THE DISSOLUTION OF METAL DECONTAMINATION SLUDGES STORED IN TANKS AND THEIR MANAGEMENT

R. A. Prokopowicz, B. Phillips
Atomic Energy of Canada Limited,
Chalk River, Ontario, Canada.

ABSTRACT

The decontamination of stainless steel components is accomplished by the use of alkaline permanganate solutions, followed by an application of solutions of complexing agents such as citric acid or oxalic acid. Spent decontamination solutions comprising residues from both steps were combined in several waste storage tanks, where they have been in storage for several years. In those tanks, a reaction between residual permanganate and unreacted complexing agents produced sludges, consisting mainly of manganese dioxide, that reside in the tanks along with supernatant liquid. In a campaign that was conducted a few years ago, the accumulated waste solution was partially treated and disposed. This treatment consisted of decanting only the supernatant liquid and transporting it to a liquid waste treatment facility that employed a Thin Film Evaporator (TFE) to concentrate the liquid and ultimately produce a bitumen-encapsulated solidified waste form for storage. A study of treatment options for the remaining sludge is reported here. The requirement was to determine a simple means of treating the sludge using existing routine processes and equipment. This will be a significant step toward the decommissioning of the decontamination waste storage tanks. The available equipment at the liquid waste treatment facility was not designed to process sludge or slurries containing a large volume fraction of solids. Laboratory testing was carried out to find a means of dissolving the decontamination waste sludges, preferably in situ, and filtering undissolved solids to meet the feed requirements of the TFE in the liquid waste treatment facility. A concentrated citric acid solution was applied to sludge samples, without the use of externally applied mixing of the reagent and sludge. In all of the samples of actual decontamination waste sludge that were tested, a quantity of undissolved material remained after treatment with citric acid. The quantities were relatively small in volume, and easily removed by coarse filtration. Tests of these residues indicated that, while they were still radioactive, the radioactivity had been decreased relative to that of untreated sludges. Processing of the sludges, following their treatment with citric acid, involved extraction from the storage tanks and filtration to remove the small quantity of undissolved residue. The conditioned liquid stored in a holding tank is currently being processed through the TFE where its volume will be reduced and it will be mixed with a bitumen emulsion to produce a solid waste form suitable for storage in 205 L drums.

1. INTRODUCTION

As part of the legacy wastes currently stored at Chalk River Laboratories (CRL), there are seven tanks that contain Metal Decontamination Wastes (MDW). The MDW consist of sludges and supernatant liquid. Four tanks (designated A, B, C and D) contain liquid wastes and sludges that were generated by the decontamination of reactor metals. Three other tanks (designated E, F and G) contain waste that is largely the same, but contaminated by a heel of waste that was generated from fuel reprocessing operations. These seven tanks contain a total of about 2.1 m^3 of sludge and 10.3 m^3 of supernatant liquid.

Between 2003 and 2007, significant quantities of supernatant MDW liquid were successfully treated at the Waste Treatment Centre (WTC) at CRL. Liquid wastes are concentrated in a Thin Film Evaporator (TFE) at the WTC and stabilized in a bitumenized solid waste form. Based on the treatability of the MDW supernatant liquids, it would be desirable to treat the sludge in a similar manner. The goal of this treatment is to reduce the risks and liability issues associated with these seven tanks. Success achieved with this treatment may be considered a key step toward the decommissioning of the seven tanks.

Preliminary studies on the dissolution of a surrogate (inactive) MDW sludge were completed. The purpose of these studies was to establish that the sludge could be dissolved in either nitric acid, oxalic acid or a mixture of the two, and to determine a range of acid concentrations that would accomplish the dissolution in a reasonable amount of time. Results of the preliminary studies indicated that nitric acid was capable of achieving complete dissolution of the surrogate MDW sludge. The inactive sludge was prepared by reacting an alkaline permanganate solution with solutions of the same complexing agents used in metal decontamination processes at CRL. On the basis of those results, tests were conducted in which nitric acid was applied to the active MDW sludge samples, under the same conditions used to dissolve the surrogate MDW sludge; however, limited success was achieved.

