PILOT-SCALE DECONTAMINATION SOLUTION
TEST RESULTS HGTP-93-0702-02

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SUMMARY

Grout processing equipment, including mixers, pumps, and piping, will require maintenance. Residual grout in these components must be removed to reduce dose to maintenance workers and allow hands-on maintenance. The purpose of this work was to test a proposed method of decontaminating grout processing equipment. The proposed method uses a weak acid (citric acid) to dissolve the grout. Laboratory coupon tests found that a 6 N citric acid solution heated to 60°C and used with vigorous agitation achieved almost quantitative (>95%) removal of grout within 3 h.

Pilot-scale decontamination tests were conducted using a 6 N citric acid solution heated to 60°C and used with as much agitation as possible to see if residual grout remaining after the 106-AN pilot scale runs could be removed. Two 3-h decontamination cycles were conducted with the effectiveness evaluated after each cycle. The solution was effective in removing thick deposits of grout from many components to a thickness of less than 1 mil. The removal of grout from the grout pump and surge tank was essentially complete. Components of the pump, including the rotor, the intake cavity, and the stator, were completely clean with no evidence of degradation. Testing of pump effectiveness showed no loss of performance.

Some deposits of grout remained in the dry-blend inlet area and lid of the mixer. The duct at the grout mixer outlet also had large quantities of grout that were not removed. However, poor contact with the decontamination solution is thought to be the cause of these deposits.

Based on the two pilot-scale decontamination cycles, the results are encouraging for the use of this method. Before full-scale implementation, a "cold" full-scale demonstration is recommended to ensure the decontamination solution adequately contacts the equipment and to ensure that no unforeseen problems exist.

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1.0 INTRODUCTION AND SCOPE

Decontamination solution testing constitutes a task of the Hanford Grout Technology Program (HGTP) at Pacific Northwest Laboratory (PNL).^(a) The HGTP provides technical support to the Westinghouse Hanford Company (WHC) Grout Disposal Program. Cementitious grout has been identified as the waste form for low-level radioactive waste. The grouted waste will be entombed in underground burial vaults. Grout processing equipment, including mixers, pumps, and piping, will require periodic maintenance. Decontamination of components is needed to reduce radiation dose to maintenance workers. The purpose of this work was to develop and test methods for decontaminating grout processing equipment.

The proposed method of decontamination is to use a mild chemical solution, such as a weak acid, to dissolve the grout. The method should effectively remove grout without causing degradation of grout processing equipment. A criterion as expressed in Allen et al.^(b) was that the thickness of grout should be less than 2 mil, or less than 1 mil on components with high surface area, such as pumps and mixers. These limits were based primarily on dose considerations. A desirable goal is to reduce the dose as low as possible to permit hands-on maintenance.^(c) We recommend that hands-on maintenance be considered feasible if the dose rate (distance of 30 cm) is less than 100 mrem/h. (Note the actual worker exposure can be reduced by adding shielding.) The dose limit corresponds to a total amount of residual grout less than approximately 35 g in any component.^(c)

A laboratory study, based on an earlier limestone-based grout formulation, was conducted in FY-91 and early FY-92.^(b) This '91, '92 study used grouts made with a dry-blend formulation of 40 wt% limestone flour, 28 wt% blast furnace slag, 28 wt% fly ash, and 4 wt% Type II Portland Cement. This

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- (a) Pacific Northwest Laboratory is operated for the U.S. Department of Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830.
 - (b) A report by R. P. Allen, L. K. Fetrow, H. E. Kjarmo, and K. H. Pool entitled *Decontamination Solution Development Studies*. Pacific Northwest Laboratory, PNL-8008, to be published.
 - (c) A private communication with R. E. Potter, Westinghouse Hanford Company.

study found that a moderate concentration ($\leq 1 \text{ N}$) of either citric or sulfamic acid was successful in removing grout from coupon specimens. The study also compiled and reviewed information on compatibility and found only citric acid was compatible with the (EPDM) stator material in the grout pump and with stainless steel. Owing to decontamination effectiveness and compatibility, solutions of citric acid ($\text{CH}_2(\text{COOH})\text{C}(\text{OH})(\text{COOH})\text{CH}_2(\text{COOH})$) at concentrations up to 6 N were recommended for further testing. The study also recommended that citric acid solution be tested pilot-scale.

