WSRC-TR-99-00317

Qualification of Reillex® HPQ Anion Exchange Resin for Use in SRS Processes

William J. Crooks III
Edward A. Kyser III
Steven R. Walter

Westinghouse Savannah River Company
Aiken, SC 29808

March 10, 2000

DISCLAIMER

Available for sale to the public, in paper, from: U.S. Department of Commerce, National Technical Information Service, 5285 Port Royal Road, Springfield, VA 22161
phone: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Available electronically at http://www.doe.gov/bridge
Available for a processing fee to U.S. Department of Energy and its contractors, in paper, from: U.S. Department of Energy, Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062
phone: (865)576-8401
fax: (865)576-5728
email: reports@adonis.osti.gov

EXECUTIVE SUMMARY

As part of the resin qualification process for HB Line Phase II, the thermal stability of Reillexf HPQ anion exchange resin in nitric acid solutions was evaluated using the Reactive System Screening Tool (RSST). The RSST allows for efficient screening of runaway reactions as a function of temperature. Resin qualification is based on a favorable comparison of the RSST reaction profiles of Reillexf HPQ to Ionacf A-641, a resin previously qualified for use in HB Line.

Resin/nitric acid mixtures were heated in the RSST and the temperature-pressure responses were determined as a function of resin type, nitric acid concentration, cerium(IV) loading, and damage caused by previous irradiation of the resin. Above 100 ^oC, Reillexf HPQ, irradiated Reillexf HPQ, and Ionacf A-641 showed similar reaction profiles as a function of temperature. Reillexf HPQ showed no obvious inertness to chemical degradation relative to Ionacf A-641. Below 100 ^oC, a low intensity, low-temperature exotherm (80 ^oC, 2 ^oC/min) was observed only for Reillexf HPQ, suggesting the presence of a small amount of easily-oxidizable material.

A detailed study of the low-temperature exothermic reaction of Reillexf HPQ and nitric acid identified nitric oxide (NO) and carbon dioxide (CO_2) as gaseous reaction products. In addition, spectroscopic analysis identified a carbonyl group in the solid resin reaction product, suggesting the presence of a carboxylic acid. This product characterization suggests the low-temperature exotherm is due to the oxidation of the ethylbenzene pendant groups of the Reillexf HPQ, forming NO, CO_2 and a benzoic acid pendant group. To evaluate this possibility, the nitric acid reaction with diethylbenzene as a model compound was tested in the RSST. Indeed, the diethylbenzene-8 molar nitric acid reaction showed a low-temperature exotherm, and generated NO, CO_2, and a mixture of mono- and dicarboxylic acids as reaction products. Furthermore, literature precedents have reported the oxidation of ethylbenzene with various oxidizing agents.

For Reillexf HPQ, irradiated Reillexf HPQ, and Ionacf A-641 resins, the time to maximum rate generally decreased as nitric acid concentration increased. For Reillexf HPQ, the higher nitrate concentration tests (Ce(IV)/8M HNO_3 and 12 M HNO_3) showed an overlap between the low and high temperature exotherms, leading to a concern that the lower temperature reaction may initiate the higher temperature reaction. However, long term isothermal resin tests at 100 ^oC in the RSST did not cause the high temperature runaway reaction until the resin went dry. When in contact with solution, the energy released from the low-temperature exothermic reaction is not sufficient to activate the high-temperature reaction. The more important issue with the low temperature exotherm is gas evolution. Pressurization in the ion exchange column may force liquid out of the column or lead to over-pressurization.

The RSST data was used to estimate the maximum volume and rate of gas evolution. This calculation of gas volumes and gas generation rates is based on the adiabatic temperature rise during the RSST test. Assuming the low temperature exotherm is due to ethylbenzene oxidization by nitric acid to give NO, CO_2, and benzoic acid as the

products, the calculated maximum volume of gases generated from a 20-liter column at 80 ^{o}C is about 53 L ± 23 and the average gas generation rate of 2.3 L/min ± 1.5.

