DECONTAMINATION SOLUTION DEVELOPMENT STUDIES

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SUMMARY AND CONCLUSIONS

This study was conducted for the Westinghouse Hanford Company (WHC) by Pacific Northwest Laboratory (PNL) as part of the Hanford Grout Technology Program (HGTP). The objective of this study was to identify decontamination solutions capable of removing radioactive contaminants and grout from the Grout Treatment Facility (GTF) process equipment and to determine the impact of these solutions on equipment components and disposal options. The reference grout used in this study was prepared with simulated double-shell slurry feed (DSSF) and a dry blend consisting of 40 wt% limestone flour, 28 wt% blast furnace slag, 28 wt% fly ash, and 4 wt% type I/II Portland cement.

An acceptable decontamination solution for the GTF must be effective, have negligible corrosion or other adverse impacts on the process equipment materials and components, and comply with all regulatory and disposal requirements. Decontamination scoping studies conducted during FY 1990 identified citric and sulfamic acid as the most promising candidates for grout removal. Expanded Impact Level II studies using citric and sulfamic acid decontamination solutions were conducted during FY 1991 to 1) determine dissolution rate as a function of temperature (20-60°C), acid concentration (0.5-6 N), amount of agitation, and cure condition (<3-day and 28-day cured); 2) determine the quantity of acid required for complete grout dissolution; 3) characterize the dissolution process waste stream; 4) conduct a materials compatibility literature review for the candidate decontamination solutions; and 5) determine if sufficient Cs can be leached from the grout. The principal results and major conclusions and recommendations for each of these five study areas are summarized below.

Dissolution Rate - A selective ion potentiometric technique using Ca^{2+} as the marker element was used to quantitatively measure the progress of the reference grout dissolution reaction in citric and sulfamic acid. Measured coupon dissolution rates ranged from 1.5 to 18 g/s/m², increasing with acid strength (sulfamic > citric), acid concentration, and reaction temperature. The dissolution rates were higher for grout in the uncured condition for all dissolution conditions, and this difference was accentuated in unstirred solutions.

Tests with coated pipe sections demonstrated that complete removal of cured grout to leave a clean, bright metal surface was not always achieved under low agitation conditions.

Conclusions:

- With adequate agitation, either sulfamic or citric acid at moderate concentrations ($\leq 1\text{ }N$) and temperatures less than the maximum attainable 60°C solution temperature will remove uncured or cured 6-mm-thick reference grout deposits within the specified 3-h decontamination period.
- For low agitation conditions, complete removal of adherent, cured grout to leave a clean, bright metal surface cannot always be achieved even for the higher acid concentrations.

Recommendation:

- Pilot-plant studies are recommended to investigate the effect of the expected variation in solution agitation conditions and flow velocities along the GTF decontamination solution flow path (direct agitation, spray, pumped flow, gravity flow) on the adequacy of grout removal.

Dissolution Capacity - Titration studies showed that 7.5 equivalents of acid are required to react with 1 kg of the reference grout. Coupon tests, however, indicated that the dissolution process does not go to completion at the lower eq/kg ratios. The ratio must be increased to 15 eq/kg for sulfamic acid and 30 eq/kg for citric acid to ensure complete dissolution. For the lower concentration sulfamic and citric acids, this dissolution capacity in conjunction with the decontamination tank volume would be sufficient to remove the equivalent of 2 mm of grout on the internal surfaces of the GTF equipment and piping. Using the higher concentration 6 N citric acid would permit the removal of up to 380 kg of grout, representing an average grout thickness of more than 1 cm, while leaving sufficient capacity in the liquid collection tank for pH adjustment.

Conclusions:

- The projected decontamination solution volumes and concentrations required to remove up to 1-cm-thick deposits of the reference grout are compatible with the capacities of the decontamination and liquid collection tanks, including the additional volume needed for waste conditioning operations.

- Although the use of lower concentration acids is preferred from a materials compatibility standpoint, higher concentrations may be required to provide sufficient dissolution capacity if the average residual grout thickness exceeds 2 mm.

Decontamination Waste - The composition and physical characteristics of the untreated and neutralized decontamination waste were determined for correlation with the operational and regulatory requirements for transfer to the tank farm, transfer to the grout vault, or incorporation into the grout. Grout dissolution in 0.5 N sulfamic acid and 1.0 N citric acid produced solids representing ~10% of the original grout weight. Neutralization of the filtered decontamination solutions with caustic to a pH of ~12 produced a gelatinous precipitate containing primarily Ca, Si, Al, and Mg. Both the as-reacted solids and the precipitate produced by the neutralization reactions could be suspended by agitation. The Cs in the grout did not preferentially partition to the solids in either the as-reacted condition or after neutralization.

Conclusions:

- The citric or sulfamic acid grout decontamination processes and subsequent neutralization operations do not produce gels or precipitates that would be unusually difficult to remove from the liquid collection tank or to transport through piping.
- The required pH adjustment volumes for treatment of the spent decontamination solutions are compatible with the available volumes in the liquid collection tank.
- The Cs in the grout remains primarily with the filtrate and does not preferentially partition to the solids either in the as-reacted condition or after neutralization.

Materials Compatibility - Information on the compatibility of the candidate decontamination solutions with the major identified GTF materials was obtained from the corrosion literature and other knowledgeable sources, including the grout pump manufacturer. Nitric acid is incompatible with natural rubber, Hypalon, ethylene propylene terpolymer (EPDM), and carbon steel. Sulfamic acid is incompatible with Hypalon and carbon steel and may be incompatible with EPDM, depending on the service conditions. Citric acid is incompatible with carbon steel and is recommended for static service only in contact with natural rubber and Hypalon.

Conclusion:

- Of the acids evaluated, only citric acid appears reasonably compatible with the identified sensitive GTF materials such as the elastomer used for the grout pump stator. Short exposure times should help mitigate other compatibility concerns.

Recommendations:

- Further efforts should be made to identify any additional GTF materials (adhesives, seals, packings, gaskets, bearings, bushings, etc.) that might prove incompatible with the proposed citric acid decontamination solution.
- Because of the difficulty of simulating localized GTF time, temperature, and flow conditions in the laboratory, pilot-plant studies are recommended to more directly evaluate the effects of these process-specific conditions on materials compatibility with the proposed citric acid decontamination solution.

Leaching - Cesium-containing cured and uncured grout specimens in powdered and cast form were exposed to deionized water and 0.5 *N* KCl to determine the feasibility of reducing dose levels by a simple leaching operation. For powdered material, Cs removal ranged from ~35% of the original inventory for the leaching of cured grout in deionized water at either room temperature or 60°C, to a maximum removal of 90% for the leaching of uncured grout in 0.5 *N* KCl at 60°C. Cesium removal was more difficult for the 6-mm-thick cast grout deposits with one surface exposed to the leachant. Cesium leaching removed 14% to 60% of the original inventory, with the higher values observed for the leaching of uncured grout in deionized water at 60°C.

Conclusions:

- The observations that Cs removal is more difficult for cured grout and that complete removal cannot be achieved even for powdered grout suggest that some of the Cs is incorporated in chemically or physically bound forms that may not be amenable to leaching.
- Although Cs leaching of cast material only removed 14% to 60% of the original inventory, it might function as part of the postdecontamination rinsing process to further reduce dose levels associated with residual grout pockets or films.

Based on the overall study results for the reference grout formulation, 3 to 6 *N* citric acid under adequate agitation conditions appears to provide the best combination of adequate dissolution rates and reaction capacity, acceptable waste form, and compatibility with the identified GTF materials.

GLOSSARY

ACI	American Concrete Institute
ARF	Analytical Request Form
DIW	deionized water
DSSF	double-shell slurry feed
EPDM	ethylene propylene terpolymer
eq	equivalents
FY	fiscal year
GTF	Grout Treatment Facility
HEPA	high-efficiency particulate air filter
HGTP	Hanford Grout Technology Program
ICP	Inductively Coupled Argon Plasma Emission Spectrometry
ID	inside diameter
LCT	Liquid Collection Tank
mpy	Mils Per Year
NACE	National Association of Corrosion Engineers
PNL	Pacific Northwest Laboratory
ppm	parts per million
PSW	phosphate-sulfate waste
QA	Quality Assurance
TOC	total organic carbon
WHC	Westinghouse Hanford Company

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1.0 INTRODUCTION

This study was conducted for the Westinghouse Hanford Company (WHC) by Pacific Northwest Laboratory (PNL)^(a) as part of the Hanford Grout Technology Program (HGTP). The objective of this study was to identify decontamination solutions capable of removing radioactive contaminants and grout from the Grout Treatment Facility (GTF) process equipment and to determine the impact of these solutions on equipment components and disposal options.

An acceptable decontamination solution for the grout equipment must:

1. effectively decontaminate grout-encrusted internal process equipment and piping surfaces to dose levels that would permit necessary maintenance. Decontamination could potentially be accomplished either by leaching the radionuclides from the grout or by removing the grout along with its radionuclide inventory. A separate process step could be required to further decontaminate the exposed metal surfaces after grout removal
2. have negligible corrosion or other adverse impacts on the process equipment materials and components, including sensitive items such as seals, packings, gaskets, and instrumentation
3. comply with all regulatory and disposal requirements, including those applicable to the reaction products. Possible disposal options include transfer to the tank farm, transfer to the grout vault, or incorporation in the grout. Neutralization or other treatment of the spent solution and reaction products may be required.

Grout decontamination scoping studies were conducted during FY 1990. The grout used in these studies was prepared with simulated double-shell slurry feed (DSSF) and a dry blend consisting of 40 wt% limestone flour, 28 wt% blast furnace slag, 28 wt% fly ash, and 4 wt% type I/II Portland cement. Dissolution rates for grout with this composition were evaluated for acetic, citric, hydrochloric, nitric, phosphoric, sulfamic, sulfuric, and tartaric acid. Based on these preliminary tests, citric and sulfamic acid were selected as the most promising dissolution candidates for grout removal.

(a) Operated for the U.S. Department of Energy by Battelle Memorial Institute under contract DE-AC06-76RLO 1830.

The following studies were conducted during FY 1991 to further address effectiveness and acceptability issues for the candidate citric and sulfamic acid decontamination solutions:

Dissolution Rate. The rate at which the reference grout is attacked and dissolved by citric and sulfamic acid was determined as a function of temperature (20° to 60°C), acid concentration (0.5 to 6 N), amount of agitation, and cure condition (<3-day and 28-day cured grout). A selective ion potentiometric technique, in which Ca^{2+} was the marker element, was used to quantitatively measure the progress of the grout dissolution reaction.

Dissolution Capacity. The quantity of citric or sulfamic acid required for reaction with the grout was determined as a basis for estimating the decontamination solution volumes and concentrations required for complete removal of the grout in the GTF process equipment and piping. Neutralization titrations were performed to measure the theoretical grout dissolution capacity of the acids, and coupon dissolution tests were conducted to determine the volumetric excess required to ensure complete dissolution.

Decontamination Waste. The composition and physical characteristics of the untreated and neutralized decontamination waste were evaluated for compatibility with the operational and regulatory requirements for transfer to the tank farm, transfer to the grout vault, or incorporation in the grout. Major test objectives were to identify conditions and treatments that could result in the formation of gels or precipitates that would be difficult to suspend, pump, or otherwise remove from tanks and piping, and to determine required pH adjustment volumes.

