In-Situ Remediation of Mixed Radioactive Tank Waste, Via Air Sparging and Poly-Acrylate Solidification

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ABSTRACT

This paper describes remediation activities performed in accordance with the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) on an underground storage tank (UST) from the Idaho National Laboratory's Test Area North (TAN) complex. The UST had been used to collect radioactive liquid wastes from and for the TAN evaporator. Recent analyses had found that the residual waste in Tank V-14 had contained quantities of tetrachloroethylene (PCE) in excess of F001 treatment standards. In addition, the residual waste in Tank V-14 was not completely solidified. As a result, further remediation and solidification of the waste was required before the tank could be properly disposed of at the Idaho CERCLA Disposal Facility (ICDF).

Remediation of the PCE-contaminated waste in Tank V-14 was performed by first adding sufficient water to fluidize the residual waste in the tank. This was followed by high-volume, in-situ air sparging of the fluidized waste, using air lances that were inserted to the bottom of V-14. The high-volume air sparging removed residual PCE from the fluidized waste, collecting it on granular activated carbon filters within the off-gas system. The sparged waste was then solidified by educting large-diameter crystals of an acrylic acrylate resin manufactured by WaterWorks America™ into the fluidized waste, via the air-sparging lances. To improve solidification, the air-sparging lances were rotated during the eduction step, while continuing to provide high-volume air flow into the waste. Eduction was continued until the waste had solidified sufficiently to not allow for further eduction of WaterWorks™ crystals into the waste. The tank was then disposed of at the ICDF, with the residual void volume in the tank filled with cement.

INTRODUCTION

The PM-2A Tanks site, located at Test Area North (TAN) within the Idaho National Laboratory, includes two 190,000-L (50,000-gal) abandoned, underground storage tanks that stored concentrated low-level radioactive waste from and for the TAN evaporator system. The tanks, identified as V-13 and V-14, remained in service from 1955 to 1975, until operation of the evaporator was shut down because of operational difficulties and spills [1]. Following evaporator shutdown, most of the liquid and sludge contained in these tanks was pumped into 55-gal drums, solidified with cement, and buried in the Radioactive Waste Management Complex. The remaining liquid and sludge in the tanks was then solidified with diatomaceous earth in 1981. The total residual volume of solidified waste left in these tanks was estimated at 14,500 L (3800 gal) [2].

Figure 1 shows one of the PM-2A tanks being removed from its original location at TAN. The PM-2A tanks were removed from their original locations without attempting to disturb the existing residual waste in each tank. The residual PM-2A tank wastes were suspected of being contaminated with radionuclides, heavy metals, semi-volatile organic compounds, and polychlorinated biphenyls. As a result, they were designated for remediation in accordance with the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA). Surprisingly sampling demonstrated that even though the heavy metals, semi-volatile organic compounds and polychlorinated biphenyls did not require treatment, the V-14 tank did contain sufficient volatile organic compounds so as to require treatment. While the

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Fig. 1. Removal of a PM-2A tank from its original location at TAN.

waste had been designated F001-listed; they were not expected to retain volatile organic contaminants (VOCs), due to their use in support of TAN evaporator operations. Sampling of the residual waste in Tank V-13 confirmed that its waste was solid, and contained non-appreciable quantities of VOCs (less than 0.25% of F001 treatment standards). However, residual waste sampling of V-14 identified the presence of 58 mg/kg of tetrachloroethylene (PCE) in Tank V-14 (an F001-listed contaminant), with a 90% Upper Confidence Level (UCL)[b] of 108 mg/kg. The PCE concentration in V-14 was far in excess of the F001 treatment standard (6 mg/kg) that needed to be met before it could be disposed of at the ICDF. A large volume of unabsorbed liquid was also found in V-14, which did not comply with the Waste Acceptance Criteria for disposing of the waste at the ICDF.

Therefore, while it was safe to dispose of the waste in Tank V-13, the waste in Tank V-14 would have to undergo further treatment and solidification before it could be properly disposed of. As a result additional treatment had to be designed for the residual waste in Tank V-14. This paper discusses the design, mockup testing, and application of the treatment and solidification process that was used on Tank V-14 waste.

CONCEPTUALIZATION OF THE PROPOSED REMEDIATION APPROACH

The original remedy for the PM-2A tanks was to remove and treat the tank contents, prior to excavating the tank [3]. The original approach involved initial removal of the top half of each tank, followed by vacuum extraction of the contents of each tank [4]. In early 2004, the remedy was revised allowing the

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[b]   90% UCLs are typically used to verify that Environmental Standards have been met.

PM-2A tanks to be excavated and removed with their contents intact [5]. The revised approach facilitated the requirements for closure of the PM-2A tank system, while allowing for contaminated soil remediation around the PM-2A tanks to be completed earlier than with the contents removal approach.

Once excavated, the PM-2A waste could be disposed of at the ICDF without treatment (and within the existing tanks) provided it met waste acceptance criteria (WAC) for the ICDF. Requirements for disposing of the untreated waste within the PM-2A tanks included verifying that F001 contaminant concentrations were below their respective treatment standard concentrations, that the residual waste in each tank was completely solidified (no free liquids), and that the residual void space in each tank would be filled with grout. If the waste did not meet F001 treatment standards, it had to be treated via some form of chemical oxidation or desorption to remove F001 contaminants from the waste, prior to disposal [6]. Analyses of the wastes found that waste in V-13 could be disposed of without treatment, but that V-14 needed to be both treated (to reduce PCE concentrations below 6 mg/kg) and completely solidified (due to continued presence of free liquids in V-14).