In contrast to the Reillex® HPQ tests, Ionac® A-641 and for irradiated Reillex® HPQ showed no increase in reactivity in the presence of cerium(IV). Neither Ionac® A-641 nor irradiated Reillex® HPQ exhibit the low-temperature exotherm under any conditions. This absence of the low temperature exotherm suggests that the small amount of easily oxidized material is not present in Ionac® A-641 and is destroyed during the irradiation of Reillex® HPQ. Therefore, the radioactive decay on a plutonium-loaded column of Reillex® HPQ may also initiate the oxidation of the easily-oxidized material as a function of dose rate, leading to gas generation and pressurization in the ion exchange column.

Maintaining the resin bed temperature below 70 ^{o}C, the low temperature exothermic reaction between nitric acid and Reillex® HPQ can be minimized. Operation at lower temperatures will ensure a greater margin of safety. However, irradiation from plutonium loaded on the resin may also cause the oxidation of the easily oxidized component. The relationship between radiation dose and off-gas volume, composition, and generation rate was not studied.

A nitric acid digestion pretreatment was developed that eliminated the low-temperature exothermic reaction without destroying the bead size or shape. The performance testing of this treated resin showed no loss of performance, and is described in an another report.

Table of Contents

List of Tables

List of Figures

1. Introduction

The Phase II portion of the HB-Line facility was built in the early 1980's to process plutonium and neptunium from nitric acid solutions into oxide suitable for storage in a vault. Although the other portions of HB-Line were started up in the mid 1980's and have operated since that time, the anion exchange and precipitation processes in Phase II were never started up. As part of the material stabilization efforts, Phase II is currently being started up. A new anion exchange resin is needed because the resins that were proposed for use 10 years ago are limited by performance characteristics, disposal requirements, or are no longer commercially available. SRTC is responsible for qualifying all resins prior to their use in Nuclear Materials Stabilization and Storage (NMSS) processes. Qualification consists of both process suitability and thermal stability with nitric acid. This report describes the thermal stability qualification of Reillex**f** HPQ, the new resin proposed for processing plutonium and neptunium in the HB Line facility.

2. Background

Incidents involving undesirable self-accelerated exothermic reactions between organic resins and nitric acid solutions have been well documented.[1,2,3,4] The motive for studying resins and nitric acid mixtures under upset conditions is to establish a margin of safety during plant process operation. The thermal stability qualification of Reillex**f** HPQ is based on a favorable comparison of thermal effects with Ionac**f** A-641, one of the resins that was used previously. This qualification process compares the thermal effects resulting from the reaction of nitric acid solutions with Reillex**f** HPQ (NO_3^- form) and Ionac**f** A-641 (NO_3^- form), respectively. Using a Reactive System Screening Tool[5] (RSST), the thermal responses to various upset conditions were determined and compared as a function of nitric acid concentration, cerium (IV) loading (as a simulant for plutonium (IV)), and damage caused by previous irradiation of the resin.

3. Description and History of Resins

Ionac**f** A-641 is a robust strong-base macroporous anion exchange resin **1**, sold by Sybron Chemicals Inc. It is composed of a cross-linked styrene-divinylbenzene polymer

---

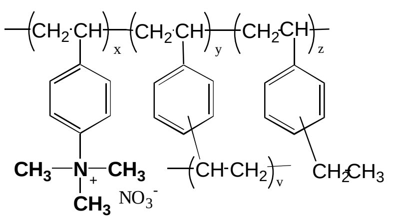
[1] H.T. Fullam, G. Jansen, Jr. and W.J. Van Slyke, Thermal Instabilities in Anion Exchange Processing, Conference on Ion Exchange in the Process Industry. Society of Chemical Industry, London, July 16-18, 1969.

[2] F.W. Miles, "Ion-Exchange-Resin Failures in Processing Actinides, Nuclear Safety, 1968, 9, 394-406.

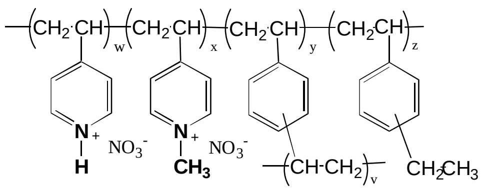
[3] D.C. Bartholomew, E.J. Kosiancic, B.J. McMurray, D.D. Wodrich and W.M. Harty, Explosion of Ion Exchange Resin in Americium Recovery Service, Hanford Plant, August 30, 1976. Report, Atlantic Richfield Hanford Co., Richland, WA, 1976.

