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FINAL REPORT OF CHEMICAL SAFETY
FOR TECHNETIUM-99 RECOVERY
BY ANION EXCHANGE

W. J. Van Slyke

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FINAL REPORT OF CHEMICAL SAFETY FOR
TECHNETIUM-99 RECOVERY BY ANION EXCHANGE

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January, 1967

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ABSTRACT

The chemical self heating hazards for a proposed Technetium-99 recovery process were thoroughly analyzed experimentally and by digital computer simulation. The important factors found were reaction kinetics and stoichiometry, flow rate, and system dimensions. Process thermal behavior is presented graphically for each ion exchange material examined, and the possible process hazards and their prevention is discussed.

TABLE OF CONTENTS

LIST OF FIGURES	v
LIST OF TABLES	vi
INTRODUCTION	1
SUMMARY, CONCLUSIONS AND RECOMMENDATIONS.	2
DISCUSSION.	4
Hazards in Anion Exchange-Nitric Acid Systems	4
Experimental Procedures.	4
Reaction Kinetics for Nitrate Form Resin in Contact with Nitric Acid Solutions	4
Calorimeter Measurements.	6
Process Cycle Simulation Tests.	8
Results	8
Reaction Kinetics	8
Critical Temperature - Vessel Radius Relation	12
Ion Exchange Heat Effects and Physical Properties	18
Inflammability and Detonation Sensitivity	18
Process Cycle Simulation.	19
ACKNOWLEDGMENTS	33
REFERENCES.	34
APPENDIX A	35

LIST OF FIGURES

1.	Technetium Recovery Cycle by Anion Exchange	2
2.	Experimental Apparatus for Resin-HNO ₃ Reaction Kinetics Determinations	5
3.	Stirred Calorimeter	7
4.	Heat Generation Rate as a Function of Temperature for Several Ion Exchange Materials with 7M HNO ₃	9
5.	Initial Heat Generation Rate as a Function of Temperature for One Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin in Several Nitric Acid Concentrations	10
6.	Critical Vessel Radius as a Function of Vessel Wall Temperature for Ion Exchange Vessels Containing One Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin in Several Nitric Acid Concentrations, Submerged	13
7.	Critical Vessel Radius as a Function of Vessel Wall Temperature for Ion Exchange Vessels Containing One Lot (Batch 3) of Drained Resin B, 20-50 Mesh, Anion Exchange Resin at Several Nitric Acid Concentrations	14
8.	Critical Vessel Radius as a Function of Vessel Wall Temperature for Ion Exchange Vessels Containing One Lot of Resin C, 20-50 Mesh, Anion Exchange Resin in 7M HNO ₃ , Submerged and Drained	15
9.	Critical Vessel Radius as a Function of Vessel Wall Temperature for Ion Exchange Vessels Containing One Lot of Resin F, 20-50 Mesh, Anion Exchange Resin in 7M HNO ₃ , Submerged and Drained	16
10.	Critical Vessel Radius as a Function of Vessel Wall Temperature for Ion Exchange Vessels Containing One Lot of Resin D, Cation Exchange Resin in 7M HNO ₃ Solutions, Submerged and Drained	17
11.	Temperature-Length Profiles during Hydroxyl-Form Resin B Nitration with 0.24M HNO ₃ at 1.77 gal/min-ft ²	20
12.	Calculated Nitrate Ion Exchange Peak Temperatures as a Function of Position for Several HNO ₃ Inlet Concentrations. Resin B Bed, Initially in Hydroxyl Form	21
13.	Calculated Temperatures as a Function of Time for Hydroxyl Form Resin B with Several HNO ₃ Inlet Concentrations	22
14.	Liquid Temperature Rise for the Proposed Ion Exchange Column for 7M HNO ₃ at 50 gal/min and Three Lots of Resin B, 20-50 Mesh, Anion Exchange Resin	24

LIST OF FIGURES (cont.)