A scoping study [1.] conducted in 2003 on the dissolution of similar sludge stored at the U.S. DOE Hanford site revealed that citric acid was the most suitable chemical agent for the dissolution of sludges composed primarily of manganese dioxide.

2. PRELIMINARY MEASUREMENTS AND CHARACTERIZATION OF SLUDGE SAMPLES

The tests reported here involved the collection of active MDW sludge samples from each of the seven storage tanks, and analysis of those samples to determine their compositions and key physical parameters.

2.1 Chemical Compositions of the MDW Sludge Samples

The chemical composition of the MDW sludge samples was characterized by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) to determine the concentrations of a variety of metals. Table 1 shows the measured concentrations of metals in the MDW sludge samples, for those metals having concentrations in excess of 0.1 $g \cdot L^{-1}$ of sludge. Other metals that are present in trace quantities below this limit have not been included.

2.2 Radiological Components in the MDW Sludge Samples

Solid MDW samples were all solubilized prior to analysis by the following radiochemical methods.

MDW sludge samples were screened for their total ("gross") alpha activities. To accomplish this, 50 µL aliquots were evaporated onto stainless steel planchettes, and heated to approximately 900°C in the flame of a Bunsen burner to destroy salts and ensure adherence of the deposits to each planchette. The total activity of the alpha-emitting radionuclides was measured using a silicon surface barrier alpha-spectrometer which had been calibrated using an Amersham electroplated alpha-emitting radionuclide standard containing ^{244}Cm, ^{241}Am and ^{239}Pu.

Table 1. Analysis of the Major Metallic Components in the Seven MDW Sludge Samples.

TANK	Metal Concentration in LDW Sludge ($g•L^{-1}$)								
	Mn	**Fe**	**Na**	**K**	**Cr**	**Ni**	**Ca**	**U**	**Zn**
A	37.9	2.2	25.2	3.6		0.2	0.3		
B	19.8	0.2	14.6	2.0					
C	28.9	2.7	5.3	1.0					
D	18.8	1.0	7.1	1.3		0.1			
E		2.9	6.8	2.2	0.3	0.3		7.5	
F		5.6	11.9	3.6	0.3		0.1	0.1	
G	1.0	5.7	5.4	0.1	0.2	0.2	3.8		0.6

Samples were also screened for total beta activity by Liquid Scintillation Counting (LSC). 0.5 mL aliquots of each MDW sample were diluted to 5.0 mL with distilled deionized water and mixed with 15.0 mL of an appropriate scintillation cocktail. The total activity was measured on a Beckman model 2800 LSC. The activities of ^{63}Ni in the solutions obtained from the MDW sludge samples were determined by Liquid Scintillation Counting (LSC) analysis. Nickel was isolated from the sample matrix by loading onto dimethylglyoxime (DMG) precipitation columns as the stable Ni-DMG complex. After elution of the other cations and anions by washing, the nickel was then stripped off using 3 $mol•L^{-1}$ HNO_3.

Strontium was chromatographically separated from other β and γ-emitters on a dynamically modified, C-18 reversed-phase High Performance Liquid Chromatography (HPLC) column, using a hydroxyisobutyric acid / octanesulfonic acid modified eluent. Following this separation, the ^{90}Sr activity was determined by LSC.

Gamma activities were measured on a HPGe (ORTEC co-axial 15% relative efficiency detector) gamma-spectrometer, after correction for background and normalization to the sample volume and weight.

