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**Characterization of 200-UP-1 and 200-
ZP-1 Operable Unit Aquifer Sediments
and Batch Adsorption Distribution
Coefficients for Contaminants of
Concern--Fiscal Year 2006 Progress**

W. Um
R. J. Serne

September 2006



Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

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Introduction

New groundwater wells were drilled by Fluor Hanford in the 200-UP-1 and 200-ZP-1 Operable Units (OUs) in 2006 to better monitor the plumes of hexavalent uranium [U(VI)] and carbon tetrachloride (CCl₄) that have been the focus of past pump-and-treat remediation activities. Fluor Hanford, Inc., sent Pacific Northwest National Laboratory (PNNL) two core samples from two new wells, 299-W22-86 (borehole C4971) and 299-W22-87 (borehole C4977) in the 200-UP-1 OU, and four core samples from one new well, 299-W11-47 (borehole C4990) in the 200-ZP-1 OU.

The PNNL analysis of the core samples involved two tasks. The Tier 1 task included core opening and aquifer sediment characterization for some chemical and physical properties. The Tier 2 task included more detailed characterization such as mineralogy, selective iron extraction, and measurement of adsorption distribution coefficients (K_{ds}) for two radionuclides, technetium-99 (⁹⁹Tc) and U(VI).

Site-specific adsorption K_d data for ⁹⁹Tc and U(VI), complemented by geochemical, geologic, mineralogic, hydrologic, and physical characterization information, are presented in this report. The results of the PNNL analysis can be used to develop a robust, scientifically defensible database to allow risk predictions and to aid in future remediation decisions for the 200-UP-1 and 200-ZP-1 operable units.

Materials and Methods

Six core samples from the new wells were opened in the PNNL laboratory (325 Building, 300 Area) and described by a PNNL geologist as they were being subsampled for various characterization parameters. Two additional outcrop samples, Cold Creek silt and caliche sediments, collected at White Bluffs were also characterized. These two samples are representative of two important lithologies that had not been sampled in recent boreholes and key strata for controlling radionuclide migration within the Hanford Site 200-UP-1 and 200-ZP-1 OUs. All the methods used for the analysis in this report are the same as those described in Um et al. (2005).

Results and Discussion

Sample Description

Core sample information and descriptions are presented in Table 1. After opening, each core was photographed with a digital camera. The cores are shown in Figures 1 through 6 and the two additional sediments from White Bluffs are shown in Figures 7 and 8. Because one core sample from borehole C4971 was identified as slough, that C4971 core sample was not used for either the Tier 1 or 2 tasks. The borehole C4977 sample was intact and identified as silty sand gravel. Because four core samples from borehole C4990 at different depths had similar texture, individual core samples were used only for Tier 1

characterization, and a mixed composite sample was used for the Tier 2 task. All four of the C4990 samples were fine sandy silt, representative of silt in the Ringold Formation. Well-sorted fine sandy silt was found in the Cold Creek sample. Silt highly rich in CaCO_3 was dominant in the white/ivory-colored caliche sample from the White Bluffs site.

Tier 1 Characterization

Tier 1 characterization results (moisture content, total/organic carbon, and specific surface area of the sediments, and pH, alkalinity, and electrical conductivity (EC) of the sediment's water extract) are given in Table 2. Moisture content and surface area, as well as pH, alkalinity, and electrical conductivity (after 1:1 water extract), were collected directly when the cores were opened, so these results are listed by individual core sample at different depths for borehole C4990. One composite sample from borehole C4990 (less than 2 mm) also was prepared and used for total carbon analysis and other Tier 2 tasks. The pH, alkalinity, and EC values measured in 1:1 water extracts are generally similar to those found in water extracts of uncontaminated sediments from the Hanford Site, including previously characterized sediments from the 200-UP-1 OU aquifer. Higher moisture content (10–38%) for samples from boreholes C4977 and C4990 compared to other vadose zone samples (1–5%) is attributed to the aquifer core samples being collected below the groundwater table and not all the entrained water escaping during the removal of the split spoon sampler from the casing. Because relatively high organic carbon (0.19 %), determined from taking the difference between total carbon and inorganic carbon, was found in the sample from borehole C4977, it is suggested that more detailed studies for CCl_4 sorption/desorption be conducted using this sample. High organic carbon might be from CCl_4 contamination (or just from natural organic content in this sample). Significantly high inorganic carbon was found in the White Bluffs caliche sample, 72–88% CaCO_3 content based on total inorganic carbon results and x-ray diffraction (XRD) analyses (see the XRD discussion in **Tier 2 Characterization** below). Relatively high total/inorganic carbon in Cold Creek silt is attributed to the presence of some caliche in this sample. The Cold Creek silt sample was obtained in close proximity (within a few meters) to the Cold Creek caliche sample in the White Bluffs. Because of high inorganic carbon content present, the alkalinity measured in the 1:1 water extract showed the highest value in the caliche sample. Because major ion, especially Ca^{2+} in the caliche sample can be dissolved in 1:1 water extracts, the highest electrical conductivity also was found in the caliche sample. The pH values were similar to those 200-UP-1 OU samples previously characterized [see discussion in Um et al. (2005)]. Similar surface area results were found for the individual core sample collected at different depths from borehole C4990. High surface area values in C4990 samples, approximately one order of magnitude higher than those for the C4977 sample, are attributed to fine silty sand dominant in the C4990 sample (Table 1).