15.	Critical Liquid (7M HNO ₃) Holdup Time for an Insulated Bed of One Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin at Several Levels of Radiolytic Heating	25
16.	Critical Liquid (5M HNO ₃) Holdup Time for an Insulated Bed of One Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating	26
17.	Critical Liquid (3M HNO ₃) Holdup Time for an Insulated Bed of One Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating	27
18.	Critical Liquid (2M HNO ₃) Holdup Time for an Insulated Bed of One Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating	28
19.	Critical Liquid (7M HNO ₃) Holdup Time for an Insulated Bed of One Lot of Resin F, 20-50 Mesh, Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating	29
20.	Critical Liquid (7M HNO ₃) Holdup Time for an Insulated Bed of One Lot of Resin C, 20-50 Mesh, Anion Exchange Resin at Several Levels of Radiolytic Heating	30
21.	Critical Liquid (7M Technical HNO ₃ , As-Mixed) Holdup Time for One Lot of Resin D Cation Exchange Resin at Several Levels of Radiolytic Heating	31
22.	Critical Liquid (7M Technical HNO ₃ , Sparged) Holdup Time for One Lot of Resin D Cation Exchange Resin at Several Levels of Radiolytic Heating	32

LIST OF TABLES

I.	Reaction Constants for Several Ion Exchange Materials with Nitric Acid Solutions	11
II.	Heat of Self-Charring Reaction for Two Dry Nitrate Form Anion Exchange Materials in Nitrogen Atmosphere	11
III.	Summary of Supplementary Data for Resin B Anion Exchange Resin, 20-50 Mesh	18

FINAL REPORT OF CHEMICAL SAFETY
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W. J. Van Slyke

INTRODUCTION

The uncontrollable exothermic chemical reaction is a perpetual threat and challenge to many chemical processes and to the safe storage of a variety of chemicals. Explosives and solid-propellant factories have suffered occasional devastating fires and explosions in spite of stringent safety precautions.

Any heat generating chemical reaction which accelerates with increasing temperature can be hazardous, but this characteristic of the organic resin-nitric acid system was not recognized until just a few years ago. The heat produced in this system by exothermic reaction is practically undetectable at moderate temperatures and in laboratory scale equipment at 100 °C, and it usually is not noticeable in small diameter critically safe ion exchange equipment. Nevertheless, there have been some chemical excursions where the hazard has not been realized and, in most instances, where the operating conditions were abnormal.

These strong base organic anion exchange resins were not specifically intended for service in strong nitric acid which shortens their useful life, but a strong incentive exists for using them because of the value of the product, the cost savings of other eliminated process steps, and increased product purity.

An ion exchange process for technetium-99 recovery and purification has been demonstrated both in pilot scale by Hanford Laboratories, General Electric Company⁽¹⁾ (now Pacific Northwest Laboratory of Battelle-Northwest) and in full scale equipment by the Chemical Processing Department (now Isochem Inc.). This process would use nitric acid with the organic anion exchange resin in two of its steps, prompting Isochem Inc. to request this investigation of the process hazards.

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

The anion exchange process cycle illustrated in Figure 1 was examined to find any combinations of circumstances which could lead to strongly exothermic reactions and serious ion exchange vessel pressurization. The reaction kinetics of several organic anion exchange materials with 7M HNO_3 were measured. All but one (Resin E) of these anion resins were found to be reasonably safe for the technetium process cycle, with suitable process control. The reaction kinetics of one batch of one anion exchange resin was measured at several lower acid concentrations, and the behavior of one cation exchange resin was evaluated in 7M HNO_3 at the request of Isochem Inc.

FIGURE 1
Technetium Recovery Cycle by Anion Exchange

Hazardous situations can occur under the following circumstances:

1. If hydroxyl form resin is converted to the nitrate form with strong nitric acid instead of the intended 0.25M HNO_3 .
2. If resin in strong nitric acid is allowed to stagnate in large diameter vessels.
3. If ion exchange vessels containing organic resin in strong nitric acid are operated with high radioactive heating rates and for long liquid residence times.

The process will normally be safe to operate, but precautions should be taken to prohibit unusual operating conditions which could cause severe exothermic effects. Thorough temperature instrumentation can provide the means to detect a developing hot spot in the ion exchange vessel in time to prevent a chemical excursion. Temperatures should be recorded continuously on the vessel centerline at closely spaced intervals, preferably every foot. Temperatures should also be watched closely when HNO_3 is flowing into the vessel. Temperature recording can be used to indicate completion of some of the ion exchange processes since the associated thermal effects are magnified in the ion exchange process. The temperature wave can be followed easily, and it will signal the completion of the process step when it has passed the outlet liquid temperature probe.

