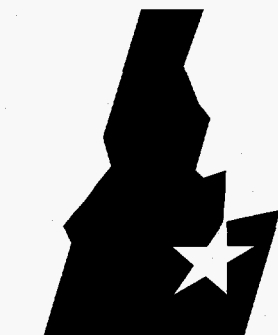


September 1996



**Idaho
National
Engineering
Laboratory**

Testing and Comparison of Seventeen Decontamination Chemicals

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Rick L. Demmer

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**Testing and Comparison of
Seventeen Decontamination Chemicals**

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Published September 1996

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ABSTRACT

This report details the testing and evaluation of seventeen decontamination chemicals. Tests were conducted with SIMCON (simulated contamination) coupons under controlled conditions to compare cleaning effectiveness, overall corrosion potential for plant equipment, interim waste generation and final waste generation.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS	iii
ABSTRACT	v
EXECUTIVE SUMMARY	vii
ACRONYMS	viii
1.0 INTRODUCTION	1
2.0 EXPERIMENTAL METHODS	2
3.0 DISCUSSION OF RESULTS	2
3.1 CORPEX™ Chemicals	4
3.2 Water	5
3.3 Nitric Acid	5
3.4 Nitric Acid and Oxalic Acid	6
3.5 TURCO™ Alkaline Rust Remover	6
3.6 Nitric Permanganate	7
3.7 Tartaric Acid	7
3.8 Formic Acid	8
3.9 Hydrogen Peroxide	8
3.10 TURCO™ 4502	9
3.11 Citric Acid	10
3.12 Aluminum Nitrate	10
3.13 Nitric Acid-Hydrofluoric Acid	10
3.14 TECHXTRACT™ 100, 200, 300	11
3.15 Fluoroboric Acid	12
4.0 RESULTS AND SUMMARY	13
5.0 RECOMMENDATION	14
6.0 REFERENCES	14

EXECUTIVE SUMMARY

This report covers experimental work comparing seventeen different decontamination chemicals. Twelve of these chemicals have some novelty, or are not currently in use at the Idaho Chemical Processing Plant (ICPP). Five are more common decon solutions used as a baseline for effective comparison. Decontamination factors, waste generation values, and corrosion rates are tabulated for these chemicals. Recommendations are given for effective methods of decontamination with non-sodium or low-sodium decontamination chemicals.

The most effective decon chemicals in these tests were two commercially available "systems" and two fluoride containing solutions. The most effective solution was CORPEX 921, a novel chelant solution. Next were fluoroboric acid, TECHXTRACT solution (100, 200, 300) and nitric acid-dilute hydrofluoric acid. Several other solutions were found to be an improvement over current ICPP decon chemistry. The CORPEX 921 and fluoroboric acid solutions unfortunately led to large amounts of waste (some of it high sodium) in waste processing. TECHXTRACT chemicals do not produce large amounts of waste, but would require long PEW bleeding times because of corrosion concerns. Waste issues for TECHXTRACT and CORPEX solutions will continue to be researched in FY'97.

ACRONYMS

DF (Df)	Decontamination Factor
ICPP	Idaho Chemical Processing Plant
NWCF	New Waste Calcine Facility
SIMCON	Simulated Contamination
LMITCO	Lockheed-Martin Idaho Technologies Company
XRF	X-ray Fluorescence
mpy	mills per year (corrosion)

Testing and Evaluation of Seventeen Decontamination Chemicals

1.0 INTRODUCTION

The Idaho Chemical Processing Plant (ICPP) Decontamination Development Group has the task of evaluating and assisting in implementing new decontamination techniques for waste minimization and effectiveness. For the past two decades, the Decontamination Development Group has tested various methods of decontamination for the ICPP and supported decontamination projects in the many processes. Since process equipment was typically flushed to remove radioactive contamination prior to major repair work, evaluations were primarily focused on chemical decontamination methods. There has been extensive work at the ICPP during the '70s and '80s on chemical decontamination testing (including electropolishing) with an emphasis placed on effective decontamination of ICPP first cycle process equipment.¹

Current emphasis is on minimization of chemical decontamination waste because of restrictions on the use of hazardous chemicals and ICPP waste handling issues. The use of chemical decon methods usually entails the generation of large quantities of secondary (in addition to the contaminant and substrate) waste. The increased regulation and concern about secondary waste has caused many nuclear facilities to abandon many of their former chemical decon methods. At the ICPP, this emphasis has taken the form of research and application of several nonchemical based decon methods (light ablation, CO₂ pellet blasting and liquid abrasive blasting) and also novel chemical flushing methods.