[4] P.G. Rhoades, P.E. Ruhter, M.W. Shupe, R.E. Gerton, Investigations of the Chemical Explosion of an Ion Exchange Resin Column and Resulting Contamination of Personnel in the 242-Z Building, August 30, 1976. Report, Energy Research and Development Agency, Richland Operations Office, Richland, WA, 1976.

[5] Manufactured by Fauske and Associates, Inc., 16W070 West 83rd Street, Burr Ridge, IL, 60521



1



2

backbone structure with a high concentration of quaternary amine exchange sites for anions, -$[N(CH_3)_3]^+$. This polystyrene-based anion exchange resin has excellent performance characteristics, and mechanical and chemical stability. While this resin has been used in the nuclear industry for many years, it is known to undergo a runaway reaction in hot nitric acid solutions and suffers from loss of performance due to radiological damage.

Reillex**f** HPQ is also a strong-base macroporous anion exchange resin **2**, and is sold by Reilly Industries Incorporated. It is composed of a copolymer backbone of 1-methyl-4-vinylpyridine (70%) and a divinylbenzene mixture (30%). Approximately, 63% of the amine sites are methylated, forming pyridinium cations, which function as the principal anionic exchange sites. Unquaternarized amines protonate in concentrated nitric acid solutions, also resulting in anionic exchange sites. During the polymeric resin synthesis, the “divinylbenzene mixture” reactant is actually composed of 80% divinylbenzene positional isomers and 20% ethylvinylbenzene positional isomers.

Reillex**f** HPQ was developed as a result of collaboration between Los Alamos National Laboratory and Reilly Industries, Inc. in an effort to increase the safety and process efficiency during the recovery and purification of plutonium.[6] The merits of a vinylpyridine-based resin were first identified in the 1950’s. A 1977 report showed polyvinylpyridine-based anion exchange resins (Permutit**f**) had excellent performance characteristics, in addition to resistance to both chemical attack and radiological damage.[7] Marston predicted that the most reactive functional group on the vinylpyridine and vinylstyrene-based resins are the aromatic rings. Due to the greater electron deficiency of the pyridine aromatic ring relative to the benzene aromatic ring, it is expected that the polyvinylpyridine-based resin will be more resistant to electrophilic aromatic substitution relative to the vinylstyrene aromatic ring. Although resin exposure to typical nitric acid process solutions and conditions does not favor nitration of aromatic rings or the formation of highly energetic compounds.

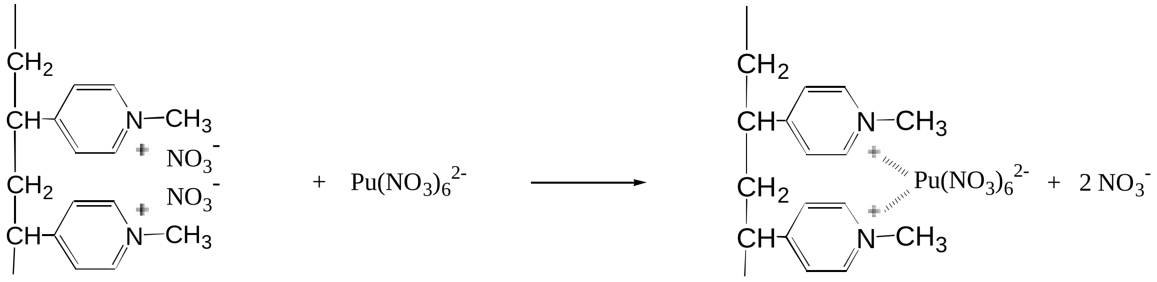
In concentrated nitric acid solutions (> 6 molar), plutonium (IV) is complexed by six nitrates to form the anionic complex, $Pu(NO_3)_6^{2-}$. Ion exchange resins which are