The nitrate conversion step, for example, will normally cause a 20-50 ° temperature rise at the liquid outlet until the resin has been completely nitrated. If temperatures rise much more than that in the vessel or at the outlet, excessively concentrated or poorly mixed nitric acid should be suspected as the cause. If so, the process may experience a continued temperature increase and vessel pressurization. The best known remedy for excessively rising temperatures during operation is a reverse flow of cold water through the ion exchange vessel.

Pressure relief should be incorporated into the ion exchange vessel facilities. Based on the resin kinetics experiments conducted, adequate pressure relief may be provided for this ion exchange vessel size by a 200 psig rated 12-inch diameter rupture disk venting into an unrestricted volume. This will be sufficient to provide instant quenching of the

of the reaction of moist Resin B with 7M HNO_3 . A lower pressure rating can be used if necessary to meet the ion exchange vessel pressure rating. Dry resin which is burning can be quenched with water, although it is very difficult to get the resin dry enough to burn.

DISCUSSION

HAZARDS IN ANION EXCHANGE-NITRIC ACID SYSTEMS

A previous report⁽²⁾ presented basic methods and calculations used in this work. Generally, organic anion exchange resins present a certain hazard when used in the nitrate form in moderately concentrated nitric acid. Their reaction with nitric acid produces heat and, as the reaction accelerates, generates copious quantities of gases. These gases can build up extremely high pressures and the heat produced can ignite the organic resin under some conditions. The implications of the reaction are especially serious since the nitrate form anion exchange resin is a self-contained fuel and oxidizer system.

Both this and the previous study⁽²⁾ have identified some mechanisms which can produce the elevated temperatures required to initiate the reaction. These are briefly: a chemically supercritical stagnant system diameter; the presence of a second, more severe oxidizing chemical; and the combination of ion exchange heating, critical flow rate, and chemical concentration. All these phenomena required study. The hazards studied were found to be well-defined and can be readily circumvented.

EXPERIMENTAL PROCEDURES

Reaction Kinetics for Nitrate Form Resin in Contact with Nitric Acid Solutions

The tests were done in an improved apparatus by the same "pipe test" method used previously.⁽²⁾ The equipment used, as shown in Figure 2, was a jacketed 5-inch diameter stainless steel pipe equipped with thermocouples, a rupture disk assembly connecting with a large "catch tank", and a manually operated pressure release valve and line. The jacket was arranged so that steam could be admitted at controlled pressure for precise and uniform jacket temperature control. Cooling water was admitted to the jacket to rapidly cool the apparatus after completion of each test. Several thermocouples were

placed at the centerline to record the reaction temperatures and rate of temperature rise. Two additional thermocouples were placed in the steam jacket to allow its temperature to be monitored and adjusted.

FIGURE 2
Experimental Apparatus for Resin-HNO₃ Reaction Kinetics
Determinations

The resin to be tested was converted to the nitrate form by washing the resin in a static bed at room temperature with 0.75M HNO₃ for about 1 hour followed by a 1-hour wash with the specified concentration of HNO₃, also at room temperature. The resin was then drained, placed in the equipment and the test conducted with as little delay as possible. The single lot of the one cation exchange resin examined, Resin D, was too reactive to equilibrate with 7M HNO₃ and test in this way. The reaction kinetics of this strongly acid, phenolic type resin were evaluated calorimetrically as described under "Calorimeter Measurements" on page 6.

Reaction pressure in the equipment was indicated by a 600 psig pressure gage. The 1/2-inch stainless steel tubing pressure release line bypassing the rupture disk assembly was routinely used to conclude each test, allowing the chemical reaction to quench itself by evaporative cooling. The reaction products receiver tank was maintained under a partial vacuum during each test by a steam jet which also scrubbed the reaction offgases for removal of the nitrogen oxides produced by the experiments. Reaction quenching by pressure release through the 1/2-inch tubing bypass line was quick and effective in every experiment, even when test pressures had climbed to well above 300 psig.