The primary reason for investigating novel decontamination methods was the difficulty of processing typical decontamination liquid waste containing sodium and potassium salts through the waste calcining facility. "Sodium waste" requires large amounts of chemical additives to prevent bed agglomeration and produce a satisfactory calciner product. Future decontamination activities at the ICPP could result in the production of over 1 million gallons of sodium-bearing waste using the current decon techniques of chemical/water flushes and steam jet cleaning.

Many of the techniques presented here are not particularly unusual. As early as 1955 combinations of nitric acid, citric acid, sodium hydroxide, tartaric acid, oxalic acid, periodic acid, and hydrofluoric acid were used to decontaminate the ICPP systems to allow manned entry of the cells.² But while the concepts are not novel, few real comparisons have been made between these methods. This report presents a "baseline" comparison using the methods detailed in "Testing

and Evaluation of Eight Decontamination Chemicals", WINCO-1228, September 1994. This current evaluation includes and updates most of the information obtained in the first set of tests.

2.0 EXPERIMENTAL METHODS

An experimental method was chosen to allow a reasonable comparison of the effectiveness of the decon chemicals while limiting variables. To facilitate this, a test involving SIMCON 2, a simulated contaminant matrix on stainless steel coupons³, was devised to compare these criteria. All chemicals were tested under the following conditions:

- Approximately 50 ml of solution was used.
- Solutions were stirred continuously during the tests.
- Solutions were heated to 55° C for a duration of 3 hours.

Two SIMCON 2 coupons were used for each test of a given chemical. Coupons were placed in a 150 ml beaker on a hotplate in the solutions under the above conditions for the full duration of the test, then rinsed with distilled water, and left to air dry. The chemical solutions included: TURCO 4502, tartaric acid, formic acid, citric acid, hydrogen peroxide, TURCO ARR, CORPEX Smearaway™, CORPEX 918™, TECHXTRACT™ 100, 200,300, nitric acid, nitric acid/oxalic acid, nitric permanganate, hydrofluoric acid/nitric acid, fluoroboric acid and aluminum nitrate.

The coupons were analyzed for removal of the SIMCON contaminants using X-ray fluorescence (XRF). Results on the amount of SIMCON before tests were compared to the results after cleaning. A decontamination factor (Df) was calculated from these results. The two analytes (Cs and Zr) used on the SIMCON 2 were removed at different rates. In general, cesium was easier to remove than the zirconium; therefore, Df results are reported by element.

The comparisons of expected relative waste volumes are based on both experience and modeling of solutions performance in the Process Equipment Waste (PEW) Evaporator and New Waste Calciner. Values for both evaporation and calcination are given separately for the various solutions. Much of the waste generation data is calculated using ASPEN process modeling software.^{4,5,6}

3.0 DISCUSSION OF RESULTS

This section is divided into discussions of the various chemicals used in the tests. Table 1 describes the overall results of the comparison of decontamination factors (Df, the ratio of before and after results) and waste generation. The waste

comparison is based on the use of 1000 gallons of the particular reagent in a 12,000 gal evaporator feed batch. For many of the solutions these values went to the minimum (0.03) volume because no significant concern prevented the greatest expected boildown (30:1). The waste values are expressed on a cubic meter (m³) of waste per m³ of original solution basis.

Table 1, Laboratory Chemical Decontamination Studies.