Based on these results, considerable effort was spent looking at options for removing PCE from the V-14 waste. Suggested options included using thermal blankets on top of the waste or against the excavated tank (to thermally remove PCE from the tanks), injecting hot air or steam into the waste (to drive off the PCE), and solidifying the waste with a grout that would provide high temperature curing (also sufficient to drive off the PCE). All of these potential technologies had drawbacks. They ranged from asphalt being present on the underside of V-14 (limiting the ability to heat the tank with an external blanket) to contamination control concerns associated with injecting air or steam into the relatively solid waste. Based on the technology evaluation, it was decided that the preferred approach would be to re-fluidize the waste in V-14, and then use high-volume air-sparging to strip the waste of its PCE. Following sparging, the waste was to be re-solidified using a poly-acrylate resin. Fluidizing the waste minimizes contamination control concerns associated with injecting high-volume air or steam into a relatively solid waste residue, while also minimizing mass transfer resistances within the waste residue (producing a state more prone to mixing, during high-volume air sparging). The purpose of high-volume sparging was to provide sufficient mixing of the fluidized waste, during sparging, while also accelerating the rate of PCE removal from the waste. The use of a poly-acrylate resin for solidification was to minimize the volume and mass increase associated with solidification to less than 10%.

THEORETICAL BASIS FOR USING AIR-SPARGING TO VOLATILIZE PCE

In general, VOCs in the fluidized waste stream exist in either a free phase, an adsorbed phase, or a dissolved phase. The initial concentration within each phase depends on both the composition within each phase, and the inherent properties of each contaminant (including liquid-solid equilibria).

According to the literature [7], successful use of the air sparging technology depends on the ability of the system to effectively deliver air to the treatment area and the ability of the subsurface materials to effectively transmit contaminants into the sparge air. The basic equation defining the overall mass transfer coefficient for contaminant transfer out of the waste is as follows:

$$K_L \cdot a = \cfrac{1}{\cfrac{1}{k_D \cdot k_s \cdot a_s} + \cfrac{1}{k_L \cdot a_L} + \cfrac{1}{H \cdot k_g \cdot a_g}} \qquad \text{(Eq. 1)}$$

where:

$K_L \cdot a$ = Overall liquid mass transfer coefficient; a_L = Surface area of the liquid phase;

k_D = Liquid-solid partition coefficient; H = Henry's Law constant;

k_s = Solid phase mass transfer coefficient; k_g = Gas phase mass transfer coefficient;

a_s = Surface area of the solid phase; a_g = Surface area of air bubbles; and

k_L = Liquid phase mass transfer coefficient.

Scale-up of the contaminant transfer out of a sparged slurry is in turn based on the liquid Sherwood number (Sh_L), which is a function of both the overall mass transfer coefficient (K_L) and the gaseous Reynolds number (Re_G), as follows [8]:

$$Sh_L = \frac{K_L \cdot d_B}{c \cdot D_L} = a + b \cdot Re_G{}^c \cdot Sc_L{}^d \cdot \left(\frac{d_B \cdot g^f}{D_L{}^h} \right)^j \qquad \text{(Eq. 2)}$$

where:

d_B = bubble diameter; c = total concentration, moles/L;

D_L = liquid diffusivity; a = 2 (dimensionless coefficient);

b = 0.0187 (dimensionless coefficient); c = 0.779 (dimensionless coefficient);

d = 0.546 (dimensionless coefficient); g = gravitational constant (9.81 m^2/s);

f = 1/3 (dimensionless coefficient); h = 2/3 (dimensionless coefficient); and

j = 0.116 (dimensionless coefficient).

As shown by the equations, contaminant mass transfer out of the waste matrix is a function of the transfer of absorbed contamination from the solid substrate, the transfer of dissolved contamination from the liquid substrate, and the transfer of free-phase contaminants into the sparge air. It is also a function of bubble diameter, liquid diffusivity and Reynolds number.

During air sparging, the air bubbles that pass through the waste absorb contamination from all phases that they come in contact with (primarily the dissolved and free-liquid phases). The efficiency of air sparging depends to a large extent on the contact time and resultant surface area of the bubble in contact with the liquid-phase materials. Volatilization from the liquid phase to the gaseous phase is the predominant mass transfer mechanism during air-sparging for VOCs with high Henry's Law constant values, such as PCE (the Henry's law constant for PCE is 16.9 L-atm/mole, at ambient temperatures).

While air sparging is underway, the VOCs in the aqueous phase are also being transferred by advection and/or diffusion through the porous media within the waste, prior to their being volatilized at the air-liquid interface. As contaminants are removed from the liquid phase, absorbed contaminants gradually diffuse out of the solid phase, in an attempt to re-establish equilibrium conditions with contaminant concentrations in the liquid phase. Though not the primary release mechanism, the rate of diffusion of

PCE out of the absorbed phase is the controlling rate for removing PCE from residual PM-2A waste in V-14. This is due to both the extensive amount of PCE present in the absorbed phase and the relatively slower rate of contaminant release from the absorbed phase to the liquid phases.

