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USE OF CITRIC ACID FOR LARGE PARTS DECONTAMINATION

By

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ABSTRACT

Laboratory and field studies have been performed to identify and evaluate chemical decontamination agents to replace ammonium carbonate, an environmentally unacceptable compound, in the decontamination facility for large process equipment at the Portsmouth Gaseous Diffusion Plant. Preliminary screening of over 40 possible decontamination agents on the basis of efficiency, availability, toxicity, cost, corrosiveness, and practicality indicated sodium carbonate and citric acid to be the most promising. Extensive laboratory studies were performed with these two reagents. Corrosion rates, decontamination factors, uranium recovery efficiencies, technetium (^{99}Tc)/ion exchange removal effects, and possible environmental impacts were determined or investigated. Favorable results were found in all areas. Detailed monitoring and analysis during two-week trial periods in which sodium carbonate and citric acid were used in the large parts decontamination facility resulted in similar evaluation and conclusions. Because it has unique and efficient cleaning properties not possessed by sodium carbonate, and because it eliminated several operational problems by incorporating two acidic decontamination reagents (citric and nitric acids) instead of one basic reagent (sodium or ammonium carbonate) and one acidic reagent (nitric acid), citric acid was selected for extended (one-year) field testing. On the basis of its excellent performance in the field tests, citric acid is recommended as a permanent replacement for ammonium carbonate in the decontamination facility for large process equipment.

INTRODUCTION

Ammonium carbonate ($(NH_4)_2CO_3$) and dilute nitric acid (HNO_3) have long been the decontaminants of choice for process equipment in the gaseous diffusion industry because they are excellent solvents for most uranium fluorides.[1] From plant start-up to 1977, large process equipment components from the cascade of the Portsmouth Gaseous Diffusion Plant, operated by the Goodyear Atomic Corporation (GAT), were routinely decontaminated with solutions of those two reagents. Decontamination operations have always been carried out in the X-705 Building, which provides facilities for (1) decontaminating process equipment and miscellaneous items, such as clothing and auxiliary equipment which have been contaminated with uranium or other radioactive materials, and (2) reclaiming enriched uranium residues from spent decontamination solutions.

The large equipment cleaning area of the building contains the decontamination spray tunnel facility and related equipment used for disassembly and cleaning of compressors, converters, and gas coolers — the three major process equipment components. The spray tunnel consists of five connected booths. A roller chain running the length of the spray tunnel facility moves dollies on which the equipment is transported from one booth to the next. All tunnel equipment is constructed of stainless steel, and the tunnel spray facility is equipped with steam heaters and ductwork so that heated decontamination solutions can be used, if needed.

Until 1977, the five spray tunnel booths were operated as follows: In booths #1 and #2, ammonium carbonate sprays were used to decontaminate compressors and converters. But, in booth #3, nitric acid spray was used to decontaminate process gas coolers, which are constructed primarily of aluminum and are, therefore, subject to corrosion by carbonate. Booth #4 was a water rinse booth, and booth #5 was a forced warm air drying booth. The carbonate and nitric acid booths recirculated at a solution flow rate of approximately 250 gallons per minute. Solutions from these booths were dumped to storage columns for eventual processing at the uranium recovery facility. The rinse booth did not recirculate, but discharged directly to a retention pond (the X-701-B Holding Pond). Depending on the uranium and/or total dissolved solids contents, the decontamination solutions were periodically transferred from the tunnel booths to the uranium recovery system. After recovery of the contained uranium by the tributyl phosphate (TBP) extraction method, the solutions were treated and discharged to the X-701-B Holding Pond from which some of their components ultimately entered local waterways. A schematic of solution flow from the spray tunnel booths as described above is shown in Figure 1.

While for many years the decontamination process described above proved satisfactory for removing and recovering uranium from large process equipment, recent increases in the number of cascade parts cleaned because of current changeout programs* resulted in increased discharge of waste solutions from the X-705 facility and, in turn, caused concern over possible

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*Cascade Improvement Program/Cascade Uprating Program (CIP/CUP)

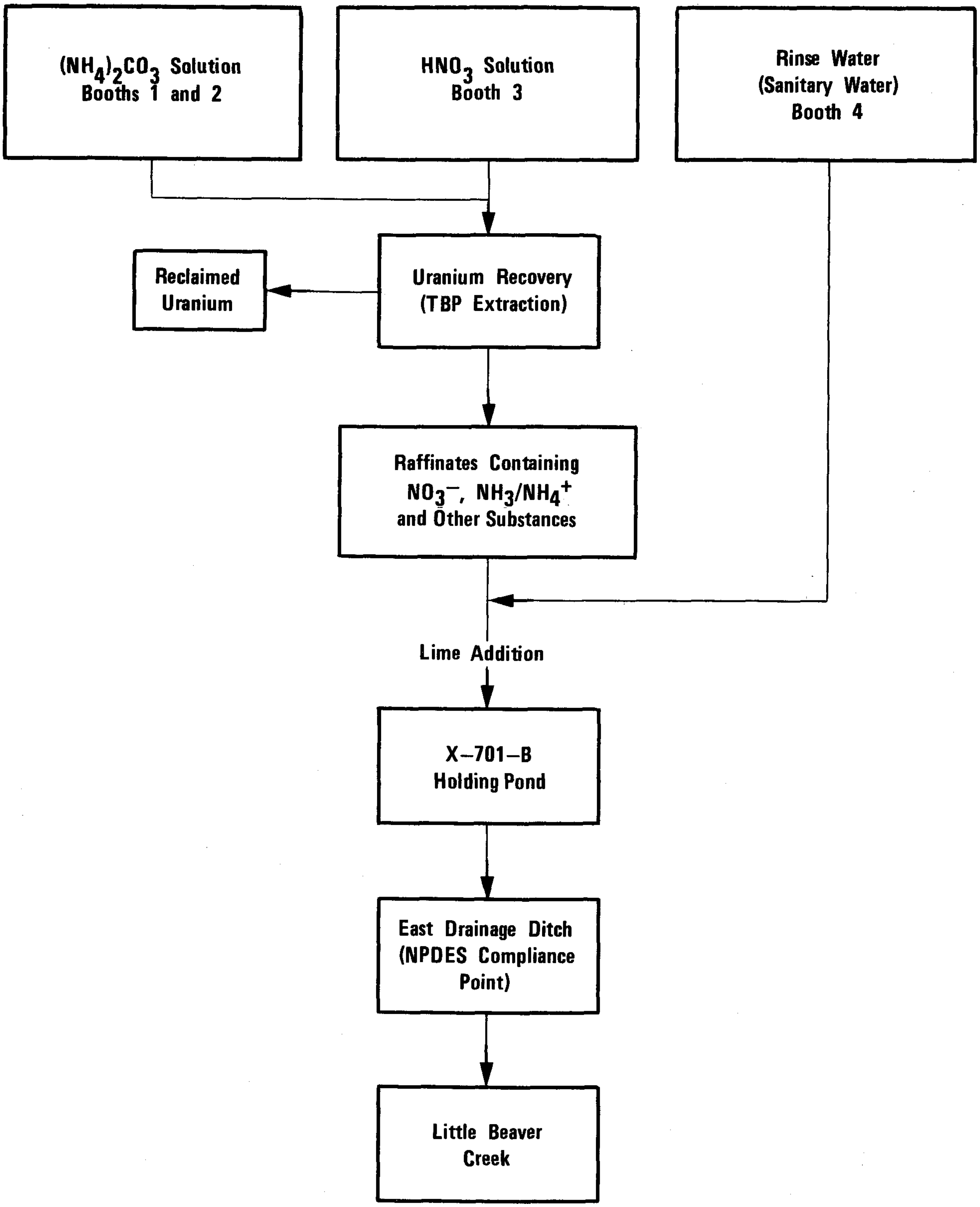

FIGURE 1 PRE-1977 SOLUTION FLOW FROM THE X-705 SPRAY TUNNEL BOOTHS

impact to the local environment. In an in-depth study[2] of the aquatic environment of Little Beaver Creek, which receives flow from the X-701-B Holding Pond via the Portsmouth plant's East Drainage Ditch (Figure 2), Battelle Memorial Institute of Columbus concluded that a severe environmental stress observed in the creek was due to effluent entering from the holding pond. However, of approximately 20 identified pollutants present in the effluent, only ammonia/ammonium ion (NH_3/NH_4^+) exceeded known toxic levels in fresh water environments and was, therefore, believed to be the cause of the observed stress. These findings were further substantiated by an independent investigation conducted by the GAT Process Technology Department.[3] Because the source of most (95%) of the effluent ammonia was identified as waste discharge from the ammonium carbonate booths of the X-705 spray tunnel (3000-5000 lbs./month), the need for an alternative decontamination agent became apparent. Alleviation of ammonia-caused environmental stress in Little Beaver Creek was the major incentive for this work.

However, other factors also prompted the search for a new decontamination agent for the X-705 tunnel facility. One such factor was a need for more effective removal of radioactive contaminants other than uranium, particularly technetium (^{99}Tc), from cascade equipment. Furthermore, it was initially also hoped that if a suitable acidic agent could be found for cleaning aluminum, then both ammonium carbonate and nitric acid could be replaced, and several significant benefits would thereby be realized: in the tunnel operation, booth carryover resulting in mixing, reaction between the basic carbonate and nitric acid solutions, and resultant solutions degradation would be eliminated; in the proposed ^{99}Tc removal operations, use of a single chemical loading medium would simplify ion exchange procedures and eliminate the mixing of acids and bases; and for the planned biodenitrification facility for removal of nitrate from X-705 waste streams, possible downsizing and concomitant cost reduction might result from decreased nitric acid usage in the spray booths.

After consideration of all the above factors, this study was initiated in an attempt to find a decontamination agent which could replace ammonium carbonate, and possibly also nitric acid, in the tunnel facility. The material selected would have to fulfill the following basic requirements: it would have to possess suitable decontamination properties, yet display low toxicity, low foaming, and corrosiveness not to exceed that of the decontaminant(s) to be replaced; it would have to be environmentally acceptable; and, it would have to be compatible with the tributyl phosphate (TBP) uranium recovery system.

DISCUSSION

LITERATURE SURVEY

As a first step in the selection process, a literature survey of both the classified literature and material in the public domain was conducted to determine if studies had been performed since the Manhattan Project on uranium decontamination agents. Although literature on decontamination in the nuclear field is extensive and detailed, the vast majority concerns the

