployment of the cores.

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List of Abbreviations

RadFLEx	Radionuclide Field Lysimeter Experiment
SRNL	Savannah River National Laboratory
SRS	Savannah River Site
XRD	X-ray Diffraction

1.0 Introduction

Vadose zone contamination is a continual source of contamination to groundwater if left untreated. Infiltrating rainwater is the primary mobilizer of contaminants previously deposited into the vadose zone, transporting the contaminants to the underlying aquifers. This mobilization is expected to worsen for many contaminants with the increasing acidity in rainwater. Treatment of deep vadose zone contamination is costly as the logistics of assessing the deep aquifer are complex and often rely on injected water as a carrier medium, limiting the areal impact. Utilizing the rainwater to carry treatment to the deep vadose zone could simplify contaminant immobilization.

Recently, limestone gravel was used as a stabilization cover to complete a removal action at the acidified D-Area coal yard at the Savannah River Site (SRS)[1]. The goal of the removal action was to treat an acidified vadose zone that had been exposed to coal leachate. Calcium carbonate soil amendment was mixed into the upper 4 ft of the vadose zone. The predominantly calcium carbonate limestone gravel cover was used to close out the project and be a source of additional carbonate ions to treat the acidified soil. Soil pH sampling demonstrated a further increase in soil pH for the top 1 ft of material relative to the other 3 ft treated soon after application of the cover, likely from the dissolution of the limestone gravel. Similar limestone gravel covers could also immobilize contaminants in the vadose zone. The same carbonate ions used to treat the acidified coal yard soils will decrease the solubility of many contaminants, effectively immobilizing them in the vadose zone. The carbonate ions will increase the pH of the infiltrating water which will increase the number of sorption sites for cations on the surface of many soil minerals. This can also result in the precipitation of divalent cations as carbonate salts. Sr-90 is a prime candidate for in situ immobilization with the application of the limestone cover as $SrCO_3$ has a low solubility, and retention in the vadose zone can lead to drastically lower groundwater concentrations as the isotope decays.

This project investigates the relative migration of Sr-90 between the control and limestone applied cores with the objective of demonstrating that carbonate ions from surface applied limestone gravel can both reach and immobilize vadose zone contaminants. This mid-project update documents the selection of cover materials and deployment of soil cores to the RadFLEx.

2.0 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in Savannah River Site manual E7 2.60. Savannah River National Laboratory (SRNL) documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

This work was requested by DOE-Technology Development Office under Work Authorization # HQ231837.This report documents Tasks 1 and 2 and fulfills Task 3 in the Task Technical and Quality Assurance Plan (TTQAP), Rev. 0 SRNL-RP-2023-01239.[2] Results are recorded in Electronic Laboratory Notebook M8433-00697-05 & J3933-00551-45.

3.0 Materials

3.1 Cover Materials

Leachate tests were performed to screen possible cover materials. Both limestone gravel and marble gravel are predominantly calcite (calcium carbonate) and may lead to the high concentration of carbonate and an increased pH leachate desired for sequestering Sr-90 in the vadose zone. However, some limestone contains, or is mostly, magnesium calcium carbonate leading to a lower pH and less impact on stomium affinity for the soil. Several limestones (and marbles) were tested for leachate pH over 3 weeks. Samples were prepared by adding 20 grams of each amendment to a centrifuge tube, spiking in 20 mL of water, mixing the vessel on a rotatory mixer, and monitoring the pH of the aqueous phase at 1 hr, 2 hrs, 24 hrs and 7 days. After 7 days the tubes were centrifuged, decanted and the water was replaced. After rotating for another 7 days, the pH was measured, liquid decanted and the process repeated. Four possible calcite/limestone gravels were tested: limestone screenings from the production of agricultural lime from Mississippi Limestone, limestone taken from the gravel cover on the D-Area coal yard which was re-crushed after being exposed to the environment for approximately 4 years, Georgetown limestone, and marble chips supplied by Martin Marietta. Each was crushed and sieved for particle sizes between 2.8 mm to 9.5 mm.