The pilot plant had residual deposits of grout from four test runs that had been conducted. Results of these tests are described in another report.^(a) The pilot plant had processed an initial amount of more than 2000 gal of grout followed by three more runs each of about 350 gal grout at 1-week intervals. The grout mixtures in all but the last run were produced by mixing simulated 106-AN tank waste with dry-blend consisting of 14 wt% attapulgite clay, 20 wt% cement, and 66 wt% class F fly ash at a mix ratio of 8.7 lb/gal. A dry-blend composition of 11 wt% attapulgite, 20.7 wt% cement, and 68.3 wt% class F fly ash with a mix ratio of 8.4 lb/gal was used for the last run. After each run, the system was rinsed once-through with 25 gal water. Then 15 gal water was added, circulated through the system for 10 minutes, and dumped.^(a) The fly ash and the clay are relatively inert; i.e., they do not readily react with mild acids to evolve CO_2 as limestone does. Therefore, the decontamination solution may not be as effective as it was on the limestone-based formulation. Therefore, additional laboratory coupon tests were conducted using citric acid with the present formulation. It was found that 6 N citric acid solution heated to 60°C and used with maximum agitation achieved almost quantitative removal of grout from coupon specimens within 3 h. Therefore, pilot-scale tests were conducted using 6 N citric acid solution heated to 60°C and used with as much agitation as possible. The maximum temperature that could be attained in the full-scale grout processing

(a) A report by L. M. Bagaasen entitled *106-An Grout Pilot-Scale Test*. HGTP-93-0501-02. Pacific Northwest Laboratory, to be published.

facility is considered to be 60°C.^(a) Results of the pilot-scale decontamination solution tests and the laboratory tests are presented.

(a) A report by R. P. Allen, L. K. Fetrow, H. E. Kjarmo, and K. H. Pool entitled *Decontamination Solution Development Studies*. Pacific Northwest Laboratory, PNL-8008, to be published.

2.0 TEST PROCEDURES

A limited number of laboratory tests were performed using citric acid solutions with the reference grout. The testing procedures were previously described.^(a) Specimens of grout were cast onto stainless steel coupons and masked with metallographic mounting resin to expose 8.0 cm² of grout to the 300 mL of stirred citric acid solution. Dissolution rates were determined by measuring the Ca⁺⁺ ion concentration in solution using a potentiometric selective ion probe. Tests were 3 h long. The quantity of citric acid was approximately a factor of 50 in excess of stoichiometric, assuming complete reaction of the calcium in the grout.

Before decontamination solution testing was started, the pilot-scale equipment had been dismantled, and photographs were taken of the insides of processing components. The photographs showed significant accumulations of grout, estimated to be a total of approximately 5 kg.^(b) The 10 gal of 6 N citric acid decontamination solution later used for testing is about a factor of 10 in excess of stoichiometric, assuming complete reaction of the calcium. In the Full-scale Grout Processing Facility (GPF), the amount of decontamination solution to be used is approximately 600 gal.^(a) Assuming the same stoichiometry as for the pilot-scale test, approximately 300 kg of grout could be removed. Note that citric acid has three equivalents per mole, with pK_a values of 3.1, 4.7, and 5.4.^(c) Thus, 6N citric acid is 2M. Conservatively assuming only the first dissociation occurs, at least a three-fold excess of citric acid equivalents would be required to react with and dissolve the basic calcium (as CaCOH₂, CaO, or CaCO₃) in the grout. Note also that the grout deposits had cured for about 6 months before decontamination solution testing. It may have been useful to incorporate decontamination testing as an integral part of the pilot-scale lifts. Using decontamination solution after each

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- (a) A report by R. P. Allen, L. K. Fetrow, H. E. Kjarmo, and K. H. Pool entitled *Decontamination Solution Development Studies*. Pacific Northwest Laboratory, PNL-8008, to be published.
 - (b) A report by L. M. Bagaasen entitled *106-An Grout Pilot-Scale Test*. HGTP-93-0501-02. Pacific Northwest Laboratory, to be published.
 - (c) C. D. Hodgman, ed. 1963. *Handbook of Chemistry and Physics*. p. 1753. Chemical Rubber Co., Cleveland Ohio.

water rinse would have reduced grout accumulation. However, programmatic priorities delayed work on decontamination solution testing for 6 months. The appearance of the various components (see schematic, Figure 1) before decontamination testing is summarized below:

1. The dry-blend inlet to the grout mixer had thick deposits, upwards of an inch thick. Especially, the rectangular inlet to the mixer was filled, leaving a circular hole about the size of the circular inlet above.
2. The grout mixer surfaces, including the augers, the lid, and the paddles, were about half coated with a layer of grout approximately 1/16 in. thick. The areas not coated with grout were spattered with smaller amounts, and the metal parts looked rusty.
3. The funnel-shaped outlet from the grout mixer had a thick layer about an inch thick in the upper part, and the lower part was rusty looking with deposits up to about 1/16 in. thick.
4. The surge tank cone-shaped bottom had splotches of grout and was rusty looking. The lid and sprayer were coated with a thin layer of grout about 1/16 in. thick.
5. Grout deposits were about 1/2 in. thick at the grout pump inlet and over an inch thick inside the pump.
6. The flange just downstream of the grout pump had deposits on each side on the lower half of the pipe ID about 1/2 in. thick. Also a pebble-shaped piece about 1 in. in diameter was in the section leading away from the pump.
7. The grout pipe, 3/4 in. Schedule 40, was free of grout buildup.