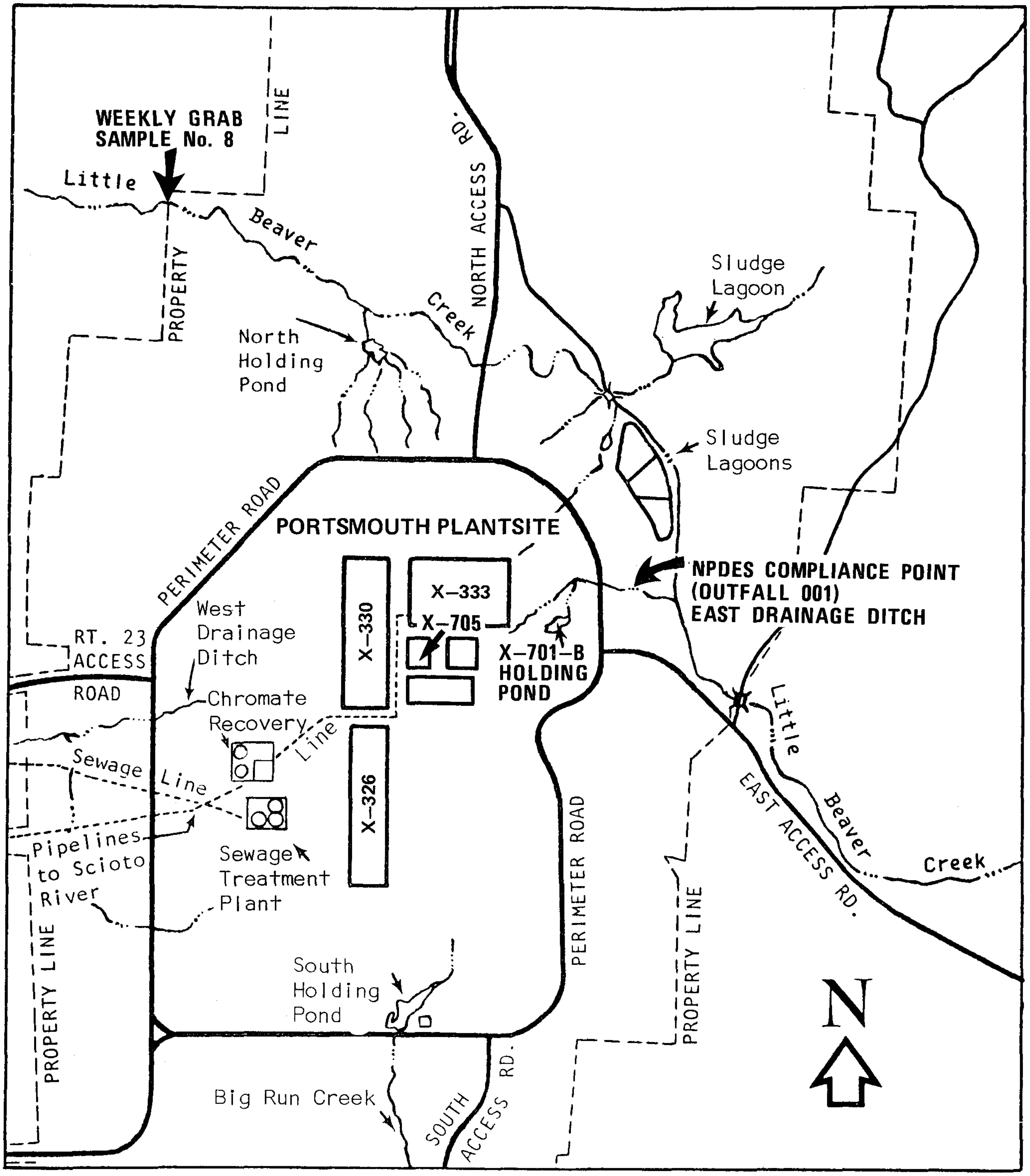

FIGURE 2 RELATIONSHIP BETWEEN X-701-B HOLDING POND AND LOCAL WATERWAYS; LOCATIONS OF ENVIRONMENTAL SAMPLING POINTS FOR AMMONIA

removal of fission products from reactor system surfaces. No information applicable to the decontamination of uranium fluorides from nickel, Monel, steel, or aluminum surfaces with agents other than ammonium carbonate or nitric acid could be found. However, general information was gathered on uranium chemistry, decontamination in general, corrosion, and surface and environmental chemistry. These data were used to compose a preliminary list of reagents with possible applicability to the problem.

INDUSTRY CONTACTS SURVEY

Before laboratory work was initiated, approximately 40 companies with recognized abilities in industrial cleaning were contacted to determine possible applications for their products. While several indicated interest and sent samples of products, no proprietary agent exhibiting significant uranium decontamination ability and also possessing all other required qualities could be found.[4]

LABORATORY EFFORTS

Preliminary Agents Screening: The general literature on decontamination indicated that complex ion formation is regarded as the most effective means of contaminant removal from metal substrates. Because uranium is a cation (UO_2^{++}) in solution, an effective decontaminant must provide an anion for its soluble complex formation. Although the complexing power of anions has not been systematically explained, it is theorized to be a function of the ionic charge modified by the specific binding nature (geometry, configuration) of the anion.[5] An approximate empirical sequence in the order of increasing power of complex formation for anions would be as follows:

$$ClO_4^- \ll Ac^- < Cl^- < NO_3^- < HSO_4^- < HCO_3^- \sim P_2O_7^{-4} < HTart^- <$$
$$H_2Cit^- < HCit^{-2} < Cit^{-3} < AcAc^-$$

From the above information and currently accepted theories of decontamination, the preliminary listing of 43 potential decontamination reagents shown in Table 1 was prepared. All compounds on the list had proven or suspected ability to solubilize or aid in the removal of +4, +5, and +6 valent fluorides of uranium, either by ionic dissolution, complexation, chelation, surface cation exchange or surface tension effects. The formulation scan included, among others, compounds of the following types: alternate carbonates, aminocarboxylic acids, β-diketones, hydroxycarboxylic acids, polyphosphates, and aminoalcohols.

In practice, the number of complexing anions for a decontamination study is limited by such factors as cost, availability, corrosiveness (i.e. selectivity of the anion for the cation to be removed over the metal substrate cation) and the requirement that the complex be soluble. The particular decontamination application concerned in this study also eliminated several agents due to their interference with the distribution coefficient of the TBP uranium recovery system, their high foam characteristics, or their high toxicity.

TABLE 1 PRELIMINARY FORMULATION SCAN FOR POTENTIAL DECONTAMINATION AGENTS

(1) Hot Water

(2) Sodium Carbonate

(3) Potassium Carbonate

(4) Aluminum Nitrate

(5) Hydrogen Peroxide (5%)

(6) Monosodium Phosphate

(7) Sodium Hexametaphosphate

(8) Sodium Tripolyphosphate

(9) Propylene Carbonate

(10) Acetylacetone (2, 4-Pentanedione)

(11) Potassium Sodium Tartrate (Rochelle Salt)

(12) Sodium Citrate

(13) Citric Acid

(14) Oxalic Acid

(15) Lactic Acid

(16) Salicylic Acid

(17) Tartaric Acid

(18) Maleic Acid

(19) Succinic Acid

(20) Propionic Acid

(21) Acetic Acid

(22) Formic Acid

(23) Sodium Diethanolglycine + Salts (DEGS)

(24) Ethylenediamine Tetraacetic Acid (EDTA) + Salts

(25) Diethylenetriamine Pentaacetic Acid (DTPA) + Salts

(26) Nitrilotriacetic Acid (NTA) + Salts

(27) Hydroxyethylenediamine Triacetates

(28) Versene Solutions

(29) 8-Hydroxyquinoline

(30) Dimethylacetamide

(31) Ammonium Citrate

(32) 1, 2-Propanediamine

(33) n-Propanecarboxylic Acids

(34) Hexafluoroacetylacetone

(35) Hydrogen Hexafluorophosphate

(36) Ethyleneglycol-bis (aminoethyl)-tetraacetic Acid

(37) Sulfosuccinic Acid Derivatives

(38) Aminotrimethyl Phosphonic Acids

(39) 1-Hydroxyethylidene-1, 1-Diphosphonic Acid (HEDP)

(40) Sodium Oleate

(41) Sodium Lauryl Sulfate

(42) Alkyl Benzene Sulfonates

(43) Sulfamic Acid

Bench-Scale Decontamination Studies of Selected Reagents: As a result of the above-mentioned restrictions, a number of compounds on the original screening list were eliminated from further consideration. However, 20 compounds which had met the preliminary criteria were subsequently selected from the list for actual laboratory investigation into their decontamination properties.

Coupons of nickel, Monel and cast aluminum, measuring 3.00 inches x 5.00 inches were lightly sandblasted, cleaned, dried, and degreased. Because the surface substrate to be cleaned is an important parameter to be considered in decontamination, all coupons were given identical contamination treatments, i.e., 48-hour exposures in 1 atmosphere of 1.25% assay UF_6 at 150°F. In addition, Monel coupons were contaminated by a 30-day evaporative soak in a 50 g/l solution of uranyl fluoride. These coupons were used for comparing solubilization of the deposited uranium by the different decontaminants.

After decontamination, each coupon was lightly air-blown to remove any loose dust contamination, and its entire surface was scanned with a Samson alpha survey meter, Model JS-301-1 (Nuclear Instrument and Chemical Corporation, Chicago, Illinois) with a 4-inch x 4.5-inch window. Counting of all coupons during the project was performed with the same meter, which was periodically calibrated.

To attempt to quantify and compare the decontamination potentials of the 20 selected agents, a 25-liter polypropylene laboratory spray booth, which could simulate conditions found in the X-705 tunnel facility, was fabricated. Decontamination factors (DFs) were calculated by dividing the alpha surface counts per minute on the coupon before and after decontamination, (i.e., DF = counts before/counts after). Thus, the higher the decontamination factor, the more efficient the action of the decontamination agent.

The DFs for the agents and the four tested surface substrates can be found in Table 2. All results are numerical averages obtained from four coupons and include the standard deviation.[4] The coupons were exposed to a spray of 10 liters/minute, which covered a square area of 18 inches on a side located 15 inches from the spray nozzle. These conditions were more rigorous than those found in the X-705 spray tunnel. All solutions were at ambient temperature (70°F) unless otherwise noted. As a reference and an indicator of decontamination resulting strictly from physical removal by the sprayed solution, the action of water at ambient temperature is included.

Information to be noted includes the increase in decontamination efficiency seen with an increase in temperature for sodium carbonate, the generally excellent results observed with most of the organic carboxylic acids (citric, oxalic, acetic), decontamination factors actually below that of water for some of the chelating agents (EDTA, NTA, DTPA), indicating a "fixation" of the contamination probably due to the higher stability constants (K) of the base metal complexes relative to those of the uranyl complexes, (i.e. K, Fe^{++}/EDTA or Ni^{++}/EDTA >> K, UO_2^{++}/EDTA); and the relatively low DFs of the inorganic carbonates compared to the higher DFs of several of the carboxylic acids. The lower DFs obtained for most decontaminants on water-contaminated Monel coupons indicate that the heavy contamination resulting from the evaporative soak in uranyl fluoride is more difficult to remove than that resulting from gas-phase UF_6 exposure.

TABLE 2 DECONTAMINATION FACTORS FOUND IN LABORATORY SPRAY BOOTH RUNS

	Decontamination Factors (DFs)[a]				
Decontaminant	Nickel	Monel	Water-Contaminated Monel	Cast Aluminum Blades	Total
H_2O	1.1 ± 0.02	2.3 ± 1.6	10.0 ± 4.7	1.4 ± 0.3	14.8 ± 6.6
$Na_2CO_3 \cdot 10\ H_2O$ (0.2M)	4.1 ± 0.1	14.1 ± 0.4	6.5 ± 4.9	1.6 ± 0.2	26.3 ± 5.6
$Na_2CO_3 \cdot 10\ H_2O$ (0.2M)) (165°F)	37.8 ± 5.2	127.2 ± 10.1	7.8 + 1.6	2.1 ± 0.5	174.9 ± 17.4
$(NH_4)_2CO_3 \cdot H_2O$ (0.2M)	4.2 ± 0.1	11.6 ± 3.9	3.6 ± 3.4	1.5 ± 0.2	20.9 ± 7.6
Sodium Citrate (0.2M)	1.3 ± 0.1	4.1 ± 0.8	4.6 ± 0.6	1.3 ± 0.3	11.3 ± 1.8
Citric Acid (0.2M)	15.5 ± 6.7	116.7 ± 8.3	8.7 ± 7.6	2.0 ± 0.5	142.9 ± 23.1
Acetic Acid (0.2M)	8.2 ± 1.0	38.1 ± 4.8	10.3 ± 1.8	1.7 ± 0.1	58.3 ± 7.7
Maleic Acid (0.2M)	11.6 ± 6.9	106.3 ± 20.8	7.5 ± 2.6	2.3 ± 0.3	127.7 ± 30.6
Succinic Acid (0.2M)	13.9 ± 0.5	4.2 ± 1.6	1.1 ± 0.1	1.3 ± 0.3	20.5 ± 2.5
Oxalic Acid (0.2M)	12.8 ± 1.2	110.4 ± 21.2	7.8 ± 1.2	1.7 ± 0.8	132.7 ± 24.4
Lactic Acid (0.2M)	8.7 ± 1.7	4.9 ± 0.9	1.3 ± 0.1	1.0 ± 0.1	15.9 ± 2.8
Salicylic Acid (0.2M)	10.5 ± 1.2	4.0 ± 0.5	1.3 ± 0.1	1.1 ± 0.1	16.9 ± 1.9
Tartaric Acid (0.2M)	15.6 ± 1.8	38.2 ± 5.1	8.6 ± 1.3	2.0 ± 0.6	64.4 ± 8.8
H_2O_2 (5%)	6.1 ± 4.5	2.9 ± 0.3	2.5 ± 0.5	2.0 ± 0.9	13.5 ± 6.2
Acetylacetone (5%)	33.6 ± 9.3	15.5 ± 0.7	4.9 ± 0.3	1.4 ± 0.3	55.4 ± 10.6
Diethylenetriamine Pentaacetic Acid (DTPA) (2%)	1.4 ± 0.5	2.7 ± 0.8	1.7 ± 0.7	1.6 ± 0.1	7.4 ± 2.1
Nitrilotriacetic Acid (NTA) (2%)	1.5 ± 0.6	2.6 ± 0.7	1.8 ± 0.3	1.5 ± 0.2	7.4 ± 1.8
Ethylenediamine Tetraacetic Acid (EDTA) (3%)	8.8 ± 1.3	1.7 ± 0.4	1.6 ± 0.6	1.5 ± 0.2	13.6 ± 2.5
1-Hydroxyethylidene-1,1-diphosphonic Acid (HEDP) (2%)	8.0 ± 1.7	1.5 ± 0.3	1.4 ± 0.8	1.6 ± 0.1	12.5 ± 2.9
Sodium Diethanolglycine (DEGS) (2%)	1.8 ± 0.3	2.5 ± 0.5	2.0 ± 0.6	1.5 ± 0.2	7.8 ± 1.6
EDTA (Methyl Phosphonic) Acid (2%)	2.0 ± 0.4	3.5 ± 0.6	2.8 ± 0.7	1.9 ± 0.3	10.2 ± 2.0

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[a] DF = Surface alpha counts before decontamination ÷ surface alpha counts after decontamination.