While the rate of PCE volatilization from the liquid to air-phase is relatively easy to predict (based on sparge rates and Henry's law), the rate of contaminant transfer from the absorbed phase is much more complicated to predict. This is primarily due to an inability to accurately define mass transfer mechanisms from the absorbed phase into the liquid, which is further complicated when non-ideal mixing conditions are present within the slurry. The complicated flow path of air during air sparging also makes it difficult to model the fundamental processes involved. As a result, predicting the rate of PCE removal experienced during air sparging is relatively uncertain using classical principles. Where possible, it is better to use laboratory-scale studies to predict the overall release rates of contaminants from the slurry, during sparging.

LABORATORY-SCALE TESTING OF AIR SPARGING IN V-14 WASTE

In support of the V-14 air-sparging process, a series of laboratory-scale air-sparging tests were performed on samples of the V-14 residual waste [9]. The purpose of these laboratory-scale tests was to define the expected rate of air sparging needed to remove PCE from the waste, within an appropriate time period (less than 28 days). Included in the evaluation was the effectiveness of both air-sparging without fluidizing the waste and air sparging after the waste had been fluidized.

The tests involved 1 kg of V-14 waste containing approximately 48 mg/kg of PCE. The 1 kg of waste was first divided into two portions of similar quantity, with the first portion left as is, and the second portion fluidized with water. Small volumes of each of these materials were placed into a 7.6-cm (3-in.) diameter glass vessel and sparged with 2-6 L/min of air for pre-determined periods, during which samples of the sparged waste were taken at periodic time intervals, to define PCE removal rates under both dry-sparge and wet-sparge conditions. Results of the laboratory-scale tests are shown in Table I.

Table I. Summary of Lab-Scale Sparging Tests.

Dry Sparging Test	PCE Concentration (µg/kg)	1st Wet Sparging Test	PCE Concentration (µg/kg)	2nd Wet Sparging Test	PCE Concentration (µg/kg)
Initial Concentration	48,000	Initial Concentration	25,000	Initial Concentration	41,000
With 22 hrs Sparging	120	With 49 hrs Sparging	1,070	With 5 hrs Sparging	6,080
With 96 hrs Added Sparging (118 hrs total)	12	With 21 hrs Added Sparging (70 hrs total)	580	With 60 hrs Added Sparging (65 hrs Total)	4,960
		After Adding 250 ml Water	400	After Adding 300 ml Water	3,090
		With 95 hrs Added Sparging (165 hrs total)	350	With 94 hrs Added Sparging (159 hrs total)	1,370
				With 51 hrs Added Sparging (210 hrs total)	120

Results of the dry-sparging tests found that a 126 g V-14 sample with an initial PCE concentration of 48,000 µg/kg could be reduced to a PCE concentration of 120 µg/kg after only 22 hrs of sparging. A PCE concentration of 12 µg/kg was reached within the next 96 hrs of sparging (118 hrs total). This was accompanied with minimal particulate carryover, at a relatively constant air sparging rate of 2 L/min.

For the first set of wet-sparge tests, the sludge samples were diluted with 250 ml of water, prior to initiating sparging. The sample was then sparged at a varying rate of 2-6 L/min. The initial PCE concentration in the slurry of 25,000 ug/kg (less than that of the dry tests, due to water addition) was reduced to 1070 µg/kg within 49 hrs of sparging and 580 µg/kg following an additional 21 hrs of sparging (70 hrs total). After adding 250 ml of water to re-fluidize the slurry (due to water loss), the resultant PCE concentration was 400 µg/kg; an additional 95 hrs of sparging (165 hrs total) reduced PCE concentrations in the slurry to 350 µg/kg.

The second set of wet tests started with a fluidized sludge containing 41,000 µg/kg of PCE (after adding 220 g of water). The higher concentration of PCE in this test (vs. the first wet test) suggested a higher volume of free liquid PCE in this sample. To improve PCE removal efficiency, a modified air sparge tube was used. The modified sparge tube had similar dimensions as that used in the previous tests, except for the presence of eight holes drilled near the capped end of the tube, and two 3-mm (0.125-in) holes at each 90º angle along the tube surface with 6.3-mm (0.25-in) hole separations. A more constant sparge rate was also used during this test. After less than 5 hrs of sparging, the PCE concentration had dropped to 6,085 µg/kg. An additional 60 hrs of sparging (65 hrs total) resulted in the PCE concentration dropping to only 4,960 µg/kg, however. This may be due to the diminished amount of liquid still present in the waste. After adding 300 ml of water (to re-fluidize the waste), the PCE concentration of 3,090 µg/kg dropped to 1,370 µg/kg, after 94 hrs of sparging, and 120 µg/kg after an additional 51 hrs of sparging.

Results of the dry and wet sparge tests showed that effective PCE removal was possible with air sparging of the PM-2A waste. Although the dry sparge tests appeared to reduce PCE concentration more rapidly than the wet tests, there were concerns that sparging the non-fluidized waste could leave pockets of untreated PCE behind in the tank, while also increasing particulate entrainment in the sparge air. As a result, a decision was made to fluidize the waste in V-14, prior to initiating sparge operations.