Materials Compatibility. A materials compatibility literature review was conducted for the major identified GTF materials (stainless steel, ethylene propylene terpolymer [EPDM], Hypalon, natural rubber) to identify compatibility problems or other possible adverse effects from exposure to the candidate decontamination solutions.

Leaching. Studies were performed to explore the feasibility of removing the soluble Cs by leaching the reference grout in deionized water (DIW) or 0.5 N KCl at room temperature and 60°C.

This report summarizes the initial scoping studies that resulted in the selection of the candidate decontamination solutions, and documents the detailed studies conducted to address the dissolution rate, dissolution capacity, decontamination waste, materials compatibility, and Cs leaching issues.

2.0 SCOPING STUDIES

PNL and WHC experts met to define the requirements for the decontamination solution study and to review grout decontamination tests performed previously by WHC. A literature search also was conducted to identify potential degradation agents for grout. Based on this background information, scoping tests were initiated to evaluate the dissolution characteristics of grout in acidic and basic solutions. Physical degradation tests also were performed.

The scoping studies, which were conducted in accordance with the requirements of PNL-MA-70, *Quality Assurance*, Part 2, "Good Practices Standard," culminated in the selection of citric and sulfamic acid as the most promising candidate decontamination solutions for further evaluation under the more rigorous Impact Level II requirements. The following sections describe this preliminary scoping work.

2.1 BACKGROUND INFORMATION

PNL and WHC staff established the following criteria for the decontamination solution development studies:

Essential:

The process must:

- remove grout, by contact, from close-tolerance surfaces (pump rotor-stator and mixer blades) to $13 \pm 13 \mu\text{m}$ (0.5 ± 0.5 mil) and all other surfaces to $25 \pm 25 \mu\text{m}$ (1 ± 1 mil). The primary objective is to reduce exposure sufficiently to permit contact maintenance. Reduction of the grout buildup to facilitate subsequent operations is a potential added benefit
- cause little or no degradation of internal GPF equipment and materials
- use solution in the liquid form, requiring no mixing
- permit treatment of the used solution within the GPF to allow transfer to tank farms. Note: the transfer of solids to the tank farms may not be allowed.

Ideal, But Not Essential:

The process should:

- be nonhazardous and nontoxic
- be deliverable in 208-L (55-gal) drums
- use less than 2650 L (700 gal) to decontaminate the internal surfaces of the grout equipment
- cause little or no damage to external surfaces and exposed wiring and instrumentation.

WHC provided drawings with associated information to show decontamination solution circulation paths and heating arrangements, tank configurations, solution level requirements, potential methods for removing residuals from tank bottoms, process equipment ventilation capabilities, and methods for introducing Ph adjustment and other additives. A schematic of the decontamination solution flow path is shown in Figure 2.1.

Other key information obtained on process requirements and constraints includes the following:

- It may be necessary to decontaminate the floor and sump of the mixer module, and the exterior surfaces of wiring, instrumentation, and equipment in addition to all internal piping and equipment surfaces.
- If feasible, the entire decontamination operation should be accomplished within a single shift. A two-stage process might be required, i.e., grout removal followed by decontamination of the exposed metal surfaces. There will be 8 to 9 decontamination cycles per year.
- At least 1100 L (300 gal) of decontamination solution are required to contact all surfaces potentially coated with grout. The liquid collection tank has a 2650-L (700-gal) maximum working volume, but some space must be reserved for pH adjustments to the spent decontamination solution.
- The decontamination tank, which is the only tank with heating capability, is not in the solution recirculation loop. Because of heat losses in the system, the maximum decontamination temperature will be ~60°C. The decontamination tank may have to be filled to full 1900-L (500-gal) capacity in order to use the heater.

FIGURE 2.1. Decontamination Solution Flow Path

- The grout buildup occurs primarily in the mixer and the surge tank. The piping seems to be self-cleaning due to the scouring action of the grout.
- The grout formulation may change in the future. The scoping and Impact Level II tests should be performed using the current "reference grout" formulation, consisting of 1 L of simulated DSSF mixed with 1080 g of dry blend composed of 40 wt% limestone flour, 28 wt% blast furnace slag, 28 wt% fly ash, and 4 wt% type I/II Portland

cement. The compositions of the simulated liquid waste and the dry constituents from other HGTP studies are given in Tables 2.1 and 2.2, respectively.

Information also was obtained from WHC staff and correspondence files regarding a 1988 decontamination test using Turco 4502 (basic) and Turco 4521 (acidic) decontamination solutions. The GTF grout pump failed to operate after completion of this test. Suggested possible causes of the pump failure included stator swelling due to the elevated solution temperature (~60°C),

TABLE 2.1. Composition of Simulated DSSF Waste

<u>Species</u>	<u>Composition, g/L</u>	
	<u>Analyzed</u>	<u>Nominal</u>
Al	22.4	20.3
B	0.136	0.105
Ba	0.6	0.6
Ca	0.6	0.2
Cr	1.26	1.15
Fe	1.49	1.41
K	11.5	9.7
Mg	0.32	NA
Mn	3.01	2.75
Mo	0.068	0.049
Na	122	122
Si	0.50	0.56
Zn	2.93	1.63
Cl ⁻	5.36	3.86
NO ₂ ⁻	27.2	23.0
PO ₄ ⁻³	5.4	5.6
NO ₃ ⁻	186	154
SO ₄ ⁻²	5.1	5.1
TOC ^(a)	1.56	1.28

(a) Total organic carbon as EDTP and citrate.

TABLE 2.2. Oxide Composition of Blast Furnace Slag, Class F Fly Ash, and Cement Used in These Studies

Oxide	Composition, wt% ^(a)		
	Slag	Fly Ash	Cement
Al ₂ O ₃	13.4	23.5	3.3
B ₂ O ₃	*	0.5	0.105
BaO	0.117	0.169	0.084
CaO	43.4	8.05	65.4
Fe ₂ O ₃	0.377	5.73	4.08
K ₂ O	0.89	0.98	0.65
MgO	5.62	1.57	1.38
MnO ₂	1.03	0.088	0.072
Na ₂ O	0.401	3.02	0.32
P ₂ O ₅	*	0.94	*
SiO ₂	33.3	47.8	22.2
SrO	0.078	0.31	0.035
TiO ₂	1.08	4.43	0.22
TOTAL	99.693	97.087	97.846

(a) Determined by inductively coupled plasma (ICP) analysis.

* Below detection limit.

chemical attack of the elastomer, an improper interference fit between the rotor and stator, or debonding of the stator from the pump tube.

In an effort to ensure that future decontamination efforts would not cause similar failures, WHC staff contacted the grout pump manufacturer, Robbins & Myers, Inc., to obtain their assessment of the cause of the pump failure. The manufacturer concluded that a combination of factors contributed to the pump failure. The original design specifying a tight rotor-to-stator fit was intended to compensate for the rapid wear of the stator by the abrasive grout. The decontamination solutions apparently attacked the chrome plating on the rotor, leaving a rough surface that increased the friction between the rotor and the stator. The decontamination solutions also may have decreased the hardness and increased the surface coefficient of friction of

the elastomeric stator material. Debonding of the stator from the pump tube apparently was not a factor in the pump failure.

The manufacturer's evaluation suggested that elimination of the chrome plating on the rotor, a relaxation of the rotor-to-stator compression fit, and the selection of compatible decontamination solutions would satisfactorily resolve the problem. Based on this assessment, a new nonplated rotor and a new stator with increased clearance were manufactured. Carbon steel was used for the stator tube instead of stainless steel to enhance the bond with the EPDM. There are, however, seals that should keep the decontamination solution from contacting either the epoxy used to bond the stator to the stator tube, or the tube body itself.

2.2 LITERATURE SURVEY

A literature search was conducted by Hanford Technical Library staff to identify potential degradation agents for grout. The most helpful information was found in the following four references:

Cordon, William A. 1966. Freezing and Thawing of Concrete: Mechanisms and Control, Monograph No. 3, American Concrete Institute (ACI), Detroit, Michigan.

Murdock, L. J. 1960. Concrete Materials and Practice, Edward Arnold Publishers, Ltd., London.

Orchard, D. F. 1958. Concrete Technology, Volume I, F. J. Parsons, Ltd., London.

Scanlon, John M. 1987. Concrete Durability, Volume I, Katherine and Bryant Mather International Conference, Atlanta, Georgia.

These references indicate that concrete can be degraded by a variety of physical and chemical processes, including freeze/thaw cycles and exposure to acids, bases, sulfate solutions, oils, and deicing salts. The following sections discuss the scoping studies that were conducted to explore the relative magnitude of these degradation effects to help identify candidate grout degradation processes.

2.3 PHYSICAL PROCESSES

Tests were performed to evaluate the grout degradation potential of three physical methods: thermal shock, freeze/thaw cycling, and dehydration. The effect of severe thermal shock was tested by cycling a grout coupon three times between liquid nitrogen and boiling water. This treatment fractured the grout into particles ≤ 3 mm in diameter. Additional tests were then conducted on a grout-coated pipe section to determine if thermal expansion differences due to the presence of a grout/pipe interface would have an effect. These tests resulted in significant cracking, but only minor spalling, of the grout after six cycles between liquid nitrogen and boiling water. The grout coating was fragmented and totally loosened from the pipe wall, but remained intact until removed from the pipe section. It then crumbled into pieces ranging from very small particles to sections 10 to 15 mm square. The larger pieces were very friable.

The effect of freeze/thaw cycles was evaluated by immersing a grout coupon in liquid nitrogen and then allowing it to warm in air to room temperature. Five cycles resulted in some cracking of the grout, but no extensive disintegration. Conducting the same test on a grout-coated pipe section produced very little cracking of the grout and no spalling. This difference in behavior for the cast grout coupon and the grout-coated pipe section may reflect the heat-sink effect of the heavy metal pipe.

The effect of dehydration on the grout was tested by passing warm, dry air around a grout coupon for 18 h. Although the coupon weight decreased by 21%, there was no noticeable physical degradation of the grout.

Although these physical process tests show that some cracking and degradation of the grout can be induced by thermal shock and freeze/thaw cycling, the low probability of complete removal of the grout and the difficulty of implementing these techniques in the field make them unlikely candidates for decontamination of GTF equipment and components.

2.4 BASIC/SALT SOLUTIONS

Grout dissolution tests based on concrete corrosion information found in the literature search described in Section 2.2 were performed using 3.8 N

sodium hydroxide, 2.7 *N* potassium hydroxide, and 2.5 *N* sodium sulfate. The grout coupons underwent no weight loss or change in thickness after 18 h of immersion, nor did the solution change color. No change was observed in a coupon exposed 2 h to the sodium hydroxide solution at 60°C. Subsequent tests performed using 10.0 *N* sodium hydroxide and 10.0 *N* potassium hydroxide produced equivalent results, further confirming that basic solutions are not effective in substantially dissolving or degrading the limestone-containing grout formulation.