Decontamination tests were conducted on the pilot plant. A schematic of the system is given in Figure 1. The decontamination solution, 6N citric acid, was heated to about 60°C using a stainless-steel-sheathed immersion heater. The decontamination solution was circulated through the dry-blend inlet into the grout mixer and simultaneously sprayed into the surge tank. The solution flowed through the grout mixer, the surge tank, and the grout pump, and returned to the decontamination solution tank. The grout mixer, the surge tank stirrer, and the grout pump were turned on during testing. Periodically, about every half hour, high flow was briefly sent through the waste feed inlet to the grout mixer. Decontamination solution samples (a total of 12 about 50 mL each) were taken at periodic intervals and put into polyethylene bottles. The samples were later taken to the chemical laboratory for

analysis of Ca^{++} using an ion probe. The acidity of some samples was also tested. After the cycle was completed, the solution was pumped back into the decontamination solution tank. Then the system was rinsed twice with recirculating water.

The first decontamination test involved the entire system, circulating the solution through all the components as described above. After the test was completed, the equipment was dismantled and photographed. Thick deposits were at the dry-blend inlet, primarily because a round duct led into a larger rectangular duct. Since the full-scale system has a rectangular duct leading into a rectangular dry-blend inlet, the dry-blend inlet was modified. A thick deposit of grout residue was also found at the flange downstream of the grout pump. A second decontamination cycle tested separate components. The grout pump area and the grout mixer area were tested separately. Also, the dry-blend inlet to the grout pump was changed so a rectangular duct now meets a rectangular duct. This change more closely matches the dry-blend duct configuration in the production-scale system.

The equipment was also dismantled and photographed after each pilot-scale decontamination solution test. Pumping characteristics of the grout pump were tested before starting grout operations and after completing the third decontamination test. After completing all testing, the grout pump was dismantled and photographed.

3.0 TEST RESULTS

3.1 LABORATORY TESTS

A set of coupon tests were conducted using the reference grout and different conditions: acidity (1 to 6 N), temperature (20 to 60°C), and agitation of the citric acid decontamination solution. The results are shown in Figures 2a and 2b. Removal rates increase with increasing acidity, temperature, and agitation (Figure 2a). Agitation appears to strongly affect initial dissolution rates. However, the best measure of decontamination effectiveness is the extent of reaction. Complete reaction for the test conditions would correspond to a Ca^{++} ion concentration of approximately 0.06 M. As shown in Figure 2b, near-quantitative removal of grout was achieved only under optimum conditions: maximum acidity, 6 N, highest temperature (60°C), and maximum agitation. Based upon these results, the pilot-scale tests were run with 6 N citric acid with a target temperature of 60°C and high flow rates (approximately 10 gpm).

3.2 FIRST PILOT-SCALE DECONTAMINATION CYCLE

As previously discussed, a schematic of the pilot-scale system is shown in Figure 1. The decontamination solution was injected into the grout mixer dry-blend and the surge tank using the high pressure pump. The solution flowed through the grout mixer and surge tank and was pumped back to the decontamination solution tank using the grout pump. The valves to the surge tank and dry-blend inlet were adjusted to have a combined flow of decontamination solution through the system of about 10 gpm. The flow in excess of 10 gpm passed through a pressure relief valve back into the decontamination solution tank. The grout mixer and surge tank stirrer were turned on during testing. Once every half hour, a surge of decontamination solution was sent through the grout mixer by opening the waste feed inlet valve.

The solution became very muddy within a few seconds after startup. The recirculating solution soon became an abrasive slurry of suspended grout that offers additional scrubbing for the surfaces that the solution contacts.

Slurry samples taken from the tests all contained significant amounts of solids that settled out and did not dissolve. These solids are presumably non-reactive grout components.

After about 80 min of testing, operators found that the sprayer nozzles in the surge tank were clogged with small pieces of polyethylene. The source of the plastic was drill shavings resulting from holes bored in a small plastic carboy used to prevent large pieces of grout from being drawn into the high-pressure decontamination solution pump. To alleviate this problem, caps were removed from six of the sprayer nozzles, leaving a 1/32-in. orifice in the uncapped nozzles. For the duration of the test, the decontamination solution sprayed through these uncapped nozzles without clogging.

The grout pump amperage during the test is shown in Figure 3. The amperage provides an indication of whether the solution would adversely impact pump performance. Testing started when the grout pump was turned on at minute 125. Testing was stopped for about 25 min at minute 205 to fix the surge tank sprayer nozzles. Testing then resumed until a total of 3 h testing was completed. The peaks at minute 370 and 390 reflect water rinses done after completing decontamination solution testing. The pump amperage was essentially constant during testing, indicating the decontamination solution did not adversely impact pump performance. Pump discharge pressure and flow rate are shown in Figure 4. Both are essentially constant during the first 80 min. After fixing the clogged nozzles in the surge tank, the flow through the system was readjusted to a higher level. This higher flow rate and corresponding system pressure were relatively constant for the final 100 min.