The initial one week leaching experiment revealed that the fresh limestone from Mississippi limestone imparted the most rapid change in aqueous pH (Figure 1). The first week leaching tests provide an indication of how quickly the possible soil cover material will impact the transport of the undelaying contaminants. Both the Mississippi limestone and marble provide the quickest impact to the pH, with the limestone maintaining its a higher pH. The field limestone demonstrates a slower impact likely due to its exposure to rain, removing the highly reactive portions of the material. Finally, the Georgetown limestone has the lowest impact of leachate pH and is likely composed of dolomite rather than calcite. There was little difference between the marble and limestone over the long-term leachate tests. For the more rapid impact on water pH, the Mississippi limestone was selected for use in the lysimeters.

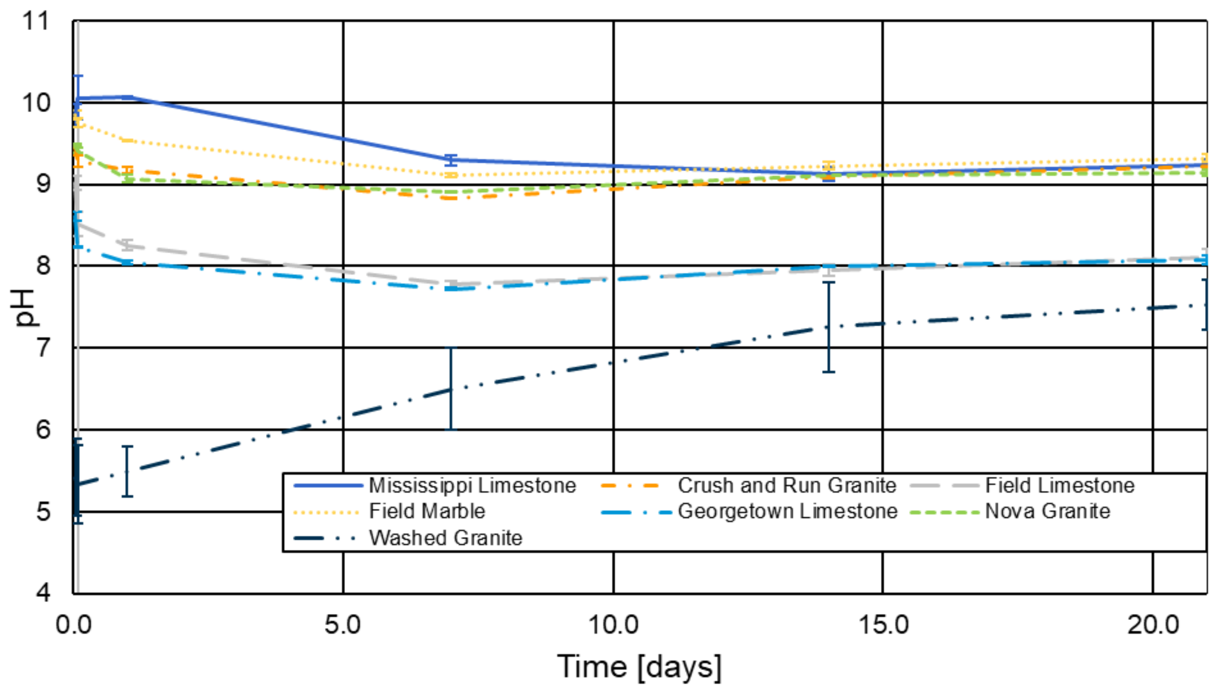

Figure 1. Leachate pH for limestone and granite amendments

Granite gravel was identified as a possible inert cover. An inert gravel of similar size to the limestone gravel was selected to minimize differences in infiltration rate across the cores to allow for a direct comparison of transport. Granite crush and run and Nova granite both from Martin Marietta were tested with identical leachate methods used to screen the limestone. Leachate tests revealed that granite increased pH, behaving similarly to the calcite containing limestone and marble gravels. Such leachates results suggest that granite covers may be capable of increasing the pH of infiltrating water. This increase likely arises from small amounts of carbonate impurities in the granite. To remove the possible calcite impurities, the granite was washed with 0.016 M nitric acid 3 times, followed by 3 washes with deionized water. After these washes, the leachate pH then remained slightly acidic to neutral for the duration of the test. This washed granite was used for the comparison soil cores.

3.2 Soils

Soils were obtained to simulate the vadose zones at 3 different sites: the SRS in South Carolina, the Hanford Site in Washington State, and the Sellafield Site in Cumbria, England. SRS soils were obtained from the SRS core repository. Cores were a composite of soil cores selected from F-Area at SRS from the installation of monitoring wells FSB101A, FSB123C, and FSB115C and included material from 10-30’ below the surface. The Hanford solids were the spoils from the excavation of the Integrated Disposal Facility excavation. Soils simulating those found on the Sellafield site were collected from an outcrop exposure just north of the site itself (Figure 2).