2.5 ACIDIC SOLUTIONS

Concrete can be severely degraded by the reaction of acids with the calcium compounds in the cement and hydration products. The limestone-containing reference grout would be even more susceptible to attack by acids. This potential grout degradation process was evaluated initially by exposing grout coupons to 6 *N* acetic, citric, hydrochloric, nitric, phosphoric, sulfuric, and tartaric acids and to 1.5 *N* sulfamic acid (representing saturation at room temperature). Less than 25 min of exposure to hydrochloric, nitric, or phosphoric acid at 22°C was required to completely dissolve >0.4-cm-thick coupons of grout containing simulated DSSF waste. Dissolution times for the citric and sulfamic acid were in the 50- to 65-min range. Substantially longer times were required for grout dissolution in sulfuric, acetic, and tartaric acid.

The effect of acid concentration on grout dissolution at 22°C was investigated using 0.5 *N* solutions of the same acids previously tested at the higher concentrations. The dissolution rates decreased substantially for all of the acids, and the grout coupons were only partial degraded after more than 20 h of exposure. Low-concentration carbonic acid also was tested as a possible grout dissolution agent because of its simplicity and low cost. Common bottled seltzer water (pH 4.2) and water containing dry ice (pH 4.9) were used as sources of carbonic acid. Neither solution proved effective. To produce stronger carbonic acid would require pressurization of the grout system to unacceptable limits.

The effect of temperature on grout dissolution was evaluated using citric, nitric, and sulfamic acid at 60°C. The rate increase with temperature

was most pronounced for nitric acid. The average dissolution rate for 3 *N* nitric acid at 60°C was 8.3 times higher than the rate at 22°C, compared with a rate difference of 4.2 times for citric acid at the same 3 *N* concentration. The average dissolution rate for the sulfamic acid over the same temperature interval increased by a factor of 2.2 at its 1.5 *N* saturation limit. The sulfamic acid at 60°C and 1.5 *N* was substantially more effective than citric acid, and almost equaled the performance of nitric acid at the same concentration and temperature.

2.6 PROCESS SELECTION

The results of the scoping studies reported above suggest that most of the acids investigated would be effective in dissolving grout containing simulated DSSF waste, particularly at higher acid concentrations and temperatures. The following factors were therefore considered in selecting acids for further evaluation:

- Hydrochloric acid presents a stress corrosion cracking risk for the 304L and 316L stainless steel GTF system components.
- Nitric acid, because of its effectiveness for grout dissolution and apparent compatibility with existing waste streams, could be considered a prime candidate for decontaminating grout-coated stainless steel. However, as discussed in Section 6, nitric acid is not compatible with GTF elastomers.
- Sulfuric acid can form calcium sulfate, a highly insoluble precipitate that could coat the grout and prevent continued dissolution. This may explain the low dissolution rate observed for even the more highly concentrated solution.
- Acetic acid is slow and attacks only certain constituents of the grout, leaving a lower density, highly friable but intact solid residue.
- Tartaric acid is slow and offers no offsetting advantages.
- The 6 *N* hydrochloric, nitric, phosphoric, and sulfuric acids tend to form a gel at room temperature after grout dissolution.

Based on these considerations, citric and sulfamic acid were identified as the best candidate solutions for grout removal by acid dissolution. They provide acceptable dissolution rates, are not extremely corrosive to carbon

steel, are relatively inexpensive, and present minimum handling problems; and the residual grout is a very fine particulate that seems easily transported by flowing solutions.

2.7 CITRIC/SULFAMIC ACID STUDIES

Additional scoping tests were performed to further explore the suitability of citric and sulfamic acid for grout removal from GTF equipment. Grout-coated stainless steel pipe sections were exposed to citric and sulfamic acid to compare the grout dissolution behavior with the earlier results obtained with cast grout coupons. The grout formulation remained the same, but the use of grout-coated stainless steel pipe sections rather than individual coupons more accurately represented actual field conditions. The grout-coated pipe sections were prepared by continuously rotating a sealed grout-containing pipe during the curing process. The grout coating was uniform near the ends of the pipe but varied in thickness from 4 to 14 mm near the center. The grout exhibited the same type of ridges and valleys in the coating that will likely exist in field equipment.

Citric acid was tested on the grout-coated pipe sections at room temperature (22°C) and concentrations of 3.0 *N*, 4.5 *N*, and 6.0 *N*. Sulfamic acid was tested at room temperature at concentrations of 1.0 *N* and 1.5 *N*. For each case, a 3.8-cm (1.5-in.) length of the grout-coated, 5.1-cm (2-in.)-diameter stainless steel pipe was immersed in the decontamination solution. During dissolution, the surface area of the grout in contact with the solution continuously changed as the coated areas were dissolved, exposing the pipe walls. The determination of quantitative dissolution rates was therefore difficult, but overall dissolution times could be determined and qualitatively compared with the results obtained for the cast grout coupons.

During these dissolution tests, it was noted that the reaction became very slow or ceased when inadequate acid volumes were used, due to partial neutralization of the acid. When adequate volumes of acid were used, total dissolution required 2 to 2.5 h. The grout was completely removed from the pipe sections, leaving very clean walls. No residue of any kind could be

detected by visual observation of the surfaces or from swiping the surfaces with clean laboratory wipes. The only agitation in these tests was caused by gas evolution.

It was also observed that grout dissolution in the acidic solutions resulted in substantial gas evolution, presumably carbon dioxide from the reaction of the acid with the calcium carbonate. Since it is necessary for safety reasons to ensure that no hydrogen is generated, a sample of the evolved gas was collected using a filter flask as the reaction chamber. A stainless steel sampling vial was evacuated and the valve closed. Grout pieces were added to 6 *N* citric acid, after which the closed system was evacuated to approximately 28 Torr and then isolated. After the pressure had increased to approximately 480 Torr and dissolution appeared complete, the evacuated vial was opened to collect a sample of the evolved gas.

Mass spectrometric analyses (Table 2.3) confirmed that the evolved gas was 96.3 mol% carbon dioxide as expected. The hydrogen concentration was <0.01 mol%, verifying that the evolved gases should not present an explosion hazard in the GTF. The 700 cfm, high-efficiency particulate air (HEPA)-filtered ventilation system serving the surge and liquid collection tanks should be more than adequate to handle any gas evolved from the decontamination process.

TABLE 2.3. Mass Spectrometric Gas Analysis

<u>Gas</u>	<u>Composition (mol%)</u>
CO ₂	96.3
Ar	0.01
O ₂	0.02
N ₂	0.95
CO	<0.10
He	<0.01
H ₂	<0.01
CH ₄	<0.01
N ₂ O	0.20
NO _x	2.55

In addition to the dissolution tests, scoping tests were conducted to determine if dilution accompanying rinsing or neutralization of the waste decontamination solutions would cause the formation of difficult-to-handle precipitates or gels. Representative waste solutions were prepared by dissolving grout in 6 *N* citric and 1.5 *N* sulfamic acid to give respective dissolved grout concentrations of ~ 0.04 g/cm³ and ~ 0.06 g/cm³. These solutions were diluted with DIW 5:1 and 20:1. No precipitate formation or other unusual behavior was noted. The as-prepared and diluted acid solutions were neutralized with anhydrous sodium carbonate. No precipitates formed, and the neutralization process was easily controlled.

2.8 PREVIOUS FORMULATIONS

Scoping studies also were conducted to evaluate the effectiveness of citric and sulfamic acid in removing the nonlimestone-containing grout formulations tested earlier in the GTF and the pilot-scale test equipment. The residual grout currently in the GTF equipment ("PSW Grout") consists of 1 L of liquid mixed with 864 g of a dry blend composed of 41 wt% cement, 40 wt% fly ash, 11 wt% attapulgite clay, and 8 wt% Indian red pottery clay. The residual grout from the 300 Area pilot-scale test ("DSSF Pilot-Scale Grout") consists of 1 L of liquid mixed with 1084 g of a dry blend composed of 47 wt% fly ash, 47 wt% blast furnace slag, and 6 wt% cement.

Coupons representing these formulations were tested like the limestone-containing formulation (Section 3.2) by encapsulating them in an acid-resistant resin with only one surface exposed to the acid to better reflect actual field decontamination conditions. The citric and sulfamic acid attacked these formulations, but removed only selected grout constituents. The initial dissolution rates decreased due to the formation of a visible layer of inert material on the exposed coupon surface. This suggests that the decontamination solution flow rates for nonlimestone-containing grout will need to be sufficient to dislodge this inert material in order to maintain adequate dissolution rates. Tests of these two earlier formulations using strong basic solutions also were conducted. As with the limestone-containing grout, these basic solutions were ineffective for either dissolution or degradation of the grout.

Based on the information obtained from the scoping studies, a Test Plan focusing on citric and sulfamic acid decontamination solutions was prepared for the FY 1991 QA Impact Level II decontamination studies. The subsequent sections of this report present the details of these Impact Level II studies.

3.0 DISSOLUTION RATE STUDIES

3.1 SCOPE

Dissolution rate studies for the reference grout were conducted using citric and sulfamic acids as a basis for estimating decontamination cycle times. The rate at which the reference grout is attacked and dissolved was determined as a function of acid type (citric versus sulfamic), concentration (0.5 to 6 *N*), temperature (20° to 60°C), amount of agitation, and grout cure condition (<3-day versus 28-day cured grout). Assumptions and constraints for the dissolution rate studies included the following:

- The maximum grout thickness requiring total dissolution is 6 mm.
- The maximum allowable dissolution time is 3 h in order to complete the GTF decontamination cycle within a single shift.
- The maximum attainable solution temperature is 60°C, based on the inability to reheat the circulated decontamination solution.
- Solution agitation will vary from high flow conditions at the exit of the grout pump to minimal agitation in areas of gravity flow.

3.2 PROCEDURE

Cast grout specimens and grout-coated stainless steel pipe sections of the reference grout formulation in the uncured (<3-day) and 28-day cured conditions were prepared by the Grout and Laboratory Studies Task using procedure HGTP-90-03-06. The ~6-mm (0.24-in.)-thick by 3.2-cm (1.26-in.)-diameter sectioned cast specimens were encased in metallographic mounting resin with one face ground to expose a defined (8.0 cm²) surface area. These mounted specimens were immersed in stirred 300-cm³ volumes of citric or sulfamic acid at test temperatures of room temperature (21° to 25°C), 42°C, or 60°C.

The progress of the grout dissolution reaction was quantitatively monitored using a selective ion potentiometric technique (Appendix A) with Ca²⁺ as the marker element. The maximum amount of calcium that would be released from a specimen by complete dissolution of all of the grout constituents is given in Table 3.1.