Temperatures recorded in the decontamination solution tank and in the surge tank are shown in Figure 5. The original solution was heated above 60°C before the start of testing, but it quickly cooled to about 45 to 50°C when the solution was circulated through the pilot plant. The solution remained in this temperature range for the entire test.

After the first decontamination test was completed, only 6 to 7 gal out of the original 10 gal were recovered. We believe about three gal evaporated

during the 3 h testing. The high evaporation rate, about 1 gph, may have resulted from using spray nozzles in a system that is not totally sealed from the ambient air.

Samples of solution were taken and analyzed for calcium content. Results are shown in Figure 6. The raw data show a very fast increase in calcium ion concentration in the first 30 to 60 min, followed by a slower increase. However, about 3 gal of solution were lost in 3 h. Assuming the loss was due to evaporation of water at a rate of 1 gph, the concentration of calcium would increase even if no further dissolution of grout were occurring. When corrected for an assumed constant evaporation rate of 1 gph, the concentration is approximately constant after about 30 min. Note that since the rate and the amount of evaporation are not precisely known, the uncertainty is estimated as about 30%. The conclusion is that most of the reaction occurred in the first 30 min, and little reaction occurred thereafter. This result differs from the laboratory coupon tests, which showed a leveling off after 3 h. Reaction rates appear to be much faster in the pilot scale tests.

To check calcium solubility, we dissolved calcium nitrate in 6N citric acid to a concentration of 3.5 M. No precipitate formed. Therefore, the solubility of calcium citrate in 6N citric acid is more than a factor of ten higher than test conditions. Samples of sediment that had settled out from the solution were examined for calcium content and $1.5 \pm 0.1\%$ was found. This amount is less than one fourth of the original content. We also checked to see if the solids would resuspend. After two months, shaking samples easily resuspended the material.

Note also that before testing, the quality of the grout residue was variable. The grout had dried out for about 6 months, thereby allowing it to crack, and possibly delaminate from surfaces. Also, the initial surface area of the residual grout was comparatively high. All these factors contributed to the very fast rates of removal at the beginning of the first pilot-scale test.

The acid normality of the solution was also analyzed by titration (see Figure 7). The raw data show the acidity decreased at first, followed by a slow increase owing to evaporation. The actual normality varied from about

5.4 to 6.5 during the test. When we correct for evaporation effects, the acid concentration is about constant after the first 30 min. The slow decline may imply that some decontamination continues at a slower rate. Owing to the uncertainties in evaporation rate, noted above, this slow decline may not be significant.

After the first pilot-scale decontamination solution test was completed, the components were dismantled and photographed. Selected photographs of key components before and after the decontamination test are presented in Figures 8a and b to 15a and b to allow a direct comparison of the effectiveness of the decontamination. A discussion of the observations follows.

- Figures 8a and 8b - The dry-blend inlet to the grout mixer had thick deposits. The dry-blend inlet had a round (~3 in.) pipe going into a rectangular hole (~4 in. x 6 in.). Grout had filled the rectangular channel, leaving only a circular opening. Thus, grout was several inches thick at the dry-blend inlet to the grout pump. The screw-feed auger surfaces were completely coated with grout. After the first decontamination test, the solution had removed some of the very thick grout deposits in the channel, but about half of the material remained. Note that in the actual application, this grout will not be as radioactive, since this area is still upstream of the waste feed inlet. Thus, a thicker deposit could be tolerable here. After the first decontamination, the auger was mostly clean with only small splotches of grout.
- Figures 9a and 9b - The grout mixer cover before and after testing is shown. Before testing, surfaces inside the grout mixer were generally coated with a layer of grout about 1/16 in. thick and rusty looking. After the first decontamination test, the components inside the mixer looked shiny with no rust color. Small amounts of grout remained on the cover, augers, and mixer paddles. Most of the grout was removed from the lid, except for a thick deposit that remained in the area of the dry-blend inlet.
- Figures 10a and 10b - The inside of the mixer, with the augers and mixer paddles, is shown. The decontamination solution removed most of the grout from these components.
- Figures 11a and 11b - The funnel-shaped outlet from the grout mixer had a thick layer about an inch thick in the upper part, and the lower part was rusty looking with deposits up to about 1/16 in. thick. The first decontamination removed some grout from the lower portion, but a thick deposit remained at the upper portion. There also was a 1/2 in. thick deposit on one side of the 3-in. pipe leading from the outlet. It is possible that these areas did not get good contact from the decontamination solution.

- Figures 12a and 12b and Figures 13a and 13b - The surge tank cone-shaped bottom had splotches of grout and was rusty looking. After testing, the surge tank looked shiny and clean. The lid and the sprayer were coated with a thin layer of grout about 1/16 in. thick. After the first test, these areas were mostly clean except for a small area that was not washed on the back side of the sprayer.
- Figures 14a and 14b - Before testing, the grout pump inlet (Figure 14a) had deposits over an inch thick. After testing (Figure 14b), the inlet was free of grout.
- Figures 15a and 15b - The flange just downstream of the grout pump had deposits on each side on the lower half of the pipe ID about 1/2 in. thick. The side looking back towards the grout pump is shown before and after the first test in Figures 15a and 15b. The test removed about half the grout.