Chemical Reagent	Df S2-Cs	Df S2-Zr	evaporated volume(m ³)	calcine volume(m ³)
CORPEX 918	1.7	1.3	0.03	0.08
CORPEX Smearaway	2	1.7	0.03	0.02
water	3.5	1.2	0.03	0
Nitric acid	4.7	1.3	0.03	0
nitric/oxalic	5	1.2	0.67	0.18
Turco ARR	5.5	1.2	0.5	0.35
nitric permanganate	6.4	1.2	0.0125	0.019
tartaric acid	6.5	1.2	0.03	0
formic acid	6.7	1.1	0.03	0
hydrogen peroxide	6.7	1.2	0.03	0
Turco 4502	7	1.4	0.45	0.34
citric acid	8.8	1.3	0.03	0
aluminum nitrate	11.4	1.4	0.273	0.23
nitric 800ppm hydrofluoric	14.2	5.9	0.0525	0.0058
TECHXTRACT 100,200,300	17	6	0.03	0.018
fluoroboric acid	18.3	24	2	0.26
CORPEX 921	44.3	7.8	0.1	2.1

Calcine waste generation is not as straightforward as it initially seems. For example, the use of sodium and potassium salt based decon reagents (typically alkaline KMnO₄) yields excessive calcine. Approximately 3.5 moles of aluminum nitrate are required to calcine a mole of sodium or potassium. Calculating the amount of volume of calcine as a result of the mass (density) of solution added to make up for the sodium, results in about 0.25 liters of calcine for each mole of sodium. This adds up fast for wastes containing significant amounts of these

chemicals. Also, many chemicals (hydrofluoric acid) should be complexed with other reagents (aluminum nitrate) after their use. This complexation results in significant volume increases. The assumption is also that enough solids are present in the concentrated waste (corrected for high fluoride waste) to make a good calcine without additives.

3.1 CORPEX™ Chemicals

The CORPEX™ Chemical Company, Research Triangle Park, North Carolina, provided chemicals and technical assistance in testing their proprietary chemicals. The technical staff at CORPEX™ performed one test where approval of the anticipated waste stream could not be obtained at the ICPP. CORPEX™ provides a decontamination service and supplies a line of about a dozen different chemicals with thorough consultation. Three different CORPEX™ chemicals were tested in this study.

Two chemicals tested were CORPEX™ 918 and CORPEX™ Smearaway™. Although these chemicals are primarily designed for "spray-on, wipe-off" application to remove loose and organic contaminants, these tests simulated their use in a "soak and flush" type of application. In this type of process, they were diluted to about 10% of their original concentration, as the cost of soaking with full strength chemicals would be prohibitive. In these tests, these chemicals were able to remove less than half of the cesium contamination, making them less effective than hot water. This is probably because they are non-polar decon reagents designed to work on loose, organic type contaminants. This indicates that although much success has been obtained with these chemicals for degreasing and spray and wipe decon, they are not suited for flushing applications.

CORPEX™ 921, however, was quite effective on the SIMCON coupons achieving the highest degree of decontamination. The results indicate that this was the most effective reagent for removing cesium contamination, and scored very highly for zirconium contaminants as well. CORPEX™ 921 is a proprietary chelating reagent. It has a unique molecular structure, which is superior in decontamination to most other chelants investigated at the ICPP. Other DOE sites, Hanford, Oak Ridge and Peduca, have used it with good results.⁷ The tests undertaken to compare its effectiveness on SIMCON coupons were performed by CORPEX™ personnel at their facility, and analyzed at the INEL. Some complicated waste issues led to this unusual test protocol.

CORPEX™ 921 is an advantageous method of removing contamination, but

waste concerns currently prevent its implementation at the ICPP.⁸ A large amount of potassium permanganate oxidant is required to oxidize this organic chemical to its components. This oxidant is unfavorable for use in calcination as it significantly increases the volume. A satisfactory substitute oxidizer is being researched.

3.2 Water

This test set a baseline which was missing in earlier evaluations. Because the coupons were rinsed with water, and lightly brushed, it was assumed that all the "loose" contaminants were removed. It was recognized that some amount of contaminants should be removable with hot water but simply unknown to what level. Historically, it is not unusual for a reduction of more than 50% to occur decontaminating with hot water alone, and to achieve much higher decon factors using steam. In this case, the hot water removed about 72% of the cesium and about 17% of the zirconium contaminants. This corresponds well with observation of routine decontamination at the ICPP. Typically, the cesium is readily removed but other radionuclides (like zirconium) are not as easily removed.

