AK Re-evaluation of Rocky Flats Pond Sludge: Planning for Surprises – 16218

Randall Morris
North Wind, Inc./Advanced Mixed Waste Treatment Project

ABSTRACT

The Advanced Mixed Waste Treatment Project (AMWTP) uses the Sludge Repack Process (SRP) to treat prohibited liquids in retrieved containers of sludge originally stored in the early 1970s. Many of these containers were generated in the Rocky Flats Plant 2nd Stage Sludge process. In June, 2015, operators at SRP identified containers of waste with historical IDs beginning with the prefix 742, indicating they were from the 2nd stage process, but which were marked with the words "Pond Sludge" and contained unusual waste such as rolled asphalt and plant material. This event required a reevaluation of the AK, which concluded that the pond sludge containers were from the same generating process as the rest of the 2nd stage sludge, and did not change the hazardous waste numbers, waste material parameters or waste matrix code. This case study demonstrated the uncertainty inherent in all AK because of the long time period between generation of the waste and current characterization. Records are missing, unreadable, and difficult to interpret; memories are faulty; and containers continue to surprise us with unexpected waste. AK must be continually reevaluated and updated throughout the life of the project. When disposing of legacy waste, conditions such as that described in this case study should be expected and planned for.

INTRODUCTION AND BACKGROUND

The U.S. Environmental Protection Agency (EPA), in their 1994 Waste Analysis Guidance Manual [1], broadly defined the term acceptable knowledge (AK) to include detailed information on the wastes obtained from existing waste analysis data or studies conducted on waste generated by processes similar to that which generated the waste; facility records of analysis performed before the effective date of RCRA; and waste analysis data obtained from generators of similar wastes. The Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WIPP-WAC) defines acceptable knowledge as follows: "Any information about the process used to generate waste, material inputs to the process, and the time period during which the waste was generated, as well as data resulting from the analysis of waste, conducted prior to or separate from the waste certification process authorized by EPA's Certification Decision…" [2]

Acceptable knowledge is used to characterize transuranic (TRU) mixed waste in five ways: [3]

- "To delineate TRU mixed waste streams
- To assess whether TRU mixed wastes comply with the TSDF-WAC
- To assess whether TRU mixed wastes exhibit a hazardous characteristic (20.4.1.200 NMAC, incorporating 40 CFR §261 Subpart C)

- To assess whether TRU mixed wastes are listed (20.4.1.200 NMAC, incorporating 40 CFR §261 Subpart D)
- To estimate waste material parameter weights"

Recognizing that an initial collection and evaluation of AK might not be sufficient to fully characterize TRU mixed waste throughout the life of any given project, the WIPP Waste Analysis Plan (WAP) provides for augmentation of AK using real-time radiography (RTR) and/or visual examination (VE). In addition, the WIPP WAP requires re-evaluation of AK "…if the results of waste confirmation indicate that the waste to be shipped does not match the approved waste stream, or if data obtained from radiography or visual examination for waste streams without an AK Sufficiency Determination exhibit this discrepancy." [3]

Acceptable Knowledge is often perceived by sites responsible for treating and shipping TRU mixed waste to WIPP as ending when all waste has been initially profiled. As this case study illustrates, because of the WIPP-WAP allowance for AK augmentation by RTR and VE, and the requirement for AK re-evaluation, AK can never be considered "finished."

The Problem

The Advanced Mixed Waste Treatment Project (AMWTP) uses the Sludge Repack Process (SRP) to treat prohibited liquids in retrieved containers of sludge originally stored in the early 1970s. Many of these containers were generated in the Rocky Flats Plant 2nd Stage Sludge process, which occurred in Rocky Flats Building 774 from January 1971 through July 1985. The 2nd Stage Sludge, currently identified at AMWTP with the Item Description Code RF-002, and profiled under waste stream BNINW216, was packaged by Rocky Flats in 55-gallon containers assigned drum numbers beginning with prefix 742. This material was also included in Central Characterization Program (CCP) waste stream profile ID-SRP-S3000. [4, 5, 6]

In June, 2015, operators at SRP identified containers of waste with historical IDs beginning with the prefix 742, indicating they were from the 2nd stage process, but which contained small amounts of unusual waste such as rolled asphalt and vegetation. Subsequent investigation revealed the containers were marked with the words "Pond Sludge" in addition to the usual historical drum number. Prior to this event, the only pond sludge identified in the AK had been from sewage treatment ponds and it was considered soil. [7, 8] No AK had connected pond sludge with the 2nd stage process. It was not identified in the original AK documentation from Rocky Flats or in any AK evaluation conducted since that time. This event required a reevaluation of the AK. Because, at the time, the SRP was managed by a different contractor who used the CCP AK subcontractor, this work was conducted jointly by CCP and AMWTP AK staff.