TABLE 3.1. Reference Grout Calcium Inventory

<u>Constituent</u>	<u>Wt% of Grout</u>	<u>Wt% Ca</u>	<u>Wt% Ca in Grout</u>	<u>% of Total Ca</u>
Limestone	18.21	40.04	7.29	56.8
Fly Ash	12.74	5.75	0.73	5.7
Slag	12.74	31.02	3.95	30.7
Cement	1.82	46.74	0.85	6.6
Liquid Waste	54.49	0.04	0.02	0.2
TOTALS	100.00		12.84	100.0

3.3 RESULTS

Using the 12.84 wt% calcium content value of the as-mixed reference grout gives a Ca^{2+} concentration of 0.09 M/L for the complete dissolution of a nominal 8.4-g sample of grout in 300 cm³ of acid. Figure 3.1 shows the type of rate data obtained using the calcium ion selective electrode. The increase in calcium concentration in moles per liter is plotted against dissolution

FIGURE 3.1. Increase In Dissolved Calcium Concentration With Time for the Dissolution of Cured Grout in Citric Acid at 60°

TABLE 3.2. Grout Dissolution Data for Citric Acid

Test No. ^(a)	Conc. (N)	Temp. (°C)	Rate (g/s/m ²)	Calc. Wt(g)	Meas. Wt(g)	Comments
C1-C	6	24	2.12	7.2	8.1	Complete
C2-C	1	22	1.66	7.6	8.5	Complete
C3-C	6	60	6.59	8.3	8.1	98% Complete
C5-C	6	42	5.09	7.6	8.0	Complete
C6-C	1	60	3.93	8.1	9.4	Complete
C7-C	1	60	3.31	8.5	8.5	Complete
C8-C	1	40	2.31	8.2	8.5	Complete
C11-UC	1	21	3.03	9.2	8.7	Complete
C12-UC	6	21	4.01	10.3	9.4	Complete
C13-UC	1	42	4.73	8.2	8.2	Complete
C14-UC	1	60	5.75	8.8	8.3	Complete
C15-UC	6	42	7.11	8.4	8.3	Complete
C16-UC	6	60	12.01	8.9	8.4	Complete
C18-UC	1	42	2.51	8.0	8.7	Unstirred-Complete
C19-C	1	42	2.92	NA	NA	Unstirred-Incomplete

(a) The suffix -C refers to 28-day cured grout, and the suffix -UC refers to <3-day (uncured) grout.

time in minutes for cured grout reacted with 300 cm³ of 6.0 N citric acid at 60°C. The test was repeated to illustrate the reproducibility of the procedure.

The slope of the initial linear portion of the calcium concentration versus time curve is proportional to the weight of as-mixed grout initially dissolved per unit time for the 8.0 cm² (1.24 in.²) of exposed specimen surface area. Normalizing this to grams of reference grout initially dissolved per second per square meter of exposed grout permits a comparison of dissolution rates as a function of acid type and concentration, temperature, degree of agitation, and grout cure condition.

The effect of the test variables on grout dissolution rates and the completeness of the dissolution reaction is summarized in Table 3.2 for citric

acid and Table 3.3 for sulfamic acid. The calculated weight is the amount of grout dissolved based on the maximum Ca^+ concentration in the test solution. The term "Complete" is used in the Comments column to indicate complete dissolution within the allotted 3-h cycle time.

3.4 EFFECT OF ACID TYPE

Sulfamic acid is a strong inorganic acid with $\text{pH} < 1$ for both the 0.5 and 1.5 *N* concentrations. Conversely, citric acid is a weakly ionized organic acid with $\text{pH} > 1$ even for the 6.0 *N* concentration. This difference in acid strength is reflected in the observed differences in grout dissolution rates for the two acids. Table 3.4 compares the dissolution rates for cured and uncured grout in the two acids for comparable temperatures. For each reaction temperature, the general order of increasing reaction rate is 0.5 *N* sulfamic,

TABLE 3.3. Grout Dissolution Data for Sulfamic Acid

Test No. ^(a)	Conc. (N)	Temp. (°C)	Rate (g/s/m ²)	Calc. Wt(g)	Meas. Wt(g)	Comments
S1-C	0.5	24	2.06	7.8	8.2	99% Complete
S2-C	1.5	24	4.54	7.8	8.2	Complete
S3-C	1.5	60	10.69	8.3	8.1	98% Complete
S4-C	0.5	60	3.20	7.8	8.6	Complete
S5-C	0.5	42	2.39	7.6	8.7	Complete
S6-C	1.5	42	7.13	8.3	8.5	Complete
S9-UC	0.5	21	2.20	8.1	7.8	Complete
S10-UC	1.5	21	7.01	8.7	8.6	Complete
S11-UC	0.5	60	3.58	8.3	7.9	Complete
S12-UC	0.5	42	3.14	7.9	7.9	Complete
S13-UC	1.5	60	18.00	9.4	7.7	Complete
S14-UC	1.5	42	9.79	8.6	8.4	Complete
S16-UC	0.5	42	2.55	8.8	9.5	Unstirred-Complete
S17-C	0.5	42	2.19	NA	NA	Unstirred-Incomplete

(a) The suffix -C refers to 28-day cured grout, and the suffix -UC refers to <3-day (uncured) grout.

TABLE 3.4. Comparison of Grout Dissolution Rates for Citric and Sulfamic Acid

Temp. (°C)	Acid	Conc. (N)	Rate (g/s/m ²)	
			Cured	Uncured
24	Sulfamic	0.5	2.06	2.20
24	Citric	1.0	1.66	3.03
24	Citric	6.0	2.12	4.01
24	Sulfamic	1.5	4.54	7.01
42	Sulfamic	0.5	2.39	3.14
42	Citric	1.0	2.31	4.73
42	Citric	6.0	5.09	7.11
42	Sulfamic	1.5	7.13	9.79
60	Sulfamic	0.5	3.20	3.58
60	Citric	1.0	3.31	5.75
60	Citric	6.0	6.59	12.01
60	Sulfamic	1.5	10.69	18.00

1.0 *N* citric, 1.5 *N* sulfamic, and 6.0 *N* citric. The rates for the 0.5 and 1.0 *N* concentrations are similar, while the rates for the 6 *N* citric average about 60% to 70% of the rates for the 1.5 *N* sulfamic.

3.5 EFFECT OF ACID CONCENTRATION

The effect of acid concentration on the dissolution rates of cured and uncured grout is illustrated in Figure 3.2 and Table 3.5. The dissolution rate ratios for 6.0 *N*:1.0 *N* citric acid increase from about 1.3 at room temperature to about 2 at 60°C. For sulfamic acid, the 1.5 *N*:0.5 *N* ratios increase from about 2 at room temperature for cured grout to 5 at 60°C for uncured grout, again reflecting the greater strength of the sulfamic acid. Note that solubility considerations limit sulfamic acid to a maximum normality of 1.5 at room temperature, whereas 6 *N* citric acid is only half saturated at room temperature.

3.6 EFFECT OF TEMPERATURE

The effect of temperature on the dissolution rates of cured and uncured grout is illustrated in Figure 3.3 and Table 3.6. The decontamination rates increase by a factor of 2 for 1.0 *N* citric acid and by a factor of 3 for 6.0 *N* citric acid in going from room temperature to 60°C. For sulfamic acid, the

FIGURE 3.2. Effect of Citric Acid Concentration on the Dissolution Rate of Uncured Grout at 21°C

TABLE 3.5. Grout Dissolution Rates as a Function of Acid Concentration for Citric and Sulfamic Acid

Temp. (°C)	Conc. (N)	Rate (g/s/m ²)	
		Cured	Uncured
<u>Citric Acid</u>			
24	1.0	1.66	3.03
24	6.0	2.12	4.01
42	1.0	2.31	4.73
42	6.0	5.09	7.11
60	1.0	3.31	5.75
60	6.0	6.59	12.01
<u>Sulfamic Acid</u>			
24	0.5	2.06	2.20
24	1.5	4.54	7.01
42	0.5	2.39	3.14
42	1.5	7.13	9.79
60	0.5	3.20	3.58
60	1.5	10.69	18.00

FIGURE 3.3. Effect of Temperature on the Dissolution Rate of Cured Grout in 1.0 Normal Citric Acid

decontamination rates increase by a factor of 1.6 for 0.5 *N* acid and by a factor of 2.5 for 1.5 *N* acid in going from room temperature to 60°C. The reduced temperature dependence again is consistent with the greater strength of the sulfamic acid. Note that the ratios for both acids are comparable for the cured and uncured grout.

3.7 EFFECT OF GROUT CURE CONDITION

The effect of grout cure condition (<3-day cured versus 28-day cured) on dissolution rates is illustrated in Figure 3.4 and Table 3.7. The rate ratio for uncured:cured grout does not seem to be sensitive to acid concentration or temperature, but averages about 1.8 for citric acid and 1.35 for sulfamic acid. The higher apparent rate for uncured grout may reflect either a faster disintegration of the grout matrix or a faster and more extensive calcium release from the grout constituents for the uncured material. The cured grout specimens used in the tests were partially dried, whereas in practice they

TABLE 3.6. Comparative Grout Dissolution Rates as a Function of Temperature for Citric and Sulfamic Acid

Temp. (C°)	Rate Ratio	
	Cured	Uncured
<u>Citric Acid - 1 N</u>		
24	1.00	1.00
42	1.39	1.56
60	1.99	1.90
<u>Citric Acid - 6 N</u>		
24	1.00	1.00
42	2.40	1.77
60	3.11	3.00
<u>Sulfamic Acid - 0.5 N</u>		
24	1.00	1.00
42	1.16	1.43
60	1.55	1.63
<u>Sulfamic Acid - 1.5 N</u>		
1.00	1.00	
42	1.57	1.40
60	2.35	2.57

would remain moist. Except as noted in Tables 3.2 and 3.3, the ~6-mm (0.24-in.)-thick cured specimens, representing worst-case conditions, were completely dissolved within the 3-h time requirement.

3.8 EFFECT OF AGITATION

Solution agitation conditions and flow velocities will vary widely along the GTF decontamination solution flow path. Internal surfaces will be exposed to pumped flow, sprays, direct agitation, and gravity flow (Figure 2.1). Since the majority of the dissolution rate tests reported in Tables 3.2 and 3.3 were performed in stirred solutions of citric or sulfamic acid, a few additional tests were conducted in unstirred solutions to determine the effect of agitation.

FIGURE 3.4. Effect of Cure Condition on the Grout Dissolution Rate in 1.0 N Citric Acid at 21°C

Figure 3.5 compares the dissolution rate behavior of cured grout in 1.0 N citric acid at 41°C. Without stirring, the grout dissolution reaction stopped abruptly at about 50% completion, leaving the balance of the grout unremoved after 3 h. Adequate agitation appears to be a less critical requirement for the uncured grout, as illustrated in Figure 3.6. For the same 1.0 N citric acid and 42°C test conditions, the unstirred dissolution rate was about one-half the rate for the stirred solution; however, the reaction with the uncured grout did go to completion after about 80 min.

Increasing the normality of the acid also reduced the agitation dependency for the cured grout. Figure 3.7 compares the dissolution rate for cured grout in stirred and unstirred 6.0 N citric acid solutions at 42°C. Although the unstirred rate was lower than the stirred rate, the dissolution reaction did go to completion. A similar agitation effect for cured grout was observed for the sulfamic acid, as illustrated in Figure 3.8 for a 0.5 N solution at 42°C. The dissolution reaction did not stop abruptly as in the case of the 1.0 N citric acid. The unstirred reaction rate was substantially reduced, however, and only about 75% of the grout was removed after 3 h.

TABLE 3.7. Comparative Grout Dissolution Rates as a Function of Grout Cure Condition for Citric and Sulfamic Acid

<u>Temp. (°C)</u>	<u>Conc. (N)</u>	<u>Uncured:Cured Rate Ratio</u>
<u>Citric Acid</u>		
24	1.0	1.83
24	6.0	1.89
42	1.0	2.05
42	6.0	1.40
60	1.0	1.74
60	6.0	1.82
<u>Sulfamic Acid</u>		
24	0.5	1.07
24	1.5	1.54
42	0.5	1.31
42	1.5	1.37
60	0.5	1.12
60	1.5	1.68

The reduced dissolution rate in the absence of stirring is probably a combined result of the partial neutralization of the unreplenished solution in immediate contact with the grout, and the accumulation of nonreactive residual grout constituents on the reaction surface. The evolution of carbon dioxide from the limestone reaction provides some localized agitation, and this may explain the beneficial effect of the higher-normality acid or the stronger sulfamic acid.