---

[6] S. Frederic Marsh, “Evaluation of a New Macroporous Polyvinylpyridine Resin for Processing Plutonium Using Nitrate Anion Exchange”, April 1989, LA-11490

[7] T.E. Gangwer, M. Goldstein, K.K.K.S. Phillay, “Radiation Effects on Ion Exchange Materials” Bookhaven National Laboratory report, BNL-50781 (1977), p. 88.

selective for $Pu(NO_3)_6^{2-}$ are polymers that typically contain trialkylammonium nitrates, $-NR_3^+ NO_3^-$. For example, the anion exchange reaction between a Reillex**f** HPQ binding site **3** and $Pu(NO_3)_6^{2-}$ **4** yields the stronger resin/$Pu(NO_3)_6$ complex **5**. The high selectivity of this resin for plutonium (IV) originates from the uniqueness of the metal anionic complex, and there are few anionic metal complexes that can compete for these cationic binding sites.



3 **4** **5**

Chemical composition and structure of a resin will control the performance characteristics, requirements for disposal, and thermochemical stability. Resins differ in the type of polymeric backbone, the type and concentration of functional groups, the extent of cross-linking, and the overall three-dimensional structure.

4. Experimental Program

The RSST was used to characterize the thermal effects of the runaway reactions between solid organic resins and nitric acid solutions. The RSST is a nearly-adiabatic calorimeter that heats an open, well-insulated 10-mL test cell within a sealed 350-mL Parr bomb. In a typical test, the Parr bomb is pressurized to minimize the endothermic process of evaporation of solvent (i.e. loss of oxidant), and the test cell mixture is stirred and heated at a constant rate. The test cell mixture and the Parr bomb are monitored for temperature and pressure, respectively. The pressure-temperature data are processed to generate plots of temperature vs. time, pressure vs. time, self-heating rate vs. temperature, rate of pressure change vs. temperature, and pressure vs. temperature.

The RSST calorimeter allows for efficient screening of runaway reactions as a function of temperature. The reaction of Reillex**f** HPQ, Ionac**f** A-641 and irradiated Reillex**f** HPQ**f** anion exchange resins (all in nitrate form) with nitric acid were compared in the RSST. The thermal effects were evaluated as a function of nitric acid concentration, cerium (IV) loading (as a simulant for plutonium (IV)), and damage caused by previous irradiation of the resin. Much of this work focused on the low-temperature exothermic reaction observed for Reillex**f** HPQ-nitric acid mixtures. Off-gases associated with this low-temperature exotherm were identified by gas chromatograph-mass spectroscopy (GC-MS), the final nitric acid concentration was determined by titration, and the solid resin residue was characterized by Fourier transform infrared (FTIR) spectroscopy. In addition, the product nitric acid solution was analyzed by a solvent extraction volatile organic method to search for soluble resin degradation fragments.

4.1 Reagent Preparations

All chemicals used in this study were reagent grade and used without additional purification except where noted. Nitric acid solutions (8 M and 12 M with and without dissolved cerium (IV)) were prepared from dilutions of stock nitric acid (69.7%, purchased from Fisher Scientific, Inc.) and ceric ammonium nitrate (99.6%, Fisher Laboratory Company, Lot Number 523930). Typical feed solutions for plutonium purification by anion exchange are 5 g Pu/L in 8 molar nitric acid. A fully-loaded column of Reillex**f** HPQ may be approximately 40 g Pu/L or 0.174 M. In concentrated nitric acid solutions, cerium (IV) and plutonium (IV) form analogous hexanitrate anionic complexes, $M(NO_3)_6^{2-}$, where M = cerium (IV) or plutonium (IV). In this study, 0.174 M cerium (IV) (24 g/L) solutions were prepared as a nonradioactive surrogate for plutonium (IV).