Approach to AK Re-evaluation

The WIPP WAP defines a waste stream as follows: "…waste materials that have common physical form, that contain similar hazardous constituents, and that are

generated from a single process or activity." [3] Given this definition, AK re-evaluation of the pond sludge required a focus on three related questions:

1. Was the waste in the containers marked "Pond Sludge" generated from the same process or activity as the rest of the waste stream?
2. Does the waste in the containers marked "Pond Sludge" have the same physical form as the rest of the waste stream?
3. Are the hazardous constituents in the containers marked "Pond Sludge" similar to those in rest of the waste stream?

These questions were approached by compiling information from several sources:

- Visual examination of the containers and the waste within them, provided information about the physical form of the waste.
- Documentation in the AMWTP Waste Tracking System (WTS) provided information about the physical form of the waste and hazardous constituents associated with other containers in the same waste stream.
- Documentation already available in the AK databases of the CCP and AMWTP provided information to help determine whether the containers marked "Pond Sludge" were considered to be from the same generating process as the rest of the waste stream and whether they differed from the rest of the waste stream in physical form or hazardous constituents.
- Augmentation of the existing AK documentation by interviews with personnel active at Rocky Flats during the time these containers were generated also helped determine whether the containers marked "Pond Sludge" were considered to be from the same generating process as the rest of the waste stream.

This information was summarized in and evaluated in two Discrepancy Reports, one written by CCP for their program and one written by AMWTP for theirs. [7, 8]

GENERATING PROCESS

Solar Evaporation Pond Description

Liquid effluent from the 2nd stage treatment process, and all other plant-generated liquid wastes not requiring treatment, was concentrated in a set of solar evaporation ponds (SEPs) near Building 774. The SEPs were constructed primarily to store and treat (via evaporation) low level radioactive process liquids from Buildings 444, 774, 881, and 883 that contained high nitrate concentrations and treated acidic wastes containing aluminum hydroxide. The SEPs consisted of three main ponds: Pond 207-A, placed into service in August 1956, Pond 207-B placed into service in June 1960, and Pond 207-C constructed in 1970. Pond 207-B was divided into three smaller impoundments, North, Center, and South. Ponds 207-A and 207-B were originally lined with asphalt planking, but this was replaced with asphaltic concrete in the early 1960s. Pond 207-C was primarily intended to provide additional storage capacity and to allow the transfer and storage of liquids

from the other ponds as necessary to perform pond repair work; Pond 207-C was not relined. [9, 10]

Not all parts of the SEPs received process waste at the same time. Pond 207-A received process wastes until 1986, at which time dewatering and sludge removal operations began. As sludge was being removed from Pond 207-A, water was also being removed by natural and forced evaporation using evaporators located in Building 374. [9, 11] As a result of these efforts, Pond 207-A was essentially empty of materials by the summer of 1988. The three 207-B ponds held process waste until 1977, when the sludge from all of the 207-B ponds was removed as part of the construction of the Reverse Osmosis (RO) facility and the related plant water recycle activities. After that time, process waste was not released into the 207-B ponds. [9, 10] Pond 207C received process waste until 1986, was not re-lined, and continued to store process liquids until the 1990s. [9, 10]

The SEPs primarily received low-level radioactive liquid wastes from Buildings 444, 774, 881, and 883; however, other RFP liquids were also discharged to the ponds. These included sanitary sewage sludge; lithium metal; sodium nitrate; ferric chloride; lithium chloride; sulfuric, hydrochloride, and nitric acids; ammonium persulfates; hexavalent chromium; and cyanide solutions. [9, 10] Water collected by a series of trenches and sumps, which intercepted natural seepage and pond leakage to prevent nitrate contamination of North Walnut Creek, and by the footing drains for Buildings 771 and 774 was also returned to Ponds 207-A and 207-B North. [9] Solvents and organics were not routinely discharged to the ponds. [10]

In addition to Rocky Flats contribution, approximately 258,700 to 261,200 gallons of liquid wastes from the Coors Porcelain Company (CPC) were disposed of in the SEPs from June 23, 1961 until June 1963. It is estimated that a minimum of 631.4 kg of beryllium were disposed of into the SEPs by CPC. [12, 13, 14]