Figure 2. Outcrop where Sellafield soil sample were taken.

The soil samples were dried in pans overnight to remove any free water. Leachate tests, similar to those performed for the cover material, were done to establish background soil pH values. SRS and Sellafield soils were both acidic, with pH around 4.5, while Hanford soils had a pH around 8.5 (Figure 3). X-Ray diffraction (XRD) aof the soils revealed that the Hanford soils contains some calcite which increases the pH compared to those from SRS and Sellafield (Appendix A).

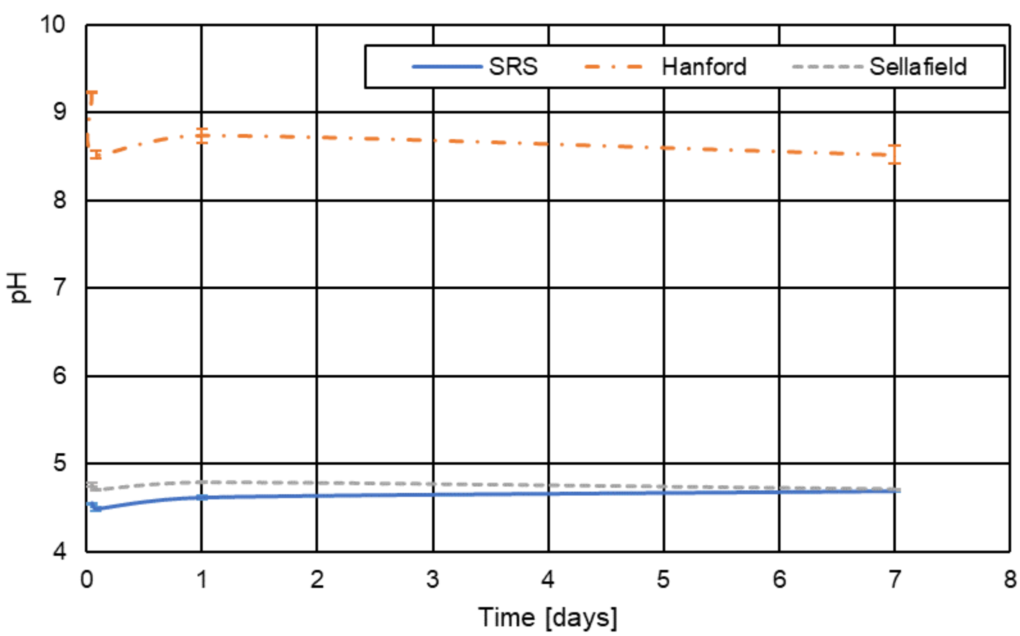

Figure 3. Leachate/soil pH for soils representing SRS, Hanford, and Sellafield sites.

4.0 Core Prep and Deployment

Six lysimeter cores were prepared for deployment at the RadFLEx facility. Two cores were prepared for each soil type (Figure 4) with one core being topped with the Mississippi Limestone, and the other topped with washed crush and run. Each core consisted of a 24" by 4" PVC pipe with a closure of 4"- 2" PVC reducer. A perforated plastic dish covered in 80x80 mesh was placed at the junction of the 4" pipe and the reducer. This was done to keep the soils contained in the pipe and only allow rainwater effluent to pass into the nylobrade tubing and into the sample bottles. (Figure 5). The cores were filled with 16 inches of clean, dry, soils from each site. A limited quantity of the Sellafield soil was available. For this reason, the Sellafield core was modified to contain 8 inches of soil on top of 8 inches of #1 silica filter pack sand. A "pita pocket" source made of 2 glass fiber filters stitched together with Teflon thread (dental floss, (Figure 6) was placed on the top of the layer the vadose zone soil. Each pita pocket was filled with 20 g of soil (2 per site) and spiked with 2.5 ml of a solution of 7.5 µCi/mL Sr-90 in 0.001M nitric acid. The Sr-90 was separated from SRS tank sludge. The pita pocket was placed on top of the 16 inches of vadose zone soil with 3 inches of clean soil placed on top.