Overall, the results of this test were very encouraging. The grout had cured for several months, the temperature was 10 to 15°C lower than the target value, and yet the decontamination was very effective in many areas. Critical areas that may need repair, such as the grout pump and the surge tank, were effectively decontaminated. Some areas where grout remained may not have contacted the solution because the grout mixer still had significant deposits of grout. It was decided to re-test specific components: the grout pump and the grout mixer areas.

3.3 SECOND PILOT-SCALE DECONTAMINATION CYCLE

The second decontamination cycle involved individual components rather than the entire integrated system. Separate runs involved first the grout pump and surge tank, then the grout mixer area.

3.3.1 Second Decontamination Cycle, Run 1 - Surge Tank and Grout Pump

The first run of the second decontamination cycle tested the grout pump and the surge tank. Results from the first decontamination cycle had shown a deposit in the area of the flange downstream of the pump. This deposit was very hard in comparison to other thick deposits. The decontamination solution was initially injected at the grout pump inlet. However, the energy added to the solution with the high pressure pump soon heated the solution to 75°C. The solution was then injected into both the surge tank nozzles and the pump inlet to increase the effective heat loss area and help control solution

temperatures at about 60 to 65°C (Figure 16). After the solution was injected into the surge tank (25 min into the run), a thermocouple was put in the decontamination solution tank to provide a second temperature monitor. Pump amperage (Figure 17), pressure, and flow (Figure 18) were essentially constant during testing.

During testing, the solution again became a turbid brownish grey color, but the amount of suspended material was much less. This is because the amount of grout represented by the deposit in the flange area (the order of 250 g) was much less than the total amount in the system (about 5 kg) before the first decontamination cycle. Results of chemical analysis, showing calcium ion content and acidity of solution samples, are shown in Figure 19. The acidity is constant throughout the test, indicating that no significant evaporation occurred. The calcium ion level was slowly increasing throughout the test. Note the quantity of calcium dissolved was a factor of 20 lower than in the decontamination cycle. The apparent rate of reaction was slower than in the first decontamination cycle. Whereas in the first cycle most of the reaction occurred in the first 30 min, in this test it was still occurring after 3 h. The rate of this test was comparable to that for the laboratory tests. It appears that this deposit of grout is more difficult to remove than the large amounts that were easily removed in the first cycle. Note this area had fluid present, and this grout may not have dried out and cracked. Photographs of the pump area will be presented later in this report.

3.3.2 Second Decontamination Cycle, Run 2 - The Grout Mixer Area

The second run of the second decontamination cycle involved the grout mixer area. A new square duct with sprayers inside was installed at the dry-blend inlet to the grout mixer. Decontamination solution was pumped from the decontamination solution tank through the nozzles in the dry-blend inlet, through the grout mixer, and back to the decontamination solution tank. Temperatures (Figure 20) were about 60 to 65°C after the first 20 min of testing. Since the flow and pressure measurement is associated with the grout pump, no time dependant data are available. Subsequent measurements with water indicated the flow rate through the dry-blend inlet was approximately 13 gpm.

Measured acidity of the solution is shown in Figure 21. The raw data shows an increase in acidity after the first 30 min. The increase in acidity is ascribed to concentration of the solution by evaporation. Assuming a constant evaporation rate of 0.5 gph, the acidity is essentially constant after the first 30 min.

The calcium ion concentrations of the solution are shown in Figure 22. The raw data and the data corrected for effects of evaporation, assuming a constant evaporation rate of 0.5 gph, are shown. Both curves show a relatively rapid reaction rate for the first hour and a slower rate thereafter. The final concentration corresponds to the dissolution of about 2.5 kg of grout.

After both runs of the second decontamination cycle were completed, the system was rinsed with water. Then the components were dismantled and a set of photographs taken. Selected photographs are shown in Figures 23 to 31. Comments follow:

- Figure 23 - This figure shows the new square duct that matched the dimensions of the grout mixer dry-blend inlet. Inlets to sprayer nozzles on each side can be seen.
- Figure 24 - The inlet to the grout mixer is now almost free of grout. Thick deposits were removed in the second decontamination cycle.
- Figure 25 - This figure shows the lid to the grout mixer after the last test. Some grout remains, particularly in the area by the dry-blend inlet. The square duct at the inlet and an area between the square dry-blend inlet and the round waste feed inlet have noticeable deposits of residual grout. The rest of the lid has some thin streaks of residual grout.
- Figure 26a and 26b - These figures show the grout mixer internal parts, including the augers and the paddles. These components are largely free of grout, with some thin streaks of residue left.
- Figure 27 - After testing, the outlet of the grout mixer still has thick deposits at the upper part and in the circular pipe below. The flow of the solution may not have contacted these surfaces.
- Figure 28 and 29 - The surge tank (Figure 28) and surge tank lid and sprayer (Figure 29) are almost free of any grout, except for a few small scattered parts of the sprayer itself that may not be contacted by the solution.