Until 1977, the liquid from the SEPs was pumped from the ponds to a steam-heated, double-drum drier in Building 774, where it was concentrated, dried, and packaged as series 745 (IDC RF-005) evaporator salt waste. Given this previously identified connection between Building 774 and the SEPs, it was reasonable to begin with the assumption that the ponds in question were the SEP. [4, 9, 10]

Pond Sludge Relationship to Building 774

A search of the AK databases identified a few documents that helped illuminate the connection between the 2nd stage process and the SEP. Fragments of a Building 774 Foreman's Logbook were discovered that identified 1328 entries from 1971 and 1972 assigned prefix 742 but with comments such as "Pond" or "Pond Sludge" that associated them with the SEP. Comparison of this logbook fragment with AMWTP's WTS revealed that 822 of those containers had been retrieved, 805 had been assayed, 805 had been subjected to RTR, and 358 were currently emplaced at WIPP. All of these containers were identified by Rocky Flats with the prefix 742, which was typical of waste generated by the 2nd stage sludge process.

Two items of correspondence were obtained indicating special processing may have been conducted with the SEP liquids or sludge, which resulted in low specific activity (LSA) 742 series sludge. The first is an August 24, 1971 letter from the U.S. Atomic Energy Commission requesting that The Dow Chemical Company, the Rocky Flats Plant operating contractor, submit a proposal to ship LSA waste to Richland (Hanford Site) for disposal. [15] This letter describes 742 series waste generated from routine processing which was greater than LSA and consistent with the current description for IDC RF-002 sludge. [4, 5] The letter also describes special 742 series waste generated as a result of emptying the SEP. The letter indicates there are "…five ponds, totaling about 8,000,000 gallons of liquid….The liquid from the first pond (2B South) is pumped into a sludge holding tank in the second stage processing", assumed to mean the 2nd stage of the Building 774 aqueous liquid waste treatment system. [4, 5, 6] "After going through the second stage processing a sludge results which is placed in drums." According to the letter, this operation started on June 27, 1971, and generated about 30 drums per day for a total of 3,000 to be generated from the first pond. Processing of all five evaporation ponds was to result in about 3,000 drums (assumed to mean in addition to the drums generated from processing the first pond). Based on analysis of the drums generated prior to the letter, Dow calculated the drums will meet the LSA criteria. [15]

The second item of correspondence consists of a proposal dated September 30, 1971, "Proposal to Ship Low Specific Activity Wastes From Rocky Flats to Richland, Washington", prepared by Dow Chemical Company, Rocky Flats Division, in response to the above described request. [16] The proposal describes the generation of greater than LSA, 742 series sludge consistent with the current description for IDC RF-002 sludge. [4, 5] The proposal continues with the 742 series description indicating "…special conditions require periodic removal of sludge from evaporation ponds. During these operations sludge from the evaporation ponds is mixed with the normal process stream. The sludge contains large quantities of solid nitrate wastes…" with depleted uranium and plutonium. "Mixing of the sludge results in about 450 drums per month….Past experience indicates about 250 drums per month are handled and shipped as LSA wastes." [16]

Former Rocky Flats personnel were interviewed regarding the potential processing of pond liquids or pond sludge in Building 774. Frank McMenus, a Building 774 process operator in the early 1970s and eventually Building 774 manager, did not believe sludge from the solar ponds was ever processed through the second stage process because the sludge would clog the system. Mr. McMenus could offer no opinion on why pond sludge would carry the 742 prefix or why the log books list pond sludge. [17] Pat Arnold, former manager of the Rocky Flats Waste Management organization was contacted regarding the processing of 207B pond sludge in Building 774. Mr. Arnold indicated, that although he was not present during this time frame, he does not know why they would have run the sludge through the Building. [18]

The Rocky Flats employee interviews and the previous AK regarding IDC RF-002 and prefix 742 sludge appear to conflict with the logbook entries and the LSA waste

proposal correspondence. However, given the demonstrated presence of series 742 containers marked with the notation “Pond Sludge” in the AMWTP inventory, it seems clear that weight should be given to the logbook entries and the LSA waste proposal correspondence. Based on these documents, liquids and sludges were periodically removed from the SEPs. These removal activities were primarily related to repair of the pond liners due to leakage, replacement of the pond linings, as part of routine waste management activities, and during "special conditions." [7, 8, 9, 10, 15, 16]

Some of the liquids removed from the SEPs were processed through the Building 774 2nd stage wastewater treatment system, including precipitation and vacuum filtration of the resultant slurry. Because process inputs to the 2nd stage process were the same regardless of the source of the liquid being processed, the sludge produced through treatment of the pond liquids would be indistinguishable from that produced through processing of routine process wastewaters. [8] Rolled asphalt and vegetation would not have survived the 2nd stage filtration process, so it also appears that some of the containers were filled with sludge scraped from the pond bottoms. The containers into which these materials were deposited were marked as pond sludge and were indistinguishable from the rest of the 742 series containers.