Carboxylate ligands have a strong affinity for actinide ions, especially if they contain several carboxylate groups and, therefore, are able to form chelates. Figure 3 depicts the stability of the uranyl complexes of several carboxylic acids and two acid derivatives (glycineamide and acetylacetone) as a function of the stability of the ligand, which is a measure of ligand basicity.[6] The line of best fit approximately follows the trend shown for monocarboxylic acids. However, with the exception of succinate, the uranyl complexes of ligands having multiple acid groups lie above the line, and irrespective of basicity, form uranyl complexes of greater stability than those formed by any of the monocarboxylic acids.

In Figure 4, the decontaminating ability of various carboxylic acids and the acid derivative acetylacetone (based on the total decontamination factors given in Table 2) is plotted as a function of ligand basicity. For monocarboxylic acids, increasing ligand basicity appears to be related to improved decontaminating ability. And, with the exception of succinate, ligands with multiple acid groups, irrespective of relative basicity, are generally better decontaminants than monocarboxylic acids.

Figure 5 shows the interesting correlation between the sets of data shown in the previous two illustrations: Decontamination efficiencies of the carboxylic acids appear to be a function of the stability of the uranyl complexes formed; the latter, are, in turn, a function of the structure of the acid. Citric acid, the only tricarboxylic acid tested, forms the uranyl complex of greatest stability and also exhibits the greatest decontamination efficiency.

As a result of these laboratory-observed decontamination factors and other previously cited factors, citric acid and sodium carbonate were selected as the two most promising agents for replacing ammonium carbonate and possibly also nitric acid in X-705 operations. Citric acid was chosen because of its results in the carboxylic acids study, and sodium carbonate was deemed worthy of further study because of its similarity to ammonium carbonate and its excellent decontamination factors at higher temperatures.

Corrosion Studies: Because cascade equipment with close tolerances is cleaned in the tunnel facility, corrosion during decontamination is a potential problem which must be closely monitored.

Detailed laboratory corrosion rate studies of the metals of interest by sodium carbonate and citric acid sprays were undertaken in the same 25-liter recirculating spray booth that was used for decontamination factors studies. All corrosion test coupons were first thoroughly deburred, cleaned, dried, and degreased, measured to the nearest thousandth of an inch and then weighed to within ±0.1 mg. Solutions either at ambient temperature or heated to 130°F were examined, as these are the two extremes of the temperature range possible in X-705 booth operations. Exposures were for four hours in a 10-liter/minute square spray pattern, which covered 18 inches on a side. The coupons were placed on a Plexiglas support 12 inches from the spray nozzle and were, thus, not galvanically coupled.