- Figure 30 - The grout pump inlet is free of grout.
- Figure 31 - The flange area downstream of the pump is largely free of grout. A small amount is still present on the side of the flange back towards the pump.

3.4 TESTING OF GROUT PUMP PERFORMANCE

After completing of decontamination solution testing described above, we evaluated the performance of the grout pump. Bleed-down was measured by pressurizing the pump to 100 psi following the pressure drop. The bleed-down time was longer than the original test before the 106-AN pilot-scale runs. Pumping speed was essentially independent of pressure from 30 to 90 psi for normal operating conditions. Therefore, pump characteristics were satisfactory after decontamination solution testing was completed.

After the performance of the grout pump was tested, the pump was dismantled and photographed. The stainless steel rotor is shown in Figures 32a and 32b. The rotor was free of any grout. The inside of the pump was also free of grout. However, a small piece of yellow plastic (possibly a screw-driver handle) was found inside the pump.

3.5 MEASUREMENT OF RESIDUAL GROUT

After testing was completed, components were disassembled, and the grout residue was scraped from the surfaces and collected. The results are presented in Table 1. Reported amounts were corrected for the fractional recovery. The actual amount collected was divided by the estimated fractional recovery. The density of the cured grout was assumed to be 1.4 g/cm^3 , reduced from the nominal value of approximately 1.5 g/cm^3 for cured grout to account for drying. Calculated thicknesses for major components, such as the grout mixer (except for an area on the lid), the surge tank, and the grout pump, are less than 1 mil. Calculated dose, gamma only, assuming a point source at a distance of 1 ft, is less than 100 mrem/h for most components. Therefore, thus most components meet the requirements for hands-on maintenance.

A few locations still have significant deposits of grout, such as the dry-blend inlet area and the outlet duct of the grout mixer. The pipe above the dry-blend inlet to the grout mixer had a thickness of 39 mil, but this

grout would not have much radioactivity because this area is upstream of the waste feed inlet. Therefore, the dose is essentially zero. The dry-blend inlet duct had an average deposit thickness of 9 mil, but this also is upstream of the waste feed inlet. Note this 9 mil thickness is less than 1% of the original thickness of an inch or more. The dose rate in this area is conservatively estimated as 62 mrem/h. A problem area existed where a 38-g deposit about 50 mil thick remained on the grout mixer lid near the dry-blend inlet. The rest of the lid had only 7 g, or an average thickness of 1.9 mil. Grout mixer surfaces, including augers and paddles, had an average thickness of only about 0.5 mil. Excluding the inlet duct and the small area near the inlet duct, the entire grout mixer had only 25.6 g of residue, corresponding to an average thickness of 0.65 mil and an estimated dose of 73 mrem/h. Hands-on maintenance of the mixer appears possible, but the area on the lid may cause problems.

The outlet duct of the grout mixer had thick deposits that were not removed by the tests. It is possible the solution did not contact either the upper part of the outlet duct or one side of the outlet pipe. These areas each contained several hundred grams of grout, and estimated doses are greater than 1 rem/h. The clean area of the outlet duct had only about 3 g of material, or an average thickness of 0.5 mil, with a dose of 9 mrem/h, well within the requirements.

Decontamination of the surge tank, including the lid and sprayer, was excellent. A total of less than 1 g of grout remained. The average thickness was 0.022 mil, and the total dose was 3 mrem/h, well within requirements for hands-on maintenance.

The grout pump had no detectible grout. Thus, it was effectively cleaned by the solution. The outlet of the pump, downstream by a flange, had a deposit about 1/2 in. thick. After the last test, only about 2 g were found. The thickness of the small 10-in.² area was about 10 mil, but the average over the entire flange area is less. The calculated dose is small, only 6 mrem/h.

TABLE 1. Residual Grout After Decontamination Testing

<u>Component, (% recov.)</u>	<u>Amount (g)</u>	<u>Area (in.²)</u>	<u>Thick. (mil)</u>	<u>Est. Dose (mrem/h)</u>	<u>Meets Req?</u>	<u>Comments</u>
Pipe above Dry-Blend Inlet (95)	270.5	302.	39.1	-0	yes	Not Radio-active
Mixer Lid, Dry-Blend Duct (95)	21.6	104.	9.0	62.	yes	>99% Removed
Mixer Lid, Near Dry-Blend Duct (95)	38.5	34.	49.3	110.	no	Problem Area
Rest of Grout Mixer Lid (95)	7.0	162.	1.9	20.	yes	
Grout Mixer Inside Surfaces (50)	18.7	1550.	0.52	53.	yes	Look Good
Mixer, Total Less Dry-Blend Duct	64.1	1750.	1.60	180.	no	Some Problems
Mixer, Less Area by Dry-Blend Duct	25.6	1710.	0.65	73.	yes	
Grout Mixer Outlet, Clean Area (95)	3.1	272.	0.50	9.	yes	
Grout Mixer Outlet, Upper Area (95)	634.7	233.	118.	1800.	no	Problem Area
Grout Mixer Outlet, Dep. in Pipe (95)	499.0	51.	426.	1400.	no	Problem Area
Surge Tank Cone (80)	0.0125	1140.	0.00048	0.04	yes	
Surge Tank Lid (80)	0.20	707.	0.0123	0.6	yes	
Surge Tank Sprayer (50)	0.72	10.	3.14	2.0	yes	
Surge Tank, Total	0.93	1857.	0.022	3.	yes	
Grout Pump	0.0	--	0.00	-0.	yes	
Flange Downstream of Grout Pump (75)	2.25	10.	9.8	6.	yes	