PHYSICAL FORM

The question of physical form is, perhaps, easiest to address. Previous AK had identified the physical form of 2nd stage sludge as homogeneous solids. The waste identified during VE contained rolled asphalt and vegetation, seemingly inconsistent with homogeneous solids. However, Rocky Flats waste management practices allowed up to 10% of the waste in any container to be of a different physical form than the form identified for the waste stream as a whole. [4] This is consistent with the current WIPP-WAC definition for Summary Category Groups, in which the physical form of the waste stream is identified as the waste form that comprises greater than 50% of the waste in the waste stream. [2]

Evaluation of the RTR results for 549 of the containers identified in the Building 774 logbook revealed no important differences between these containers and other 2nd stage sludge waste characterized at the AMWTP. The VE operators who initially reported the anomalous waste identified it as a small component of an overall homogeneous solid waste form, insufficient to result in a change in Waste Material Parameters. [6, 8]

HAZARDOUS CONSTITUENTS

Hazardous constituents and their corresponding EPA Hazardous Waste Numbers (HWNs) identified in AMWTP waste stream profile BNINW216 and CCP waste stream profile ID-SRP-S3000, of which 2nd stage sludge is a part, are presented in Table 1. [5, 6] The constituents and HWN assignments are not identical, primarily because ID-SRP-S3000 includes IDCs not included in BNINW216.

TABLE 1. Hazardous Constituents in BNINW216 and ID-SRP-S3000. [5, 6]

EPA HWN	Constituent	BNINW216	ID-SRP-S3000
D004	arsenic	X	X
D005	barium	X	X
D006	cadmium	X	X
D007	chromium	X	X
D008	lead	X	X
D009	mercury	X	X
D010	selenium	X	X
D011	silver	X	X
D022	chloroform	X	X
D026	Cresol		X
D027	1,4-Dichlorobenzene		X
D028	1,2-Dichloroethane		X
D029	1,1-Dichloroethylene		X
D030	2,4-Dinitrotoluene		X
D032	Hexachlorobenzene		X
D034	Hexachloroethane		X
D036	Nitrobenzene		X
D037	Pentachlorophenol		X
F001	1,1,1-trichloroethane	X	X
	1,1,2-trichloro-1,2,2-trifluoroethane	X	
	1,1,2-trichloroethane	X	
	carbon tetrachloride		X
	methylene chloride	X	
	tetrachloroethylene	X	
	trichloroethylene	X	
	trichlorofluoromethane		X
F002	1,1,1-trichloroethane	X	
	1,1,2-trichloro-1,2,2-trifluoroethane	X	
	1,1,2-trichloroethane	X	
	1,2-dichlorobenzene		X
	carbon tetrachloride	X	
	chlorobenzene	X	X
	methylene chloride	X	X
	tetrachloroethylene	X	X
	trichloroethylene	X	X
	trichlorofluoromethane		X
F003	ethylbenzene	X	
F005	2-ethoxyethanol		X
	benzene		X
	carbon disulfide		X
	methyl ethyl ketone		X
	pyridine		X

EPA HWN	Constituent	BNINW216	ID-SRP-S3000
	toluene	X	X
F006	electroplating sludges	X	X
F007	cyanide plating bath solutions	X	X
F009	cyanide cleaning bath solutions	X	X

Inputs to the solar evaporation pond were examined to determine whether additional EPA Hazardous Waste Numbers might be added to the BNIN216 or ID-SRP-S3000 waste streams by inclusion of this previously unidentified input process. Based on the Building 374 Evaporation process (374-04) described in the Building 374 Waste Stream and Residue Identification and Characterization book, [19] low-level aqueous waste from Buildings 122, 123, 334, 371, 440, 443, 444, 460, 559, 707, 774, 776, 778, 779, 865, 881,883, and 889 were processed by evaporation. [7] While these liquids were processed directly from the buildings and not the evaporation ponds, it is assumed these inputs would bound those process wastes historically sent to the SEP. Hazardous constituents identified include cadmium (D006), chromium (D007), lead (D008), selenium (D010), silver (D011), carbon tetrachloride (F001), chlorinated fluorocarbons (F001, F002), methylene chloride (F002), tetrachloroethylene (F002), trichloroethylene (F002), 1,1,1-trichloroethane (F001, F002), 1,1,2-trichloro-1,2,2-trifluorethane (F001, F002), and toluene (F005). All of these HWNs and constituents are assigned to waste stream BNINW216 (Table 1). [5]