Particle size distribution results determined by dry sieve/hydrometer methods are presented in Table 3. Dry sieve and hydrometer results are also shown in Figures 9 through 11. Both sand and silt size fractions are dominant in sample C4977, while the silt and clay size fractions (sum 91%) is significantly high in the C4990 sample. The Cold Creek silt sample consists mostly of sand-size particles (82%) with minor amounts of silt and clay size particles. These results are in good agreement with core sample descriptions noted by the PNNL geologist when core samples were opened (see Table 1). Because of high CaCO_3 content present as a cement matrix between grains in the caliche sample, CaCO_3 should be removed before conducting particle size distribution analysis on this sample. Particle size distribution analysis for the caliche sample was not conducted this year.

Gamma energy analyses were conducted for each of the cores and Cold Creek outcrop sediments. As expected, the results showed no detectable amount of Hanford generated gamma radionuclides..

Tier 2 Characterization

The results of selective iron extractions conducted using two different iron extraction methods (Tamm's and the citrate-bicarbonate-dithionite [CBD] extraction method) are given in Table 4. Both Tamm's and the CBD methods yielded higher iron contents in sample C4977 compared to that for the composite sample C4990. Significantly higher iron content was found in the CBD extract from sample C4977 than resulted from the Tamm's extract. Because the CBD extraction method is selective for crystalline iron oxides (goethite and hematite) and the Tamm's extraction method is selective for amorphous iron oxides (ferrihydrite), most of the iron oxides (74 %) present in sample C4977 are considered to be more crystalline iron oxides such as hematite or goethite. However, sample C4990 showed that about 70% of iron oxide present in CBD extractant is from amorphous iron oxide (ferrihydrite). The iron oxide content difference between samples C4977 and C4990 may have originated from different weathering environments or history in the two different wells. Cold Creek silt showed higher iron content than its adjacent caliche sample. Lower iron content in calcium carbonate-rich soils like caliche is likely caused by dilution of the iron by calcium carbonate cementing the void spaces between grains. The lowest iron contents found in both Tamm's and CBD methods were in the caliche sample, consistent with the above description for iron content in high-CaCO₃ soils.

Total oxide chemical compositions of the sediments were determined by microwave digestion and analysis using an inductively coupled plasma-optical emission spectrometer (ICP-OES). The results of bulk chemical composition represented as oxide percentage are given in Table 5. Major ion concentrations were similar in samples from boreholes C4977 and C4990. About 50–60 wt% SiO₂ is normal for Ringold silt samples found at the Hanford Site. Relatively low Al₂O₃ and SiO₂ contents in the caliche sample are caused by the high CaO (74 wt%) content compared to that of the adjacent Cold Creek silt.

The XRD patterns and identified minerals for sample C4977 are given in Figures 12 and 13. The sample was dominated by quartz, feldspar (orthoclase), and plagioclase (albite), with minor amounts of hornblende, mica (muscovite), and clays (montmorillonite). The XRD pattern at low angle (<30 in 2-theta) showed more distinctive peaks for clays (Figure 13). The XRD patterns for composite sample C4990 and the Cold Creek silt showed similarities to that of sample C4977, except that orthoclase is dominant in sample C4990 while microcline dominates in the Cold Creek silt sample. However, based on the similar XRD patterns, all three sediment samples are considered to have similar mineralogical composition. The Cold Creek caliche sample showed two distinctive dominant peaks representative of quartz and calcite (Figure 14). Semiquantitative XRD profile fit analysis revealed that the caliche sample consisted of about 88 wt% calcite, consistent with previous characterization results.