Quantitative determination of the alpha-emitting actinides was carried out after flame charring of the samples to remove any organic residues. The ^{238}Pu, ^{239}Pu and ^{240}Pu activities were then determined by alpha spectrometry, following solvent extraction with the quaternary amine salt di-isobutylphenoxyethoxyethyldimethylbenzyl ammonium nitrate (Hyamine 1622). Plutonium in the sample was conditioned to the +4 oxidation state using a reduction-oxidation cycle employing sulfamic acid and ferrous ammonium sulfate solutions, prior to analysis. ^{241}Am was determined by alpha spectrometry, following separation from the other actinides using extraction chromatography onto a column of tri-octylphosphine oxide on a silica gel support. The alpha spectrometry system consisted of a Nuclear Data ND6700 instrument for system control and data acquisition, equipped with a Paul Downey and Co. Surface Barrier Detector and a Tri-Met™ total alpha counter with a scintillation detector (7.5 cm ZnS screen and photomultiplier tube).

Table 2 shows the results of radiological analyses of the seven sludge samples from the MDW tanks. Values for minor radionuclides less than 1.0 $MBq•L^{-1}$ have not been included.

Table 2. Analysis of the Major Radionuclides in the Seven MDW Sludge Samples.

TANK	Radiological Activity in LDW Sludge (MBq•L^{-1})							
	^{63}Ni	^{90}Sr	^{60}Co	^{137}Cs	^{241}Am	^{238}Pu	^{239}Pu	^{240}Pu
A	1.2	1.8	44.1	17.5				
B			8.3					
C			10.8	2.0				
D	1.4		95.6					
E	1.8	70.3	22.0	15.5	5.3	1.7	12.7	21.2
F		3.6		5.6	7.0	1.9	22.0	36.7
G	1.9	38.6	68.9	36.1	1.1		1.5	2.5

2.3 Physical Properties Related to Dissolution of the MDW Sludge Samples

An estimate of the bulk densities of each of the sludge samples was made by weighing each and dividing each weight by the corresponding sample volume. Three subsample aliquots were drawn from each sludge sample immediately after agitation to homogenize the material. All of the subsample aliquots were weighed and then dried at 70°C overnight followed by raising the temperature to 105°C for 24 h. The purpose of the two-stage drying was to avoid vigorous boiling which could possibly eject some material from the sample drying vessels. After the drying step, the subsample aliquots were again weighed.

Values of the average ratio of dry to wet sample weight are presented in Table 3 along with the estimated standard deviation, standard error and relative standard error. The relative standard errors ranged from 1% to 8%, and serve as an indication that the procedure produced reasonably representative subsample aliquots.

Table 3. Physical Characteristics of the Active MDW Sludge Samples.

Tank Sample	Bulk Density (g•cm^{-3})	Dry / Wet Mass Ratio	SD	SE	RSE
A	1.9 ± 0.2	0.371	0.023	0.0130	4%
B	2.2 ± 0.2	0.084	0.011	0.0065	8%
C	2.0 ± 0.2	0.110	0.005	0.0027	2%
D	1.8 ± 0.2	0.051	0.001	0.0005	1%
E	1.9 ± 0.2	0.076	0.005	0.0029	4%
F	1.9 ± 0.2	0.055	0.003	0.0019	3%
G	1.6 ± 0.1	0.053	0.001	0.0004	1%

In the table above, SD represents the standard deviation of the triplicate dry / wet ratio measurements, SE represents the standard error (SE = SD/√n, where n is the number of samples, in the present case, 3) and RSE is the relative standard error (RSE = SE/μ, where μ is the mean of the three ratios).

The values of the dry to wet sample ratio were used in subsequent calculations of the stoichiometric amounts of various dissolution agents. The assumptions are that the dried material is composed entirely of manganese dioxide (MnO_2) and that the contribution to the dry weight from total dissolved solids in the supernatant solution is negligible. Both of these assumptions lead to an over-estimation of the true MnO_2 content; however, the dissolution strategies that follow use stoichiometric excesses of the dissolution agents.

3. DISSOLUTION TESTS OF ACTIVE SLUDGE SAMPLES

Preliminary tests were conducted previously, using a surrogate (inactive) sludge that was prepared by reacting alkaline solutions of potassium permanganate with complexing agents such as oxalic acid, citric acid, hydroxyquinoline and gluconic acid. This preparation simulated the metal decontamination process that produced the seven MDW sludges. Samples of this surrogate sludge dissolved easily in nitric acid.