Ionac**f** A-641 (chloride form) was purchased from Sybron Chemicals Inc., Birmingham, New Jersey. Two batches of Reillex**f** HPQ (chloride forms: 1995 Lot Number 50224AE and 1998 Lot Number 80302MA) were purchased from Reilly Industries. The 1995 product had a brown color and the 1998 product had a white color. In order to increase the performance characteristics, the 1998 process increased the amount of methylated amine sites. To achieve this, we speculate that the 1998 process may have required higher reaction temperature and longer reaction times than the 1995 process. Except where noted, the 1998 product was used in all experiments. Irradiated Reillex**f** HPQ (chloride form) was prepared by exposing Reillex**f** HPQ (chloride form: 1998 Lot Number 80302MA) to a cobalt-60 source for a total exposure of 10^8 RAD. To evaluate the quality assurance of the 1998 product, Reilly Industries Inc. also provided a sample of their latest 1999 Reillex**f** HPQ product (chloride form: Lot number 100698, batch number 1364.1).

4.2 Experimental Procedures

4.2.1. Resin Preparations

4.2.1.1. Standard Method for Resin Conversion from Chloride Form to Nitrate Form. The resins used in this study are commercially available as the chloride salts. Typically, approximately, 25 mL of resin (chloride form) were added to a 150-mL beaker. The resin was slurried with about 50 mL of 1 molar sodium nitrate and loaded into a glass, 30-mL ion exchange column. The chloride form resin was converted to the nitrate form resin by washing with ten bed volumes of 1 molar sodium nitrate. Excess sodium nitrate was removed by washing with ten bed volumes of water. The resin was collected by suction filtration and dried in a vacuum at approximately 70 ^{o}C for 12 hours to give a dry product. The dry product was stored in a plastic screw cap bottle until use.

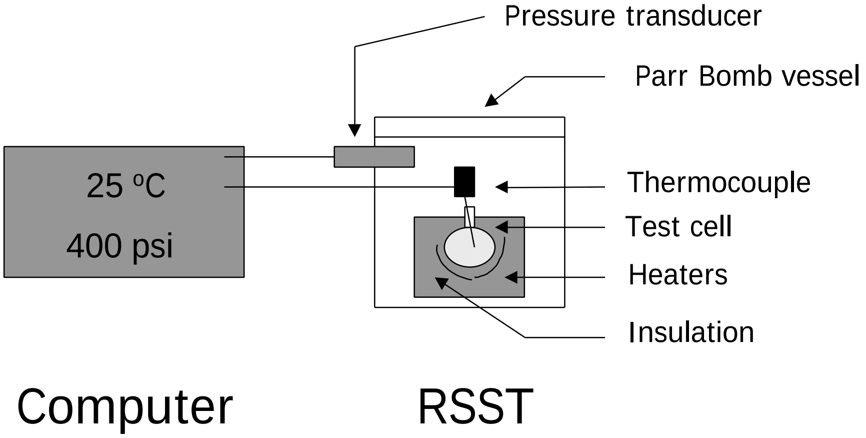
4.2.1.2. Pre-treatment of Resin Prior to Standard Chloride Form to Nitrate Form Conversion. In two of the resin tests, resin was pretreated with an organic solvent wash prior to the standard method for conversion to the nitrate form. Typically, approximately, 25 mL of resin were added to a 150-mL beaker. A 50-mL aliquot of organic solvent (methanol or acetone) was added and loaded into a glass 30-mL ion exchange column. Pre-treatment was achieved by washing the loaded resin with ten bed volumes of the organic solvent. Subsequently, this pretreated resin was converted to nitrate form using the *Standard Chloride Form to Nitrate Form Resin Conversion*, as described above.

In two other resin tests, the resin was pretreated by digesting it in a hot aqueous solvent. Typically, approximately 25 mL of resin and a 50-mL aliquot of aqueous solution (12 M HNO_3 or distilled water) were added to a 150-mL beaker. The 12 molar HNO_3 mixture was boiled for three hours with a steady generation of NO_x gas. The distilled water mixture was heated for three hours at 60 ^oC; digestion at higher temperatures resulted in violent bumping. Subsequently, each pretreated resin was converted to nitrate form using the *Standard Chloride Form to Nitrate Form Resin Conversion*, as described above.

4.2.2. RSST Testing

4.2.2.1. Charging the test cell. First, 2.38 A 0.10 grams of the dry nitrate form resin were added to a tared 14-mL RSST test cell. Second, a nitric acid solution with a known specific gravity was added dropwise to the test cell until the required mass of nitric acid solution was added. Finally, a small Teflon **f** stir bar was added.