Adsorption K_ds for Technetium and Hexavalent Uranium

Adsorption distribution coefficients (K_ds) for ⁹⁹Tc and U(VI) were measured using a Hanford groundwater (see Um et al. 2005, Table 1 for chemical composition) spiked with both contaminants together. Total concentrations of 10 µg/L and 23.8 µg/L (=10⁻⁷ M) were used for ⁹⁹Tc and U(VI), respectively, in a batch experiment with a 300-g/L solid concentration. The calculated K_ds are shown in

Table 6. The K_d s for ^{99}Tc range from 0–0.2 mg/L, consistent with ^{99}Tc K_d s measured previously on 200-UP-1 OU sediments (Um et al., 2005). Different U(VI) K_d s were found for samples C4977 and C4990 because of their distinctly different particle size fractions and iron oxide contents. Although the equilibrated groundwater chemical composition for the respective batch tests are similar, the U(VI) K_d (4.23 ml/g) for sample C4990 is much higher than that for C4977 (0.76 ml/g). This difference results from high iron oxide content and high clay/silt size fraction content as well as high surface area in sample C4990, indicating that geochemical and physical characterization for each differing sediment lithology is necessary to understand site-specific and lithology-specific K_d values for many key contaminants.

The Cold Creek caliche sample showed higher U(VI) K_d values compared to the Cold Creek silt sediment collected at the White Bluffs sampling location. Previous studies for U(VI) adsorption on CaCO_3 -rich sediments showed that U(VI) adsorption decreases with high CaCO_3 content because 1) CaCO_3 might block the reactive surface sorption sites and 2) dissolved Ca and CO_3^{2-} tend to form a soluble calcium-uranyl-carbonate complex ($\text{CaUO}_2(\text{CO}_3)_3^{2-}$) in solution (Dong et al. 2005). However, recent study by Um et al.^(a) also revealed that the U(VI) K_d on CaCO_3 -rich sediment is dependent on solution chemistry, with results showing increased U(VI) K_d values caused by CaCO_3 coprecipitation in solutions oversaturated with calcite. The high U(VI) K_d on the caliche sample might be from uranium-calcite coprecipitation. The high alkalinity (2848 mg/L) found in 1:1 water extract for the Cold Creek caliche sample suggests that U-calcite coprecipitation is quite plausible. However, more studies should be conducted to determine the potential role of caliche sediments on U(VI) sequestration.

Conclusions

A total of six core samples from 200-UP/ZP-1 OUs and two additional outcrop samples were characterized during FY2006 by PNNL. One sample (C4971) was identified as slough and not used, but the five other samples identified as intact core samples were used for further analyses. The C4977 sample is gravel-sandy silt and C4990 samples are fine-sandy silt from the Ringold formation. Although the sediments from these two boreholes have similar mineralogical composition, C4990 samples show higher values of Fe oxide content, clay/silt content, and surface area compared those in C4977.

The measured Tc K_d values ranged 0–0.2 mg/L for both samples, while U(VI) K_d for C4990 (4.23 mg/L) is much higher than that for C4977 (0.76 mg/L). A key finding from the K_d measurements is that detailed sediment and pore water characterization is necessary to understand the variation in K_d values seen in the empirical batch tests. Without the ancillary characterization of the sediments and pore waters, one might form misleading interpretations of the mechanisms that control the K_d values. Thus, physical, geochemical, and hydrological characterization of the sediments and pore waters should be conducted to increase our understanding of the site-specific K_d measurements. More details for methods and results will be provided in the formal technical report in FY 2007.

The much higher U(VI) K_d found in the caliche sample was not expected because previous studies suggested that U(VI) adsorption should decrease for sediments containing high CaCO_3 content.

^(a) Um W, RJ Serne, and KM Krupka. “Surface Complexation Modeling of U(VI) Adsorption to Hanford Sediments with Varying Geochemical Conditions.” *Environ. Sci. Technol.* Submitted.

However, this observed increase in U(VI) K_d for the caliche-rich sample can be explained by a different sequestration mechanism, co-precipitation of U(VI) with calcite rather than simple surface adsorption. More detailed studies of caliche sediments for their potential to sequester U(VI) in the Hanford and Ringold formation sediments should be conducted in the future.