The reaction kinetics of three different batches of Resin B anion resin in 7M HNO_3 were evaluated and one batch was checked in a range of HNO_3 concentrations from 2M to 7M HNO_3 . The reaction kinetics of a single batch of three other anion exchange resins in 7M HNO_3 were also measured. The reaction kinetics of one cation exchange resin, Resin D, was measured calorimetrically in both as-mixed and well-sparged 7M technical grade nitric acid.

Calorimeter Measurements

The simple calorimeter used to measure heat capacities, heats of exchange, heats of neutralization of the hydroxyl form resin, and the reaction kinetics for Resin D in 7M HNO_3 solutions is shown in Figure 3. A resistance heater with carefully measured characteristics was employed with a stable dc power supply (Perkin Model TVCR 0210-30) to calibrate the calorimeter before and/or after each measurement as necessary. The heating rate of the resistance heater was calculated from the heater voltage drop measured with a Weston Model 901 multiple range milliammeter in series with a 1004 ohm precision resistor. The heater resistance wire was protected by silicone oil filled pyrex tubing. Calorimeter temperature rate of change was measured with a Brown Electronik^R variable range and suppression recorder measuring the EMF difference between a 1/16-inch stainless steel sheathed iron constantan thermocouple and a Joseph Kaye Model PRJC 5C thermocouple reference junction. All measurements were corrected for the small rate of heat loss of the calorimeter, measured separately. A Rubicon Model 2745 mV potentiometer was used to calibrate the recorder to 1mV full scale in the EMF range of interest. The recorder chart speed was 8 in. per hour. Liquid agitation

^R Minneapolis-Honeywell Regulator Co.

FIGURE 3
Stirred Calorimeter

in the calorimeter was accomplished by a laboratory magnetic stirrer, eliminating the possibility of heat loss through a propeller shaft.

Heats of ion exchange and chemical reaction involving the resin required the use of thin wall glass bulbs containing the resin which were broken to mix resin with a reactive liquid. Resin heat capacity was measured by calculation from the change in total heat capacity of the calorimeter and its contents before and after adding a weighed quantity of the resin.

The calorimeter methods were checked by measuring the heat capacity of pure water. The validity of the break tube technique for heats of chemical reaction was confirmed by measuring acid-base heats of neutralization. Some liquid heat capacities were also measured.

A heavy duty Paar oxygen bomb calorimeter was used to measure total heats of reaction for nitrate form Resins A and B. The resin samples were equilibrated with $7M$ HNO_3 , drained, and dried to constant weight at room

temperature in a desiccator jar over concentrated sulfuric acid. The samples were "ignited" in a heavy duty combustion bomb in a well-purged nitrogen atmosphere at atmospheric pressure. The sample cups were lined with thick asbestos paper to insulate the resin from the cool cup wall and allow the reaction to proceed to completion.

Process Cycle Simulation Tests

Two complete, but shortened, test cycles were run with Resin B, using nonradioactive solutions simulating the expected final compositions. The test contactor was a 4-inch ID by 6 ft long glass column fitted with inlet, outlet, and five equally spaced centerline thermocouples. Temperatures at these points were recorded during each test cycle. Each part of the test cycle was continued until any heat effects observed had passed completely through the packed resin bed in the glass column. Flow rates were adjusted to about 1.77 gal/min-ft², the rates previously used in the plant equipment. (3)

RESULTS

Reaction Kinetics

Figure 4 graphically compares the magnitudes of the initial reaction rates in 7M HNO₃, in terms of heat generation rate, for the ion exchange materials examined. One ion exchange resin previously examined, (2) Resin A, is also included. Figure 5 gives heat generation rates for Resin B, Batch 3, in several HNO₃ concentrations. The equations for the heat generation rates may also be expressed mathematically by a pseudo-first-order Arrhenius equation in the presence of excess HNO₃:

$$q = C_0 \cdot q_0 e^{-\Delta E/RT} \quad [\text{cal/cm}^3\text{-min}] = K_0 e^{-\Delta E/RT}$$

where q is the heat generation rate at temperature T degrees Kelvin, C_0 is total heat available in the reaction, cal/cm³; q_0 is a constant coefficient, minutes⁻¹; ΔE is the activation energy and R is the gas law constant.