3.1 Sludge Dissolution in Nitric Acid and Nitric / Hydrochloric Acid Mixtures

3.1.1 Experimental Procedure

Three sample aliquots from each of the seven active MDW sludge samples were placed into centrifuge tubes. Volumes of 5.0 mol•L^{-1} HNO_3 were added, equal to 1.5 times the stoichiometric quantity required to dissolve the sludge samples. After the initial 24 h dissolution time, an additional 24 h period was used, during which agitation was applied using a laboratory flask shaker operating at a speed of 175 min^{-1}.

A second dissolution test was performed on one of the three subsamples of each sludge. In this test, additional quantities of concentrated (approximately 15.4 mol•L^{-1} HNO_3) were added to raise the acid concentration to 10.0 mol•L^{-1}.

A third test was performed in which 5.0 mL of concentrated HCl were added, subsequent to an initial attempt at dissolution using HNO_3.

3.1.2 Results and Discussion

The extent of dissolution was minimal in the case of all seven of the active sludge samples. Slight production of gas and darkening of the colour of the supernatant liquid was observed; however, there was no appreciable reduction in the total volume of solids. The application of agitation did not enhance dissolution.

Upon increasing the concentration of HNO_3 in the sample tubes, there was an additional dissolution of the solids; however, at a concentration of 10 mol•L^{-1}, the dissolution was not complete. Typical sample results are shown in Figure 1 for the Tank A sludge. The addition of 5.0 mL of HCl yielded essentially complete dissolution of the sludge.

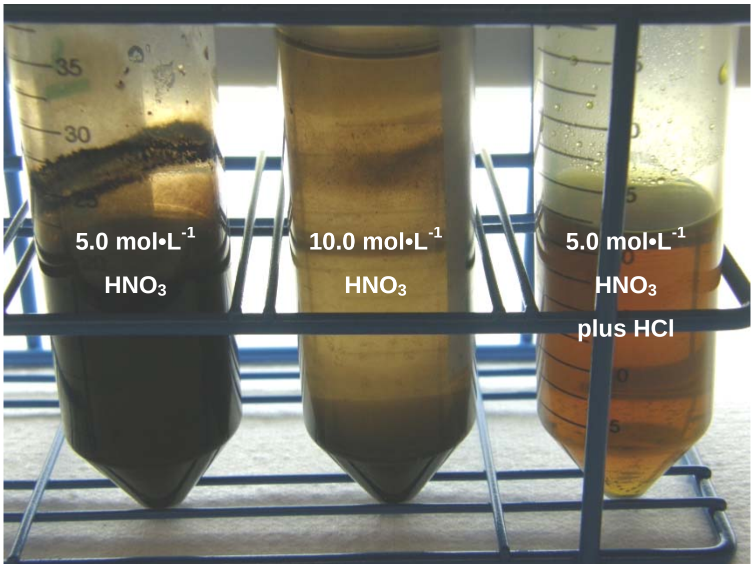

Figure 1. Dissolution of Tank A Sludge in Nitric Acid and a Nitric / Hydrochloric Acid Mixture.

3.1.3 Summary and Recommendations

Although complete dissolution of freshly prepared surrogate MDW sludge samples was easily accomplished, it does not appear that nitric acid will produce either complete or nearly complete dissolution with any of the active MDW sludge samples. Although a combination of nitric and hydrochloric acids can achieve complete dissolution, the necessary concentrations are too high to avoid unacceptable corrosion of the storage tanks and waste processing equipment.