Analysis of the laboratory data seems to indicate diffusion control through the solid. Although the mass transfer coefficient would be constant for air stripping liquids with dissolved VOCs, the data suggests that the mass transfer coefficient for PM-2A slurry is inversely proportional to something between the square root and fifth root of the sparge time, due to the slow rate of diffusion through the solid (with the fifth root providing the best fit). According to penetration mass transfer theory [8], the mass transfer coefficient is inversely proportional to the square root of sparge time, at constant sparge rates. For this reason, an inverse square root relationship was chosen. Using this relationship, it was conservatively predicted that PCE concentrations below 6,000 µg/kg (the Land Disposal Restriction guideline) could be achieved in V-14 after 4 weeks of sparging, at a sparge rate of only 5.7 standard m^3/min (200 scfm) [10].

FULL-SCALE MOCKUP TESTING

Because of the ribbed internal structure of V-14, plans were to sparge the tank using T-shaped sparge wands that would be placed in each ribbed section of V-14. Once in place, the sparge wands would be used to blow compressed air into the fluidized waste, effectively volatilizing the PCE. Volatilized PCE would be captured via granular activated carbon filters in the attached off-gas system. Once sufficient PCE was removed, the sparge air would continue to be blown into the tank (to provide effective mixing) while inducting poly-acrylate solidification material into the waste to solidify it.

A series of two mockup tests were performed on simulated V-14 waste. The purpose of the first mockup test was to finalize design of the T-shaped sparge wands, evaluating the ability of the sparge wand to effectively sparge the entire fluidized waste volume while also keeping the waste well mixed as it was being solidified. The purpose of the second mockup test was to verify system design (following modifications prescribed by the first mockup test), while also identifying system design and processing improvements that should be implemented, prior to actual V-14 remediation.

Finding a mockup tank large enough to evaluate the proposed system was simplified by the ribbed nature of the tank. Rather than evaluating the complete multiple wand system in a 16.8 m (55 ft) long tank, the mockup test would only have to evaluate the full-scale system, as applied to a single 2.7-3.4 m (9-11 ft) portion of V-14. The tank that was used for mockup testing was a fiberglass tank, 3.4 m (11 ft) in diameter by 3.8 m (12.5 ft) long. Though slightly smaller than the 3.8-m (12.5-ft) V-14 diameter, the fiberglass tank size was sufficient to provide a good evaluation of system implementability. The fiberglass tank was placed in a horizontal orientation, with a 15 cm (6 in) high circumferential rib added to the tank, 1.6 m (5.5 ft) away from the one of the tank ends. Holes were drilled into the top of the horizontally-laid tank, to provide openings for placing the T-shaped sparge wands into the tank.

The simulated waste used in mockup testing consisted of 590-700 kg (1300-1550 lbs) of water-soaked un-ground silica sand, covered with 700-830 kg (1550-1833 lbs) of diatomaceous earth. Setup of the waste simulant was performed in a manner similar to that expected in V-14, with the silica sand and water initially added to the mockup tank, followed by placement of diatomaceous earth on top of the saturated sand. The ratio of water, sand and diatomaceous earth added to each stimulant was based on existing data as to the total water content and amount of diatomaceous earth added to V-14. Once in place, the resultant simulant appeared to be more fluid than it was in V-14. This was of minimal concern, however, since additional water was then added, sufficient to completely fluidize the simulated waste, prior to initiating air sparging. Similar fluidization is expected in V-14.

The initial T-shaped wand design that was tested consisted of two flexible 50-cm (20-in) long nozzles attached on opposite sides of a 5-cm (2-in) diameter steel center pipe; two additional sparge nozzles were also placed in the bottom of the center pipe. The flexible nozzle design was unsuccessful, however, since the nozzles were too flexible to burrow down into the waste, thereby provide insufficient mixing of waste sediments during both sparging and solidification exercises. After a number of trials, a spray wand design consisting of hard metal piping throughout the T-shaped wand was used. A diagram of the selected sparge wand design is shown in Figure 2. The selected sparge wand design has two 2.5-cm (1-in.) diameter steel pipe wands, 0.76 m (2.5 ft) long, attached perpendicularly and on opposite ends of the 5-cm (2-in) diameter center pipe, forming the T-shape design. The successful T-shaped wand design had 1.4- cm (9/16-in) diameter spray nozzles placed at the end of each wand stem, two 0.6-cm (1/4-in) diameter spray nozzles placed midway on each wand stem (at 60° orientations) and two 1-cm (3/8-in) diameter spray nozzles placed in the bottom of the T-shaped wands center pipe (at 45° orientations).