3.9 PIPE TESTS

In addition to the coupon studies, stainless steel pipe sections were coated with reference grout in the cured and uncured conditions to evaluate dissolution behavior in a geometry more representative of field equipment and conditions. One of the most important objectives of this work was to determine the conditions required for complete removal of the grout coating to leave a bright, clean metal surface.

FIGURE 3.5. Effect of Agitation on the Dissolution Rate of Cured Grout In 1.0 N Citric Acid at 41°C

FIGURE 3.6. Effect of Agitation on the Dissolution Rate of Uncured Grout In 1.0 N Citric Acid at 42°C

FIGURE 3.7. Effect of Agitation on the Dissolution Rate of Cured Grout In 6.0 N Citric Acid at 42°C

FIGURE 3.8. Effect of Agitation on the Dissolution Rate of Cured Grout in 0.5 N Sulfamic Acid at 42°C

The grout-coated pipe sections were prepared by continuously rotating a sealed 5.1-cm (2.0-in.)-ID pipe containing grout during the curing process. Although the grout distribution was nonuniform along the length of the pipe, 5.0-cm (1.97-in.)-long sections with a uniform 6-mm (0.24-in.) wall thickness were prepared by reaming out the excess grout in the center.

To simulate internal flow conditions, the pipe sections were rotated on a 10.0-cm (3.94-in.) radius in a 4.5-L (1.2-gal) volume of the test solution. The minimum rotation speed was 20 rpm, with a solution drag rotation of ~10 rpm. These conditions corresponded to a simulated minimum flow velocity of ~11 cm/s (22 ft/min), or a volume flow of ~0.21 L/s (3.3 gal/min).

The grout-coated pipe sections were tested as a function of cure condition, acid type, acid concentration, and temperature. The 0.5 *N* sulfamic acid appeared to completely remove the grout in both the cured and uncured conditions at 42°C, but left a dark stain on the metal. The results for the citric acid were somewhat variable. The uncured grout was completely removed by 1.0 *N* acid at 42°C, leaving a clean, bright metal surface. The cured grout, however, was not always completely removed even after 3 h in 6.0 *N* citric acid. Adherent grout seemed to resist removal, whereas grout that was not well adhered was readily removed by undercutting.

4.0 DISSOLUTION CAPACITY STUDIES

4.1 SCOPE

The quantity of citric or sulfamic acid required for reaction with the grout was determined as a basis for estimating the decontamination solution volumes and concentrations required for complete removal of the grout in the GTF process equipment and piping. Neutralization titrations were performed to measure the theoretical grout dissolution capacity of the acids, and coupon dissolution tests were conducted to determine the actual volumetric excess needed to ensure complete dissolution.

Assumptions and constraints for the dissolution capacity studies were as follows:

- The required decontamination volumes must be compatible with the 1900-L (500-gal) capacity of the decontamination tank.
- The required decontamination volumes must be compatible with the 2650-L (700-gal) working capacity of the liquid collection tank; this must include sufficient room for any chemical additions needed for pH adjustment or other waste conditioning operations.

4.2 NEUTRALIZATION TITRATION STUDIES

The results of the scoping study suggest that the dissolution of the reference grout results primarily from the reaction of the decontamination acid with the limestone (calcium carbonate) to form water and carbon dioxide. However, the fact that the earlier grout formulations tested in the GTF and pilot-scale test equipment are partially degraded by these acids indicates that one or more of the other grout constituents also are susceptible to attack.

A back-titration technique was used to measure the theoretical acid equivalent requirement for complete dissolution of the grout and also its individual constituents. This study (ARF No. M85013-4) was conducted by reacting weighed samples of the blast furnace slag, cement, limestone, fly ash, simulated liquid waste, and dry blend with an excess of 0.1 N HCl. The reacted solution was then back-titrated with 0.1 N NaOH to determine the acid

equivalents consumed by the initial reaction. The results of the titration study are shown in Table 4.1 as eq/kg for the grout and its constituents.

The eq/kg values for the dry blend and the grout agree to within 5% with the totals calculated by summing the constituent values on a weight percent basis. The 7.5 eq/kg value for the grout translates into a minimum requirement of 7.5 L of 1 N acid per kg (0.9 gal/lb) of as-mixed grout for complete reaction. This minimum ratio would increase or decrease correspondingly with the normality of the decontamination acid.

4.3 COUPON DISSOLUTION TESTS

Dissolution capacity tests were conducted by reacting coupons of cured reference grout with varying volumes of 0.5 N sulfamic acid and 1.0 N citric acid at 42°C. As in the dissolution rate studies, the progress of the dissolution reaction was monitored by measuring the Ca^{2+} concentration.

The change in Ca^{2+} concentration with time for citric and sulfamic acid is shown in Figures 4.1 and 4.2, respectively, for eq/kg ratios ranging from 6 to 60. These results confirm, as expected, that the dissolution process does not go to completion at the lower eq/kg ratios. It appears, for the conditions used for these dissolution capacity tests, that an eq/kg ratio at least twice the theoretical 7.5 ratio is required for sulfamic acid, and four times this ratio is required for citric acid to ensure complete dissolution.

TABLE 4.1. Acid Equivalent Requirement for Complete Dissolution of the Grout and Its Constituents

<u>Component</u>	<u>Equivalents per Kilogram</u>
Grout	7.5
Liquid Waste	1.8
Dry Blend	14.3
Limestone	19.4
Fly Ash	3.8
Slag	18.1
Cement	23.0

FIGURE 4.1. Effect of the Equivalents/KG Ratio on Cured Grout Dissolution In 1.0 N Citric Acid at 42°C

FIGURE 4.2. Effect of the Equivalents/KG Ratio on Cured Grout Dissolution In 0.5 N Sulfamic Acid at 42°C

4.4 DISSOLUTION CAPACITY CALCULATIONS

Using an eq/kg ratio of 30, the weight of grout that could be removed per decontamination treatment thus would range from 35 kg (77 lb) for 1100 L (300 gal) of 1 *N* citric acid (the minimum volume of decontamination solution required to fill and operate the GTF equipment) to approximately 380 kg (840 lb) for 1900 L (500 gal) of 6 *N* citric acid (the working volume of the decontamination tank).

The actual weight of grout requiring removal can only be estimated by assuming some average grout deposition thickness on the internal surface area of the GTF equipment and piping. Table 4.2 gives the calculated internal surface area for the major GTF components based on dimensions extracted from a WHC communication (memo from A. R. Tedeschi to G. Williamson, September 12, 1990).

Using this calculated surface area and the density of the as-mixed reference grout (1.67 g/cm³), the average thickness of grout that could be removed by the maximum volume (1900 L) of acid of a specified normality can be calculated as shown in Table 4.3.

TABLE 4.2. Internal Surface Area of GTF Components

<u>Component</u>	<u>Area(m²)</u>
Surge Tank	2.55
Grout Pump	1.65
Mixer	2.93
Liquid Collection Tank ^(a)	10.68
LCT ^(b) /Mixer Module Sump	0.72
Grout Pipe	<u>0.39</u>
TOTAL	18.92

(a) Assumes bottom half exposed to grout.

(b) LCT = liquid collection tank.

TABLE 4.3. Grout Removal Thickness Versus Acid Normality for Sulfamic^(a) and Citric^(b) Acid

<u>Acid/Normality</u>	<u>Thickness (mm)</u>
Sulfamic/0.5 N	2.0
Sulfamic/1.5 N	6.1
Citric/1.0 N	2.0
Citric/3.0 N	6.1
Citric/6.0 N	12.2

(a) 15 eq/kg for sulfamic acid.

(b) 30 eq/kg for citric acid.

Although the more dilute acids would be preferred from a materials compatibility standpoint, these dissolution capacity experiments and calculations suggest that the higher normalities may be required to permit complete dissolution if the actual average residual grout thickness exceeds 2 mm (79 mils).

5.0 DECONTAMINATION WASTE STUDIES

5.1 SCOPE

The composition and physical characteristics of both the untreated and the neutralized decontamination waste were evaluated to assess compatibility with operational and regulatory requirements for transfer to the tank farm, transfer to the grout vault, or incorporation in the grout. Constraints on the physical and chemical nature of the decontamination waste include the following:

- The grout dissolution products must be physically removable from the LCT; the decontamination process or subsequent neutralization operations must not produce gels or precipitates that would be difficult to suspend, pump, or otherwise remove from tanks and piping.
- Implementation of the decontamination and neutralization processes must be consistent with valving, pumping, and sampling capabilities and procedures for the GTF.
- The required pH adjustment volumes must be consistent with available volumes in the LCT.
- The neutralization treatment must not result in a significant partitioning of the radioactive Cs to the solids to form potential high-exposure sites.

5.2 GROUT DISSOLUTION PRODUCTS

An analytical study (ARF No. M85013-3) was conducted to chemically characterize the as-reacted solids and the spent decontamination solution. Specimens of uncured reference grout were reacted in 300 cm³ of 1.0 N citric acid and 0.5 N sulfamic acid. The resulting solids were collected by filtration, dried, weighed, and then dissolved in a hydrochloric/nitric acid solution. Inductively coupled argon plasma (ICP) emission spectrometry techniques were used to determine the composition of the solids and the filtrate. The results of the chemical characterization work are shown in Table 5.1.

The solids in this study represented about 9 to 10 wt% of the dissolved grout weight. The total calcium concentration for the solids and filtrate was ~12.6% of the dissolved grout weight, which is very close to the calculated

TABLE 5.1. Composition of the Solids and Filtrate from the Dissolution of Uncured Grout in Citric and Sulfamic Acid

Element	Citric Acid		Sulfamic Acid	
	Filtrate %	Solids %	Filtrate %	Solids %
Ca	48.8	1.3	49.4	0.8
Na	20.3	0.8	21.1	0.7
Si	10.6	*	10.8	*
Al	7.0	3.0	7.6	2.4
Mg	2.6	0.3	2.7	0.2
Fe	1.2	1.3	1.2	1.0
Ti	0.8	0.6	0.4	0.6
Mn	0.5	*	0.5	*
Cr	0.2	*	0.2	*
Sr	0.2	0.1	0.2	*
Zn	0.2	*	0.2	*
B	0.2	*	0.1	*
TOTAL	92.6	7.4	94.4	5.6

* <0.1%

12.8 wt% calcium content from Table 3.1. Approximately 98% of the calcium was in the filtrate, further validating the use of the soluble Ca^{2+} ion as the marker for the dissolution rate studies.

As illustrated in Table 5.1, the filtrate for both the citric and sulfamic acid contained primarily Ca, Na, Si, and Al. The solids had an insoluble residue that was not analyzed, but the soluble portion contained primarily Al, Ca, Fe, Na, Ti, and Mg.