3.2 Sludge Dissolution Tests Using Organic Acids

3.2.1 Experimental Procedure

An aliquot of each active MDW sludge was collected and reacted with a quantity of 1.0 mol•L^{-1} citric acid solution, equal to the stoichiometric quantity needed to dissolve the sludge. Observations of the colour of the supernatant and the extent to which the solids had dissolved were made after an elapsed time of 27.5 h. Following this, a further quantity of the citric acid solution was added to bring the amount of acid to a level of four times the calculated stoichiometric requirement. Observations were again recorded after a second period of 19 h.

A second experiment was conducted using a larger quantity of each of the seven active MDW sludge samples. An aliquot of 2.6 mol•L^{-1} citric acid was added to each sludge subsample in an amount equal to three times the stoichiometric requirement based on the measured quantity of sludge in the subsample. All of the samples were allowed to react for 72 h. Following that, the undissolved solids were recovered by vacuum filtration using a 5 µm polymer membrane filter. Each sample of recovered solids was rinsed using four successive aliquots of 10 mL each of deionized water, then dried overnight at a temperature of 105°C.

Four of the seven dried samples (which yielded substantial quantities of undissolved solids) were subjected to gamma counting using a gamma spectrometer equipped with a High Purity Germanium (HPGe) detector.

3.2.2 Results and Discussion

Data for the colour of the supernatant solution and an estimate of the volumes of sludge dissolved by the successive (stoichiometric followed by fourfold excess) citric acid treatments are presented in Table 4.

As expected from the results in Section 3, there was evidence (vigorous gas evolution and colouration of the supernatant) to suggest that dissolution of the active MDW sludge occurred in all seven subsamples. In the case of the sludge samples from Tanks A and C, it appeared that the addition of quantities of citric acid in excess of the calculated stoichiometric increased the amount of solids that dissolved. In the case of all of the other samples, it appeared that there was no increase in sludge dissolution when an excess of citric acid was added. The lower citric acid concentration of 1.0 mol•L^{-1} appeared to be adequate in most cases; however, in order to minimize the total liquid volumes, a concentration such as 500 g•L^{-1} (2.6 mol•L^{-1}) was recommended for use in the field.

Table 4. Results of Active MDW Sludge Dissolution in Citric Acid.

TANK	First Addition		Second Addition	
	Supernatant Colour	Sludge Dissolution	Supernatant Colour	Sludge Dissolution
A	yellow	50%	no change	80%
B	orange	> 95%	no change	> 95%
C	yellow	10%	no change	50%
D	green	> 95%	no change	> 95%
E	yellow	10%	no change	10%
F	dark orange	70%	no change	70%
G	pale yellow	50%	no change	50%

In the second experiment, three times the stoichiometric requirement of 2.6 mol•L^{-1} citric acid was chosen for the dissolutions. Solids were recovered, washed and dried from all seven of the active MDW sludge subsamples after they were subjected to the citric acid treatment. A qualitative description of the particles in the sludge samples, their estimated maximum particle sizes and the length of time needed to filter the post-treated samples through the 5 µm filter membrane are presented in Table 5. The maximum particle sizes stated in Table 5 are estimates based on visual inspection of the samples.

Of the seven active MDW sludge samples, only the one from Tank G was difficult to filter. It is possible that a major component of the undissolved portion of the sludge samples is local sand, which could have been deposited in the storage tanks during various operations.

Table 5. Sludge Particle Characteristics and Filtration Behavior following Citric Acid Treatment.

Tank	Solids Description	Maximum Particle Size (mm)	Filtration Time (h)
A	mixture of fines and particles	3	0.5
B	fine, evenly sized particles	very fine	< 0.05
C	like A but more fines	1	0.5
D	fine, evenly sized particles	very fine	< 0.05
E	coarse sand-like	2	1.0
F	very coarse sand-like particles	5	0.5
G	extremely fine, silt-like	extremely fine	6.0

3.2.3 Estimation of the Citric Acid Requirements for Sludge Dissolution

The volume values of the initial liquid and solids in each tank are given in Table 6, as well as the estimated quantity (by volume) of solids that would remain after treatment. The amount of reagent (a solution of 500 g•L^{-1} citric acid) required for each treatment has been included in the table. The assumption used to calculate the acid requirement is that the stoichiometric equivalent will suffice in all cases except Tanks A and C, in which a threefold excess was recommended.