Results of the initial mockup test are summarized in EDF-5672 [11]. As part of the initial mockup test, solidification rates for different sized WaterWorks[TM] Crystal materials were also evaluated. This binder is non-toxic, non-biodegradable, highly resistant to the effects of radiation, and able to withstand standard freeze/thaw test environments. Testing was conducted using both course-grained WaterWorks[TM] Crystals (nominal diameter: 1000 µm) and standard fine-grained WaterWorks[TM] Crystals (nominal diameter: 400 µm). The results found that gel times for the course-grained crystals were almost ten times slower than that for the fine-grained crystals. With slower rates of solidification, the course-grained crystals provide better mixing of the waste with the poly-acrylate crystals, prior to solidification. This resulted in increased waste sediment incorporation in the solidified product, and less potential of free liquid accumulation in the bottom of the residual waste.
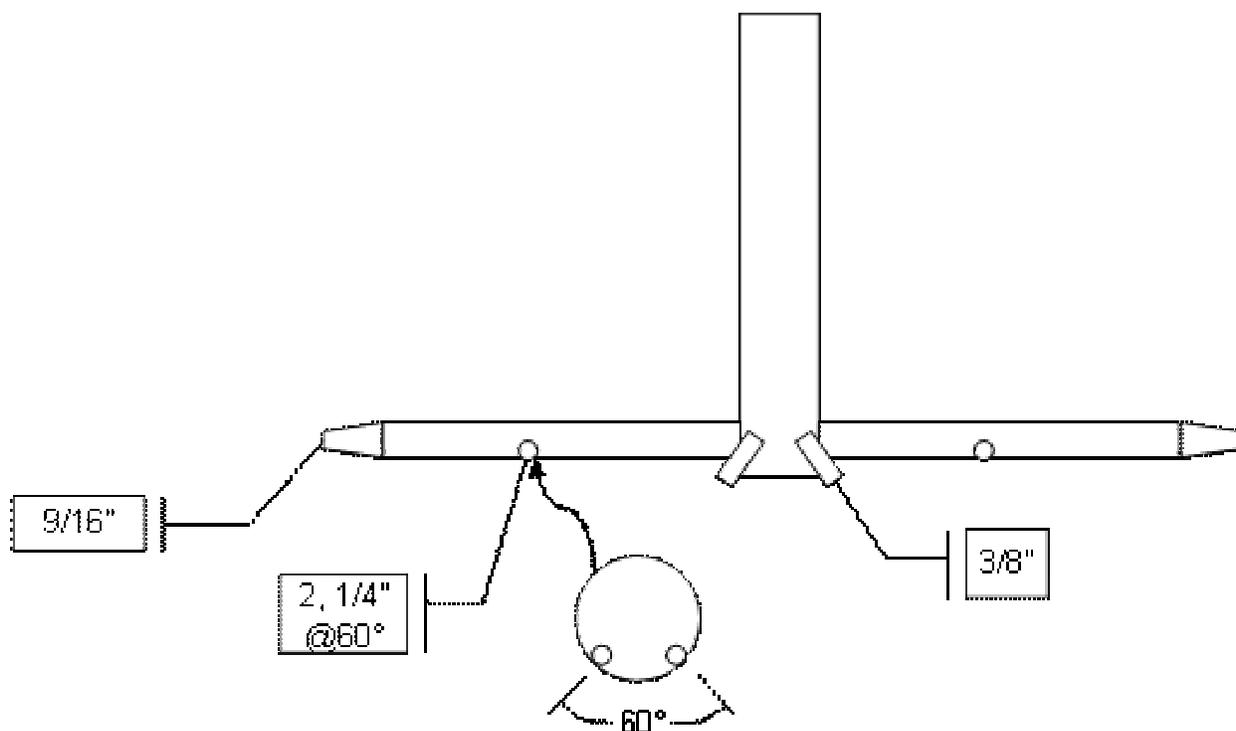
Fig. 2. T-Shaped sparge wand configuration.

During initial mockup tests, sparging and solidification operations were performed without attempting rotation of the T-shaped air lance. However, results showed that the resultant flow pattern generated by the air sparging nozzles in the T-shaped sparge wand were insufficient to mix sediments throughout the residual waste volume in the tank, no matter what level of sparging was used. Various fixed orientations were also tried, without success. The problems with inadequate mixing were particularly evident during solidification operations. In areas where mixing was insufficient within the tank, water would coalesce into settled-out sediments, limiting its ability to be solidified with WaterWorks™ crystals. The amount of unabsorbed water present in the settled sedimentary layer was high enough that core samples of the solidified waste-form failed paint-filter testing (a requirement for proving the waste to be sufficiently solid, prior to disposal). Based on these results, it was determined that mixing by direct air contact will be required for all areas of the tank, particularly during solidification operations, and that mixing will not be sufficient unless the spray wand nozzles are within 0.6 m (2 ft) of all portions of the residual waste. This resulted in the need for rotating sparge wands in the tank.

As a result, the revised sparging system that was evaluated in the second mockup test involved rotation of the air lances, during both sparging and solidification operations. The revised system involved two sparge wands being placed within each rib section, rotating during both the sparging and solidification processes. To increase mixing turbulence, the sparge rate through each wand was also increased from 2.8 standard m³/min (100 scfm) to 5.7 standard m³/min (200 scfm), resulting in a total sparge volume of (56 standard m³/min (2000 scfm).

Requiring the sparge wands to rotate during sparging and solidification operation complicated the system design, since the horizontal nature of the tank required the sparge wands to be raised and lowered, as the wand ends rotated around the curved bottom of the tank. The sparge wands also had to be designed such

that their total span was no greater than both the tank width and half the length of each ribbed section (so as to not interfere with rotation of the adjacent sparge wand within each rib section). To accomplish this design, the sparge system had swivels installed in the top of each wand, to prevent the air hoses from twisting up during each wand rotation. In addition, tool balancers were placed on each sparge wand to reduce mechanical stresses on the ends of the sparge wands, as they rose and fell through each rotation.