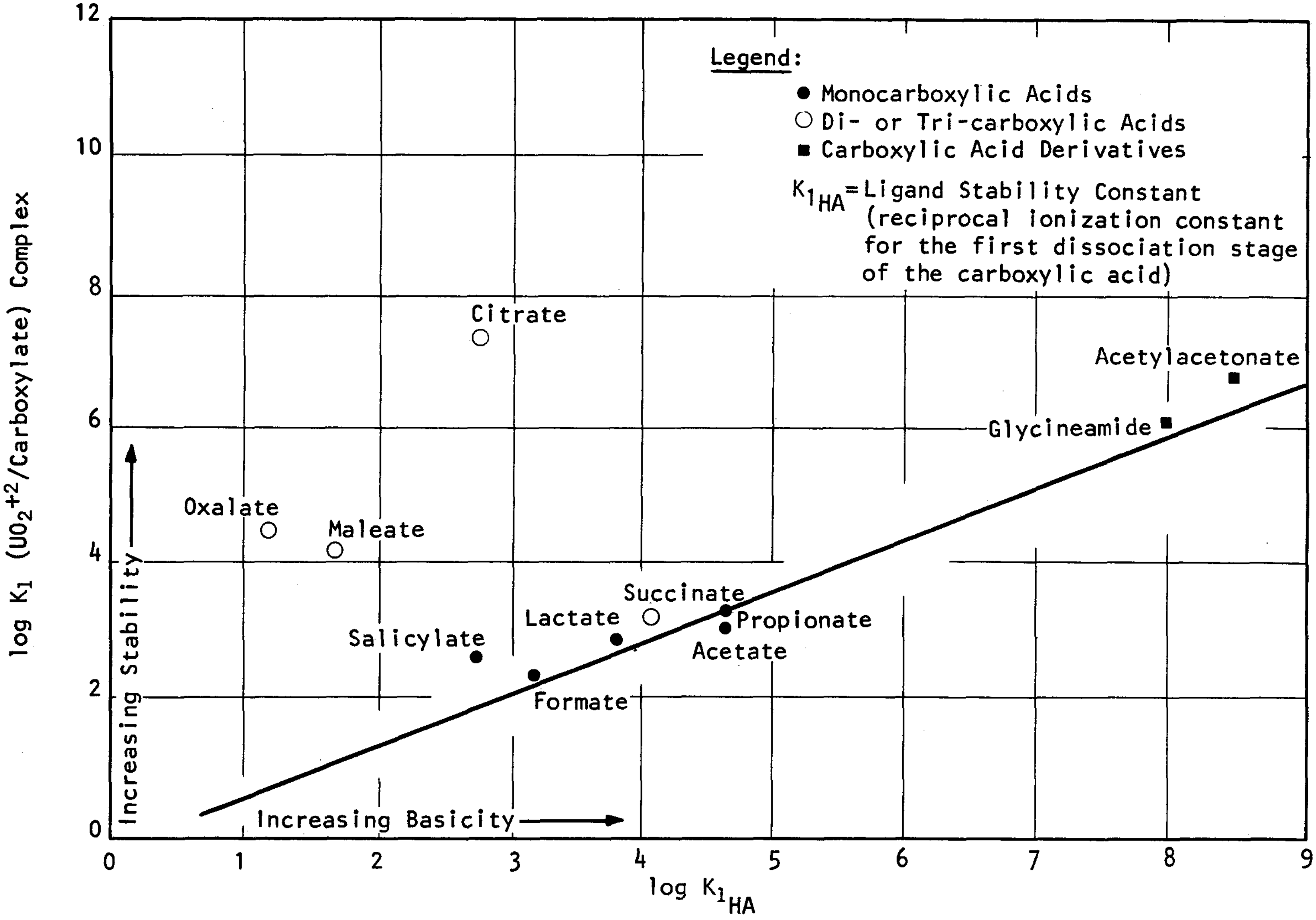

FIGURE 3 STABILITY OF THE URANYL/CARBOXYLATE COMPLEXES AS A FUNCTION OF LIGAND BASICITY

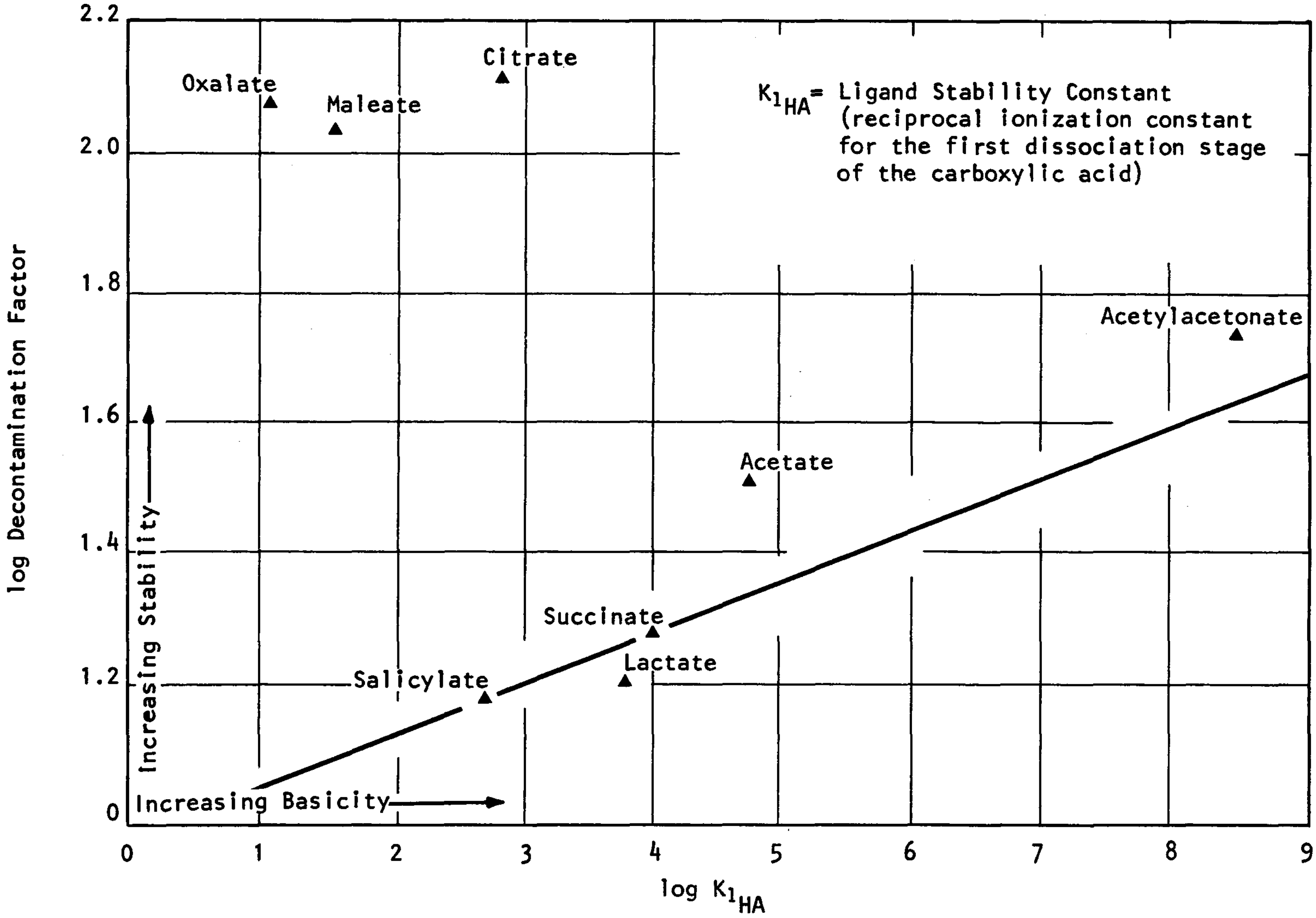

FIGURE 4 DECONTAMINATION FACTORS OF CARBOXYLIC ACIDS AS A FUNCTION OF LIGAND BASICITY

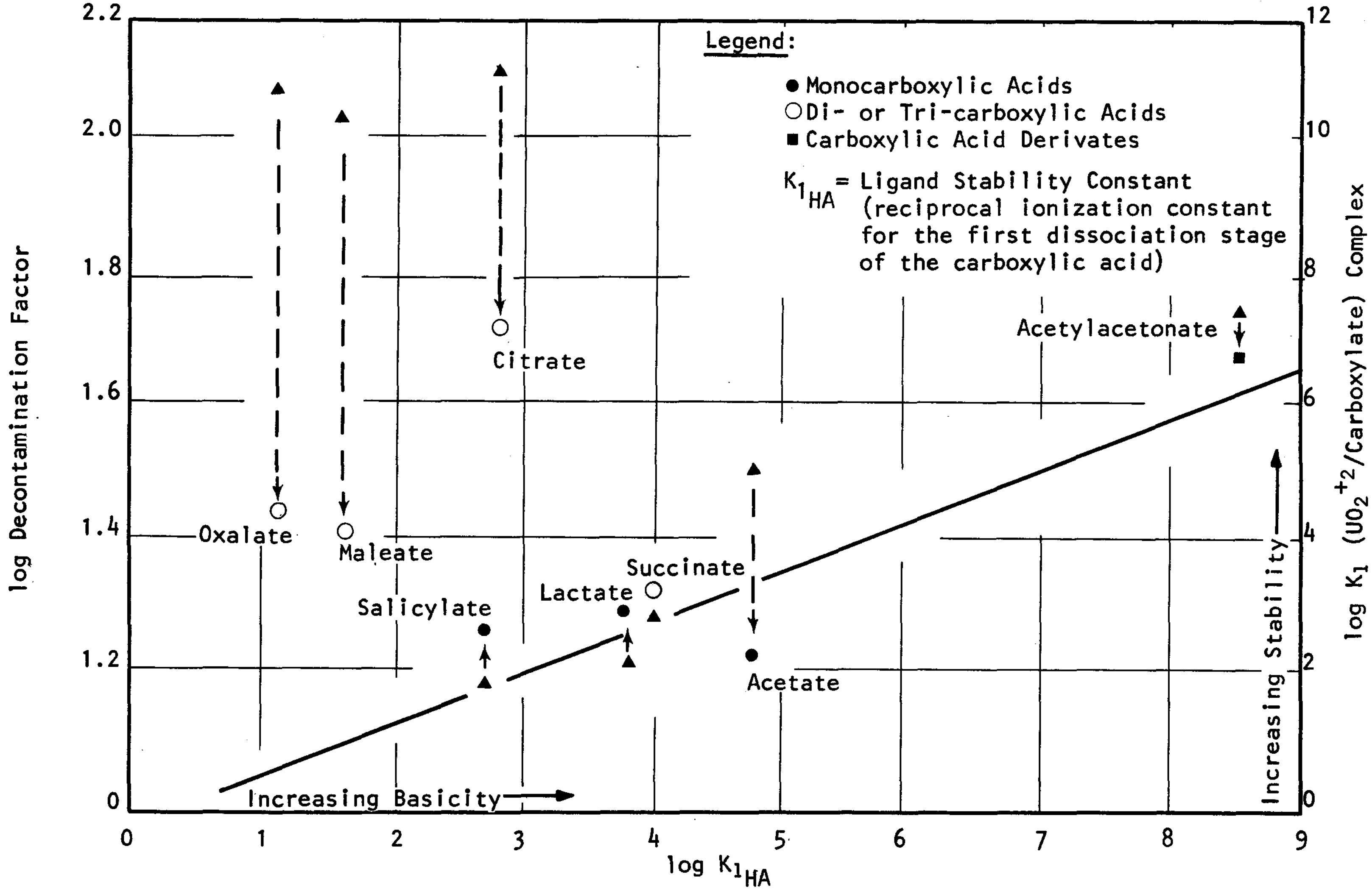

FIGURE 5 STABILITY CONSTANTS AND DECONTAMINATION FACTORS OF CARBOXYLIC ACIDS AS A FUNCTION OF LIGAND BASICITY

Results are given in Table 3 for ammonium carbonate, sodium carbonate and citric acid corrosion rates on steel, Monel, nickel and aluminum. Because carbonate sprays are known to be extremely corrosive to cast aluminum, aluminum coolers, and some alloys such as aluminum bronze,[7] corrosion rates for this combination were not measured. All results are the average of three coupons, and are compared to some published corrosion rates of Monel and steel in 3 percent citric acid solutions and the same solutions with 0.025 percent Rodine 115 (a commercially available corrosion inhibitor).[8]

TABLE 3 CORROSION RATES OF METALS IN $(NH_4)_2CO_3/Na_2CO_3$/CITRIC ACID SPRAYS[a]

$(NH_4)_2CO_3 \cdot H_2O$	Conditions	Recession Rate (mils/hr.)
Steel	0.4M @ 130°F	0.0475
Steel	0.4M @ Ambient	0.002
Monel	0.4M @ 130°F	0.095
Monel	0.4M @ Ambient	0.011
Nickel	0.4M @ 130°F	0.0805
Nickel	0.4M @ Ambient	0.009
Aluminum	(not tested due to high corrosion rates)	

$Na_2CO_3 \cdot 6H_2O$		
Steel	0.4M @ 130°F	0.0600
Steel	0.4M @ Ambient	0.0150
Monel	0.4M @ 130°F	0.0165
Monel	0.4M @ Ambient	0.0036
Nickel	0.4M @ 130°F	0.0125
Nickel	0.4M @ Ambient	0.0035
Aluminum	(not tested due to high corrosion rates)	

Citric Acid [0.4M = 7.0%]			Corrosion Inhibited[b]	
			[0%]	[3%]
Steel	0.4M @ 130°F	0.210	0.380	0.10
Steel	0.4M @ Ambient	0.0355	0.025	0.002
Monel	0.4M @ 130°F	0.009	0.002	0.002
Monel	0.4M @ Ambient	0.0015	0.002	0.002
Nickel	0.4M @ 130°F	0.0085		
Nickel	0.4M @ Ambient	0.0025		
Aluminum	0.4M @ 130°F	0.105		
Aluminum	0.4M @ Ambient	0.050		

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[a] Aerated; not galvanically coupled; 130°F or ambient temperature; 10 liters/minute flow; 12-inch distance from spray nozzle.

[b] Published values for corrosion inhibition with Rodine 115.[8]

Although corrosion rates seen in actual field conditions could vary greatly, the results tend to point to acceptable corrosion rates for all metals of concern when either sodium carbonate or citric acid is used as a decontamination agent. Reagent concentrations in all corrosion studies were in the range determined optimum for most efficient decontamination.

In January 1978 during X-705 field trials, several compressor stub shafts were etched beyond repair in citric acid solutions. A Quality Assurance (QA) committee investigating this incident concluded that nitric acid contamination of the citric acid from the nitric acid booth (through a failed drain line valve) caused the excessive shaft corrosion. In order to document this effect, a follow-up study was performed in the laboratory.[9] Results are given in Table 4 and clearly show that corrosive attack of shaft steel (mild steel) is greatly increased when even small amounts of nitric acid are mixed with citric acid. The corrosion rate of mild steel in dilute citric acid alone is quite low in accord with earlier test results (Table 3). Comparison of the data with those for electrolytic iron in nitric and citric acid solutions of comparable dilution[10] indicates that the enhanced corrosivity of the mixture is due solely to the presence of nitric acid. As would be expected, increasing the temperature from 68°F to 150°F increased corrosive attack--about 8-fold for citric acid alone and more than 300-fold for the mixture of nitric and citric acids.

TABLE 4 CORROSION RATES OF SHAFT STEEL IN CITRIC ACID AND IN CITRIC/NITRIC ACID MIXTURES

Solutions	Recession Rate for Shaft Steel (mils/hr.)
0.3M Citric Acid; 68°F	0.06 ± 0.01
0.3M Citric Acid + 3% HNO_3; 68°F	1.63 ± 0.15
0.3M Citric Acid; 150°F	0.48 ± 0.02
0.3M Citric Acid + 3% HNO_3; 150°F	>20

Permanent corrective actions recommended by the QA committee and subsequently implemented included daily monitoring of NO_3^- levels in the citric acid spray booths and increased control of tunnel operating parameters, decontamination times, temperatures, and NO_3^- concentrations.

Chemical Usage Optimization Studies: Studies to determine optimum concentration of decontamination agents were carried out. The purpose was to find the concentration of decontaminant above which further increases in chemical usage result in decreasing returns in decontamination efficiency.

The complexing anions of both citric acid and sodium carbonate are formed from the dissociation of weak acids, as represented by Equation 1:

$$HA \rightleftharpoons H^+ + A^- \qquad (1)$$

Since in dilute solutions little difference between activity and concentration exists, the dissociation constant, K_a, for the acid may be depicted by Equation 2:

$$K_a = \frac{[H^+]\ [A^-]}{[HA]} \qquad (2)$$

Rearranging produces Equation 3, which shows the inverse relationship between the anion concentration and the hydrogen ion concentration:

$$[A^-] = \frac{K_a\ [HA]}{[H^+]} \qquad (3)$$

Accordingly, as the hydrogen ion concentration decreases (i.e., as pH increases), the concentration of the complexing anion will increase, as illustrated by the data for several organic acids shown in Table 5.

TABLE 5 EFFECT OF pH ON DISSOCIATION OF CARBOXYLIC ACIDS

Acid	Percentage in Active Anionic Form			
	1%	10%	20%	50%
	pH			
Citric Acid	1.08	2.08	2.40	3.08
Oxalic Acid	0.81	0.19	0.48	1.19
Acetic Acid	2.74	3.74	4.04	4.75
Acetylacetone	6.00	7.00	7.30	8.00

Improved decontamination should result from increasing the pH and thereby increasing the concentration of the complexing anion. In fact, the concentration of the contaminating cation on the surface to be cleaned should vary inversely with the concentration of the complexing ligand assuming (1) diffusion of the cation from the metal surface is the rate determining factor (except for porous cast aluminum); (2) the undissociated acid has virtually no complexing ability; (3) the complex is formed from the singly charged anion to give an uncharged molecule; and (4) turbulent conditions are maintained to prevent diminished local anion concentrations and increased local complex concentrations.

These effects are subject to the limitation that increased hydrolysis of the aquo-complexes of the UO_2^{+2} ion will occur at increasingly higher pH levels.

This phenomenon is a function of the stability of the complex (the stronger the complex formed, the higher the tolerable pH) and will result in the formation of polynuclear complexes with hydroxy bridges in neutral (pH 5-8) solutions and a subsequent lowering of the solubility of the complex. This effect reaches a maximum at pH >7.0 and results in the eventual precipitation of insoluble uranates. There is, therefore, a combination of an optimum pH and an optimum anion concentration for the most effective uranium removal and complex solubility.

Laboratory studies were thus conducted on steel, nickel, aluminum, and Monel coupons in the experimental (laboratory) spray booth to measure decontamination efficiency versus agent concentration. Plots of the resulting data (decontamination factors versus molarity of agent) reveal that for citric acid at ambient temperatures and for sodium carbonate at 125°F (Figures 6 and 7, respectively) the optimum agent concentration (point of curve inflection) is approximately 0.20 - 0.35 Molar.

The X-705 spray tunnel has the capability to heat the decontamination solutions, thus affording increased cleaning efficiencies. Sodium carbonate solutions are, of course, subject to decomposition and, at low CO_3^{-2} concentrations, UO_2^{+2}/CO_3^{-2} complexes can also polymerize and form precipitates.[11] The decomposition rate of sodium carbonate was measured under simulated spray booth conditions at 130°F (Figure 8) and was found to be acceptable, assuming normal booth solution changeout frequency and acid booth solution carryover.

Fluoride increases, pH changes, and $[CO_3^{-2}]$ decreases were also studied in solutions of citric acid and in sodium carbonate to which UO_2F_2 was added by slow, controlled hydrolysis of UF_6. Carbonate analyses were performed according to ASTM Procedure D513-71, Method E. Fluoride and pH analyses were performed with specific ion electrodes, and uranium analyses were of the versene/peroxide type. No values were found to deviate from normal tunnel operating parameters provided that solution changeout was performed before the uranium concentration reached 10,000 ppm. (Normal solution changeout ranges from 3,000 - 7,000 ppm uranium.)

Uranium Recovery System Effects: All tunnel solutions contain 2,000-7000 ppm mixed assay uranium when pumped to the solution recovery facility for extraction of the uranium (as a uranyl nitrate complex) with 25% tributyl phosphate (TBP)/Stoddard's solvent. Thus, any agent used in tunnel operations must be compatible with the TBP extraction process, and must not significantly change the distribution coefficient of the uranium between the aqueous and organic phases.