References

Dong W, WP Ball, C Liu, Z Wang, AT Stone, J Bai, and JM Zachara. 2005. "Influence of Calcite and Dissolved Calcium on Uranium(VI) Sorption to a Hanford Subsurface Sediment." *Environ. Sci. Technol.* 39:7949-7955.

Um W, RJ Serne, BN Bjornstad, HT Schaef, CF Brown, VL LeGore, KN Geiszler, SR Baum, MM Valenta, IV Kutnyakov, TS Vickerman, and MJ Lindberg. 2005. *Characterization of 200-UP-1 Aquifer Sediments and Results of Sorption-Desorption Tests Using Spiked Uncontaminated Groundwater*. PNNL-15502, Pacific Northwest National Laboratory, Richland, Washington.



Figure 1. Core Sediment (slough sample) Collected from Borehole C4971



Figure 2. Core Sediment (intact sample) Collected from Borehole C4977



Figure 3. Core Sediment (intact sample) Collected from Borehole C4990 (404.7-405.2 ft bgs)



Figure 4. Core Sediment (intact sample) Collected from Borehole C4990 (405.2-405.7 ft bgs)



Figure 5. Core Sediment (intact sample) Collected from Borehole C4990 (405.7-406.2 ft bgs)



Figure 6. Core Sediment (intact sample) Collected from Borehole C4990 (406.2-406.7 ft bgs)



Figure 7. Outcrop Sample (Cold Creek silt) Collected from White Bluffs



Figure 8. Outcrop Sample (caliche) Collected Adjacent to Cold Creek Silt at White Bluffs