4.0 DISCUSSION

The requirement for decontamination is to remove the grout to permit hands-on maintenance. Low dose rate minimizes worker exposure and simplifies maintenance operations. Higher dose rates make maintenance more difficult, but not impossible. Removal of grout implies removal of contamination, i.e., ^{137}Cs . A recommended criterion is that the residual amount in any component be less than 35 g. This requirement was met for the grout pump and the surge tank. This requirement was also met for most of the grout mixer, except for deposits that remained on the lid near the dry-blend inlet and the dry-blend inlet duct itself. The process was effective in removing thick deposits of grout in the dry-blend inlet area and in the grout pump. However some problem areas remained. Some thick deposits of grout in the duct of the grout pump outlet were not removed even after a total of 6 h testing. Probably these areas were not effectively contacted by the decontamination solution. If the solution does not contact the area, lengthening the time will be of no benefit. However, the deposit at the outlet of the grout pump was mostly removed in the second 3 h test. It may be anticipated that heavy deposits could be removed by operating longer than 3 h, provided there is good contact. Based on the results of the dry-blend inlet, adding sprayers would be expected to remove the grout from problem areas such as the mixer outlet duct.

Except for a few areas noted above, the solution was effective in removing grout, even at 50°C. In the first decontamination cycle, rates of grout removal were faster than in laboratory coupon tests. This rapid initial rate may have been a result of thick deposits of grout that were poorly adhered. It is also possible that recirculating the grout solution, with the abrasive components of suspended grout, is effective. The test of the grout pump flange area had slower rates, possibly because this deposit was of a more dense and well-adhered material.

The removal of grout from the grout pump was complete. It initially had deposits an inch thick or more. Testing the pumping effectiveness showed no loss of performance. Components of the pump, including the rotor and the stator, were completely clean with no evidence of degradation.

The citric acid solutions may not be suitable for disposal in the grout vaults owing to the organic content and the reactivity with grout components. Interim storage would involve neutralizing and putting in a tank. Some precipitates could form as the pH is adjusted for disposal. As a check, two samples of solution from the first test were filtered and NaOH added until the pH was approximately 12. The solutions did become slightly cloudy, indicating some small amount of precipitation is possible. The used decontamination solutions will contain both suspended solids and granular materials that will have to be handled. A small amount of precipitate is not likely to change handling requirements. The amount of citric acid could be minimized by processing the solutions to remove or destroy the citric acid. The solutions should be re-used as much as possible to minimize the total amounts requiring disposal.

5.0 CONCLUSIONS AND RECOMMENDATIONS

Pilot-scale tests of decontamination solution were conducted. Laboratory tests identified optimum conditions: 6 N citric acid at about 60°C with maximum agitation. These conditions were used in two pilot-scale decontamination cycles, although the temperature was about 10°C below the target temperature for the first cycle. The 6 N citric acid decontamination solution was recirculated, and sprayers were used to maximize the agitation and the effectiveness of contact with surfaces. The conclusions and recommendations are

1. The reference decontamination solution, 6 N citric acid heated to about 60°C, is effective in removing grout. Even thick deposits were removed to a thickness of less than 1 mil.
2. Critical components were effectively decontaminated by the process. The surge tank and the grout pump were essentially cleaned of grout. Most of grout mixer was cleaned, but a few problem areas remained for this component.
3. In some areas, grout deposits remained, particularly in the grout mixer outlet duct. Also, an area on the grout mixer lid had a deposit that was not removed. The solution probably did not effectively contact these areas. Adding more sprayers or other design changes should allow better solution contact and permit more complete decontamination.
4. The grout pump was effectively cleaned by the process without any loss of performance or evidence of corrosion.
5. Based on two cycles, no adverse corrosion or other degradation effects were observed. Information on lifetime of components, such as the grout pump stator, is not available. Additional laboratory corrosion studies would be required to determine such limits.
6. Citric acid solutions may not be suitable for disposal in the grout vault owing to its organic content and its reactivity with grout components. Therefore, amounts should be minimized and the solution should be re-used if possible. The possibility of separating, reacting, or otherwise processing the used solutions to remove or recycle the citric acid can be investigated.
7. Drying the grout may improve removal rates. Additional testing with dried grouts can be pursued if rate enhancement is required.
8. Overall, the results are encouraging. The use of 6 N citric acid as a solution to remove radioactive grout looks very promising. Testing on a full-scale system is recommended to ensure the decontamination solution adequately contacts the equipment.