Laboratory tests were made to determine the effect of citric acid on the extraction efficiency of the TBP process. Data from these tests, given in Table 6, showed that, as expected, the extraction efficiency for uranium in citric acid alone was significantly lower (by 80-90%) than that normally experienced in the plant with nitrate solutions of uranium. However, should this problem occur, it can be overcome if the citrate solution is brought to 2.5-3.0% nitrate concentration, prior to transfer to the uranium recovery system. Uranium recovery on the order of 99.0-99.5% is then realized. Because

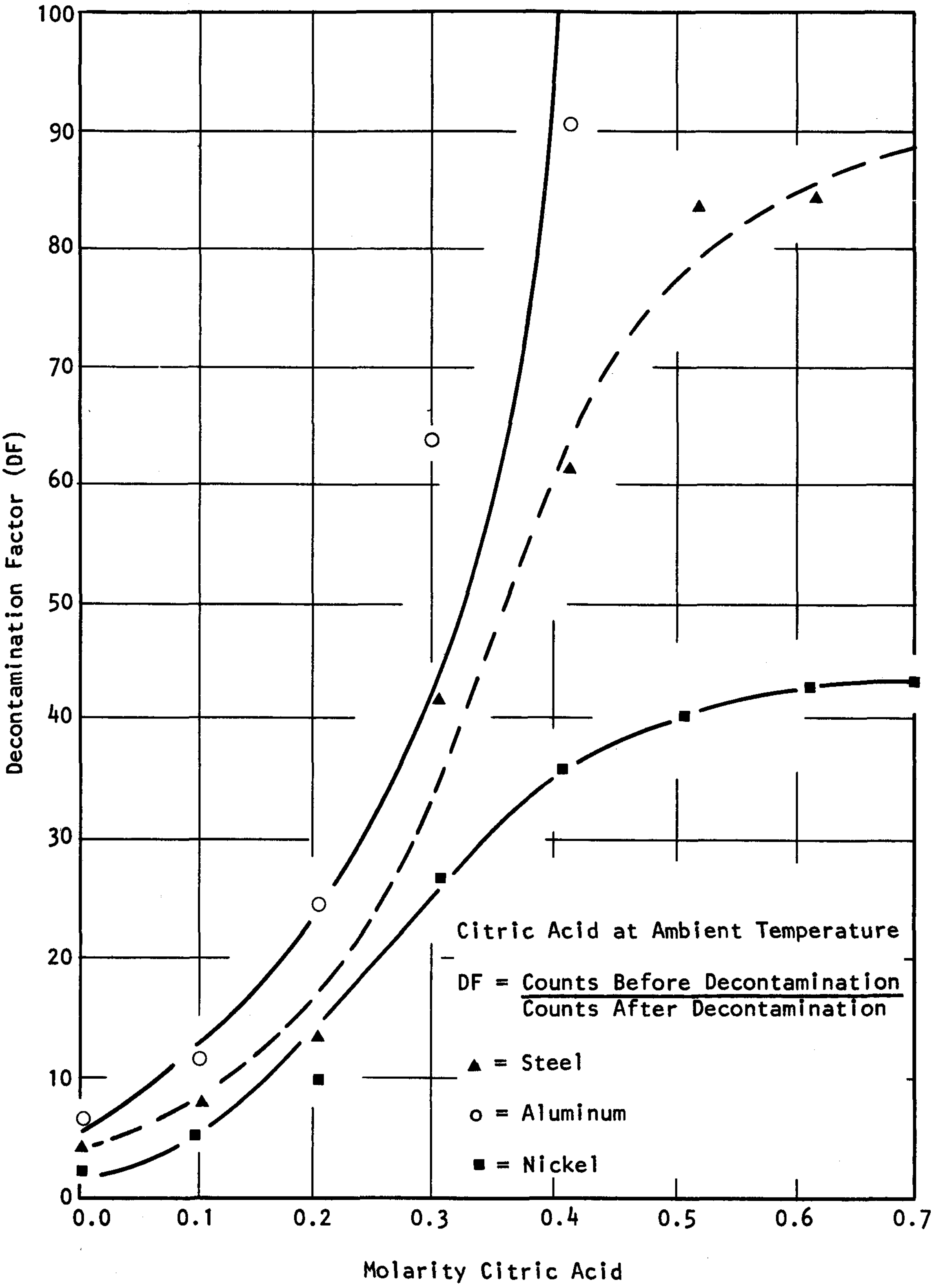

FIGURE 6 OPTIMIZATION OF CITRIC ACID CONCENTRATION

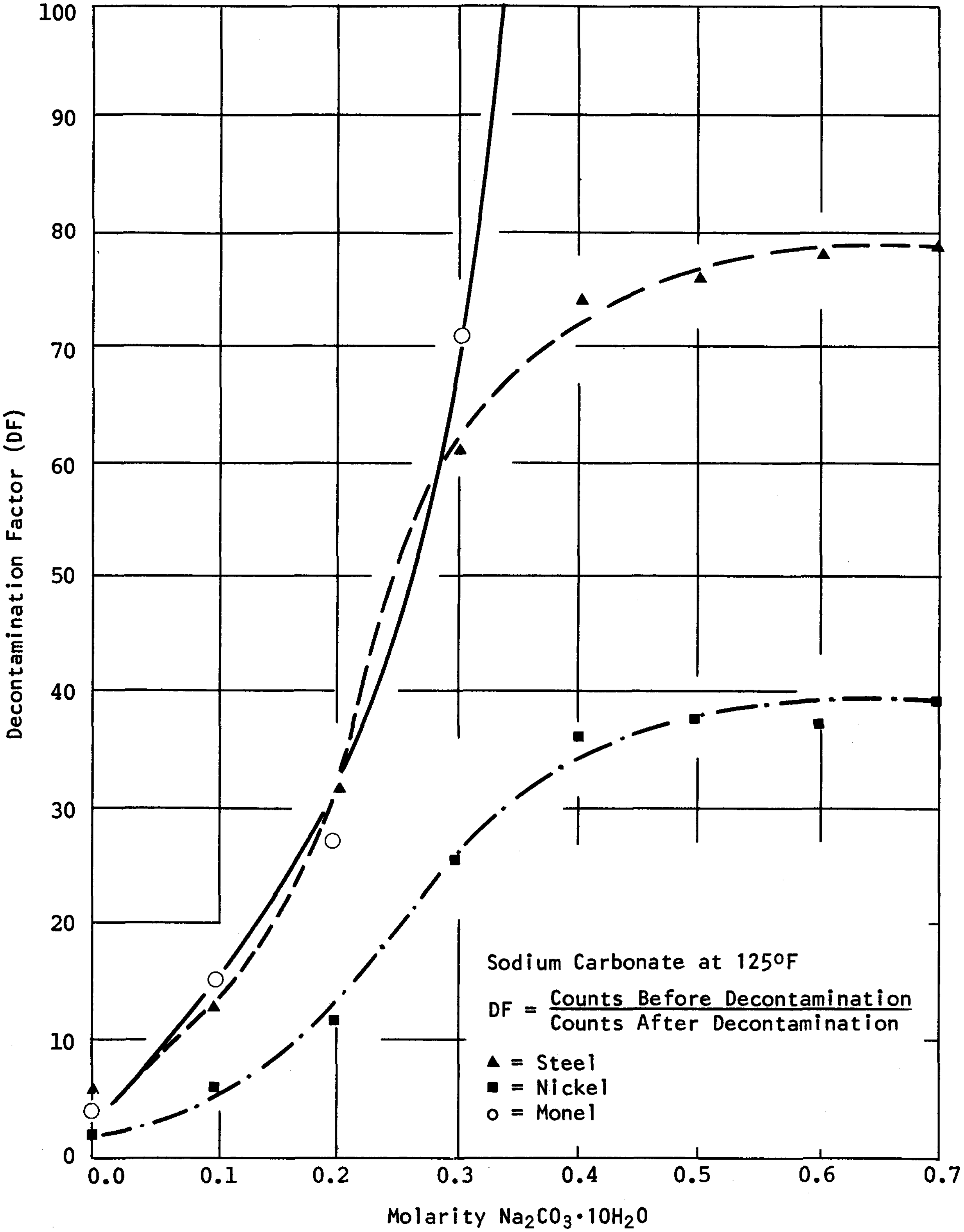

FIGURE 7 OPTIMIZATION OF $Na_2CO_3 \cdot 10H_2O$ CONCENTRATION

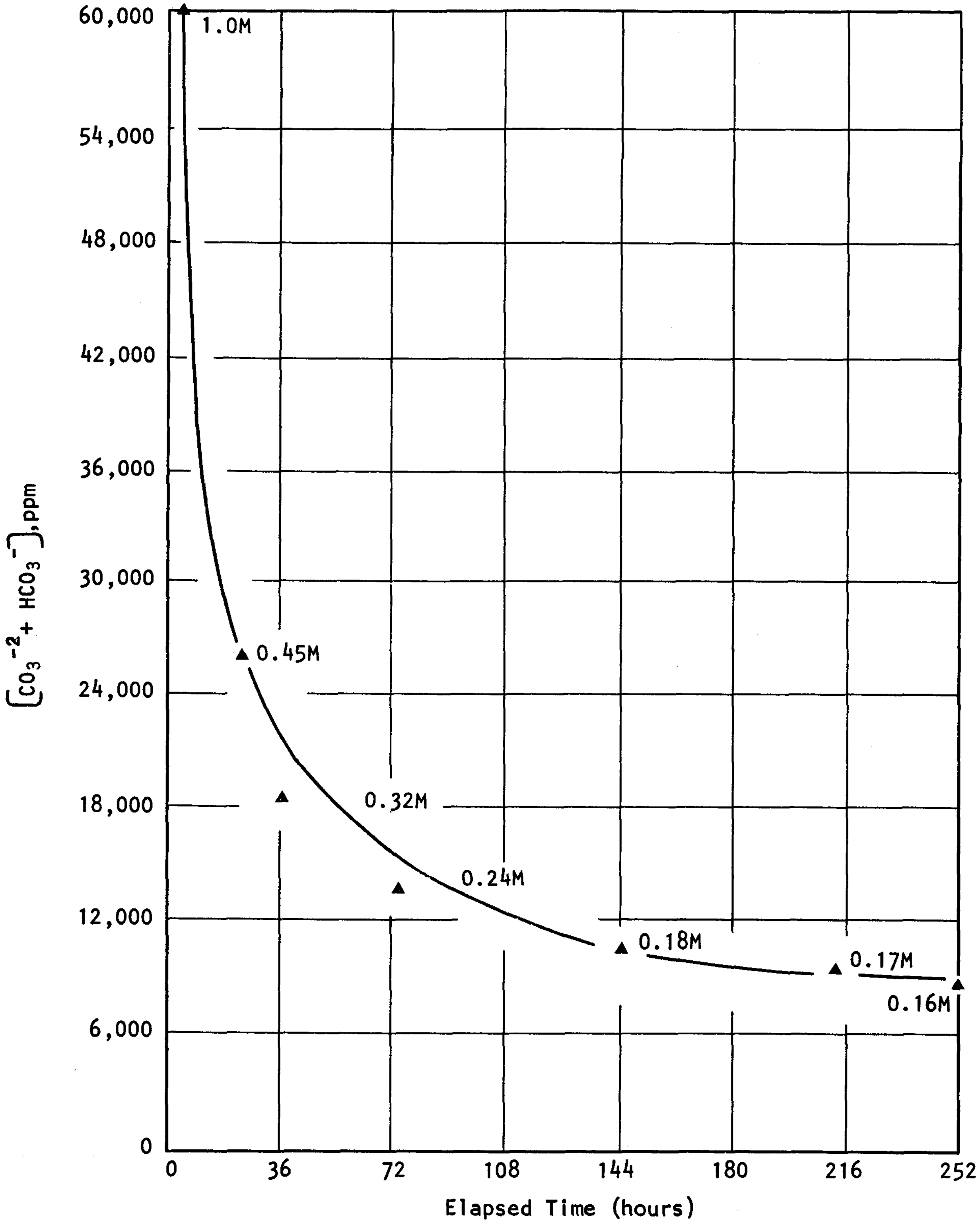

FIGURE 8 SODIUM CARBONATE DECOMPOSITION AT 130°F

of its chemical similarity with ammonium carbonate, sodium carbonate was expected to be compatible with the TBP system and was not studied in this regard.

TABLE 6 EFFECT OF INCREASING NITRATE CONCENTRATIONS ON URANIUM RECOVERY FROM CITRIC ACID SOLUTIONS BY TBP EXTRACTION PROCESS

Citric Acid (Molarity)	NO_3^- (%)	U Extracted (%)
0.25	0.1	5.6
0.25	0.5	17.1
0.25	1.0	62.0
0.25	2.5	99.5
0.25	5.0	99.5

Technetium Operations Effects: While preliminary field observations indicate an acceptable decontamination efficiency of citric acid for surfaces contaminated with technetium (^{99}Tc), data are limited and final conclusions await further testing when such surfaces become available. Another factor to be considered in citric acid use in X-705 is associated with the loading of technetium on Amberlite 401-A anionic exchange resin. This method is planned for future ^{99}Tc removal and control operations in X-705 aqueous process and waste streams. Replacement of both the nitric acid and carbonate booths with citric acid would enable the realization of another advantage; namely, the replacement of two differing loading media and their associated mixing problems and complexities with a single medium. Loading capacity of ^{99}Tc on Amberlite 401-A resin in a 0.30M citric acid medium was found to be somewhat greater than that in nitric acid medium, but significantly less than that in carbonate medium. The citric acid loadings were clearly acceptable for presently planned uses and anticipated column changeout frequencies. Results for the citric acid study are shown in Figure 9.