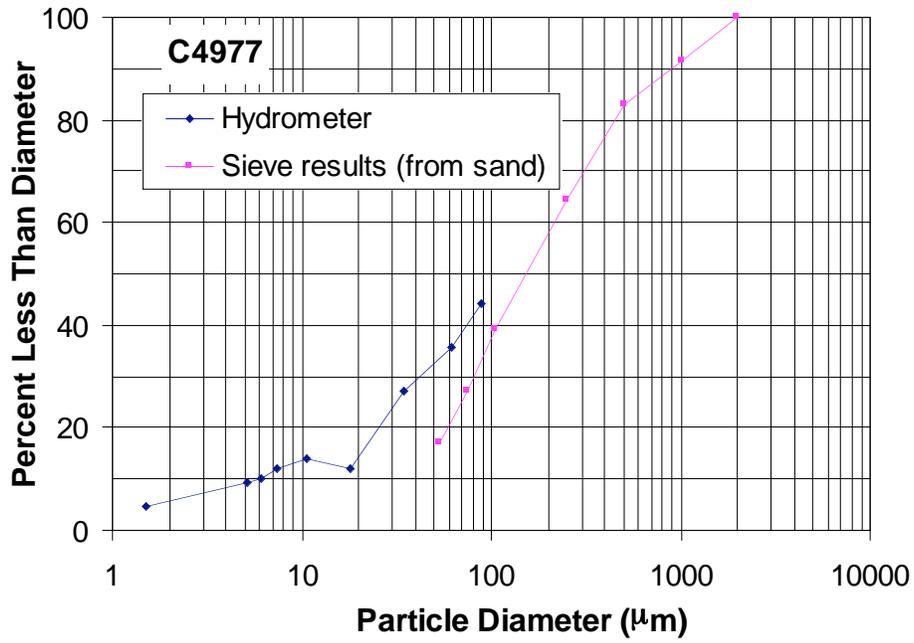


Figure 9. Particle Size Distribution for Borehole C4977 Sample

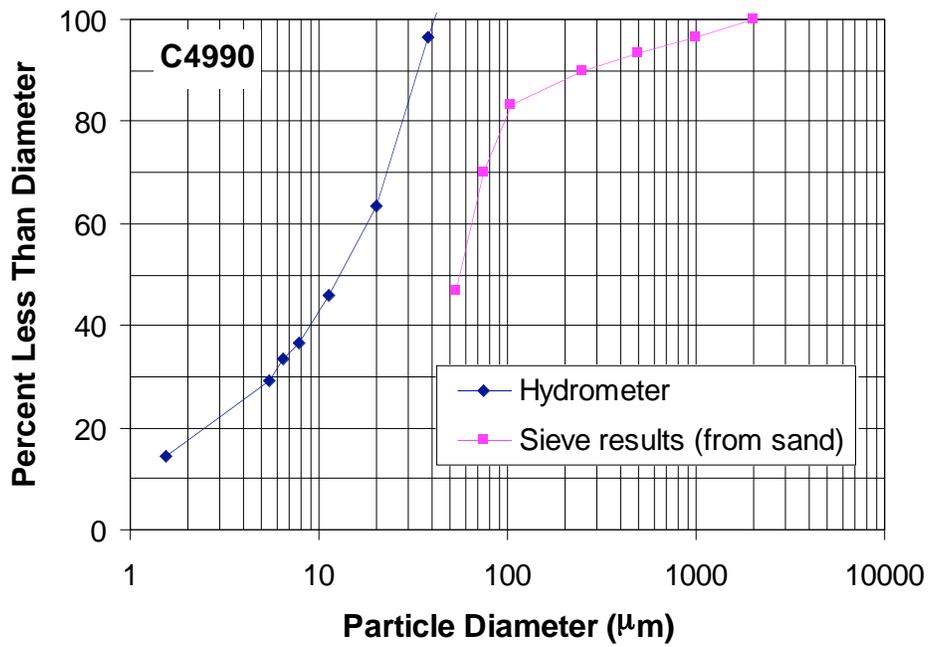


Figure 10. Particle Size Distribution for Borehole C4990 Sample

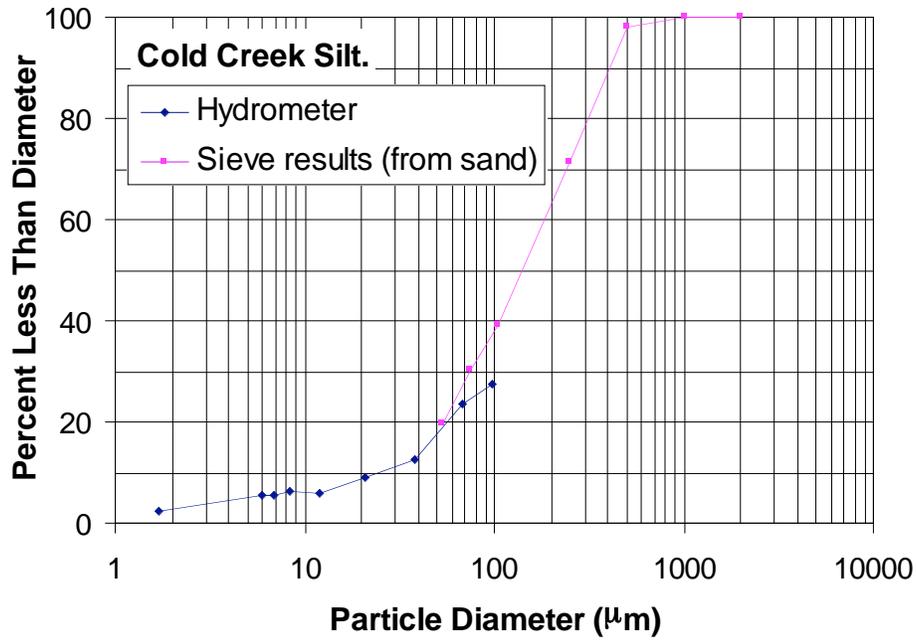


Figure 11. Particle Size Distribution for Cold Creek Silt Sample