Table I lists the constants for the reactions for each type and lot of resin tested when wetted with the nitric acid solutions listed. C_0 and q_0 are combined into one value, K_0 .

FIGURE 4
Heat Generation Rate as a Function of Temperature for Several Ion
Exchange Materials with 7M HNO₃

FIGURE 5
Initial Heat Generation Rate as a Function of Temperature for One
Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin in
Several Nitric Acid Concentrations

The total heats of reaction, C_o , were measured for Resin A and Resin B, and are presented in Table II. The K_o values for these two resins in Table I may be divided by C_o to determine q_o .

TABLE I
REACTION CONSTANTS FOR SEVERAL ION EXCHANGE
MATERIALS WITH NITRIC ACID SOLUTIONS

<u>Ion Exchange Resin</u>	<u>$K_o -$ g-cal/(cm³) (min)</u>	<u>$\frac{\Delta E}{R}, ^\circ K^{-1}$</u>	<u>HNO₃ Concentration moles/liter</u>
<u>Resin B</u>			
Batch 1	2.1×10^9	8.5×10^3	7.0
Batch 2	2.7×10^6	5.8×10^3	7.0
Batch 2	no observable reaction		.24
Batch 3	5.25×10^3	3.04×10^3	7.0
Batch 3	1.05×10^4	3.52×10^3	5.0
Batch 3	6.24×10^{10}	9.84×10^3	3.0
Batch 3	4.66×10^9	8.99×10^3	2.0
Resin E	4.10×10^8	5.70×10^3	7.0
Resin D	2.27×10^9	5.88×10^3	7.0 as-mixed technical grade HNO ₃
Resin D	5.48×10^8	5.88×10^3	7.0 sparged technical grade HNO ₃
Resin C	6.41×10^4	3.90×10^3	7.0
Resin F	5.27×10^{12}	10.28×10^3	7.0
Resin A	9.84×10^{14}	1.43×10^4	7.0

TABLE II
HEAT OF SELF CHARRING REACTION FOR TWO DRY NITRATE FORM
ANION EXCHANGE MATERIALS IN NITROGEN ATMOSPHERE

<u>Ion Exchange Resin</u>	<u>Heat of Reaction, C_o</u>	<u>Standard Deviation</u>
Resin A	456.6 g-cal/g	* 13.8 g-cal/g
Resin B	374.1 g-cal/g	* 4.7 g-cal/g

Wide variations in reaction kinetics were observed for the three different lots of Resin B tested, emphasizing the sensitivity of the reaction to slight deviations in ion exchange material composition which have no appreciable effect on ion exchange properties. Similar variations will probably be observed for different lots of any of the ion exchange resins, and the heat generation rates presented in Figure 4 and the reaction kinetics of Table I should be considered representative only of the particular batch of each material tested.

The two curves shown for Resin D emphasize the variation that can be caused by nitric acid solutions of the same nominal concentration. These tests, done calorimetrically rather than by the enclosed vessel or pipe test method, exposed the ion exchange resin to $7M$ HNO_3 prepared by diluting concentrated technical nitric acid to the specific gravity of $7M$ HNO_3 . The curve for the higher heat generation rate is typical for the reaction rate of that batch of Resin D in the $7M$ HNO_3 without any further treatment. The lower curve was obtained when the $7M$ HNO_3 was thoroughly sparged with air, presumably lowering its nitrous acid content. The measurements were made for the initial reaction rates, typical of that batch of the resin in the nitric acid solutions as mixed.

Critical Temperature - Vessel Radius Relation

Figures 6 and 7 present the calculated critical temperature-radius relation for stagnant beds of submerged and drained Resin B, Batch 3, 20-50 mesh, in equilibrium with four nitric acid concentrations. Figures 8 and 9 give the critical temperature-radius function for Resin C and Resin F exchange resins respectively. Figure 10 shows the critical temperature-radius function for Resin D cation resin in $7M$ technical HNO_3 and sparged $7M$ HNO_3 , submerged and drained.