Results of the second mockup test are summarized in EDF-5877 [12]. Initial rotation rates of 2-3 rpm were not sufficient to guarantee rotation of the air-lances, as the wands would stall whenever they rotated into an orientation perpendicular to the horizontal axis of the tank (where rotational stresses were at a maximum). Effective sparge wand rotation was achieved at a rate of approximately 20 rpm, however. The resultant increase in sparge wand rotation, combined with a sparge rate of 5.7 standard m^3/min (200 scfm) per wand, was sufficient to provide a high level of agitation within the surrogate waste. The rotational air sparging system was successfully demonstrated for a period of over 30 minutes, without any stalling of the air lances.

Solidification operations during the second mockup test were performed using the course-grained WaterWorks[TM] material. Initial eduction rates into the tank (through the two sparge wands were around 8.6 kg/min (19 lb/min), before settling to a "steady-state" rate of 5.7 kg/min (12.5 lb/min), within 2.5-3.5 minutes after starting eduction operations. However, the rate dropped substantially, 12-15 minutes after initiating eduction, and eventually stopped altogether, as the tank waste solidified. The primary reason for this slowdown in eduction rate is due to the rapidly solidifying surrogate waste materials, which provides substantially greater pressure drop within the surrogate waste stream. The increased pressure drop minimizes the flow rate of compressed air that is available for eduction, thereby decreasing the flow rate of WaterWorks[TM] crystals into the surrogate waste. Sparge wand rotation also stopped, as the waste solidified.

Post-solidification measurements indicated that the resultant waste form had a mixing ratio slightly under the targeted ratio of 10 parts free water to 1 part WaterWorks[TM], far below the maximum ratio of 50:1 recommended for solidifying liquids. Piezometer and paint filter test measurements of the solidified waste form (taken 24 hrs after solidification) found that all of the liquid in the simulated V-14 tank waste had been successfully absorbed.   In addition, a cursory examination of the solidified waste form showed that it was relatively homogeneous, indicating that adequate mixing had been achieved.

On the basis of the second mockup test, plans were made to proceed forward with in situ sparging and solidification of the V-14 waste, using ten T-shaped sparge wands placed in the five ribbed section of V-14. The sparge wands were to be rotated at a nominal rate of 20-30 rpm, while supplying a nominal air-sparge rate of 5.7 standard m^3/min (200 scfm) to each wand.

REVALUATION OF REQUIRED SPARGE TIME, AT INCREASED SPARGE RATES

As previously discussed, a total sparge rate of only 5.7 standard m^3/min (200 scfm) was needed to complete sparging operations within 28 days. Since then, however, the sparge rate had been increased ten times, to 57 standard m^3/min (2000 scfm), or 5.7 standard m^3/min (200 scfm) per wand, in order to maintain sufficient mixing of the fluidized waste during sparging and solidification operations. Because of the substantially increased sparge rate, a new estimate was made of the required sparge time needed to achieve PCE concentrations in the waste below 6 mg/kg (the F001 treatment standard for PCE).

The new calculation was made using the same mass transfer coefficients determined from lab-testing of actual V-14 waste. Results of this evaluation are also documented in EDF-5558 [10]. Based on the results of these tests, it was estimated that only 8 hrs of sparge time would be needed to complete PCE removal operations.

IN SITU AIR SPARGING OF V-14 WASTE

In situ remediation of the V-14 waste was conducted within the V-14 tank, at a facility located at the ICDF complex. Treatment of the waste was performed in August and September of 2005. The in situ treatment of V-14 waste tank consisted of air sparging the waste, using ten sparging lines that were placed into the waste from the top of the V-14 tank. Figure 3 shows how tank V-14 was setup, in preparation for in situ air-sparging and eventual solidification. The figure shows hoppers for storing the WaterWorks[TM] material that is to be educted in the tank, during solidification, and air sparge lines going into the tank through the sparge wands that are inserted in the top of V-14.

Fig. 3. Setup of the V-14 remediation system.

To fluidize the waste, a total of 13,200 L (3,500 gal) of water was added to the tank prior to and during air-sparging operations. tank. Plans were to process the waste using a total sparge rate of 57 standard m^3/min (2000 scfm), using 5.7 standard m^3/min (200 scfm) per wand. The off-gas system that was used on this system included a demister to knock out entrained water from the sparging process, a high-efficiency particulate air (HEPA) filter system to remove radioactive particles, and granulated activated carbon (GAC) filters to remove the PCE from the off-gas, prior to its release to the atmosphere.

The ten sparge wands were to be continuously rotated throughout the sparging process. Due to the viscosity of the waste slurry, however, the motors were unable to turn the sparging units for greater than two hours at a time, before shutting down. A project decision was made to turn the sparging units by hand, during the sparging phase, rather than continuously, to avoid damage to the sparging motors. This was necessary to keep the continuous rotation available for use in the solidification phase of treatment, where continuous mixing is crucial. The ten sparging units were manually rotated 45° every four hours,

to guarantee that the sparge air came in contact with the entire fluidized V-14 waste volume. Non-continuous rotation of the sparge wands, during air-sparging operations, was found to be sufficient in volatilizing PCE out of the fluidized V-14 waste.