The quantities of citric acid solution needed for each tank *i* were calculated according to:

$$\boldsymbol{Q_i = n_i V_i \left(\frac{\rho_i \epsilon_i}{C}\right)} \qquad (1)$$

where Q_i is the volume of citric acid solution (in L); n_i is the stoichiometric coefficient used for the dissolution; V_i is the volume of sludge to be dissolved (in L); ρ_i is the density of the sludge (in g•L^{-1}); ϵ_i is the ratio of the weight of MnO_2 per unit weight of wet untreated sludge; and C is the concentration of the citric acid solution (in g•L^{-1}).

There is an implicit assumption that the density of the sludge samples and the densities of the corresponding residual solids are essentially the same. For that reason, the calculated volume fraction of each sludge remaining undissolved after treatment is the same as the mass fraction that was experimentally determined in this test.

None of the treatments was able to accomplish complete dissolution of the sludge subsamples. In the cases of the sludge samples from Tanks C, E and F, the dissolution was approximately two thirds, one third and virtually none, respectively. Although the treatment appears to have no effect on the material in Tank F, the total volume of that sludge is the least amongst all seven of the MDW.

The rightmost column in Table 6 contains an estimate of the total dissolved solids concentration that will be in the solution in each tank after the citric acid treatments. This estimate was calculated according to:

$$\boldsymbol{TDS_i} = \frac{\boldsymbol{S_i \rho_i + T_i L_i + C Q_i}}{\boldsymbol{L_i + Q_i + S_i}} \tag{2}$$

where TDS_i is the total dissolved solids concentration in Tank i (in $g \bullet L^{-1}$); S_i is the volume of solids that dissolved (equal to the difference between the initial and residual volumes, in L); T_i is the concentration of dissolved solids in the supernatant liquid in tank i; L_i is the volume of supernatant liquid in tank i; and the terms ρ_i, C and Q_i are as defined for Equation (1).

Table 6. Predicted Amounts of Citric Acid Needed to Dissolve the Sludges, Estimated Total Liquid and Residual Solid Volumes and Total Dissolved Solids in the Treated Solutions.

TANK	**Total Solids** (L)	**Initial Liquid Volume** (L)	**Stoichiom. Excess Factor**	**Reagent Added** (L)	**Total Liquid Volume Estimate** (L)	**Residual Solids Estimate** (L)	**Total Dissolved Solids** ($g \bullet L^{-1}$)
A	380	950	3	400	1 676	54	26
B	60	640	1	6	703	2	484
C	900	6 650	3	289	7 490	349	31
D	360	490	1	16	864	2	11
E	170	1 000	1	12	1 079	103	20
F	30	494	1	2	496	30	28
G	220	90	1	9	306	13	4

Note: The stoichiometric excess factor represents the number of moles of citric acid added per mole of MnO_2.

The quantities of reagent solution needed to dissolve the sludges in Tanks A and C are the largest contributing volumes to the total volume required of approximately 6 600 L. This is partly due to the use of a threefold excess, and because the weight ratio of MnO_2 per unit volume of sludge is higher for Tank A than any of the other six storage tanks.

The dried samples of recovered undissolved solids from Tanks A, C, E and F were analyzed, along with corresponding samples of the untreated sludge samples, using a gamma spectrometer. Results are shown in Table 7.

Table 7. Gamma Spectrometry Results for Selected Untreated Sludge Samples and Undissolved Solids Recovered after Treatment with Citric Acid.