In each case, the curve plotted represents the stability boundary where any increase in either vessel wall temperature or vessel radius can cause an unstable or self-accelerating chemical reaction. The instability occurs at the set of conditions where heat is generated more rapidly than it can be rejected by the system. Since the heat generation rate of the chemical system generally increases more rapidly with increasing temperature than the conduction

FIGURE 6

Critical Vessel Radius as a Function of Vessel Wall Temperature for Ion Exchange Vessels Containing One Lot (Batch 3) of Resin B, 20-50 Mesh, Anion Exchange Resin in Several Nitric Acid Concentrations, Submerged

FIGURE 7

Critical Vessel Radius as a Function of Vessel Wall Temperature for Ion Exchange Vessels Containing One Lot (Batch 3) of Drained Resin B, 20-50 Mesh, Anion Exchange Resin at Several Nitric Acid Concentrations

FIGURE 8
Critical Vessel Radius as a Function of Vessel Wall Temperature for
Ion Exchange Vessels Containing One Lot of Resin C, 20-50 Mesh,
Anion Exchange Resin in 7M HNO₃, Submerged and Drained

FIGURE 9
Critical Vessel Radius as a Function of Vessel Wall Temperature for
Ion Exchange Vessels Containing One Lot of Resin F, 20-50 Mesh,
Anion Exchange Resin in 7M HNO₃, Submerged and Drained

FIGURE 10
Critical Vessel Radius as a Function of Vessel Wall Temperature for
Ion Exchange Vessels Containing One Lot of Resin D, Cation
Exchange Resin in 7M HNO₃ Solutions, Submerged and Drained

heat loss rate, stability can only be regained by a change in system geometry, by an increase in the conduction temperature drop if the instability has not progressed far, or more conveniently by increased heat removal by forced convection or evaporation.

Ion Exchange Heat Effects and Physical Properties

Table III lists supplementary measurements which were made to allow analysis of the process with ion exchange Resin B. The heat capacity and thermal conductivity measurements made for Resin B were assumed to be typical of the other resins for calculational purposes.

TABLE III
SUMMARY OF SUPPLEMENTARY DATA
FOR RESIN B ANION EXCHANGE RESIN, 20-50 MESH

<u>Property</u>	<u>Measured</u>	<u>Measured</u>	<u>Measured</u>	<u>Mean</u>	
Settled bulk density- dry nitrate form	.820 .813	.799 .805	-- .811	.81	g/cm ³
Settled bulk density in 7M HNO ₃ nitrate form resin	1.229	1.230	1.232	1.23	g/cm ³
Heat capacity, dry nitrate form resin	.55	.50	.52	.52	g-cal/(g) (°K)
Thermal conductivity, ⁽⁵⁾ settled chloride form resin, water-washed and drained	.050 .012	.057 .014	.053 .013	.053 .013	Btu/(hr) (ft ²) (°F/ft) g-cal/(min) (cm ²) (°K/cm)
Thermal conductivity, ⁽⁵⁾ settled chloride form resin in water	.24 .059	.24 .059	.24 .059	.24 .059	Btu/(hr) (ft ²) (°F/ft) g-cal/(min) (cm ²) (°K/cm)
Heat of ion exchange conversion of chloride form resin to nitrate form resin by 1M HNO ₃	1.31	1.25	--	1.28	g-cal/cm ³

Inflammability and Detonation Sensitivity

Two liters of Resin B, in equilibrium with 7M HNO₃ were drained and spread in a thin layer in a large stainless steel pan to dry. After drying

four days, the resin was neither flammable nor sensitive to the shock of a number six blasting cap. After seven days drying in this way, the resin was still not quite able to support combustion and was not shock sensitive to a number eight blasting cap.⁽⁴⁾ It was found to be flammable when dried even more thoroughly, however.