The treatment system had sampling ports upstream and downstream of the GAC filters. Gas samples were monitored for PCE upstream of the GAC filters to determine when treatment was complete. Sensidyne™ samples were collected every hour for the first 8 hours of sparging, and every 4-5 hours after that until the end of treatment. A summary of the off-gas data is shown in Table II. The levels of PCE detected in the sampling collection point upstream of the GAC went from 260 ppmv PCE on the first sample collected (at the start of treatment) to less than 2 ppmv after approximately 12 hours of operation. After 30 hours of treatment, the PCE levels in the off-gas were below 1 ppmv. Air-sparging operations were continued for 75 hrs. Post-GAC air samples also verified that the GAC filters were absorbing the bulk of the volatilized PCE.

Table II. Pre- and Post-GAC Air Samples, During Air-Sparge Operations.

Hours of Sparging	Pre-GAC PCE Concentrations (ppmv)	Post-GAC PCE Concentrations (ppmv)
0	260	0.5
1	55	0
2	40	0
3	30	0
4	19	0
5	7	0
6	7.5	0
7	4	0
8	5	0.25
12.5	2	0
16.5	2	0
17.5	2	0
22.5	3	0
26.5	1	0
30.5	1	0
35.5	0.75	0
40.5	0.4	1.5
47	0.6	1.5

In addition, a Fourier Transform-Infra Red (FTIR) off-gas monitoring system was utilized for part of the off-gas monitoring, in support of colorimetric sampling. Monitoring with the FTIR system started approximately 20 hours after the start of treatment and continued through the remaining 55 hrs of air sparging. The resultant data indicated peak PCE concentrations of 18.2 ppmv in the off-gas, 20 hrs after commencing air sparging operations, to 1.96 ppm at the end of air sparging operations. A graphical representation of the FTIR data is shown in Figure 4.
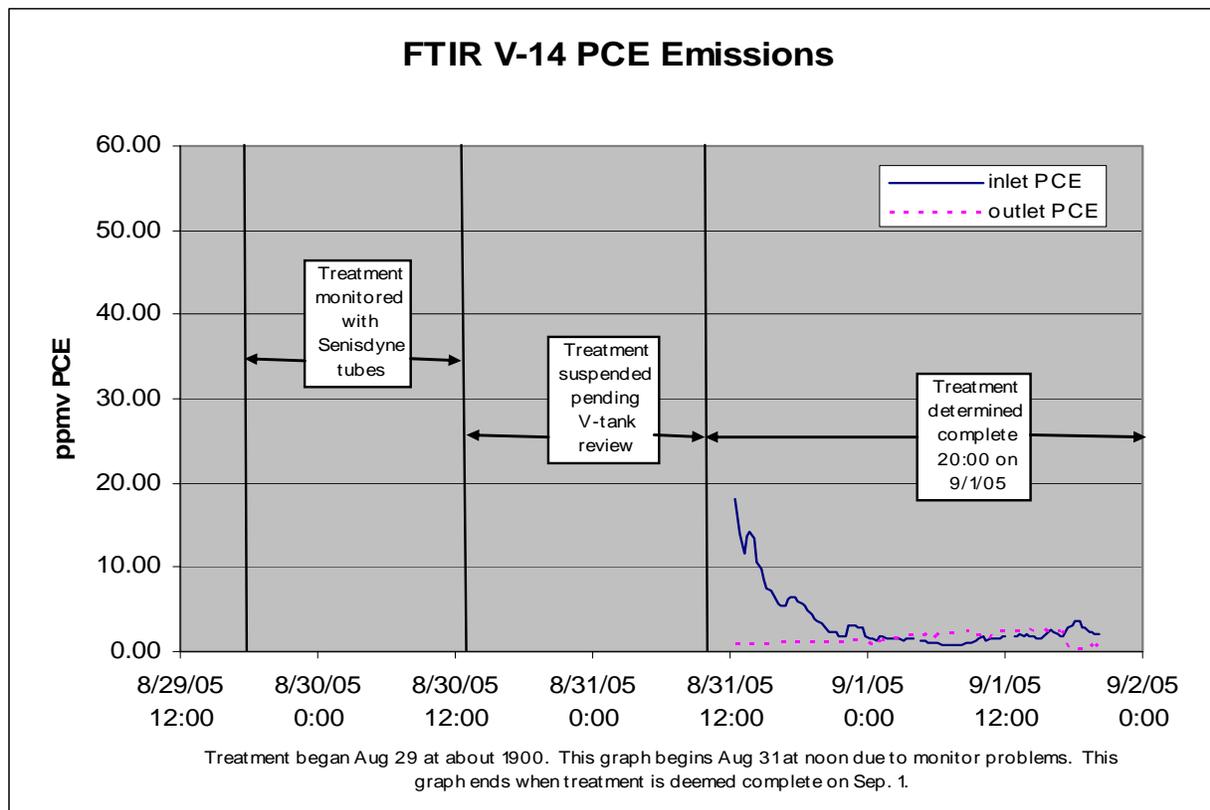
Fig. 4. FTIR off-gas monitoring results for PCE during V-14 air-sparging operations.