3.3 Nitric Acid

Nitric acid (HNO_3) is the most commonly used decontamination chemical at the ICPP. Hundreds of thousands of gallons of HNO_3 are consumed in the process of decontamination. Six molar nitric acid was tested as a baseline, in the same manner as the water. It is a fair decon reagent but is not truly corrosive to the stainless steel. It does not attack the passivation layer (which is probably where the contaminants are held) but usually promotes its growth. It is possible that some contaminants may even become more firmly entrenched rather than removed by the use of nitric acid. Also, at the ICPP, the solution which left the residual contaminants was generally nitric acid based. This indicates that nitric acid should be of little effectiveness in redissolving contaminants. Test results indicate that this reasoning is fairly accurate. In terms of the cesium and zirconium removal, nitric acid ranked near the bottom with only three chemicals, including water, being less effective.

Most of the historical success of decon with nitric acid at the ICPP centers around its use to dissolve residues. Many of the processes in use at the ICPP leave solid material that is somewhat soluble in nitric acid. Results from sampling of decontamination solutions from 1982 to 1991 show that nitric acid is second only to alkaline tartaric acid in removing contamination from the ICPP headend processes. This is no doubt partly because it was used nearly ten times as often as any other chemical, and some thirty times as often as tartaric acid.¹ But the effectiveness of nitric acid to dissolve solids and residues should not be minimized.

This is particularly true in the case of dissolving calcine at the NWCF, which is our largest current problem.

The largest disadvantage of nitric acid use is its significant contribution to the amount of tank farm waste. As the solution that is relied upon more often than any others, it is overused well after its effectiveness on residues is complete. Common practice in ICPP decontamination is to repeat HNO₃ flushing throughout an entire decon campaign, generating the thousands of gallons extra with no value returned.

3.4 Nitric Acid and Oxalic Acid

A solution of 3.5 M HNO₃ · 0.5 M oxalic acid was evaluated during this experiment. Combinations of organic acids and mineral acids (citric and oxalic acids with nitric acid) have been documented previously. This particular formulation was tested in plant use during the 1980's.⁹ Good results were obtained both in plant and in the SIMCON tests. It combines a general reductive property with a strongly acidic dissolution and complexation capability. A higher waste generation was expected because of the limited solubility of oxalic acid.

These tests on the nitric-oxalic acid mixture place the solution in about the same position as the 1994 study. A Df of 4.5 (for Cs) was determined in 1994, where a Df of 5 was determined in this study.

3.5 TURCO™ Alkaline Rust Remover

TURCO Alkaline Rust Remover (ARR) was fairly effective at removing decontamination from the SIMCON coupons. It was tested at a concentration of 60 g/l. It has been particularly effective at removing scale and contaminants held in the scale and rust. This is partly due to alternating from an acidic process to a basic one. ARR tends to dissolve the oxides without removing an appreciable amount of base metal. Also, many of the radionuclides (like ruthenium) are more soluble in base than in acid systems.

The largest issue concerning the use of TURCO ARR is excess sodium waste. TURCO ARR contains about 70 % sodium hydroxide and is often used in greater quantities than the 60 g/l commonly recommended. In the case of descaling the PEW evaporator, for instance, solutions of up to 240 g/l ARR are used. This translates to about 4.2 M sodium, which is about twice the concentration of the current, unacceptably high, waste.

3.6 Nitric Permanganate

Traditional alkaline permanganate (AP) decon solutions are generally preferred to acidic permanganate because of their lower corrosion of metals (due to their basic nature). Corrosion remains fairly well controlled with AP solutions even when used at high concentrations. However, strongly alkaline solutions are inherently high in sodium and potassium hydroxide, resulting in high waste volumes. For this reason, adapting the oxidizing chemistry of the alkaline permanganate reagents to a nitric acid system could offer large benefits.