4.2.2.2. Loading the test cell into the calorimeter. A dual-bottom heater was wrapped around the test cell and secured with a heater belt. The test cell assembly was wrapped with an aluminum foil square. The wrapped test cell was placed into the insulation jacket, and sealed into the insulation sheath, with the four heater wires exiting through the grommet. The four heater wires were connected to the corresponding wires of the heater glands, and the insulation sheath assembly was lowered into the bottom of the Parr bomb. The Parr bomb was attached to the nitrogen line and was placed on a stir plate. Stirring



was confirmed by visual inspection. A thermocouple was threaded through an extension tube and secured onto the top of the test cell. Temperature and pressure sensors were connected, the Parr bomb was sealed, and charged with nitrogen.

4.2.2.3. RSST operation. The test was initiated after the change in pressure with time, or pressure rate ($\Delta P/\Delta t$), was less than 0.20 psi/min. The system was considered at thermal and pressure equilibrium. Unless otherwise noted, tests were run from room temperature to 300 ^{o}C with an imposed heating rate of 0.5 ^{o}C/min under 400 psig (nitrogen gas). Preliminary RSST testing of resin/8 M nitric acid mixtures indicated that some vapor saturation (“boiling”) occurred under 300 psig but could be avoided by running the tests at 400 psig. Vapor saturation increased the endothermic stripping of the water/nitric acid solvent and interfered with observation of exotherms. Generally, tests were run in “automatic shutdown mode” with shutdown criteria of 280 minutes, 650 psig, or 300 ^{o}C.

4.3. Experimental Data

The RSST resin test conditions are described in Table 1. Each resin/nitric acid mixture was heated at a constant rate of 0.5 ^{o}C/min under 400 psig of nitrogen gas in a sealed Parr bomb, unless otherwise noted. Ionac**f** A-641, Reillex**f** HPQ, and irradiated Reillex**f** HPQ were each tested in 8 and 12 molar nitric acid solutions in the presence and absence of 24 g/L cerium (IV) (0.174 molar). Some tests were performed multiple times. Additional tests in Table 1 evaluated other characteristics of the runaway reaction including pressure dependency, the effect of heating at low-temperature for a long duration, and the effect of various pre-treatments prior to thermal stability testing using the RSST.

5. Results

5.1. Reproducibility of the Method

The reproducibility of the RSST method for the characterization of the runaway reaction between resin and nitric acid solutions was evaluated for Reillex**f** HPQ (nitrate form) in 8 molar HNO_3. The runaway behavior is characterized by Figures 1–4, which are annotated to identify the important features. In addition, the important parameters for the low-temperature and high-temperature exotherms are summarized in Tables 2 and 3, respectively.

The comparison of the time to maximum rates (TMR) between tests is only valid when heating mixtures of similar mass and heat capacity. The maximum temperature, self-heating rates, pressure, and pressure rates are valid for comparisons of solutions with different heat capacities. Furthermore, for comparing different resin reactions, the test conditions that should be duplicated include the mass of reactants, ratio of reactants, pressure of containment, imposed heating rate, and mixing rate.

The reproducibility tests with Reillex® HPQ in 8 M HNO_3 were run under the same conditions. The absolute errors in the TMR, maximum temperature, maximum self-heating rate ($\Delta T/\Delta t$), maximum pressure, and maximum pressure rates ($\Delta P/\Delta t$) in Tables 2 and 3 are reported as ± one standard deviation. These errors are a measure of the reproducibility of RSST testing of the Reillex® HPQ-8 M HNO_3 system, and do not include the propagation of errors within individual tests.