In order to be certain all inputs were addressed in this analysis, the Backlog Waste Reassessment Baseline Book (BWRBB) was reviewed for pond liquid or pond sludge. Chapter 6 identifies historical process inputs to Pond 207A including waste from Buildings 122, 123, 443, 444, 447, 559, 561, and the 700 and 800 areas. These process wastes include ignitable liquids such as acetone, methanol, ethanol, hexane, methyl ethyl ketone (F005), as well as acids, bases, and spent plating wastes (F006, F007, and F009). No additional HWNs would result based on these process inputs. [7, 11]

The sludge and liquids from the SEPs were sampled as part of site closure in the mid 1980s and in 1991. [9] As described above, Pond 207-A held process wastes during the 1980s sampling event and Pond 207-C held process wastes during both the 1980s and the 1991 sampling events. The three sections of Pond 207-B, on the other hand, were relined and did not hold process wastes after 1977. The results from these sampling events were used to bound beryllium and nitrate concentrations in the SEP pond sludge (Table 2).

Introduction of liquid waste from the Pluto Project into the SEPs by CPC raised the possibility of high beryllium concentration in the pond sludge. [12, 13, 14] Based on the results in Table 2, the pond sludge contained a maximum beryllium concentration of 1570 ppm (0.157%). [7, 9] Therefore the concentration of beryllium in this waste stream is less than 1%.

High nitrate concentration in the pond sludge was possible due to the slow evaporation of pond water. Measured nitrate concentrations in the sludge were a

maximum of 97,000 ppm (9.7%) (Table 2) The Energetic Materials Research and Testing Center (EMRTC) at the New Mexico Institute of Mining and Technology tested nitrates for classification as a 49 CFR 173 oxidizer in accordance with Method 1040. This testing determined that nitrates present below 35.5% in zeolite and 55% in grout were not oxidizers. [20, 21] Therefore, it was determined that "Pond Sludge," at a maximum 9.7% nitrate, could not be an oxidizer.

TABLE 2. Analytical Results from SEP Sampling. [9]

Pond	Analyte	1984 -1988 Results	1991 Results
207-A (liquid)	Total cyanide	ND – 1.7 ppm	0.478 ppm
	Nitrate	ND - 21,739 ppm	1,000 ppm
	pH	8.3 - 11	9.9
	Beryllium	ND - 0.1 ppm	NA
207-A (sludge)	Total cyanide	NA	NA
	Nitrate	8,800 ppm	NA
	pH	9.5	NA
	Beryllium	309 – 1,570 ppm	NA
207-C (liquid)	Total cyanide	ND – 1.9 ppm	9,650 ppm
	Nitrate	0.4 – 21,400 ppm	2,600 ppm
	pH	7.7 – 12.5	10.2
	Beryllium	ND – 0.6 ppm	NA
207-C (sludge)	Total cyanide	NA	3,200 ppm
	Nitrate	NA	97,000 ppm
	pH	NA	NA
	Beryllium	NA	ND

NA = Not analyzed, ND = Not detected

CONCLUSION AND RECOMMENDATIONS

This AK re-evaluation concluded the inclusion of "pond sludge" does not result in a change to the EPA HWN assignment to either waste stream BNINW216 or ID-SRP-S3000. Asphalt and vegetation, believed to be from the SEP liners and bottoms, comprise a small fraction of the waste, and do not affect the waste material parameter estimate or the Waste Matrix Code assignment for the waste streams. Therefore, containers marked as "Pond Sludge" are an acceptable part of waste streams BNINW216 and ID-SRP-S3000.

This case study demonstrated the uncertainty inherent in all AK because of the long time period between generation of the waste and current characterization. Records are missing, unreadable, and difficult to interpret; memories are faulty; and containers continue to surprise us with unexpected waste. AK must be continually reevaluated and updated throughout the life of the project. When disposing of legacy waste, conditions such as that described in this case study should be expected and planned for.

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