Nitric acid-potassium permanganate (NP) decon solutions have been tried in the nuclear industry with notable success. Decontamination factors for the NP system at the Ringhals 2 (Sweden) nuclear reactor system were 6.4 to 7.3, while AP Df stood at 1.9 to 2.3.¹⁰ Decon solutions of AP and NP are also often used with reductive solutions such as low oxidation metal ion (LOMI) processes. LOMI decontamination campaigns show little difference in well managed NP and AP decontaminations. The Results reported for this test are the individual results for NP of Df 6.4 and 1.2. However, when the test was repeated using a second oxidizing step, the Df went to 17.8 and 6.2. These results would change its relationship to the other chemicals, and place NP near the top of the decon reagents.

These solutions present a significantly lower sodium waste problem than the typical TURCO DECON solutions. Though they contain potassium permanganate as the oxidizer, they do so without the overwhelming potassium hydroxide that creates the high waste volumes such as for TURCO 4502. This results in a final calcine waste volume is 18 times less for NP than for AP.

3.7 Tartaric Acid

The use of organic acids is a novel, though not unknown, approach to reductive chemical decontamination at the ICPP. Tartaric acid has the composition of $C_4H_6O_6$ and is commonly used as a *dextrorotatory* isomer¹¹. As with most of the organic acids, it acts to dissolve material as an acid but it also acts as a reductant and will complex metals. Plant decontamination records document successful use of tartaric acid both at the ICPP and at other facilities.

Of the organic acids tested during this study, tartaric was the least effective on the SIMCON coupons. Formic and citric acids were both more effective, however, generally, the organic acids were fairly effective and surpassed several of the standard methods of decontamination.

3.8 Formic acid

Another organic decontamination reagent tested was formic acid. Formic acid is the simplest organic acid, with a formula of CH_2O_2 , and acts as either a weak acid (a dissociation constant of about 10 times that of acetic acid)¹⁰ or an aldehyde. It will dissolve most metals, and acts as a reductant, but is not as good a chelant as most other organic acids

In these tests, formic acid ranked better than most other organic acid solutions tested and about mid-scale as a good decontamination reagent. The decontamination factor for cesium was better than most of the common decon reagents, and on par with the most effective reagents historically used at the ICPP. Historically it has been quite successful at decontaminating materials other than the stainless steel used in these tests. Hanulik has also proposed the use of formic acid for the decon of concrete.¹²

An additional advantage of using formic acid comes from the ease of processing the waste solutions. Formic acid is easily oxidized to water and carbon dioxide. The ICPP waste processing systems are an oxidizing matrix, so the formic acid should be readily oxidized to the water and carbon dioxide, giving a net "zero" volume in terms of evaporation and calcination.

3.9 Hydrogen Peroxide

Hydrogen peroxide has been used in decontamination practices for many years. It has a dual role, part of which is seen in the efficiency of the solution tested in this study. The overall effectiveness of the 1% hydrogen peroxide solution was higher than expected, exceeding that of most traditional methods. The second role of the hydrogen peroxide has been to reduce strongly oxidizing decon reagents (like ceric nitrate) to more benign species (cerrous nitrate), or to oxidize certain other strongly reducing reagents (like formic acid). This is accomplished by varying the conditions (using different catalysts) under which either the oxidation or the reduction are performed.

While the efficacy of the hydrogen peroxide was proven for decontamination during these studies, a more powerful use could be in combination with another oxidizing or reducing decon reagents. This would provide a two step decon, similar to the AP/oxalic acid treatments more commonly used, but with potentially much less waste. For example, formic acid would be used first, providing a good decontamination factor (DF cesium 6.7), and then be flushed to a waste processing tank. The hydrogen peroxide would be used next (Df cesium 6.7) achieving a combined theoretical Df 45. The hydrogen peroxide would be flushed to the tank already containing the formic acid and with an

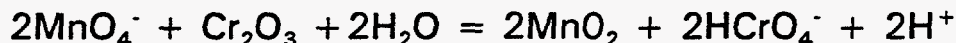
appropriate catalyst would oxidize the formic acid to hydrogen and CO₂. Assuming that the proportions were correctly combined, neither reagent would be left, as the hydrogen peroxide would be reduced to water and oxygen.