6.0 FIGURES

Pilot-Scale Decontamination Solution Test

—✕— Valve Normally Closed

—◇— Valve Normally Open

FIGURE 1. Schematic of the Pilot-Scale System

FIGURE 2a. Initial Grout Dissolution Rate for Coupon Specimens as a Function of Temperature and Acid Normality

FIGURE 2b. Final Calcium Ion Concentration as a Function of Temperature and Acidity

FIGURE 3. Grout Pump Current Draw During First Decontamination Cycle

FIGURE 4. Grout Pump Discharge Pressure and Flow During First Decontamination Cycle

FIGURE 5. Citric Acid Solution Temperatures During First Decontamination Cycle

FIGURE 6. Measured Calcium Ion Concentration for the First Pilot-Scale Decontamination Cycle; Raw Data and Data Corrected for an Assumed Water Evaporation Rate of 1 gal/h

FIGURE 7. Citric Acid Concentration (N) for the First Pilot-Scale Decontamination Cycle; Raw Data and Data Corrected for an Assumed Evaporation Rate of 1 gal/h

FIGURE 8a. Grout Mixer Dry-Blend Inlet Before Decontamination Testing

FIGURE 8b. Grout Mixer Dry-Blend Inlet After First Decontamination Cycle

FIGURE 9a. Grout Mixer Cover Before Decontamination Testing

FIGURE 9b. Grout Mixer Cover After First Decontamination Cycle

FIGURE 10a. Grout Mixer with Cover Removed Before Decontamination Testing

FIGURE 10b. Grout Mixer with Cover Removed After First Decontamination Cycle

FIGURE 11a. Outlet from Grout Mixer Before Decontamination Testing

FIGURE 11b. Outlet from Grout Mixer After First Decontamination Cycle

FIGURE 12a. Surge Tank Before Decontamination Testing

FIGURE 12b. Surge Tank After First Decontamination Cycle

FIGURE 13a. Surge Tank Lid and Sprayer Before Decontamination Testing

FIGURE 13b. Surge Tank Lid and Sprayer After First Decontamination Cycle

FIGURE 14a. Grout Pump Inlet Before Decontamination Testing

FIGURE 14b. Grout Pump Inlet After First Decontamination Cycle

FIGURE 15a. Flange Just Downstream of Grout Pump Before Decontamination Testing

FIGURE 15b. Flange Just Downstream of Grout Pump After First Decontamination Cycle

FIGURE 16. Citric Acid Solution Temperatures During Second Decontamination Cycle, Run 1 - Grout Pump Area

FIGURE 17. Grout Pump Current Draw During Second Decontamination Cycle

FIGURE 18. Grout Pump Discharge Pressure and Flow During Second Decontamination Cycle

FIGURE 19. Measured Calcium Ion Concentration and Acidity for the Second Pilot-Scale Decontamination Cycle, Run 1, Testing Grout Pump Area

FIGURE 20. Citric Acid Solution Temperatures During Second Decontamination Cycle, Run 2 - Grout Mixer Area

FIGURE 21. Citric Acid Concentration for the Second Decontamination Cycle, Run 2 - Grout Mixer Area, As Measured and As Corrected for an Assumed Evaporation Rate of 0.5 gal/h.

FIGURE 22. Calcium Ion Concentration for the Second Decontamination Cycle, Run 2 - Grout Mixer Area, As Measured and As Corrected for an Assumed Evaporation Rate of 0.5 gal/h

FIGURE 23. Modified Rectangular Duct Above Grout Mixer Dry-Blend Inlet

FIGURE 24. Grout Mixer Dry-Blend Inlet After Second Decontamination Cycle

FIGURE 25. Grout Mixer Cover After Second Decontamination Cycle

FIGURE 26a. Grout Mixer with Cover Removed After Second Decontamination Cycle

FIGURE 26b. Grout Mixer Paddles After Second Decontamination Cycle

FIGURE 27. Grout Mixer Outlet Duct After Second Decontamination Cycle

FIGURE 28. Surge Tank After Second Decontamination Cycle

FIGURE 29. Surge Tank Lid and Sprayer After Second Decontamination Cycle

FIGURE 30. Grout Pump Inlet After Second Decontamination Cycle

FIGURE 31. Flange Downstream of Grout Pump After Second Decontamination Cycle

FIGURE 32a. Grout Pump Rotor Being Removed After Second Decontamination Cycle

FIGURE 32b. Grout Pump Rotor After Second Decontamination Cycle

FIGURE 33. Inside of Grout Pump After Second Decontamination Cycle

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