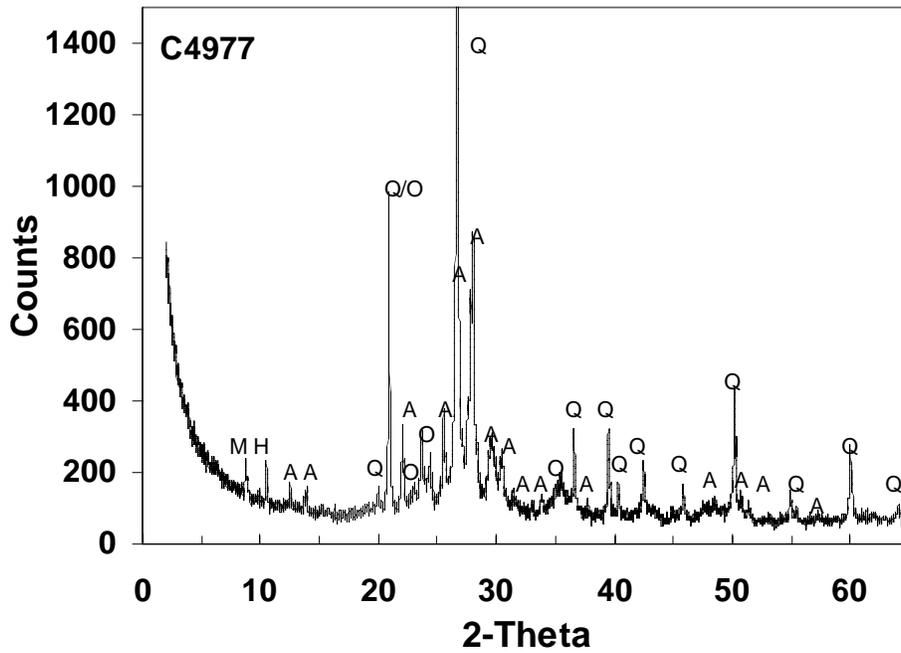


Figure 12. X-Ray Diffraction Pattern of Borehole C4977 Sample and Identified Minerals. M = muscovite; H = hornblende; A = albite; Q = quartz; O = orthoclase.

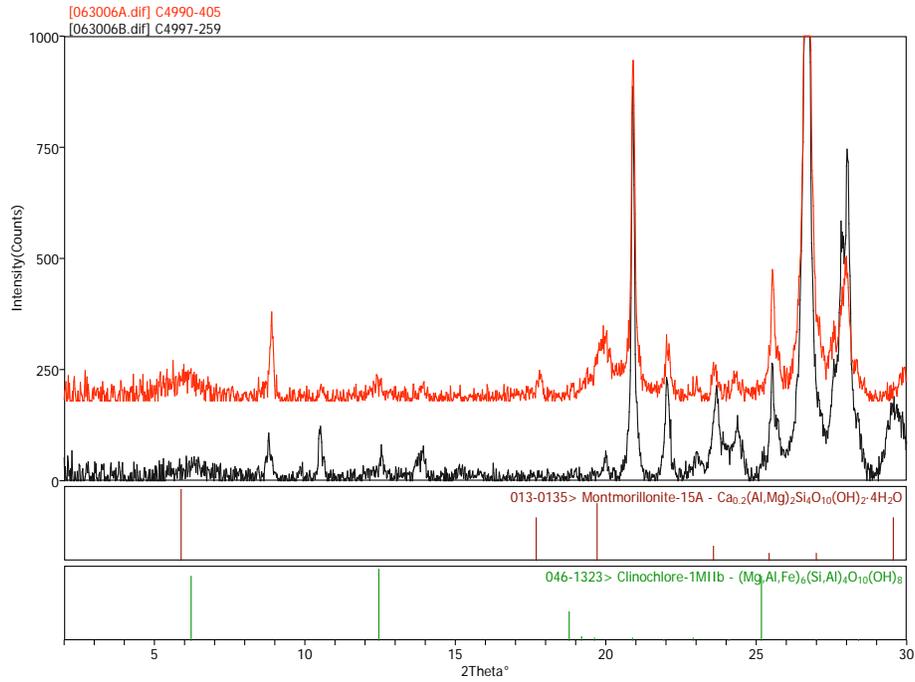


Figure 13. X-Ray Diffraction Patterns of Montmorillonite and Clinochlore from Boreholes C4977 and C4990 in Low Angle