The reproducibility of RSST test with this resin/nitric acid system under an initial backpressure of nominally 410 psig is represented in Figures 1-4. In Figure 1, a small temperature excursion is observed at 127 ± 6 min (3% error), reaching a maximum temperature of 80 ± 4 ^{o}C (4% error). A large temperature excursion is observed at 240 ± 8 min (4% error), reaching a maximum temperature of 248 ± 1 ^{o}C (0.4% error). Figure 2 shows that both the low and high-temperature excursions are associated with pressure excursions, evidence for the generation of gaseous reaction products. Figures 3 and 4 identify the intensity of the temperature and pressure excursions, perhaps the most informative plots for characterizing reactive systems. A low-temperature exotherm is observed with a self-heating rate 2 ± 1 ^{o}C/min (50% error), and a small but observable pressure rate increase of 0.3 ± 0.1 psi/min (33% error). In addition, a high-temperature exotherm is observed with a self-heating rate of 105 ± 40 ^{o}C/min (30% error), a pressure rate increase of 274 ± 21 psi/min (7% error), and a maximum pressure of 570 ± 6 psig (1% error). The experimental determination of the TMR, maximum temperature and maximum pressure for this reaction in the RSST were determined with relatively high precision. However, the maximum self-heating rates and maximum pressure rates were determined with much less precision and must be viewed more qualitatively. This loss in precision can be attributed to heat losses due to differences in sample stirring and heater configuration around the test cell. In addition, even under 400 psi backpressure, the resin/nitric acid system is tempered (solvent is vaporizing) in the RSST. Differences in the tempering rate result in differences in the composition of the cell contents at the time of the exotherms, and contribute to variations in experimental self-heating and pressure rates. Although the experimental values are less precise for the low-temperature exotherm, the RSST was sufficiently sensitive to identify this exotherm with measured self-heating rates as low as 1 ^{o}C/min, only slightly higher than the imposed self-heating rate of 0.5 ^{o}C/min.

5.2. Pressure Dependency of the Resin/Nitric Acid Reactions.

One of the limitations of this screening method is evaporative loss of solvent from the test cell during the RSST test. Running the test under a large backpressure of nitrogen minimizes evaporation. Table 4 summarizes the pressure-temperature-time characteristics for the Reillex® HPQ-nitric acid reaction as a function of pressure. Figure 5 depicts the effect of backpressure on the time to maximum rate. At 0 psig, the flat portion of the plot is due to saturation of the vapor phase, limiting the temperature rise. No exotherm was observed after 280 minutes, although essentially all solvent had been stripped. With larger backpressures of 200 and 400 psig, the temperature rise was not limited by vapor saturation until 215 and 250 ^{o}C, respectively.

Table 1. Resin Tests Performed in the RSST Calorimeter.

RSST Test Number	Reactant	[HNO_3] M	[Ce] g/L	Mass Resin g	Mass HNO_3 (aq) g	Sp. Gr. HNO_3 (aq) g/mL	Plotted In Figure No.
#113	Ionac® A-641	8	0	2.86	7.61	1.24	7-10, 15-18, 21-23
#111	Ionac® A-641	12	0	2.86	12.67	1.33	11-14,19,20
#133	Ionac® A-641	8	24	2.86	10.03	1.28	15-18,34,35
#131	Ionac® A-641	12	24	2.87	12.67	1.36	19,20
#115	Reillex® HPQ	8	0	2.86	7.38	1.24	1,-10, 36, 38-44, 45
#135	Reillex® HPQ	8	0	2.86	7.38	1.24	1-4
#143	Reillex® HPQ	8	0	2.86	7.38	1.24	1-4
#137	Reillex® HPQ	8	0	2.86	7.37	1.24	1-4
#191	Reillex® HPQ, (air-dried)	8	0	2.87	7.38	1.24	1-4
#117	Reillex® HPQ	12	0	2.86	9.73	1.33	11-14, 24-26
#123	Reillex® HPQ	8	24	2.86	7.38	1.28	21-23,34,35
#125	Reillex® HPQ	12	24	2.86	9.74	1.36	24-26
#119	Irrad. Reillex® HPQ	8	0	2.86	7.35	1.28	7-10, 27-32
#121	Irrad. Reillex® HPQ	12	0	2.86	7.36	1.33	11-14, 30-32
#127	Irrad. Reillex® HPQ	8	24	2.87	7.36	1.28	27-29,34,35
#129	Irrad. Reillex® HPQ	12	24	2.86	9.76	1.36	31,32
#161	Reillex® HPQ, 200 psi	8	0	2.88	7.41	1.24	5,6
#163	Reillex® HPQ, 0 psig	8	0	2.88	7.35	1.24	5,6
#141	Reillex® HPQ, 0.25 ^oC/min, hold 100 ^oC for 10 h	8	0	2.86	7.37	1.24	33
#145	Ionac® A-641, 0.25 ^oC/min, hold 100 ^oC for 10 h	8	0	2.74	6.32	1.24	33
#147	Reillex® HPQ, Boiled in 12 M HNO_3	8	0	2.87	10.80	1.24	38
#165	Reillex® HPQ, Boiled in water	8	0	2.86	7.37	1.24	37
#167	Reillex® HPQ, MeOH washed	8	0	2.86	7.38	1.24	37