Screening samples of the air-sparge V-14 waste were also collected daily, starting approximately 10 hrs after air-sparging operations had commenced. The purpose of these screening samples was to provide evidence that treatment standards had been met. Small (less than 40 ml) fluidized V-14 samples were collected by pumping liquid from a location on top of the tank through tubing lowered into the sparged liquid in the tank. Following collection, the samples underwent same-day analysis for PCE concentration, at the INL's Remote Analytical Laboratory. The results of this sampling are shown in Table III. Analysis are shown in terms of both a solid sample and a liquid sample As shown in the Table, the concentration of PCE in the fluidized waste was under 11 mg/kg after 10 hrs of sparging, below 5 mg/kg after 34 hrs of sparging, and under 1 mg/kg after 58 hrs of sparging.

Table III. PCE Concentrations in V-14 Waste (Screening Data), During Air-Sparging Operations.

Hours of Sparging	PCE Concentration (mg/kg)	
	Solid Phase	Liquid Phase
~10	5.2	11
~34	4.6	NA
~58	0.99	0.17

CONFIRMATION SAMPLING OF THE AIR-SPARGED V-14 WASTE

Confirmation sampling of the air-sparge V-14 waste was performed after the off-gas data indicated that minimal levels of PCE were being volatilized via air-sparging and the screening data indicated that PCE concentration in the fluidized waste was below 6 mg/kg. The purpose of the confirmation sampling was to confirm that air-sparging treatment was successful and that LDR treatment standards would be met, once the waste was solidified. The wet-sparging treatment was expected to reduce the concentration levels of PCE adequately to comply with the LDR of 6 mg/kg in approximately 8 hrs. However, if laboratory data indicated that the levels of PCE were not acceptable, additional treatment and sampling would be performed until acceptable levels were achieved. Multiple samples were collected to measure data comparability.

The air-sparged waste was sampled from three sample ports located in the top of V-14. Sampling was performed using a specially-fabricated tool that could be extended into and remove material from the tank. During sampling, the "solids tool" was maneuvered such that the samples were collected from two side angles per hole, for a total of six distinct samples. A duplicate (split) sample was also collected from one of the locations, for a total of seven sample sets. To address questions related to buildup of solids near the ribs, one of the samples was taken adjacent to one of the ribs. Due to extensive mixing of the fluidized waste, separate liquid and solid samples were not available for collection. Instead, the seven samples that were collected from the treated waste represented both solid and liquid phases.

Confirmation sampling was performed following the commencement of air-sparging operations. A statistical analysis of the analytical data indicated that the 90% UCL concentration of PCE in Tank V-14 was 1.09 mg/kg, using spike-adjusted data. As a result, the V-14 waste appears to have been air-sparged sufficiently to reduce PCE concentrations below the LDR treatment standard of 6 mg/kg.

SOLIDIFICATION OF THE AIR-SPARGED V-14 WASTE

Following confirmation that the PCE concentration in the waste was below the 6 mg/kg, the fluidized and air-sparged waste was readied for solidification. Because of water losses during air-sparging operations, the residual waste in V-14 appeared to be relatively viscous. To guarantee initial fluidity during solidification, an additional 1,900 L (500 gal) of water was added to assist in mixing in the WaterWorks[TM] Crystals.

Solidification was performed by simultaneously educting course-grained WaterWorks[TM] crystals (nominal diameter: 1000 µm) into the fluidized waste through all ten sparge wands. During solidification operations, the sparge wands were continuously rotated to insure that the WaterWorks[TM] was mixed into the entire fluidized volume of V-14 waste. As with the second mockup tests, the course-grained WaterWorks[TM] Crystals were educted into the fluidized V-14 waste until the resultant pressure drop in the sparge lines eliminated further eduction, as the waste was solidified.

Total time for solidifying the entire volume of fluidized V-14 waste was around 70 minutes. Following the completion of solidification, a layer of unincorporated WaterWorks[TM] material appeared to cover the poly-acrylate waste form. Including the addition of 15,100 L (4,000 gal) of water, and the suspected water loss of 3,700 L (1000 gal) during air-sparging operation, the ratio of free water to WaterWorks[TM] Crystals in V-14 was estimated to be 9:1. This ratio is close to the 10:1 ratio that was suggested from mock-up testing. As a result, there was no need for paint filter tests to be performed on the solidified waste, prior to its disposal at ICDF. A video inspection of the solidified waste form, within V-14 indicated no visual presence of free liquids. The combination of conformational PCE sampling prior to solidification, along with no free liquids in the solidified waste allowed for V-14 to be accepted at the ICDF for final disposal.

CONCLUSIONS

Results of a series of laboratory studies and full-scale mockup tests were sufficient to demonstrate the in situ remediation of PCE-laden tank wastes could be performed by fluidizing the waste, air-sparging the fluidized waste to remove PCE, and then solidifying the treated waste with a poly-acrylate solidification material. In situ remediation of the V-14 tank waste was then performed, using the system design developed as a result of full-scale mockup testing. The resultant remediation was successful in lowering PCE concentrations in the waste below the LDR treatment standard of 6 mg/kg, while also solidifying the treated waste sufficiently to be disposed of at the ICDF. Similar sparging and solidification processes have been applied to other tank wastes at the INL that contain F001-listed VOCs.

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