The wet volume of solid decontamination waste produced by reacting specimens of uncured reference grout in 300 cm³ of acid was measured as a function of acid type, acid concentration, and reaction temperature (Table 5.2). For citric acid, the waste volumes ranged from 0.1 to 0.3 cm³/g of grout, with the higher values observed for the 6 N acid. The corresponding

TABLE 5.2. As-Reacted Solid Waste Volumes for the Dissolution of Uncured Grout in Citric and Sulfamic Acid

<u>Conc. (N)</u>	<u>Temp. (°C)</u>	<u>As-Reacted Vol. (cm³)</u>	<u>Specimen Wt. (g)</u>	<u>Ratio (cm³/g)</u>
<u>Citric Acid</u>				
1	21	0.89	8.7	0.10
1	60		8.3	0.11
6	60	1.32	8.4	0.16
6	21	2.82	9.4	0.30
<u>Sulfamic Acid</u>				
0.5	60	1.70	7.9	0.22
1.5	21	2.20	8.6	0.26
1.5	60	2.10	7.7	0.27
0.5	21	3.00	7.8	0.38

as-reacted solid waste volumes for sulfamic acid ranged from 0.2 to 0.4 cm³/g of grout. For the sulfamic acid, there was no obvious correlation with either acid concentration or temperature.

Visual examination of the waste from the various grout dissolution tests showed that the solids that formed were granular and, upon settling, sometimes formed two or more distinct layers. All the as-reacted solids were readily suspended by moderate agitation.

5.3 NEUTRALIZATION PRODUCTS

Filtrate from the tests reported in Section 5.2 was neutralized to a pH of ~12 with 50% NaOH. This produced a gelatinous precipitate that was collected and analyzed using the same procedures described in Section 5.2. As shown in Table 5.3, the relative composition (excluding sodium) of the precipitate is essentially the same as that of the original filtrate, consisting primarily of Ca, Si, Al, and Mg.

The volume of gelatinous precipitate produced by the neutralization reactions was measured as a function of acid type, acid concentration, and

TABLE 5.3. Relative Compositions of the Neutralization Products and the Original Filtrate from the Dissolution of Uncured Grout in Citric and Sulfamic Acid

Element	Citric Acid		Sulfamic Acid	
	Filtrate %	Solids %	Filtrate %	Solids %
Ca	67.5	21.5	67.4	37.3
Si	14.7	38.7	14.7	27.6
Al	9.7	21.8	10.4	21.2
Mg	3.6	10.6	3.7	7.5
Fe	1.7	3.3	1.6	3.1
Ti	1.1	2.3	0.6	1.1
Mn	0.7	0.8	0.7	1.2
Cr	0.3	0.1	0.3	0.4
Sr	0.3	0.1	0.3	0.1
Zn	0.3	0.7	0.3	0.4
B	0.3	0.0	0.1	0.1

reaction temperature (Table 5.4). For citric acid, the wet precipitate volumes after 2 days of settling ranged from 14% to 46% of the original acid volume, with the higher values observed for the lower acid concentration. The corresponding precipitate volumes for the neutralized sulfamic acid ranged from 50% to 100% of the original acid volume. As in the case of the volume of as-reacted sulfamic acid solids, there was no obvious correlation with either acid concentration or temperature.

The precipitate produced by neutralization of the citric acid decontamination solution was readily suspended by moderate agitation. The sulfamic acid precipitates also could be suspended, but the suspensions appeared to be more viscous.

In addition to the above chemical characterizations, the concentration of Cs in the as-reacted and neutralized filtrate and solids was measured using atomic absorption techniques. The simulated liquid waste used to make the reference grout was spiked with nonradioactive Cs to permit this determination.

Table 5.4. Precipitate Volumes for the Neutralization of Citric and Sulfamic Acid Decontamination Solution

<u>Conc. (N)</u>	<u>Temp. (°C)</u>	<u>pH</u>	<u>Caustic Vol. (cm³)</u>	<u>Precipitate Vol. (cm³)</u>
<u>Citric Acid</u>				
6	21	13.2	94	42
6	60	12.6	83	95
1	21	13.2	24	110
1	60	11.8	14	139
<u>Sulfamic Acid</u>				
1.5	21	11.4	20	150
0.5	60	12.4	4	175
0.5	21	12.5	5	190
1.5	60	12.4	22	300

For the citric acid, essentially all of the Cs inventory in the grout went with the original filtrate, and about 10% remained with the neutralized solids. For the sulfamic acid, about 3% of the Cs inventory remained with the original solids, and about 8% was retained by the neutralized solids. The Cs associated with the gelatinous precipitate may reflect in part the difficulty of adequately washing the precipitate to remove all the filtrate. These measurements show, however, that the Cs remains primarily with the filtrate and does not preferentially partition to the solids either in the as-reacted condition or after neutralization.

5.4 WASTE NEUTRALIZATION

The maximum volume of 50% sodium hydroxide *N* required to neutralize the decontamination solution to pH 12 was calculated based on using 1900 L (500 gal) of 6 *N* citric acid as the decontamination solution. Without taking credit for partial neutralization by the grout, the required chemical addition volume is ~600 L (160 gal), or within the 750-L (200-gal) volume reserve capacity of the LCT.

The data in Tables 5.2 and 5.4 can be used to demonstrate the validity of this calculation. As discussed in Section 4.2, approximately 7.5 eq/kg is

required for complete grout dissolution. This corresponds to 0.5 eq for the 66.8 g of grout referenced in Table 5.2. Subtracting this from the 5.4 eq represented by the sum of the initial decontamination solutions leaves 4.9 eq to be neutralized by the caustic. The 0.266 L of sodium hydroxide used for this neutralization represents 5.1 eq, or slightly more than the calculated 4.9 eq as would be expected for neutralization to a pH of ~12.

6.0 MATERIALS COMPATIBILITY STUDIES

6.1 SCOPE

Predicted corrosion rates and/or dimensional changes for GTF materials and components must be consistent with design requirements and allowances, or replacement of the part must be technically feasible and operationally acceptable. The internal GTF surfaces that will be in direct contact with the decontamination solution are primarily 304L stainless steel with some 316L stainless steel. The grout pump stator is EPDM bonded to a carbon steel tube. The agitator blades are Hypalon coated onto stainless steel. There also is natural rubber in the system, and there may be other as yet unidentified materials used for adhesives, seals, packings, gaskets, bearings, bushings, etc. External casings are carbon steel and aluminum, but these will not be in direct contact with the decontamination solution. The tank farm piping is carbon steel.

A literature review was conducted for the major identified GTF materials to identify possible materials compatibility problems or other adverse effects from exposure to the candidate decontamination solutions. Contacts also were made with the grout pump manufacturer (Robbins & Myers, Inc.); the Du Pont Co., Polymer Products Department; and the Parker Seal Group.

6.2 COMPATIBILITY INFORMATION

Information on the compatibility of the candidate decontamination solutions with the major identified GTF materials was obtained from the following handbooks and corrosion references:

De Renzo, D. J. 1985. Corrosion Resistant Materials Handbook. Fourth Edition. Noyes Data Corporation, Park Ridge, New Jersey.

National Association of Corrosion Engineers (NACE). 1985. Corrosion Data Survey: Metals Section. Sixth Edition. Houston, Texas.

NIBCO. NIBCO Chemical Resistance Guide for Valves & Fittings. Elkhart, Indiana.

Parker Seal Company. Seal Compound Manual. Culver City, California, and Cleveland, Ohio.

Pruett, Kenneth M. 1978 and 1983. Compass Corrosion Guide II: A Guide to Chemical Resistance of Metals and Engineering Plastics. Compass Publications, La Mesa, California.

Schweitzer, Philip A. 1986. Corrosion Resistance Tables: Metals, Plastics, Nonmetallics, and Rubbers. Second Edition. Marcel Dekker, Inc., New York and Basel.

The following is a compilation of the compatibility information from these references. Data for nitric acid are included for comparison with the citric and sulfamic acid. Penetration data are given in mils per year (mpy).

304 Stainless Steel

Citric Acid:

<20 mpy to 27°C; then >50 mpy with pitting (Schweitzer, p. 312)
6 N: <20 mpy at 60°C (NACE, p. 40)
<20 mpy to 65°C (Pruett, p. A26)

Sulfamic Acid:

20%: >50 mpy at 60°C (NACE, p. 152)

Nitric Acid:

40%: <2 mpy to 90°C (Schweitzer, p. 754)
6 N: <2 mpy at 60°C (NACE, p. 86)

316 Stainless Steel

Citric Acid:

<20 mpy to 200°C (Schweitzer, p. 312)
6 N <2 mpy at 60°C (NACE, p. 40)
Resistant (NIBCO, p. 9)
<20 mpy to 65°C (Pruett, p. A26)

Sulfamic Acid:

20%: >50 mpy at 60°C (NACE, p. 152)
20%: Resistant (NIBCO, p. 25)

Nitric Acid:

40%: <2 mpy to 35°C; <20 mpy to 100°C (Schweitzer, p. 754)
6 N: <2 mpy at 60°C (NACE, p. 86)

Carbon Steel

Citric Acid:

>50 mpy at room temperature (Schweitzer, p. 312)
6 N: >50 mpy at room temperature (NACE, p. 40)
>50 mpy above room temperature (Pruett, p. A26)

Sulfamic Acid:

1.5 N: >50 mpy at room temperature (NACE, p. 152)

Nitric Acid:

40%: >50 mpy at room temperature (Schweitzer, p. 754)
6 N: >50 mpy at room temperature (NACE, p. 86)

Natural Rubber

Citric Acid:

10% Citric: resistant to 40°C (Schweitzer, p. 315)
Recommended (De Renzo, p. 357)
Satisfactory for static service only (Parker Seal Co.)

Sulfamic Acid:

Resistant to 65°C (Schweitzer, p. 1095)

Nitric Acid:

40%: Unsatisfactory (Schweitzer, p. 755)
3 N: Unsatisfactory (De Renzo, p. 363)

Hypalon[®]

Citric Acid:

Resistant to 120°C (Schweitzer, p. 313)
Little or no effect (De Renzo, p. 299)
Recommended (De Renzo, p. 357)
60°C max. (NIBCO, p. 9)
Satisfactory for static service only (Parker Seal Co.)

Sulfamic Acid:

20%: 21°C max. (NIBCO, p. 25)

[®]Hypalon is a registered trademark of E. I. Du Pont de Nemours & Co.

Nitric Acid:

40%: Resistant to 27°C (Schweitzer, p. 755)
30%: Severe effect at 70°C (De Renzo, p. 300)
Unsatisfactory (De Renzo, p. 363)

EPDM

Citric Acid:

Resistant to 150°C (Schweitzer, p. 313)
Little or no effect (De Renzo, p. 299)
Recommended (De Renzo, p. 357)
99°C max. (NIBCO, p. 9)
Satisfactory for static and dynamic service (Parker Seal Co.)

Sulfamic Acid:

Resistant to 150°C (Schweitzer, p. 1095)
20%: Not recommended (NIBCO, p. 25)

Nitric Acid:

30%: Severe effect at 70°C (De Renzo, p. 300)
Unsatisfactory (De Renzo, p. 363)

6.3 COMPATIBILITY EVALUATION

Although the references differ for some combinations, the following reflects the consensus on the compatibility of the identified materials with citric, sulfamic, and nitric acid:

304 Stainless Steel. Corrosion rates appear minimal (<20 mpy) for citric and nitric acid at temperatures to 60°C. There is one reference to increased corrosion rates and pitting for citric acid at higher temperatures, but this should be mitigated by short exposure times.