TANK	Measured Radionuclide Activity (kBq•g^{-1})				
	^{60}Co	^{137}Cs	^{94}Nb	^{126}Sn	^{241}Am
A	28 (100)*	2.3 (1.6)	0.2 (0.3)		0.4 (0.4)
C	51 (96)	2 (10)			0.3 (0.6)
E	67 (87)	77 (190)	0.2 (0.6)	1.1 (1.6)	81 (150)
F	1.1 (1.8)	24 (41)		1.5 (1.6)	56 (14)

*The values shown in parentheses are those of the untreated sludge samples, those not in parentheses are the corresponding values for the recovered sludge samples after treatment with citric acid, filtration, washing and drying. All values are in kBq per gram of sludge (dry basis).

For the major radionuclides that contribute the bulk of the measured gamma activity, ^{60}Co and ^{137}Cs, the citric acid treatment appears to reduce the activity remaining in the rinsed residual solids. The one exception, ^{137}Cs in the Tank A residue, is relatively small and could be the result of experimental error such as sample inhomogeneity. The activities of both of the minor radionuclides ^{94}Nb and ^{126}Sn were reduced by the citric acid treatment in all four of the samples analyzed.

The behavior of the ^{241}Am upon treatment with citric acid is inconsistent among the four samples tested. In the Tank A sludge sample, there was no apparent change. Reductions were observed for the samples from Tanks C and E, however in the case of the sample from Tank F, a substantial increase was observed.

3.2.4 Summary and Recommendations

Of the reagents tested and combinations thereof, it appears that the most practical choice would be to use citric acid alone. A relatively high concentration and stoichiometric quantities, based on the estimated mass of manganese dioxide in the sludge in each tank, seems to provide adequate dissolution in most cases. In the case of Tanks A and C, results suggest that an excess of the reagent is appropriate.

All of the treatments are expected to yield some undissolvable solids which will need to be managed as part of the overall waste processing operations.

4. APPLICATION OF SLUDGE DISSOLUTION AND PROCESSING STRATEGY

4.1 In-Tank and Ex-Tank Inspections

Prior to the application of chemical treatment to dissolve the MDW sludges (to the extent possible), an external inspection of the tanks, within the vaults that housed them, was undertaken. The inspection monitored gamma radiation fields along the bottom of each tank, in order to verify that the dose rates were consistent with values estimated from the earlier radiological analyses of the sludges inside the tanks. By so doing, it was established that the planned dissolution and retrieval operations could be accomplished safely. Also, this kind of inspection served as a means of ruling out local radiation *hot-spots*, which might have been missed in earlier analysis of samples taken from inside the tanks.

For this purpose, a special remote-controlled vehicle was designed. It consisted of a motorized electric platform with four wheels, measuring approximately 15 cm by 15 cm. The vehicle was equipped with a Personal Alarming Dosimeter (PAD) normally used to monitor gamma field intensities, and two Charge-Coupled Device (CCD) cameras. One camera was used to allow remote control of the vehicle as is was maneuvered along each tank, and the other was used to transmit data from the PAD to a remote receiving station where they could be recorded. The tank inspection vehicle is shown in Figure 2.

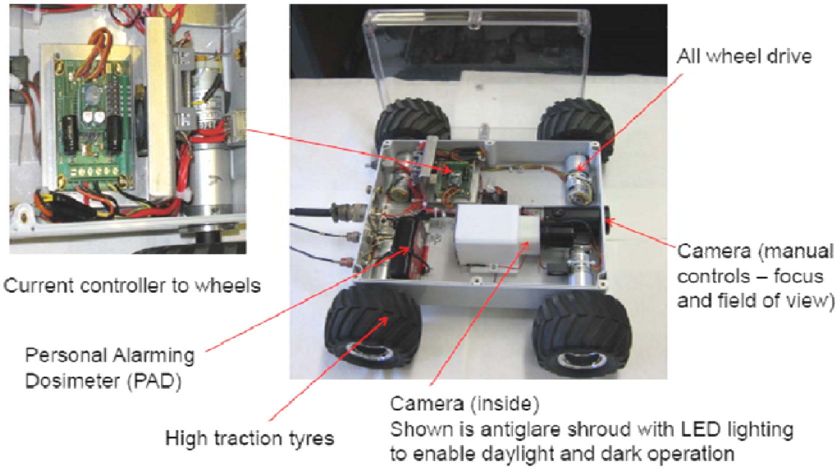

Figure 2. Ex-Tank Inspection Vehicle and its Key Components.