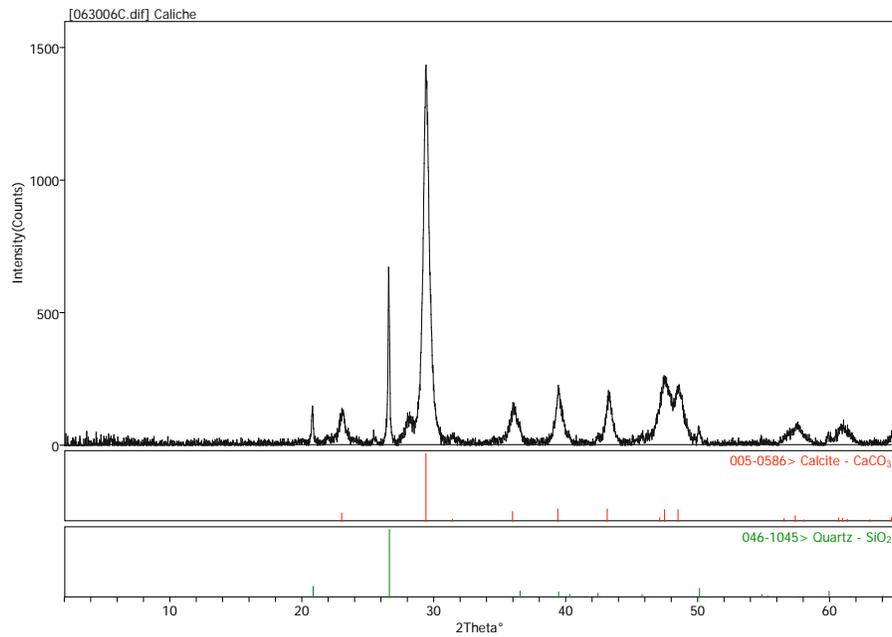


Figure 14. X-Ray Diffraction Pattern of Caliche Sample Consisting of Two Dominant Minerals (quartz and calcite)

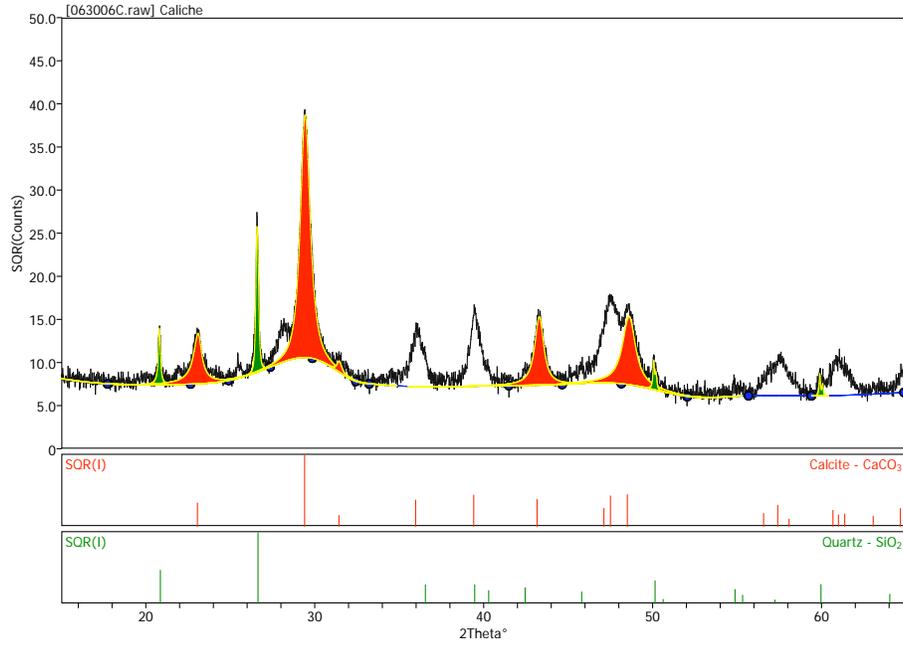


Figure 15. X-Ray Diffraction Pattern of Caliche Sample and Profile Fit Plot with Quartz and Calcite. Weak and unidentified patterns are ignored in calculation.

Table 1. Description of Core Samples

Borehole	Well ID	Depth Interval	Formation	Intact Material	Descriptions
C4971 (200-UP-1)	299-W22-86	261.5–262.0 ft bgs	Ringold Formation (Unit E)	No- Slough	Sand; medium-grained; well-sorted; 2,5Y7/4 (pale yellow); 10–15% mafic, 85–90% felsic grains; loose; couple of pebbles in bottom
C4977 (200-UP-1)	299-W22-87	258.5–259.0 ft bgs	Ringold Formation (Unit E)	Yes- Intact	Silty sandy gravel; 50% gravel, 35% sand, 15% silt; 2.5Y6/2 (brownish gray), moderately sorted; loose; sand = 10% mafic grains; gravel = 20-30% basalt clasts; loose; largest clast = 2 cm diameter
C4990 (200-ZP-1)	299-W11-47	404.7–405.2 ft bgs	Ringold Formation (Lower mud)	Yes- Intact	Fine sandy silt, well-sorted, 2.5Y6/6 (olive yellow), micaceous, compact and cohesive, non-calcareous; uppermost liner had gravelly sand along sides of core that had been dragged down from above (sample was collected from intact sandy silt from middle of liner)
		405.2–405.7 ft bgs			
		405.7–406.2 ft bgs			
		406.2–406.7 ft bgs			
Cold Creek silt	White Bluffs outcrop	Outcrop	Cold Creek Unit	Yes	Well-sorted fine sandy silt
Caliche sample	White Bluffs outcrop	Outcrop	Cold Creek Unit	Yes	CaCO ₃ -cemented sand, silt and clay