316 Stainless Steel. Corrosion rates appear minimal (<20 mpy) for all three acids over the temperature range of interest.

Carbon Steel. All three acids are corrosive to carbon steel, with greater than 50 mpy penetration rates at room temperature.

Natural Rubber. Natural rubber is incompatible with nitric acid, compatible with sulfamic acid to 65°C, and appears compatible with citric acid for specified conditions (dilute, ≤40°C, static service).

Hypalon. Hypalon is incompatible with nitric or sulfamic acid at greater than room temperature; it is compatible with citric acid at least to 60°C, although one reference suggests that it be restricted to static service.

EPDM. EPDM is incompatible with nitric acid. It may be compatible with sulfamic acid depending on the service conditions. It is compatible with citric acid for both static and dynamic service.

The most sensitive material in the GTF is the EPDM stator, since degradation of this component could lead to failure of the grout pump. Based on the literature data, only citric acid appears reasonably compatible with the EPDM. The installation of a new stator with increased clearance following the pump failure discussed in Section 2 should help compensate for any minor detrimental effect caused by exposure to citric acid. The abrasive action of the grout also would tend to remove any softened surface material.

Citric acid also is reasonably compatible with the other elastomers and identified GTF component materials, except for carbon steel. However, exposure of the carbon steel tank farm piping to the spent decontamination solution presumably would occur only after neutralization or dilution. The other mitigating factor is the expected short exposure time. Even if carbon steel components were exposed to acid with a corrosion rate of 1,000 mpy for the full 3-h decontamination period, the amount of material removed each cycle would be less than 0.5 mil. Addition of a corrosion inhibitor of the type used for industrial citric acid cleaning operations also could be employed if it were required to use citric acid rather than other more appropriate decontamination agents for carbon steel equipment. A greater concern, as noted earlier, is that there may be as yet unidentified critical materials (adhesives, seals, packings, gaskets, bearings, bushings, etc.) that might not prove compatible with citric acid.

7.0 CESIUM LEACHING STUDIES

7.1 SCOPE

Leaching studies were performed to explore the feasibility of removing soluble Cs by exposing the reference grout to DIW or 0.5 *N* KCl. The amount of the original Cs inventory removed by these two test solutions was determined as a function of exposed surface area (powdered versus cast samples), temperature (room temperature and 60°C), and grout cure condition.

7.2 PROCEDURE

Cast grout specimens containing Cs were prepared by spiking the simulated liquid waste with nonradioactive cesium chloride to give 42 ppm Cs in the uncured grout and 334 ppm Cs in the cured grout. The ~6-mm (0.24-in.)-thick by 3.2-cm (1.26-in.)-diameter sectioned cast specimens were encased in metallographic mounting resin with one face ground to expose a defined surface area to simulate field leaching conditions. These mounted specimens were immersed for 3 h in stirred 100-cm³ volumes of DIW or 0.5 *N* KCl at room temperature and 60°C. Powdered samples also were prepared and tested under identical leachant and temperature conditions. The amount of Cs removed by exposure to the leachant was measured using atomic absorption techniques (ARF No. M85031-1,2).

7.3 LEACHING RESULTS

The results of these leaching tests are summarized in Table 7.1 for the powdered grout, and in Table 7.2 for the cast specimens. Since the samples rapidly lost weight by drying, the calculated original Cs inventory is a minimum value, giving a maximum value for the percent removed.

For the powdered grout (Table 7.1), Cs removal was a minimum ($\leq 35\%$) for the cured grout in DIW at either room temperature or 60°C. Maximum cesium extraction ($\leq 90\%$) was achieved for uncured grout in 0.5 *N* KCl at 60°C. The effect of temperature was strongest (80% versus 44%) for the cured grout in 0.5 *N* KCl, whereas temperature had almost no effect for the cured grout in DIW. The percent removed was higher for the uncured grout in all cases.

TABLE 7.1. Removal of Soluble Cs by Leaching Powdered Grout in DIW and 0.5 N KCl

<u>Cure Condition</u>	<u>Leachant</u>	<u>Temp. (°C)</u>	<u>% Cs Removed</u>
Uncured	DIW	RT	≤42.7
Uncured	DIW	RT	≤38.0
Uncured	DIW	60°C	≤49.8
Uncured	DIW	60°C	≤52.2
Cured	DIW	RT	≤29.3
Cured	DIW	RT	≤38.9
Cured	DIW	60°C	≤37.4
Cured	DIW	60°C	≤32.6
Uncured	0.5 N KCl	RT	≤61.7
Uncured	0.5 N KCl	RT	≤66.4
Uncured	0.5 N KCl	60°C	≤90.2
Uncured	0.5 N KCl	60°C	≤90.2
Cured	0.5 N KCl	RT	≤47.9
Cured	0.5 N KCl	RT	≤41.0
Cured	0.5 N KCl	60°C	≤83.8
Cured	0.5 N KCl	60°C	≤77.2

TABLE 7.2. Removal of Soluble Cs by Leaching Cast Specimens in DIW and 0.5 N KCl

<u>Days After Preparation</u>	<u>Leachant</u>	<u>Temp. (C°)</u>	<u>% Cs Removed</u>
2	DIW	RT	≤14.2
2	DIW	60°C	≤58.6
29	DIW	60°C	≤39.8
29	DIW	60°C	≤54.3
2	0.5 N KCl	RT	≤17.3
2	0.5 N KCl	60°C	≤34.2
32	0.5 N KCl	60°C	≤39.9
32	0.5 N KCl	60°C	≤38.1

The nature of the leachant had a pronounced effect on Cs extraction from the powdered grout, with the amount removed increasing from 35% for cured grout in DIW at 60°C to 81% for cured grout in 0.5 *N* KCl at the same temperature. This KCl leachant effect presumably reflects an exchange of the chemically similar, but more highly concentrated, potassium ion with the Cs in the pore solutions. The findings that cesium removal was more difficult for the cured grout and that complete removal could not be achieved even for the powdered grout suggest that some of the Cs is incorporated in chemically or physically bound forms that may not be amenable to leaching, or at least would require a substantially more aggressive leachant for release.

The leaching results for the cast specimens with only one surface exposed to the leachant are given in Table 7.2. The specimens were tested after holding at room temperature for the indicated period after preparation. As in Table 7.1, the percentage removed is reported as maximum values because of sample drying.

Some significant differences were found in the leaching results for the cast grout compared with the results for the powdered material. Temperature had a greater effect on the percent Cs removal from the cast material for both leachants, and particularly for the DIW, than was observed for the powdered grout. Similarly, DIW was more effective in removing Cs than the 0.5 *N* KCl leachant, which is the reverse of the leaching behavior observed for the powdered material.

Although the reasons for these differences are not clear, the leaching results for the cast material suggest that less than half of the Cs inventory is removable from 6-mm (0.24-in.)-thick grout deposits with only one surface exposed to the leachant. This would not reduce dose levels sufficiently to permit contact maintenance. However, following a grout removal operation, leaching as part of the rinsing process might further reduce dose levels associated with any residual grout pockets or films.

8.0 CONCLUSIONS AND RECOMMENDATIONS

The following are the major conclusions and recommendations for the work documented in this report:

Conclusions:

- With adequate agitation, either sulfamic or citric acid at moderate concentrations ($\leq 1\text{ }N$) and temperatures less than the maximum attainable 60°C solution temperature will remove uncured or cured 6-mm-thick reference grout deposits within the specified 3-h decontamination period.
- For low agitation conditions, complete removal of adherent, cured grout to leave a clean, bright metal surface cannot always be achieved even for the higher acid concentrations.
- The projected decontamination solution volumes and concentrations required to remove up to 1-cm-thick deposits of the reference grout are compatible with the capacities of the decontamination and liquid collection tanks, including the additional volume needed for waste conditioning operations.
- Although the use of lower concentration acids is preferred from a materials compatibility standpoint, higher concentrations may be required to provide sufficient dissolution capacity if the average residual grout thickness exceeds 2 mm.
- The citric or sulfamic acid grout decontamination processes and subsequent neutralization operations do not produce gels or precipitates that would be unusually difficult to remove from the liquid collection tank or transport through piping.
- The required pH adjustment volumes for treatment of the spent decontamination solutions are compatible with the available volumes in the liquid collection tank.
- The Cs in the grout remains primarily with the filtrate and does not preferentially partition to the solids either in the as-reacted condition or after neutralization.
- Of the acids evaluated, only citric acid appears reasonably compatible with the identified sensitive GTF materials, such as the elastomer used for the grout pump stator. Short exposure times should help mitigate other compatibility concerns.

- The observations that Cs removal is more difficult for cured grout and that complete removal cannot be achieved even for powdered grout suggest that some of the Cs is incorporated in chemically or physically bound forms that may not be amenable to leaching.
- Although Cs leaching of cast material only removed 14% to 60% of the original inventory, it might function as part of the postdecontamination rinsing process to further reduce dose levels associated with residual grout pockets or films.
- Based on the overall study results for the reference grout formulation, 3 to 6 *N* citric acid under adequate agitation conditions appears to provide the best combination of adequate dissolution rates and reaction capacity, acceptable waste form, and compatibility with the identified GTF materials.

Recommendations:

- Pilot-plant studies are recommended to investigate the effect of the expected variation in solution agitation conditions and flow velocities along the GTF decontamination solution flow path (direct agitation, spray, pumped flow, gravity flow) on the adequacy of grout removal.
- Further efforts should be made to identify any additional GTF materials (adhesives, seals, packings, gaskets, bearings, bushings, etc.) that might prove incompatible with the proposed citric acid decontamination solution.
- Because of the difficulty of simulating localized GTF time, temperature, and flow conditions in the laboratory, pilot-plant studies are recommended to more directly evaluate the effects of these process-specific conditions on materials compatibility with the proposed citric acid decontamination solution.

APPENDIX A

CALCIUM DETERMINATION BY SELECTIVE ION POTENTIOMETRY

APPENDIX A

CALCIUM DETERMINATION BY SELECTIVE ION POTENTIOMETRY

INTRODUCTION

Selective ion potentiometry is a simple, quick, and accurate method of measuring specific ions in aqueous solutions. This technique was selected for the grout decontamination studies to monitor the dissolution rate of the grout in sulfamic acid and citric acid decontamination solutions. Calcium, which is one of the major constituents of the reference grout formulation, is used as the "marker" to follow the progress of the dissolution reaction.

Although selective ion potentiometry is a standard analytical technique, it must be adapted for each specific application to optimize sensitivity for the ion of interest and to minimize interferences from other ions. This appendix documents the work performed to adapt and optimize this analytical technique for the decontamination solutions used for the grout dissolution rate studies, to calculate the resulting calcium concentrations, and to validate the overall analytical and computational processes.

THEORY

The emf generated by a Ca^{2+} selective ion electrode plus a reference electrode in solutions of similar composition (and therefore similar liquid junction potential) conforms to the Nernst equation:

$$E = K + S \log_{10}(C_{\text{Ca}}) \quad (\text{A.1})$$

where E = measured electrode potential in mV

K = reference potential constant

C_{Ca} = molar concentration of the soluble calcium ion (Ca^{2+})

S = electrode slope constant (defined later in report).