There are potential safety concerns about the general use of hydrogen peroxide including the rapid decomposition of the material. However, at these lower concentrations (<5%) this is a very low risk. Additional concerns about the peroxide reactions with organics (some probability in ICPP waste processing equipment) which would be catalyzed by metal ions (high probability) could be an even greater problem. These safety concerns would have to be addressed by the safety analysis and risk assessment groups before hydrogen peroxide could be used.

3.10 TURCO™ 4502

TURCO 4502 is a commercially available decon chemical that is marketed by the TURCO Company of Cincinnati, Ohio. It is one of a suite of chemicals marketed under the "TURCO DECON" umbrella. These products were specifically tailored to the cleaning and decontamination needs of the nuclear industry. TURCO has since dropped their TURCO DECON line, but specially mixed chemicals (like TURCO 4502) are still available upon request. It's inclusion in this report is as a baseline, or a historical benchmark to compare with new techniques.

This chemical is in a broad family termed "AP", (alkaline potassium permanganate) that are used extensively in nuclear decontamination. "AP" chemicals contain sodium hydroxide or potassium hydroxide (5 to 20%) and potassium permanganate (1 to 5%), are typically strongly basic and oxidizing.¹³ This allows them to disrupt and dissolve metal surface films according to the equation:



The HCrO₄⁻ is more soluble than Cr₂O₃. Disrupting the metal surface film releases the trapped radionuclide particles and decontaminates the metal.¹⁰ This is often the first step of the two step alkaline permanganate/oxalic acid process that uses oxalic acid (C₂H₂O₄) (or a suitable reductant) to reduce iron oxide in the second step, disrupting the strongly held oxide according to the reaction:



Cycling the surface film chemistry in this fashion, through oxidation/reduction steps, has been demonstrated to be very effective in decontamination. Additional

discussion of reducing organic acids is given in section 3.7 and 3.8.

A test of TURCO 4502 was conducted in the ICPP laboratories to determine the effectiveness at cleaning SIMCON 2 test coupons. The TURCO Company recommends use of TURCO 4502 at a concentration of 2 lb. per gal. ICPP usage has indicated that a quarter this concentration has performed satisfactorily.¹⁴ The solutions were therefore mixed to a concentration of 1/2 lb. per gal. for bench top testing. The results indicated that while the TURCO 4502 was only moderately successful in removing cesium and zirconium from the SIMCON 2. The results reported for these tests are two staged, using the oxalic/nitric mixture as a second treatment of the coupons. The results were good, but when compared with the same treatment of NP, they only about 1/3 as effective.

As mentioned earlier, using concentrated sodium and potassium chemicals causes waste generation problems in the ICPP calcination process. Nonradioactive additives (predominantly aluminum nitrate) must be added to prevent sodium/potassium agglomeration of the calcine bed. A volume ratio of

3.11 Citric Acid

Citric acid is the most versatile and commonly used organic acid.¹¹ It has the formula $C_6H_8O_7$, and is a tri-carboxylic acid. It is an extremely good chelating agent and is a fairly good acid. Citric acid and sodium citrate are used in metal finishing as a cleaner, and have replaced many phosphates in laundry detergent.

Its use as a decontamination agent is long-standing as well. Oxalic acid and citric acid have been combined for use as the CITROX and CITROSOLV reagent, and in dilute quantities as the CANDECON process.¹⁵ It's use at the ICPP has been limited, though CITROX has been used before.

Tests of solutions of 5% citric acid showed very good decontamination effectiveness and potential waste savings. The overall Df was 8.8, exceeding most of the traditional and improved decon technologies. Citric acid has been demonstrated in a two step AP-Citrox process that used the oxidative/reductive treatment to achieve very high Dfs.¹⁶ Waste processing savings could also be approximately 1 volume of AP to 3.5 volumes of aluminum nitrate must be used.