X–705 FIELD TESTS

Sodium Carbonate Trial Period: With successful completion of all laboratory studies, field tests of 10 to 14-day periods were planned for the X-705 tunnel facility. Sodium carbonate was used in place of ammonium carbonate from April 29, 1977, to May 12, 1977. The solutions were heated to 130°F; target concentration was 0.30 Molar (75-100 lbs. per booth). (The use of hot solutions is not feasible for ammonium carbonate due to the resulting generation and concentration of irritating ammonia fumes in the X-705 high bay area.) Chemical Operations personnel monitored tunnel operations while Industrial Hygiene & Health Physics personnel evaluated cleaning efficiencies by close observations and alpha counting of decontaminated equipment. The booth solution was periodically (once each eight-hour shift) sampled and

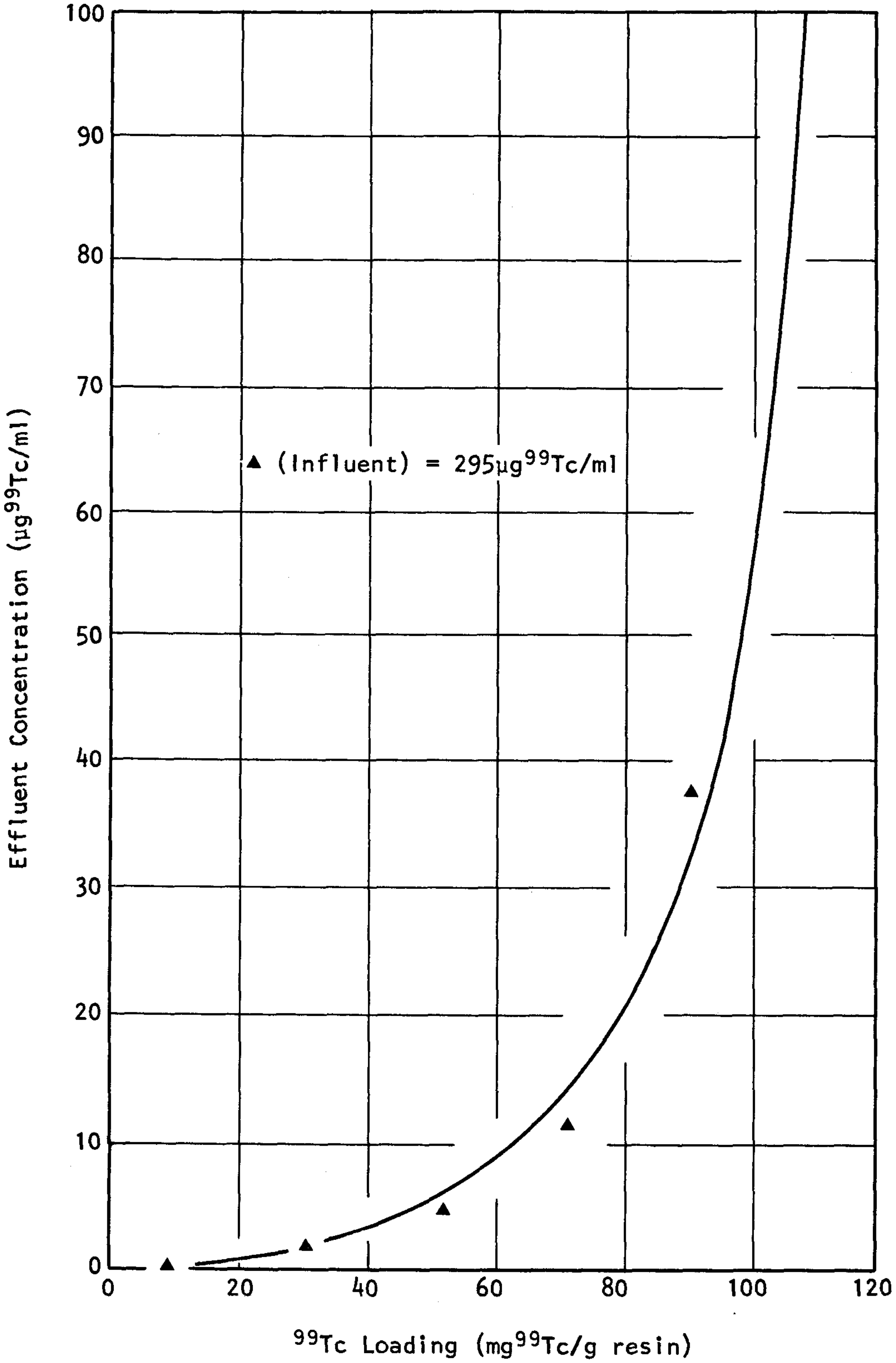

FIGURE 9 ^{99}Tc LOADING OF AMBERLITE 401-A ANIONIC RESIN IN 0.3 MOLAR CITRIC ACID analyzed for fluoride concentration, pH, uranium concentration, and total concentration of all carbonate species. Detailed records of all equipment cleaned in the tunnel, as well as sodium carbonate usage, booth solution changeouts, and makeup and contamination levels of decontaminated equipment, were kept. The records of the booth parameters monitored are shown in Figures 10 and 11. All parameters are considered by Chemical Operations and Process Technology to be within acceptable limits for efficient and satisfactory carbonate booth operation,[12] with the exception of the time period between the "0" shift of May 4 to the booth changeout at noon on May 6. These anomalies, particularly the carbonate and pH values, are believed to have been caused by addition of insufficient Na_2CO_3 for the booth changeout of May 4. It was subsequently recommended that chemical usage and booth volumes be more closely monitored to ensure proper agent concentrations.

Citric Acid Trial Period: Following the exhaustion of the sodium carbonate purchased for the trial period, the carbonate booth of the tunnel was returned to ammonium carbonate. Additional sodium carbonate was purchased and, when available, was used in the tunnel until trial use of citric acid commenced on August 16, 1977. At this time, both the carbonate and nitric acid booths were dumped, refilled, recirculated for approximately one hour, and then dumped again. Both booths were then made approximately 0.30M in citric acid. Because its heating assembly was down for maintenance, booth #1 was operated at ambient temperature. Booth #2 was operated at 130°F. All parameters were monitored as in the sodium carbonate trial period and again found to stabilize within acceptable limits. Results are shown in Figure 12. Booth solutions pumped to solution recovery were made 3% in nitric acid prior to the recovery process, and no detrimental effects were noted in solution recovery, i.e. normal uranium extraction efficiencies were observed.

Chemical Operations personnel initially considered citric acid cleaning to be generally superior to that of either sodium carbonate or ammonium carbonate and essentially the same as that of nitric acid. Citric acid-decontaminated equipment required less hand buffing and exhibited more luster and less visible contamination than did equipment decontaminated in carbonate solutions. In general, decontamination results obtained with citric acid were considered excellent by Chemical Operations and Industrial Hygiene/Health Physics personnel. However, there are no available data on the effects of citric acid on the heat transfer properties of aluminum gas coolers. Thus, until it has been demonstrated that citric acid would have no long-range, deleterious effects on gas cooler performance, nitric acid will remain the decontaminant of choice for those components.

Because of the generally favorable evaluations of the trial period, the X-705 tunnel facility has continued to be operated with citric acid in booths #1 and #2 for compressor and converter decontamination since August 1977. Corrosion of the tunnel system and the associated uranium recovery system has been monitored by X-705 personnel during this 24-month period. No observable corrosion of the systems has been noted, and systems' downtimes have not increased since the changeover to citric acid decontamination. All major components in booth systems are fabricated from stainless steel, which has excellent corrosion resistance for citric acid solutions. Other construction materials include glass, polyvinylchloride plastics, and Monel, all of which