Table 2. Tier 1 Characterization Results ^(a)

Sample ID	MC (%)	TC (%)	IC (%)	Alk (mg/L)	pH	EC (mS/cm)	SA (m ² /g)
C4977	10.0	0.19	0.00	353.8	7.60	0.08	2.62
C4990	404.7–405.2	34.9		174.7	7.72	0.16	29.4
	405.2–405.7	34.6		140.8	7.65	0.14	25.9
	405.7–406.2	37.2		112.8	7.62	0.14	29.8
	406.2–406.7	37.8		105.3	7.61	0.14	25.9
C4990 composite		0.09	0.02				
Cold Creek silt	4.42	0.64	0.52	1246.6	7.85	0.12	27.0
Caliche	1.35	8.81	8.59	2848.1	7.75	0.64	

(a) Moisture content (MC), alkalinity (Alk), pH, and electrical conductivity (EC) were measured using individual C4990 samples, while total carbon (TC), inorganic carbon (IC), and surface area (SA) were determined using one composite sample for C4990. The alkalinity, pH, and electrical conductivity were measured in 1:1 water extracts, and the alkalinity and EC values were dilution-corrected based on moisture content to reflect porewater values. Total organic carbon can be estimated by difference between total carbon (TC) and inorganic carbon (IC).

Table 3. Particle Size Distributions as Determined by Dry Sieve/Hydrometer Method ^(a)

Sample ID	Clay (%)	Silt (%)	Sand (%)				
			Very Fine	Fine	Medium	Coarse	Very Coarse
C4977	3.0	46.6	11.1	12.8	9.4	4.3	4.3
C4990 Composite	16.4	74.6	6.2	1.1	0.6	0.6	0.6
Cold Creek silt	0.2	18.0	20.0	32.7	27.3	1.8	0.0
Caliche							

(a) Specific size distribution: clay (<2 µm), silt (2–53 µm), very fine sand (53–106 µm), fine sand (106–250 µm), medium sand (250–500 µm), coarse sand (500–1,000 µm), very coarse sand (1,000–2,000 µm). Particle size distribution was conducted after gravel removed. Caliche sample was not characterized for particle size distribution because high CaCO₃ present as cements should be removed in advance.

Table 4. Results of Selective Iron Extraction Using Two Different Methods

Sample ID	Fe ($\mu\text{mol/g}$ of sediment)	
	CBD Method ^(a)	Tamm's Method
C4977	26.49 \pm 0.13	18.52 \pm 1.45
C4990 composite	149.28 \pm 8.32	38.30 \pm 1.15
Cold Creek silt	38.14 \pm 12.87	24.59 \pm 1.25
Caliche	2.14 \pm 0.05	0.74 \pm 0.02

(a) CBD method indicates citrate-bicarbonate-dithionite extraction.

Table 5. Chemical Composition of Sediments (% as oxides)

Oxides	C4977	C4990	Cold Creek Silt	Caliche
Al ₂ O ₃	12.9	14.3	16.9	1.9
SiO ₂	55.4	54.9	51.0	17.5
Fe ₂ O ₃	6.6	14.8	9.9	1.1
MnO	0.1	0.1	0.2	0.0
MgO	2.4	2.5	2.8	3.5
CaO	13.8	4.3	9.7	73.6
Na ₂ O	5.2	3.3	4.8	1.0
K ₂ O	3.2	5.1	4.4	0.8
TiO ₂	0.0	0.0	0.0	0.0
P ₂ O ₅	0.1	0.2	0.1	0.1
SrO	0.1	0.1	0.1	0.1
BaO	0.2	0.2	0.3	0.2

Table 6. Batch Adsorption Distribution Coefficients (K_d s) for Tc and U(VI) ^(a)

Adsorbents	K_d s (ml/g)		
	Tc	U(VI)	pH
C4977	0.20 ± 0.14	0.76 ± 0.05	7.94 ± 0.01
C4990	0.19 ± 0.14	4.23 ± 0.16	7.82 ± 0.04
Cold Creek silt	0.00 ± 0.00	3.54 ± 0.51	7.75 ± 0.00
Caliche	0.00 ± 0.00	6.26 ± 1.49	7.82 ± 0.09

(a) Average value with one standard deviation based on 2 replicates