3.13 Nitric Acid-Hydrofluoric Acid

The nitric acid-hydrofluoric acid solution has been examined to varying degrees for several years. Solutions of 3.5 M HNO_3 and 0.04 M have been used

as cleaning/etching solutions on stainless steel.¹⁸ To this end, this HNO₃-HF solution was posed as a candidate for examination as a nonsodium chemical decon reagent.

A solution of 3.5 M HNO₃ · 0.04 M HF and one of 3.5 M HNO₃ and 0.02 M HF was tested in is study. Tests using SIMCON 2 coupons produced comparatively high decontamination factors and good overall results. Cesium decontamination factors were the third highest of those chemicals tested. Zirconium decon factors were almost ten times higher then the next higher chemical; second only to fluoroboric acid. This makes sense due to the ZrF³⁺ complexing of zirconium in fluoride solutions.

While the efficacy of the HNO₃-HF solution is viewed as compelling, the waste volumes are especially attractive. This solution produces significantly lower waste volume than the baseline solution (TURCO 4502). As the decontamination factor is quite a bit higher, less solution would be used and even less waste produced. Another attractive feature of this solution is that it may chemically simulate Fluorinel dissolver Process (FDP) product. This would allow higher blends of sodium waste to be processed in the calciner. Prior to the cessation of fuel reprocessing, this method of blending relieved sodium waste inventory. FDP product had a complexed (aluminum nitrate added) concentration of 0.04 M free HF. This solution actually starts with that concentration of free HF, and will likely contain aluminum more nitrate to fully complex the HF.

Unfortunately, adoption of this solution as a general/all purpose decon solution is slow in developing. Concerns over the health effects of HNO₃-HF have imposed a great barrier to it's adoption. A healthy "fear" of hydrofluoric acid has been developed in operators, engineers and support personnel at the ICPP. This stems from years of working with concentrated hydrofluoric acid in the ROVER and FAST process. While it is good that such a respect has been generated for hydrofluoric acid, it is certainly not a grave concern using low (0.04 M) concentrations of the reagent. Equally, concerns have been raised as to excessive corrosion of process equipment. Excessive corrosion has occurred in ICPP process systems using hydrofluoric acid. Tests have shown that the corrosion of this solution is high (about 5 mils per month) but acceptable for short term decon.

3.14 TECHXTRACT™ 100, 200, 300

One of the most effective decontamination methods is the TECHXTRACT™ process, provided by a private decontamination firm, EET of Bellaire, TX. Formerly known as Enclean Environmental Technologies, EET has acquired a solid reputation for removing radioactive and hazardous contaminants in the nuclear and non-

nuclear industries. The TECHXTRACTtm chemistry (100, 200, 300) is a patented process that combines some 25 different chemicals to incorporate dissolution, oxidation, reduction, hydrolysis, decomposition, wetting, complexation, microencapsulation, and flotation chemistry principles.¹⁹ When complete, the process produces a non-hazardous (RCRA) matrix that contains only the waste codes of the contaminants of the original target material.

The ICPP has used the TECHXTRACTtm process to successfully decontaminate both concrete slabs²⁰ and miscellaneous tools. Several of these items were returned to the owners without restriction. EET performed a successful demonstration on the removal of technetium and uranium from nickel plated components at Oak Ridge National Laboratory (ORNL) K-25 gaseous diffusion plant. Additional structure and equipment decontamination have been performed at the Scientific Ecology Group plant at ORNL and the Ronson Metals (thorium production) facility in Newark, New Jersey.^{19,21}

The tests used in this study were significantly different than previous demonstrations, primarily because of the dilute nature of these chemicals. The TECHXTRACTtm chemicals were diluted to 15% of their original concentration (1:6.7) with water. Another unusual application was performing the steps in the order: 100,200, 300, instead of 300, 200, 100. The chemicals were diluted to use as a flush, not as a spray-on-wipe-off type application or a concentrated soak. Still, the results were excellent for the decon tests. A high Df of 17 for cesium and 7 for zirconium ranked third from the top.