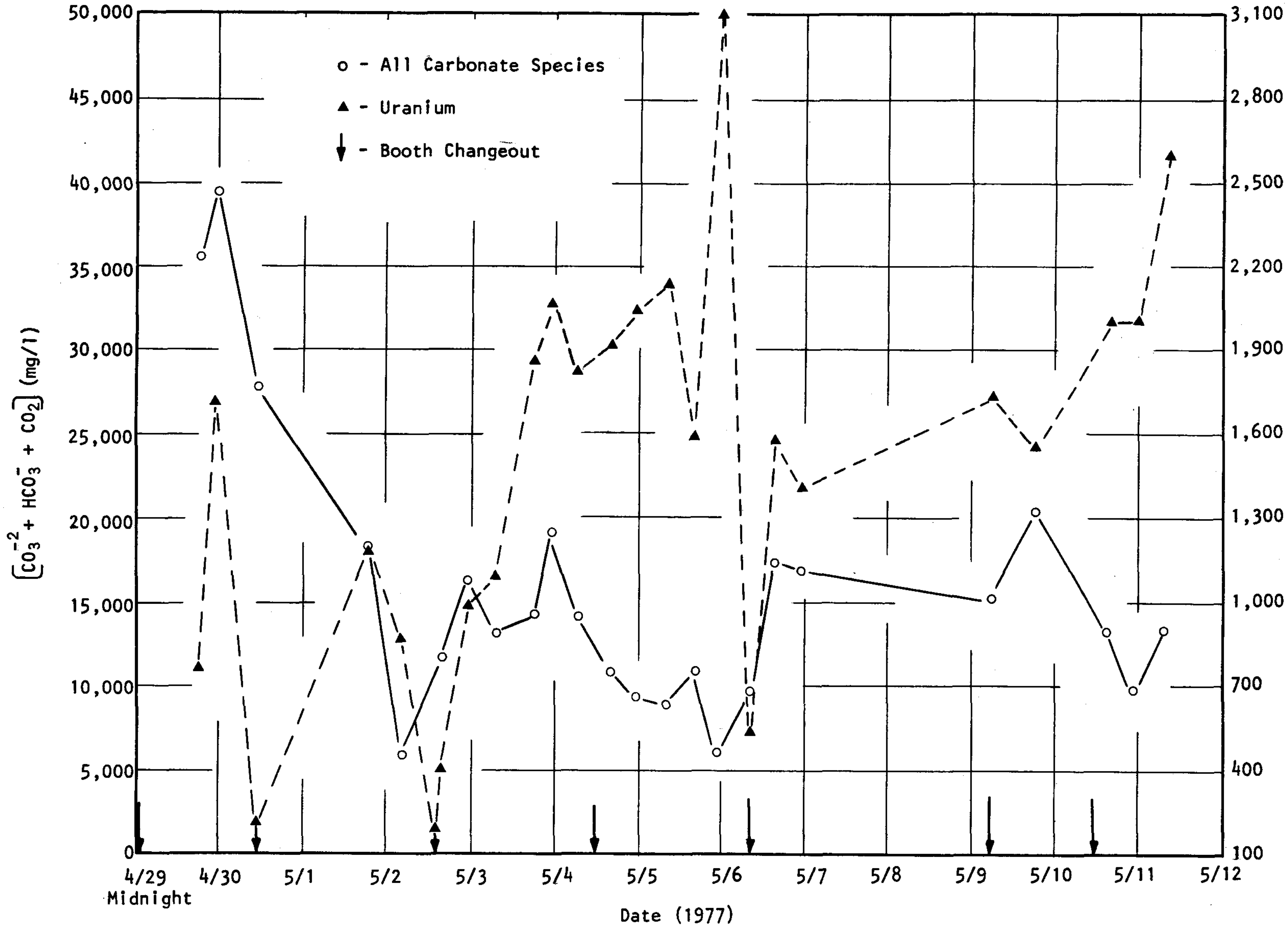

FIGURE 10 SODIUM CARBONATE TRIAL PERIOD AT X-705 SPRAY TUNNEL

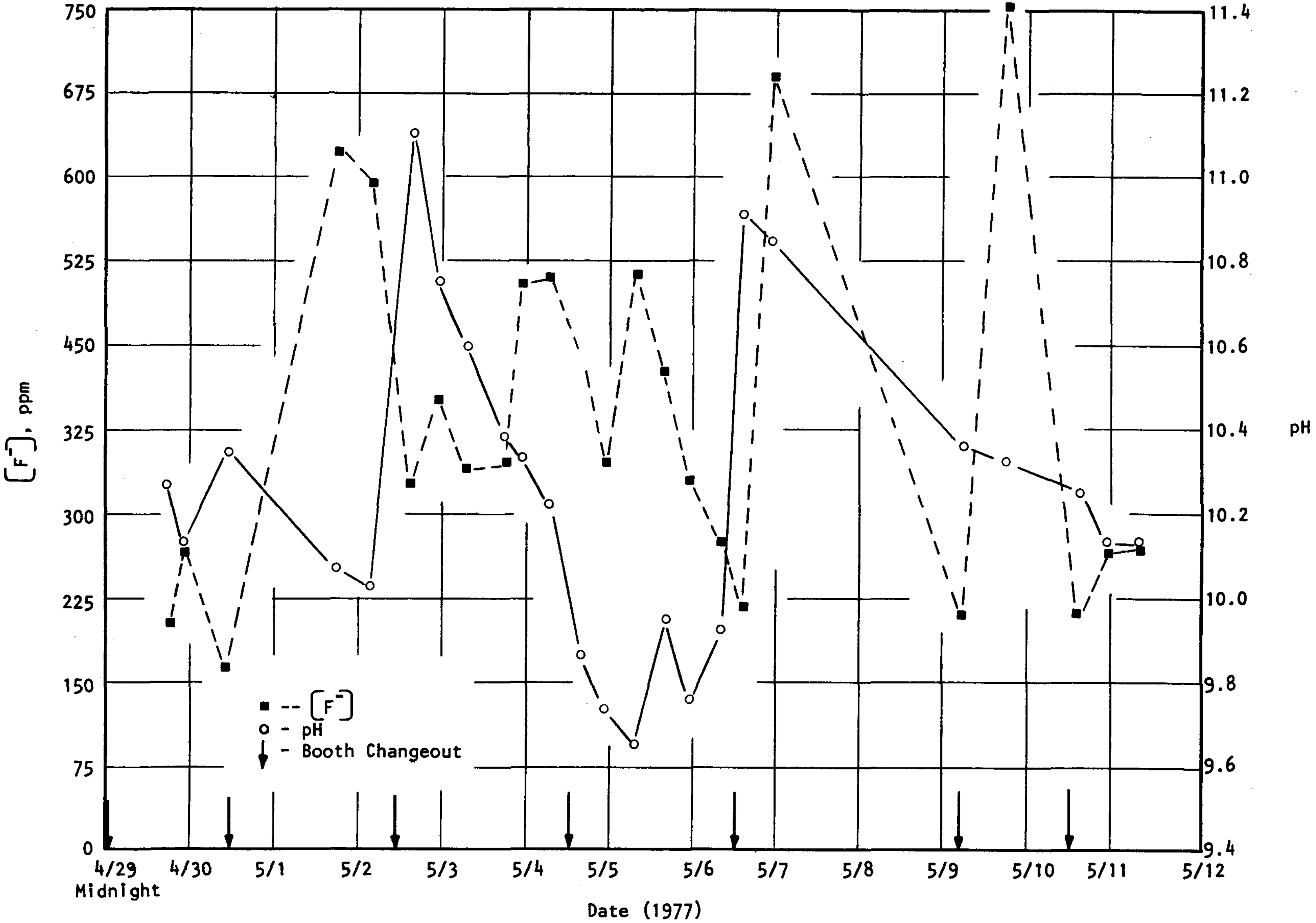

FIGURE 11 SODIUM CARBONATE TRIAL PERIOD AT X-705 SPRAY TUNNEL

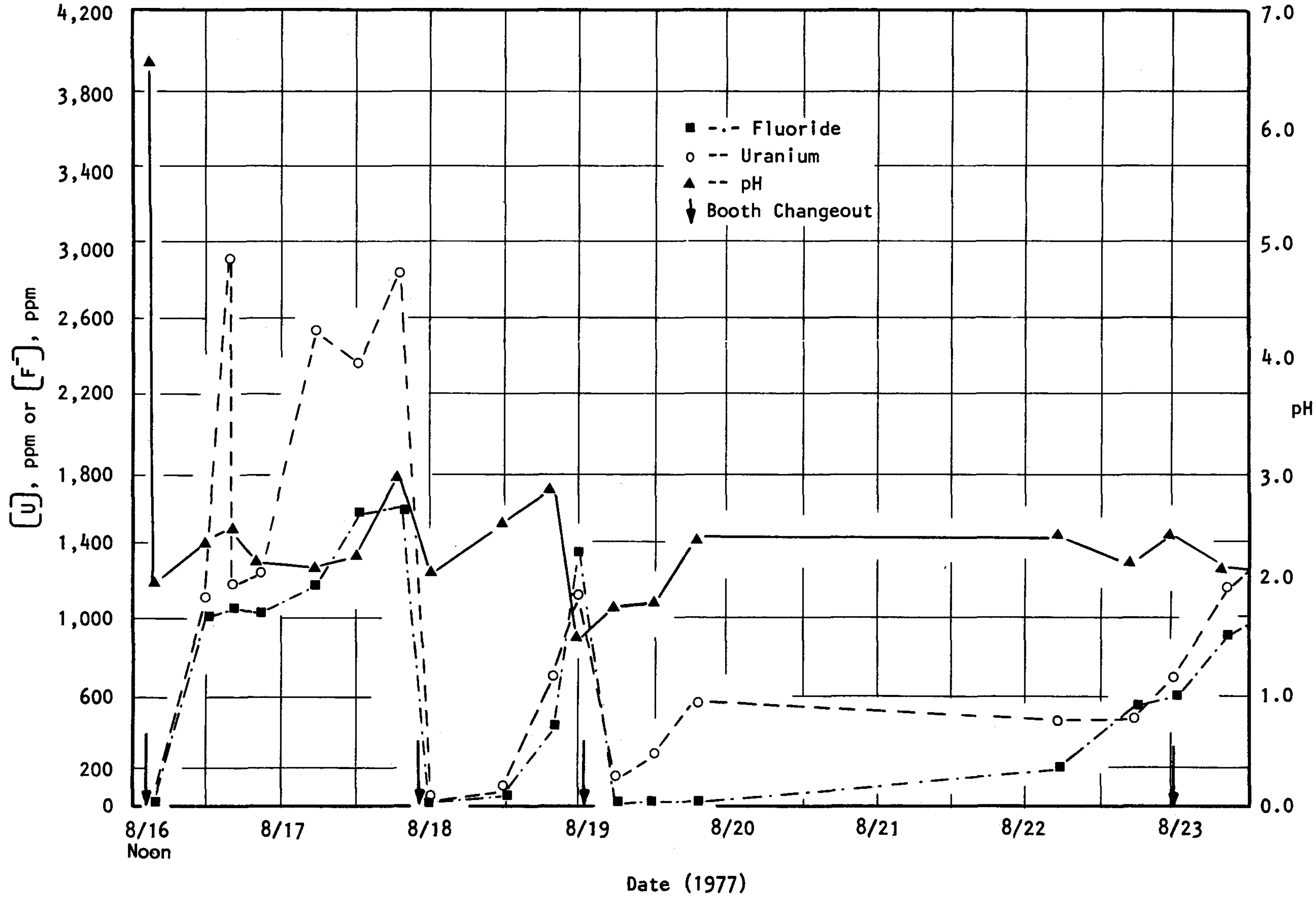

FIGURE 12 CITRIC ACID TRIAL PERIOD AT X-705 SPRAY TUNNEL

are considered compatible with the citric acid decontamination solutions. In addition, the uranium recovery columns are scheduled to be replaced in FY-80 and the stainless steel tunnel housing is to be replaced in FY-86, thus minimizing the impact of any long-term corrosion effects that might unexpectedly hamper operations.[13]

ENVIRONMENTAL EFFECTS

Background: The major incentive for initiating this study was to attempt to alleviate or minimize observed environmental stress in Little Beaver Creek resulting from X-705 ammonia discharges. These discharges were considered to be the Portsmouth plant's most serious aqueous effluent environmental problem.[14] Weekly monitoring of ammonia/ammonium ion concentrations at National Pollution Discharge Elimination System (NPDES) Outfall-001 (which includes effluent from the X-701-B Holding Pond prior to confluence with Little Beaver Creek), and the weekly grab sample at point #8 (Little Beaver Creek on plantsite), began in the summer of 1976. Locations of sample points are shown in Figure 2, page 9. Monitoring was initiated shortly after studies by Battelle and Goodyear Atomic Corporation concluded that the observed environmental stress in Little Beaver Creek was caused by X-705 ammonia effluents which flow through the X-701-B.[15] During the study, monitoring data were used for comparing ammonia-level decreases at NPDES Outfall-001 resulting from the use of alternate decontaminants.

Ammonia/Ammonium Ion Effects: The current U.S. EPA Water Quality Criterion for total ammonia ($NH_3 + NH_4^+$) in effluent streams is 1.5 mg/l; that for free ammonia is 0.02 mg/l. Total ammonia refers to the total concentration of the nitrogen component of both the NH_3 and NH_4^+ (ammonium ion) species; free ammonia refers to the nitrogen component of un-ionized ammonia. The differences are due to the fact that ammonia dissociates in water according to the equation:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Increasing temperature, increasing pH and decreasing salinity push the equilibrium toward free ammonia, which has been documented to be from 100-500 times more toxic than the ammonium ion to fresh water life indigenous to the Scioto River Valley and can be rapidly lethal in the range of 0.5-2 mg/l.[2] Thus, the EPA criteria reflect the fact that variations in season and the characteristics of the environmental waters greatly alter the effects of total ammonia concentrations upon aquatic life. Values of total ammonia which contain 0.02 mg/l NH_3 at varying pH values and temperatures are listed in Table 7.

TABLE 7 CONCENTRATIONS[a] OF TOTAL AMMONIA ($NH_3 + NH_4^+$) CONTAINING AN UN-IONIZED AMMONIA CONCENTRATION OF 0.02 mg/l NH_3

	pH						
Temperature (°C)	7.0	7.5	8.0	8.5	9.0	9.5	10.0
5 (41°F)	16	5.1	1.6	0.53	0.18	0.071	0.036
10 (50°F)	11	3.4	1.1	0.36	0.13	0.054	0.031
15 (59°F)	7.3	2.3	0.75	0.25	0.093	0.043	0.027
20 (68°F)	5.1	1.6	0.52	0.18	0.070	0.036	0.025
25 (77°F)	3.5	1.1	0.37	0.13	0.055	0.031	0.024
30 (86°F)	2.5	0.81	0.27	0.099	0.045	0.028	0.022

[a] In mg/l.

Observed levels of ammonia at NPDES Outfall-001 are plotted in Figure 13. Significant events concerning effluent ammonia levels are also shown in this figure. It is evident that the use of sodium carbonate, and later, citric acid, resulted in significant decreases in the ammonia levels.

Residual NH_3 levels in the holding pond, background NH_3 levels in both Little Beaver Creek and the Portsmouth plant's well water, and some limited uses of ammonia as a precipitation agent for uranium are responsible for remaining levels. Close monitoring is continuing at NPDES Outfall-001. All other known possible sources of ammonia have been replaced by citric acid or sodium carbonate decontamination procedures to further alleviate the discharge of ammonia.

Completion of work on a current plant line-item project involving recarbonation of sanitary water has lowered the pH in the East Drainage Ditch and has assisted in further free ammonia reduction.

Nitrate Effects: The use of citric acid in the spray tunnel has reduced usage of the nitric acid in booth #3 of the tunnel. As a consequence, levels of nitrates found at the same sample points have decreased somewhat. Total nitrate discharges are expected to be cut by approximately 500 lbs./year (which could result in a small (1%) decrease in the size of the planned FY-80 line item biodenitrification facility). Nitrate levels at NPDES Outfall-001 are shown in Figure 14, with dates of significant X-705 changes indicated.