Process Cycle Simulation

Heat effects were observed during two of the process steps. The first of these is exothermic resulting from conversion of the hydroxyl form resin to the nitrate form by 0.25M HNO_3 and the simultaneous reaction between the hydroxyl ion and the acid (Figure 1). Figure 11 shows the temperature profiles produced by this step during the experiment. The acid concentration limited the heat generation to a relatively low constant rate which produced a nitrate ion exchange conversion zone moving more slowly than the interstitial liquid. The heat produced was swept away from the reaction zone forming a broadening temperature plateau which eventually worked its way through the packed bed and produced a temperature increase at the column outlet. Then a decrease back to normal temperatures occurred which signaled completion of the nitrate-ion exchange step. Different temperatures were reached in the two experiments, possibly because of different resin pretreatment or a slightly different acid concentration, although the second experiment was intended to duplicate the first. Analysis of the time-temperature records for the calorimeter measurements of the quantity of heat evolved showed that the nitrate conversion process is approximately half order with respect to the remaining ion exchange capacity.

The results of these experiments were closely duplicated by a computer calculation which also predicted the results of nitrate ion exchange with increasingly stronger nitric acid solutions at the same flow rate. Some of these results, shown in Figures 12 and 13, include heat generation from oxidation (or resin degradation). The calculations do not include heat loss by conduction or evaporation and the calculated temperatures above the nitric acid solution boiling point may be interpreted as being equivalent to a pressure buildup or to boiling in the resin bed.

Figure 13 shows the data of Figure 12 with maximum temperature plotted versus elapsed time instead of versus position. Acid concentrations of 1M

FIGURE 11
Temperature-Length Profiles During Hydroxyl-Form Resin B Nitration
with 0.24 M HNO_3 at 1.77 Gal/min-ft²

FIGURE 12
Calculated Nitrate Ion Exchange Peak Temperatures as a Function of Position for Several HNO₃
Inlet Concentrations. Resin B Bed, Initially in Hydroxyl Form

FIGURE 13
Calculated Temperatures as a Function of Time for Hydroxyl Form Resin B with Several HNO_3
Inlet Concentrations

HNO_3 or less will produce a limited temperature rise because the ion exchange zone moves more slowly than the interstitial liquid. As the reaction zone passes, the bed cools back to the inlet liquid temperature and the resin-nitric acid reaction is quickly arrested. Elevated temperatures exist only at, and downstream from, the hydroxyl-ion-nitrate ion exchange zone. Since the resin at the exchange zone is only partially in the nitrate form and the hydroxyl form resin downstream is unreactive, resin degradation is low.

In contrast, the reaction with 2M , 3M and 5M HNO_3 flowing through the 6-ft diameter bed at 50 gal/min will cause a very rapid temperature rise. These combinations of acid concentrations, flow rate, ion exchange kinetics, and heat capacities will give a movement rate for the ion exchange zone which is very close to the heat movement rate through the bed by convection. This rate coincidence effect concentrates the heat available by ion exchange into a narrow zone where the reaction occurs, producing a heat spike which grows until some change in the system allows heat dissipation. For 3M HNO_3 , the rate of rise would be extremely fast, rising from the 20°C initial temperature to 100°C within 75 seconds after the acid reaches the column entrance. Five molar HNO_3 will cause an even faster rate of rise, reaching 100°C within 50 seconds and the heat spike also moves through the bed more rapidly than with the 3M HNO_3 . These high temperatures will promptly trigger the resin-nitric acid reaction therefore.

At still greater acid concentrations, the ion exchange zone moves more rapidly than the heat produced, and the peak temperature location begins to lag behind the ion exchange reaction zone. Seven molar HNO_3 will produce a temperature rate of rise which is less than the 5M HNO_3 and almost as low as the 3M HNO_3 , reaching 100°C in about 72 seconds. The reaction zone moves much more rapidly than with the lower acid concentrations however, and the heat left behind with the nitrate form resin eventually causes the resin-nitric acid exothermic reaction and the upswept curve shown in Figure 12.

Because the initial sources of heat are hydroxyl-nitrate-ion exchange and neutralization of hydroxyl ion by nitric acid, exposure of hydroxyl form resin to nitric acid can cause heating by ion exchange heating, chemical neutralization, and by subsequent oxidation of the resin. These mechanisms could conceivably cause ion exchange vessel pressurization, but nitric acid concentration of 1M HNO_3 or less will be safe at any flow rate.