However, waste processing at ICPP for this process prohibits absolute acceptance at this time. TECHXTRACTtm contains immisible organics and high levels of chloride, both of which prohibit its acceptance in the Process Equipment Waste (PEW) evaporator system. The solution produced an immisible organic layer during a "boildown" test with nitric acid, so it was prohibited. However, a better method of processing the chemicals together for a more effective destruction of organics will soon be tested. A new formulation without the high levels of chloride is also being developed. It is hoped that this process will be acceptable after those changes are made.

3.15 Fluoroboric Acid

Fluoroboric acid (HBF₄) is an excellent decontamination reagent with extremely high decontamination factors. The HBF₄ was tested at a significantly high concentration of 0.5 M, which makes a potential fluoride concentration of the solution 2 molar. The SIMCON 2 coupons showed a consistently high decontamination factor, cesium Df 18.3 and zirconium Df of 24 using this solution.

A commercial vendor, ALARON Co., reports decontamination factors of 50 to 100 using the fluoroboric acid process.²² The likely cause of these high factors, particularly of zirconium which responds very well to fluoride, is the high fluoride concentration. The fluoride is mainly complexed in the HBF_4 by the boron molecule. The equilibrium of free fluoride in solution is displaced as ions on the metal surface are dissolved. The HBF_4 may then release more fluoride to dissolve contaminants as others are depleted in solution.

The main disadvantage to the fluoroboric acid is the high amount of waste that is generated by its use. Under current ICPP philosophy, each fluoride molecule must be accompanied by three aluminum molecules. Not only does this produce excessive waste due to the use of eight moles of aluminum per mole of fluoroboric acid, but it doesn't take into account the presence of the boron, which of itself is an adequate complexing agent. Others argue that a complexing rate of one aluminum to three fluoride (the exact opposite of that given in ICPP manuals) is adequate. That change alone would reduce the ratio from 4 moles of aluminum to 1 mole of fluoroboric acid to 4:3. Yet to be examined is the beneficial use of this reagent for blending with sodium feed. That has a potential to decrease the overall waste production well below current levels and substantially reduce cold aluminum nitrate input into the calcine process.

A process for recycling and regenerating fluoroboric acid exists that could even decrease the amount of fluoroboric acid that goes to waste. A Swiss company, Recytec, has patented a process called "DECOHA" that electrochemically restores the acid and removes the metal and contaminants from the fluoroboric acid. This DECOHA technology has been proven in laboratory tests²³ and has been placed in use at the damaged reactor at Chernobyl. While not a perfect "closed loop" system, DECOHA offers capabilities that would provide significant recycling benefits.

4.0 RESULTS AND SUMMARY

These tests have furthered the evaluations that the Decontamination Development Group perform in the field of chemical decon. Several "baseline" solutions were incorporated into this study to show the relative effectiveness of more common solutions. Continued use of water and nitric acid (for example) is expected, and efficient when properly used. But their relative position with respect to the other chemicals is important. In general, these solutions all have their proper use, including the alkaline solutions.

A number of solutions were shown to be superior to the alkaline potassium permanganate baseline and will result in much less waste. Of particular note are the two proprietary solutions, TECHXTRACTtm and CORPEXtm 921. Additional

work will be required to adopt either of these solutions, but this study has shown that effort is well placed. Some solutions were found to be quite effective but not very well utilized. Citric, formic and tartaric can be very successful, but are seldom (if ever) used. Likewise, hydrogen peroxide should be examined further to see if the benefits would outweigh potential hazards.

5.0 RECOMMENDATIONS

The use of some novel decontamination reagents can and should be adopted in plant applications. After the 1994 report, acceptance of the novel decon chemicals was not very rapid; some of the recommendations have still not been implemented. Both the Decontamination Development Group and Operations must bear part of the responsibility to adopt new methods.

Chemical decontamination tests are expected to continue. The tests were abruptly terminated, slightly prematurely, due to the failure of the XRF equipment. Therefore some confirmation data is desired on a few of the chemicals. No opportunity was given to optimize some of the systems or to test two part processes. There are also some decon modifications that could improve the decon processes, such as spraying, foaming or recycling, which will be tested later in this program. Finally, some practical testing in the ICPP processes is anticipated next year.

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