Figure 4. Soils representing SRS (top left), Sellafield (top right), Hanford (bottom).

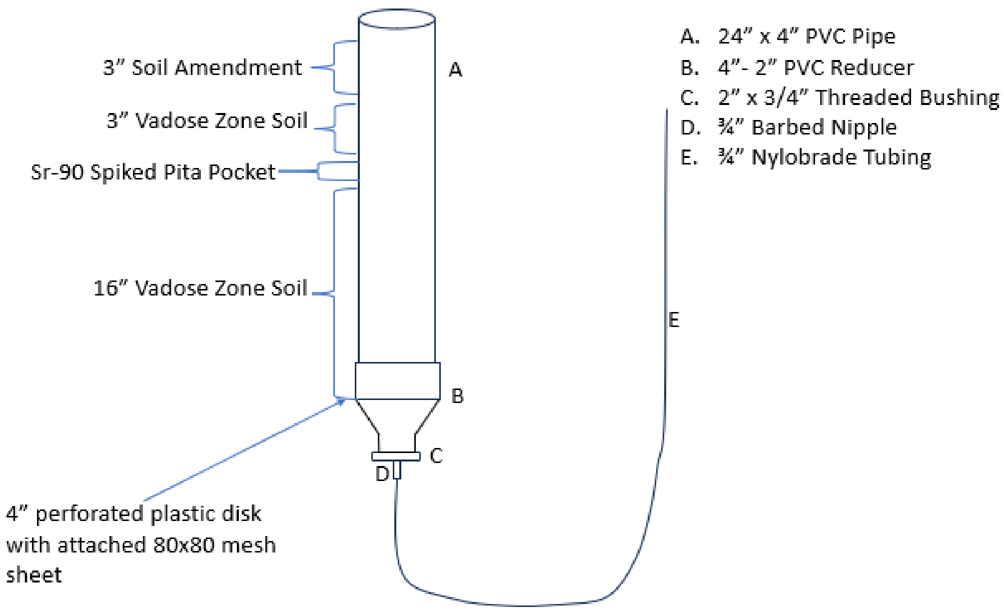

Figure 5. Soil Core Construction Diagram

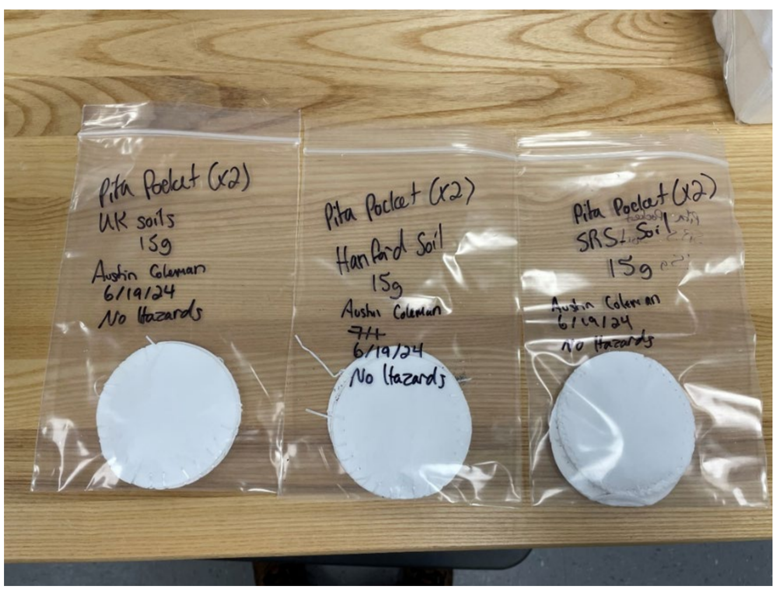

Figure 6. Pita pockets prior to spiking with Sr-90 solution.

The cores were then transported and installed at the RadFLEx facility. Post-installation, 3 inches of either limestone or washed granite was placed on the cores. The cores were uncapped and exposed to the environment on July 1st, 2024. Rainwater effluent will be collected at the end of each month and sent to SRNL's Analytical Development for analysis.

Figure 7. (Left) Soil cores being installed by SRNL operations and Radcon (Right) Cores installed on top of facility.

Figure 8. Limestone (left) and granite (right) covered cores at RadFLEx.