Results from the tank inspections indicated that there were no unexpected zones of high radiation, and that the radiation fields were consistent with values estimated from analytical data.

In addition to the measurement of radiation fields in the vaults outside the waste storage tanks, a series of video camera inspections of the tank interiors was also made. For this purpose, a miniature Pan-Tilt-Zoom integrated high-resolution colour CCD inspection camera was used. The main reason was to verify the total sludge volumes present prior to application of the citric acid for dissolution. The video cameras were also used to monitor the dispersal of the reagent into the sludge and to check for evidence of dissolution by observing gas bubbles as the reaction proceeded.

4.2 Resampling of the Sludges and Verification of Analytical Data

Before dissolved material and undissolved residual sludges were retrieved from any of the MDW tanks, samples were taken and analyzed for gross beta-gamma activity and selected alpha-emitting radionuclides. This was a check, required by the safety analysis, to demonstrate that the dissolved material could be safely transported to the WTC for further processing.

4.3 Sludge Dissolution and Waste Retrieval From the Storage Tanks

A peristaltic pump was used to meter the required quantity of 50 wt% citric acid solution into each tank. A Lutz™ pneumatic pump was used to disperse the citric acid into the sludge in each tank. In each case, the pneumatic pump was operated for a period of 0.5 h to achieve the dispersal. Following that operation, the acid / sludge mixture was allowed to stand for sufficient time for dissolution, before the liquid and undissolved residues were withdrawn from each tank.

The volumes of sludge initially present in the seven MDW storage tanks and the remaining undissolved volumes following treatment with the citric acid are presented in Table 8.

Table 8. Residual Quantities of Undissolved Sludge Following Treatment with Citric Acid.

Tank	**Tank Capacity** (m^3)	**Initial Sludge Volume** (m^3)	**Final Sludge Volume** (m^3)
A	11.0	0.38	0.20
B	11.0	0.70	0.13
C	11.0	0.90	0.38
D	11.0	0.36	0.18
E	13.8	0.17	0.13
F	15.7	0.30	0.20
G	11.0	0.22	0.05

Following the dissolution, the waste was removed from each tank through a dip tube and transfer hose assembly. A strainer was used to remove solid particles larger than 0.5 mm. The wastes were deposited into a 1.2 m^3 transfer vessel consisting of a stainless steel tank within a concrete shielded enclosure. The transfer vessel was transported overland to the location of the WTC for solidification (bitumenization) of the wastes. Batches of treated waste were placed in an interim storage tank at the WTC. A final step in the retrieval process involved flushing each tank with water, and pumping out residual waste left over from the initial removal process.

5. CONCLUSIONS

- Although the results from preliminary work with surrogate MDW sludge samples suggested that nitric acid could completely dissolve the surrogate solids, results with the active MDW sludge samples proved otherwise.
- The only combination of mineral acids that showed promise toward complete sludge dissolution was the nitric acid – hydrochloric acid mixture. This was not practical, because the presence of halides would cause damage to processing equipment.
- The most suitable choice of agent to dissolve the active MDW sludge in all seven storage tanks was a solution of 500 $g \bullet L^{-1}$ citric acid, applied under ambient temperature conditions with minimal mixing only, as required to achieve adequate reagent dispersion.
- The bulk of the material was removed from all seven of the MDW tanks. The liquid containing the dissolved solids is currently being processed into a bitumenized solid.

6. REFERENCES

[1.] Sinkov, S., *Candidate Reagents for Dissolution of Hanford Site Tank Sludges - Scoping Studies with Simulants Using Single Reagents and Their Mixtures*, Report PNNL-14378, Prepared for U.S. DOE under Contract DE-AC06-76RL01830, 2003 August.