A second heat effect noted was primarily endothermic and therefore of no concern relative to process safety. It occurred during the water wash following the 6M HNO_3 elution and consisted of a small constant height exothermic peak, about 3-5 $^\circ\text{C}$, followed by a deepening "valley" or inverse temperature peak. The minimum temperature during this step decreased at a rate of about 3-6 $^\circ\text{C}$ per foot of packed bed length.

No observable temperature rise occurred in the packed nitrate form resin column with Resin B, Batch 1, 20-50 mesh anion resin, in contact with flowing 6M HNO_3 entering at 20 $^\circ\text{C}$, and these results were confirmed by calculating a temperature rise based on the reaction kinetics of Resin B tested in 7M HNO_3 and the physical properties of the packed bed. The results of these calculations are presented in Figure 14. Notice that as much as 2 $^\circ\text{C}$ temperature rise would have been observed if Batch 3 resin had been used for the test.

FIGURE 14

Liquid Temperature Rise for the Proposed Ion Exchange Column for
7M HNO_3 at 50 gpm and Three Lots of Resin B, 20-50 Mesh, Anion
Exchange Resin

The calculated critical liquid holdup time is detailed in Figure 15 as a function of column inlet temperature for Resin B, Batch 3 in 7M HNO_3 and several levels of radiolytic heating. This graph gives the "worst known case" calculation for this resin since Batch 3 showed the highest reactivity of the three batches of Resin B and the 7M HNO_3 concentration is also somewhat more severe than the 6M HNO_3 specified for the technetium ion exchange cycle step. The calculation was also based on heat transfer by liquid convection only, equivalent to assuming that only the centerline temperatures of an infinite diameter column are being considered. The central volume of the 6-ft diameter by 8-ft long column approximates an infinite diameter column because of the relatively low bulk resin thermal conductivity. The critical holdup times plotted correspond to extremely rapid temperature rise rates occurring at high temperatures, but these times are only slightly greater than required to reach temperatures in the 150-300 °C range where gas evolution has already become rapid. These holdup times may also be interpreted as the time to deflagration for a perfectly insulated (or very large) ion exchange vessel from an initial uniform temperature equal to the inlet temperature shown on the graph.

FIGURE 15

Critical Liquid (7M HNO_3) Holdup Time for an Insulated Bed of One Lot (Batch 3) of Resin B, 20-50 Mesh Anion Exchange Resin at Several Levels of Radiolytic Heating

Figures 16 through 22 present the critical holdup time curves for the other resins tested, including Resin B, Batch 3 resin in 7M, 5M, 3M, and 2M HNO_3 .

The information provided in the figures permits estimating when a rapid temperature rise will occur in most cases. The computer programs presented previously can be used to predict or simulate the ion exchange vessel performance for other situations or where a more precise performance estimate is required. One of these, "Hotbed", has been extensively modified to handle ion exchange heating, a rate process. Copies of this updated Fortran IV source program are available from the author.

FIGURE 16

Critical Liquid (5M HNO_3) Holdup Time for an Insulated Bed of One Lot (Batch 3) Resin B, 20-50 Mesh, Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating

FIGURE 17
Critical Liquid (3M HNO₃) Holdup Time for an Insulated Bed of One Lot (Batch 3) of Resin B, 20-50 Mesh Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating

FIGURE 18
Critical Liquid ($2M$ HNO_3) Holdup Time for an Insulated Bed of One Lot (Batch 3) of Resin B, 20-50 Mesh Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating

FIGURE 19
Critical Liquid (7M HNO₃) Holdup Time for an Insulated Bed of One Lot of Resin F, 20-50 Mesh, Anion Exchange Resin as a Function of Liquid Inlet Temperature at Several Levels of Radiolytic Heating

FIGURE 20
Critical Liquid (7M HNO₃) Holdup Time for an Insulated Bed of One
Lot of Resin C, 20-50 Mesh, Anion Exchange Resin at Several Levels
of Radiolytic Heating

FIGURE 21
Critical Liquid (7M Technical HNO₃, As-Mixed) Holdup Time for One Lot of Resin D Cation Exchange Resin at Several Levels of Radiolytic Heating

FIGURE 22
Critical Liquid (7M Technical HNO₃, Sparged) Holdup Time for One Lot of Resin D Cation Exchange Resin at Several Levels of Radiolytic Heating

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APPENDIX A

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