5.0 Conclusions & Path Forward

The soil cores were prepped and deployed at the lysimeter with 2 cores representing each soil type. The cores will be deployed for 12-18 months at the facility. The water that infiltrates through the cores will be collected monthly and analyzed for Sr-90 concentrations. Once the 12–18-month deployment is complete, the cores will be removed from the facility and destructively analyzed to determine the Sr-90 depth profile. Nitrate concentrations will also be analyzed if possible. Comparison of the cores will help determine if the use of limestone is a viable method to sequester Sr-90 in the vadose zone. The assessment will be supported by batch experiments that are currently underway.

References

1. Jolin, W.C., *Calculation of soil amendment application rate and gravel cover mass for the D-Area Coal Storage Yard (484-17D)*.
2. Jolin, W., *Task Technical and Quality Assurance Plan for Surface Applied Limestone Gravel to Mitigate Contaminant Transport in the Vadose Zone*. 2024, Savannah River National Laboratory: Aiken, SC.

Appendix A: XRD

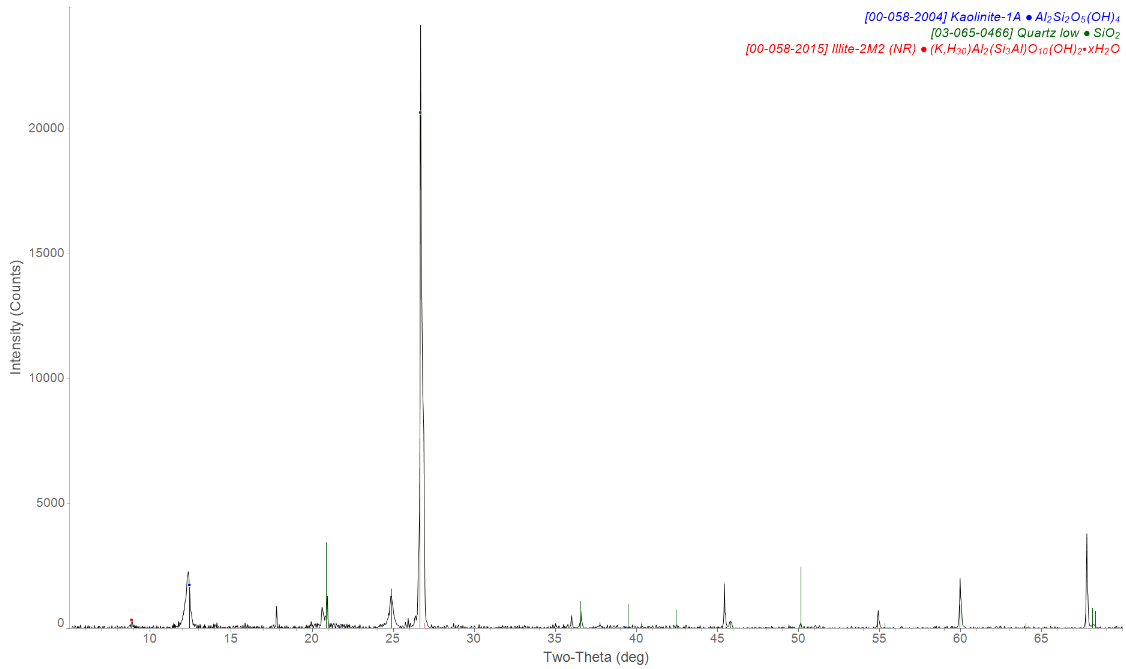

Figure A-1. SRS Soil XRD Results

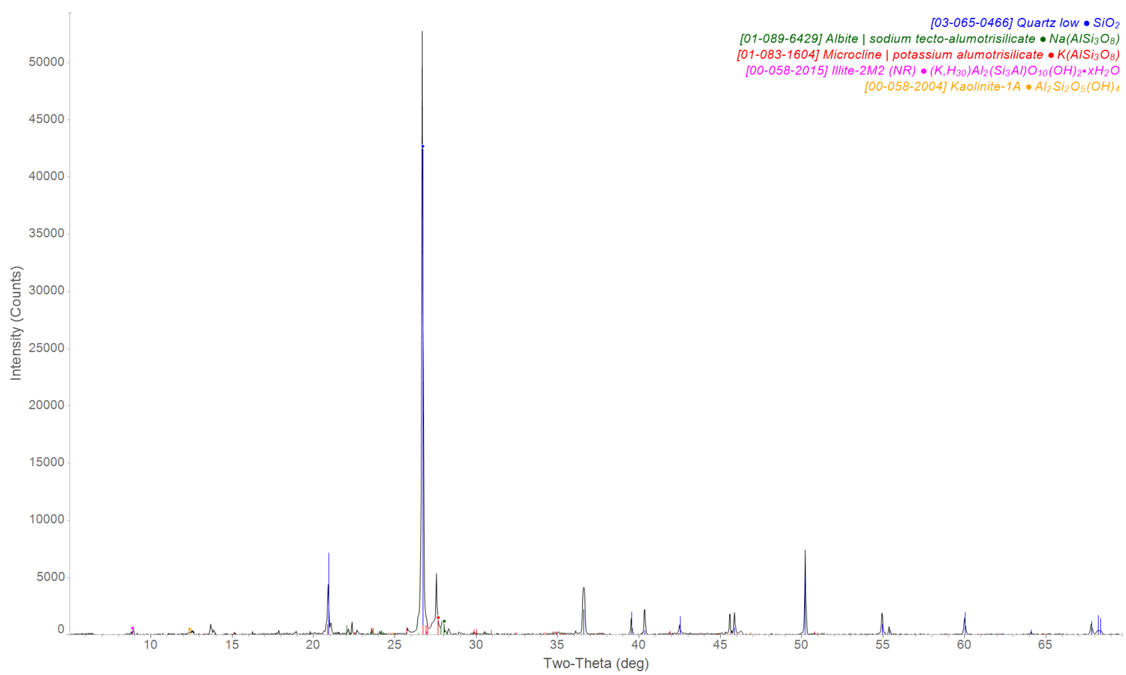

Figure A-2. Sellafield Soil XRD Results

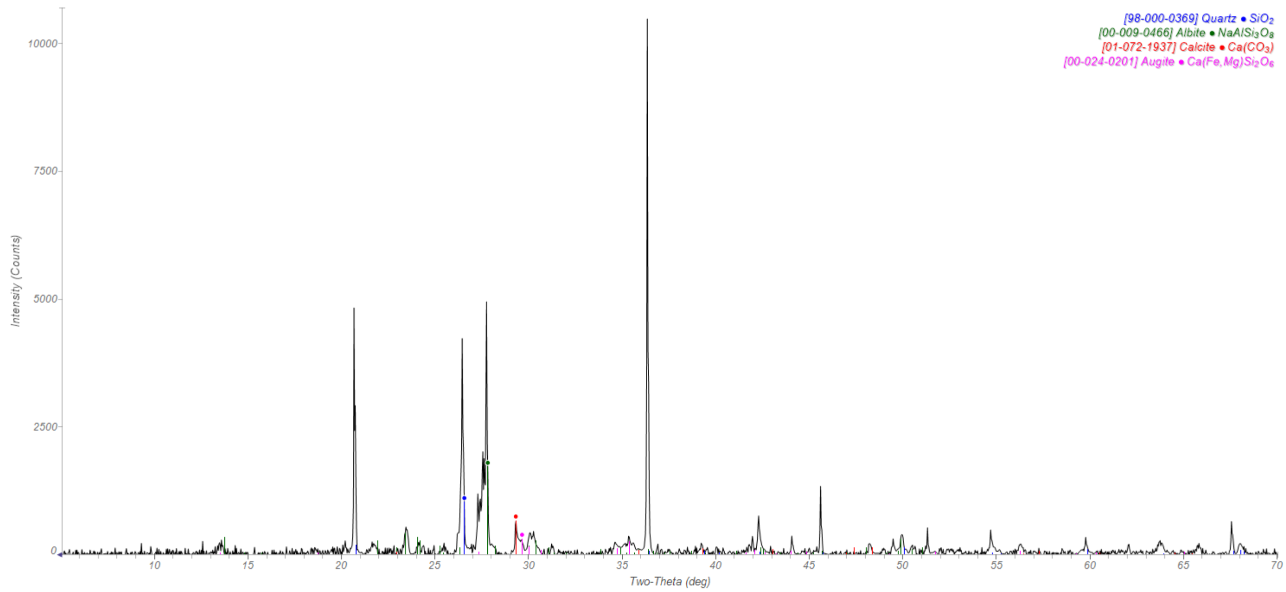

Figure A-3. Hanford Soil XRD Results

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