The specific analytical procedure used with the calcium selective ion electrode is the "known-addition" method as described in the manufacturer's instruction manual (Orion Research Incorporated, Laboratory Products Group, Model 93-20 Calcium Electrode Instruction Manual).

The known-addition method consists of the following steps:

1. Immerse the electrodes in a suitable electrolyte.
2. Add an aliquot of the unknown solution and measure the potential (E_1).
3. Add an aliquot of a standard solution containing a known concentration of Ca^{2+} and measure the new potential (E_2).
4. Repeat Step No. 3.

This sequence generates three emf values representing the test solution plus two spikes with known calcium concentrations:

$$E_1 = K + S \log_{10}(C_x) \quad (\text{A.2})$$

$$E_2 = K + S \log_{10}(C_{s1}) \quad (\text{A.3})$$

$$E_3 = K + S \log_{10}(C_{s2}) \quad (\text{A.4})$$

By taking the differences in the measured emf values for the spiked and the unspiked samples, a relatively simple equation can be derived that allows calculation of the unknown Ca^{2+} concentration, C_x ; for example,

$$\Delta E = E_2 - E_1 = S \log_{10}(C_{s1}/C_x) \quad (\text{A.5})$$

But,

$$C_{s1} = (V_E \times C_x + V_S \times C_S) / (V_E + V_S) \quad (A.6)$$

where: V_E = electrolyte volume after sample addition

V_S = standard solution volume

C_S = standard solution concentration (M).

Combining Equations (A.5) and (A.6), and solving for C_x gives

$$C_x = [(V_S \times C_S) / (V_E + V_S)] / [10^{\Delta E / S} - V_E / (V_E + V_S)] \quad (A.7)$$

The concentration of Ca^{2+} in the test solution at the time the aliquot sample was taken is then C_x from Equation (A.7) times a dilution factor reflecting the volume of aliquot added. This calculation is performed for both spike potentials, and the C_x values are averaged to give the reported calcium concentration. Comparing the two calculated C_x values also provides a check against experimental or computational errors.

The known-addition method thus permits accurate determination of the calcium ion concentration in the decontamination solution as a function of reaction time. These data are then used to calculate the rate at which calcium is released from the grout sample and, by inference, the rate at which the grout itself is dissolving.

KNOWN-ADDITION PROCEDURE, AS ADAPTED

The following is the known-addition procedure as adapted for the sulfamic acid and citric acid grout dissolution solutions.

A. Sulfamic Acid Solutions

Aliquots of the dissolution solution (0.5 cm^3) are transferred to bottles containing 25 cm^3 of 0.1 M KCl . Approximately 0.5 g of $BaCO_3$ powder is added to this electrolyte to increase the pH of the strongly acidic sulfamic acid. The bottles are appropriately labeled (aliquot number, reaction time, etc.) and set aside for later analysis.

B. Citric Acid Solutions

The procedure is exactly the same as that for sulfamic acid solutions except that BaCO_3 is not added to the electrolyte, since citric is a weaker acid.

C. Calcium Ion Concentration Measurement

1. Condition the calcium selective ion electrode (Orion Model 93-20 or equivalent) according to manufacturer's recommendations.
2. Prepare the reference electrode (Orion double junction or equivalent) according to manufacturer's recommendations, with one important exception: use 4 M KCl as the outer filling solution instead of the solution supplied with the electrode.
3. Connect the electrodes to a pH/mV meter that has a 0.1-mV resolution. Select the "mV" readout.
4. Transfer the entire contents of a bottle from Section A or B above to a small beaker. Introduce a small magnetic stir bar and place onto a stir plate set at low speed.
5. Rinse the electrodes (1 and 2 above) with deionized water, blot dry with a tissue, and place the electrodes into the stirred solution. After ~30 seconds, or when the reading stabilizes, record the potential (mV) displayed on the meter.
6. Pipet an appropriate volume of 0.10 M Ca^{2+} standard into the stirred solution. After the system has stabilized, record the potential reading and the volume of Ca^{2+} standard added. Note: The volume of 0.10 M Ca^{2+} used to spike the solution should be sufficient to cause an approximate doubling of the overall calcium concentration. This, in turn, will result in approximately +9 mV change in the measured potential. A bit of trial and error is obviously involved until experience is gained but, in general, a 50- or 100- μL spike is appropriate for samples taken early in the dissolution reaction. For aliquots taken later in the dissolution process, progressively larger spikes of 0.1 M Ca^{2+} standard are needed.
7. Repeat Step 6, adding enough Ca^{2+} standard to approximately double the overall calcium concentration again.
8. Remove the electrodes from the test solution, rinse well with deionized water, blot dry, and place the electrodes in the next solution to be analyzed.
9. Repeat Steps 6 and 7 with each test solution until all of the unknowns have been measured.

SAMPLE CALCULATIONS

The following sample calculations are based on data for a simulated dissolution test (page 138 of Laboratory Record Book No. 4002).

1. Calculation of Actual Calcium Concentration

First Addition

Start with 25 cm³ of 6 N citric acid

Add 0.5 cm³ of 0.1 M Ca²⁺

New volume = 25.0 + 0.5 = 25.5 cm³

Calcium concentration = $(0.5 \times 0.1)/25.5 = 1.9608 \times 10^{-3} \text{ M}$

Second Addition

Start with 25.5 cm³ of $1.9608 \times 10^{-3} \text{ M Ca}^{2+}$ solution

Remove 0.5 cm³ sample and add 0.5 cm³ of 0.1 M Ca²⁺

Calcium concentration = $(1.9608 \times 10^{-3} \times 25.0 + 0.5 \times 0.1)/25.5 = 3.8831 \times 10^{-3} \text{ M}$

Third Addition

Start with 25.5 cm³ of $3.8831 \times 10^{-3} \text{ M Ca}^{2+}$ solution

Remove 0.5 cm³ sample and add 1.0 cm³ of 0.1 M Ca²⁺

Calcium concentration = $(3.8831 \times 10^{-3} \times 25.0 + 1.0 \times 0.1)/26.0 = 7.5799 \times 10^{-3} \text{ M}$

Fourth Addition

Start with 26.0 cm³ of $7.5799 \times 10^{-3} \text{ M Ca}^{2+}$ solution

Remove 0.5 cm³ sample and add 2.0 cm³ of 0.1 M Ca²⁺

Calcium concentration = $(7.5799 \times 10^{-3} \times 25.5 + 2.0 \times 0.1)/27.5 = 1.4301 \times 10^{-2} \text{ M}$

Fifth Addition

Start with 27.5 cm³ of $1.4301 \times 10^{-2} \text{ M Ca}^{2+}$ solution

Remove 0.5 cm³ sample and add 4.0 cm³ of 0.1 M Ca²⁺

Calcium concentration = $(1.4301 \times 10^{-2} \times 27.0 + 4.0 \times 0.1)/31.0 = 2.5359 \times 10^{-2} \text{ M}$

Sixth Addition

Start with 31.0 cm³ of $2.5359 \times 10^{-2} \text{ M Ca}^{2+}$ solution

Remove 0.5 cm³ sample and add 8.0 cm³ of 0.1 M Ca²⁺

Calcium concentration = $(2.5359 \times 10^{-2} \times 30.5 + 8.0 \times 0.1)/38.5 = 4.0869 \times 10^{-2} \text{ M}$

2. Calculation of Electrode Slope Constant

The electrode slope constant (S) is given theoretically by

$$S = (2.303 \times R \times T)/(n \times F)$$

where R is the gas constant, T is the absolute temperature, n is the number of equivalents, and F is the Faraday Constant. For calcium with two equivalents, the theoretical value of S is 29.6 at 25°C.

The value of S may be determined experimentally from a plot of electrode potential versus $\log_{10}$ of the actual calcium concentration, as shown in Figure A.1. (The calcium concentration is calculated by correcting the concentration obtained with the standard additions by a dilution factor representing the addition of the 0.5-cm³ samples to 25.5 cm³ of electrolyte. This dilution factor is 0.5/26.0, or 1.923×10^{-2} .) The linearity of the curve confirms the proper functioning of the electrode. The value of S calculated from the slope of the experimental curve in Figure A.1 is 30.0, which is consistent with theory for a room temperature measurement. Experience shows, however, that a better fit to the experimental data is obtained by using S values in the 28.5 to 29.5 range.

3. Calculation of Measured Concentration

As discussed in the Theory section, the calcium concentration of the unknown is calculated using Equations (A.2) through (A.6). The calculations are performed for two spikes with the standard solution, and the two results are averaged to give the reported concentration.

FIGURE A.1. Electrode Slope Determination for Simulated Grout Dissolution Test

The following is a sample calculation using an S value of 28.5 for the fourth addition that produced a citric acid solution with a 0.01430 M calcium concentration.

Initial Reading

Add 0.5 cm³ of the simulated unknown to 25.5 cm³ of the electrolyte in the polybottle; measured potential = -49.4 mV; volume = 26 cm³; calcium concentration = C_x.

First Spike

Spike with 0.1 cm³ of 0.1 M standard solution; measured potential = -38.7 mV; volume = 26.1 cm³; calcium concentration = C_{s1}.

Subtracting Equation (A.3) from Equation (A.2) gives

$$\begin{array}{r} -49.4 = K + S \log_{10} (C_x) \\ 38.7 = -K - S \log_{10} (C_{s1}) \\ \hline -10.7 = S \log_{10} (C_x/C_{s1}) \end{array}$$

$$\text{or, } (C_{s1}/C_x) = 10^{10.7/28.5} = 2.3738$$

$$\text{Solving Equation (A.7) gives } C_x = 2.781 \times 10^{-4}$$

This is the concentration in the electrolyte; the concentration in the original sample based on the first spike is

$$C_{Ca1} = C_x \times 26.0/0.5 = 0.01446 \text{ M}$$

Second Spike

Spike with 0.2 cm³ of 0.1 M standard solution; measured potential = -29.1 mV; volume = 26.3 cm³; calcium concentration = C_{s2}.

Subtracting Equation (A.4) from Equation (A.2) gives

$$\begin{array}{r} -49.4 = K + S \log_{10} (C_x) \\ 29.1 = -K - S \log_{10} (C_{s2}) \\ \hline -20.3 = S \log_{10} (C_x/C_{s2}) \end{array}$$

$$\text{or, } (C_{s2}/C_x) = 10^{20.3/28.5} = 4.7497$$

Solving Equation (A.7) gives $C_x = 2.737 \times 10^{-4}$

This is the concentration in the electrolyte; the concentration in the original sample based on the second spike is

$$C_{Ca2} = C_x \times 26.0/0.5 = 0.01423 \text{ M}$$

The difference between the calcium concentrations calculated from the two spikes is 0.00023 M, or 1.6% of the average value of 0.01435 M. This small difference in the two independent measurements is an internal check on the accuracy of the data entry as well as the applicability and validity of the entire known-addition procedure.

The measured average calcium concentration, 0.01435 M, is within 0.4% of the actual 0.01430 M concentration. Figure A.2 is a plot of all six concentrations measured using the known-addition procedure versus the actual calcium concentrations. The curve essentially extrapolates to zero and has a slope near unity, further demonstrating the applicability of both the analytical procedure and the calculations used to reduce the data.

FIGURE A.2. Measured Calcium Concentration Versus Actual Concentration for Simulated Grout Dissolution Test

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