Environmental Monitoring of Citrate: Discharge of citric acid in X-705 effluents is not expected to pose environmental problems: The compound is an intermediate in the tricarboxylic acid cycle for the conversion of acetate to CO_2 and water (with the production of energy), and, as such, is found in almost all living systems. Furthermore, citric acid is rapidly destroyed under most conditions in almost all natural systems. Biodegradability of citric acid occurs very rapidly in sewage plant systems (99% of a 1000 ppm

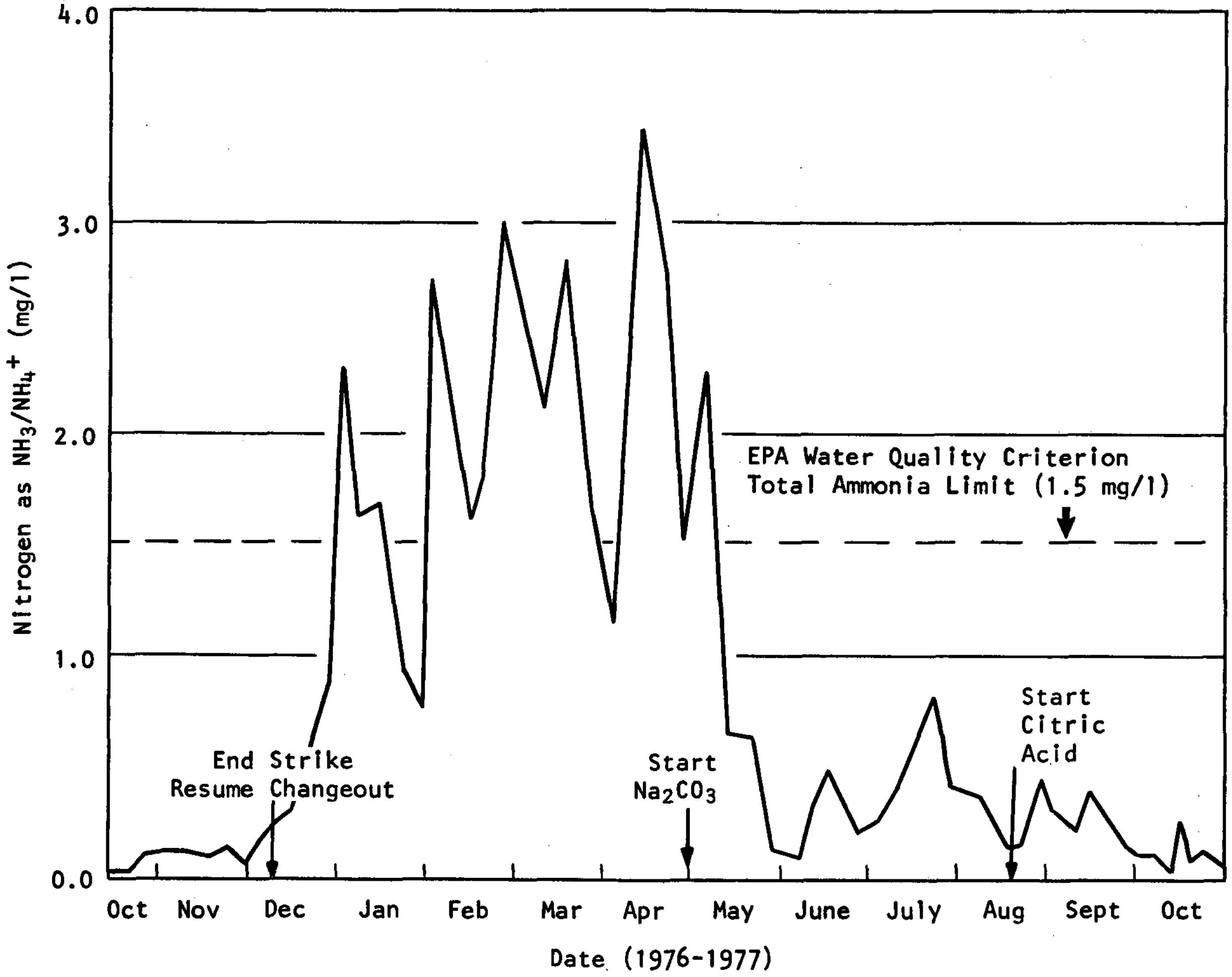

FIGURE 13 AMMONIA/AMMONIUM LEVELS AT NPDES OUTFALL-001

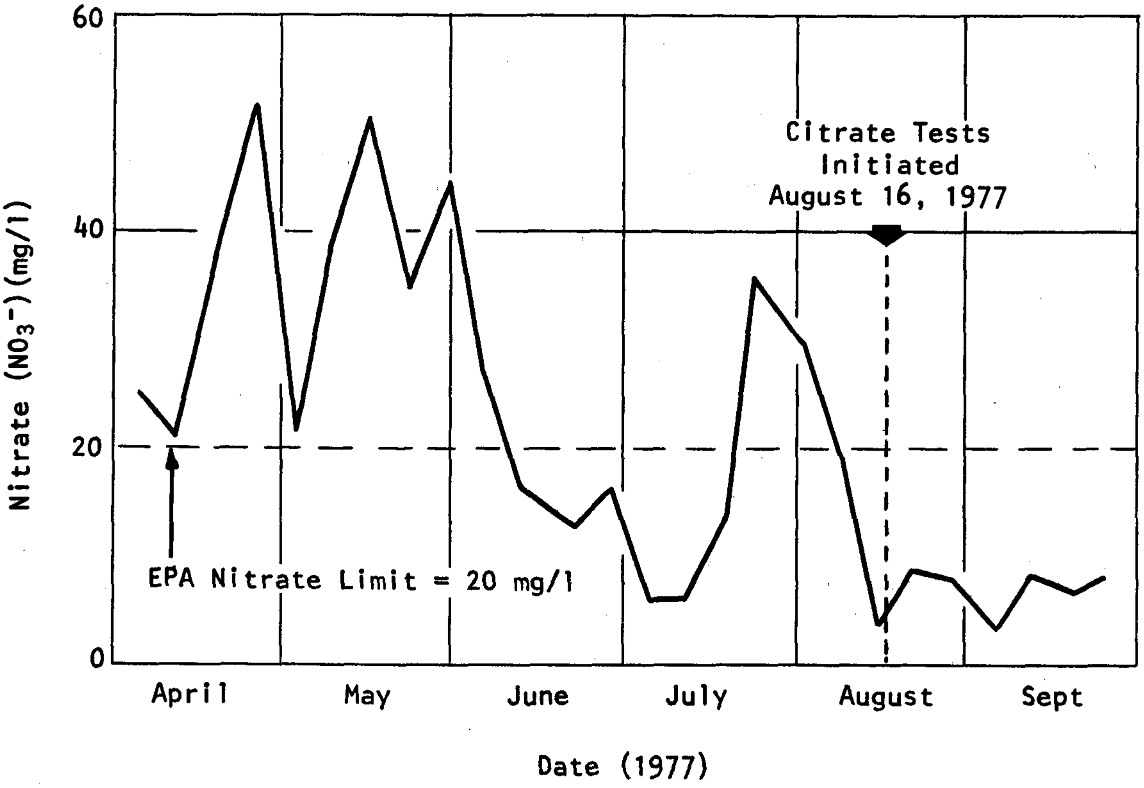

FIGURE 14 NITRATE LEVELS AT NPDES OUTFALL-001

solution in two hours).[16] River water tests have shown citric acid concentrations dropping from 10 to 0.1 ppm in less than 24 hours.[17] Finally, data demonstrating the very low toxicity of citric acid/citrates to natural biota are available.[18] Nevertheless, citric acid levels in natural receiving waters will have to be monitored. For this purpose, an analytical procedure for determination of citric acid/citrates has been developed by the GAT Chemical Analysis Department[19] and analyses have been performed. Levels of citric acid in the X-701-B Holding Pond average 80-120 ppm, while concentrations in the East Drainage Ditch are consistently at or below the lower analytical limit of 2 µg/ml.

ECONOMICS

Usage and costs of ammonium carbonate, sodium carbonate, and citric acid for X-705 tunnel operations from January 1977 through December 1978 are summarized in Table 8.

Because of difficulty in obtaining ammonium carbonate domestically, Goodyear Atomic Corporation was forced to place several foreign orders for the chemical in 1977. Bulk quantities generally cost 37-40¢/lb. Sodium carbonate is available from Diamond-Shamrock of Cleveland, Ohio, at a cost of $0.50/lb. Until the summer of 1978, only USP-grade powdered citric acid could be obtained in the United States. Major suppliers included McKesson Chemicals, Pfizer Chemicals, and Ashland Chemicals at an average price of $0.74/lb. Since then, however, Miles Laboratories of Elkhart, Indiana, has marketed a 50% (w/w) technical grade liquid citric acid solution in 55-gallon drums at $0.285/lb. This lower purity product is acceptable for X-705 decontamination operations and was trial-tested in January 1979 with favorable results. Use of this grade of citric acid would enable the realization of economic benefits greater than those listed in Table 8.

The average monthly cost for both carbonates for the seven months prior to citric acid usage was $1322. Citric acid costs from December 1977 to December 1978 averaged $1406/month, a 6.4% cost increase. However, had the Miles liquid technical grade product been used, the cost of citric acid would have been $1084/month for the same period. Estimated reduced manpower requirements due to decreased buffing of decontaminated equipment are approximately 6 hours/day. At a cost of $10/manhour, a cost savings in excess of $15,000/year[20] could be realized because of the superior cleaning properties of citric acid.

CONCLUSIONS

Citric acid is an excellent alternate decontamination agent for use in the ammonium carbonate booths of the X-705 large parts decontamination tunnel facility. A closely monitored field trial period of one year, during which citric acid decontamination solutions were used, has demonstrated efficient operation of the X-705 tunnel facility. The specifications of all operating parameters for normal use of citric acid decontamination have been established during this period.

TABLE 8 X-705 SPRAY TUNNEL CHEMICAL USAGE AND COSTS

		Usage[a] (in pounds)			
Month	Year	$(NH_4)_2CO_3$	Na_2CO_3	Citric Acid	Monthly Avg. Cost[b] for Period Indicated
January	1977	3200			$1322
February		6080			
March		3840	Begun		
April		2560	400		
May		1280	1600		
June		1280	400		
July		640	1000		
August		Discontinued	800	1000	$ 881
September			300	600	
October			0	900	
November			320	1300	
December			Discontinued	1200	$1406
January	1978			1400	
February				2300	
March				2000	
April				2400	
May				1500	
June				1300	
July				2700	
August				1600	
September				2200	
October				2400	
November				1400	
December				2300	

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[a] Estimated.

[b] Based on \$0.37/lb. for ammonium carbonate, \$0.50/lb. for sodium carbonate, and \$0.74/lb. for citric acid.

In addition to its excellent decontaminating properties, citric acid has fulfilled the other requirements for a replacement for ammonium carbonate:

1. Use of citric acid instead of ammonium carbonate has markedly reduced the ammonia/ammonium ion level in Little Beaver Creek, and has thus alleviated a serious environmental discharge problem for the Portsmouth plant. Citric acid has not been found to introduce any new environmental problems: the compound is both non-toxic and biodegradable; in fact, it is a metabolite common to most living systems.

2. Corrosiveness of citric acid to either process converters or compressors has been closely monitored and has not been demonstrated. Since, however, heated mixtures of citric and nitric acids were found to corrode mild steel, monitoring and prevention of such mixing is continuing.

3. Citric acid is compatible with the tributyl phosphate uranium recovery system. Nitric acid will normally be present or can be added in the small amounts needed to ensure high extraction efficiency. Furthermore, tests show that citric acid is also compatible with a proposed ion exchange process for the removal of ^{99}Tc from uranium recovery raffinates.

Several other benefits have been realized from citric acid usage:

1. Citric acid possesses unique cleaning properties (not characteristic of either sodium carbonate or ammonium carbonate) that minimize the need for hand buffing of decontaminated equipment and, thus, enable the realization of an estimated annual cost savings of approximately $15,000 in reduced manpower requirements.

2. More efficient tunnel operations result from use of two acids (citric/nitric) instead of a base/acid (ammonium carbonate/nitric acid) combination: booth carryover no longer results in neutralization and resultant solution degradation. Thus, with the citric/nitric acid combination, there is longer booth solution service (less frequent booth changeout) and decreased solution throughput requirement in uranium recovery.

3. Because it may be used at higher booth temperatures than ammonium carbonate (which, at equivalent temperatures, produces undesirable ammonia fumes), citric acid yields increased cleaning efficiency.

RECOMMENDATIONS

1. The major recommendation of this report is that citric acid should be used as a permanent replacement for ammonium carbonate in the X-705 spray tunnel facility.

2. Citric acid should be purchased domestically as a technical grade 50% (wt/wt) liquid. This product will give the greatest economic benefit and greatest ease of handling.

3. Appropriate measures have been and should continue to be implemented to monitor and control the level of nitric acid/nitrates in heated citric acid solutions to avoid excessive corrosion of mild steel parts.

4. Citric acid should be used on a trial basis for other X-705 cleaning operations, such as the small cylinder loop, small parts decontamination tables, laundry, etc.

5. Development Laboratory personnel should be notified when ^{99}Tc-contaminated equipment is scheduled for tunnel decontamination so that further data and controlled decontamination factor observations can be obtained and analyzed.

ACKNOWLEDGMENTS

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