Table 1 –CONTINUED. Resin Tests Performed in the RSST Calorimeter.

RSST				**Mass**	**Mass**	**Sp. Gr.**	**Plotted**
Test		**[HNO_3]**	**[Ce]**	**Resin**	**HNO_3 (aq)**	**HNO_3 (aq)**	**In**
Number	**Reactant**	**M**	**g/L**	**g**	**g**	**g/mL**	**Figure No.**
#169	Reillex**f** HPQ, Acetone washed	8	0	2.87	7.38	1.24	37
#171	Reillex**f** HPQ, + 200 uL MeOH	8	0	2.87	7.36	1.24	40
#173	Reillex**f** HPQ, + 100 uL MeOH	8	0	2.87	7.36	1.24	40
#151	Reillex**f** HPQ, + 50 uL MeOH	8	0	2.87	12.02	1.24	40
#177	Reillex**f** HPQ, + 7.39 g pump oil	0	0	3.01	0	n/a	36
#185	Reillex**f** HPQ, + 0.1 g methylbenzoate	8	0	2.86	7.35	1.24	41
#198	Reillex**f** HPQ, (heat-treated, dry)	8	0	2.87	10.14	1.24	39
#190	Reillex**f** HPQ, (air-dried, 1999 Lot No.)	8	0	2.87	9.35	1.24	
#182	No resin, + 2.93 g styrene	8	0	0	11.00	1.24	42
#178	No resin, + 1.00 g diethylbenzene	8	0	0	11.02	1.24	43
#172	No resin, + 1.45 g diethylbenzene	8	0	0	10.04	1.24	43
#180	No resin, + 2.92 g diethylbenzene	8	0	0	10.92	1.24	43
#174	No resin, + 3.08 g diethylbenzene	8	0	0	10.03	1.24	43
#160	Reillex**f** HPQ, (after 30 min, 85 ^{o}C in 8M HNO_3)	8	0	2.88	8.58	1.24	44
#150	Reillex**f** HPQ, (after 50 grams at 45 min, 85 ^{o}C 8M HNO_3)	8	0	2.88	8.08	1.24	44
#138	Reillex**f** HPQ, (LTE, ΔP determination)	8	0	2.87	7.37	1.24	

Table 2. *Low-Temperature Exotherm* **Characterization of the Reaction of Reillex**f **HPQ and 8 M HNO_3 [Imposed Heating Rate = 0.5 °C/min, 410 psig].**

RSST Test Number	Max. T (°C)	Max. P (psi)	Time to Max. Rate (min)	Max. Rate: DT/Dt (°C/min)	Max. Rate: DP/Dt (psi/min)
#115	78	421	120	3.7	0.47
#135	84	423	130	0.7	0.17
#137	81	417	123	1.0	0.27
#143	84	416	126	1.1	0.22
#191	76	437	136	1.5	0.25
Average	80	423	127	2	0.3
Std. Dev.	4	8	6	1	0.1

Table 3. *High-Temperature Exotherm* **Characterization of the Reaction of Reillex**f **HPQ and 8 M HNO_3 [Imposed Heating Rate = 0.5 °C/min, 410 psig].**

RSST Test Number	Max. T (°C)	Max. P (psig)	Time to Max. Rate (min)	Max. Rate: DT/Dt (°C/min)	Max. Rate: DP/Dt (psi/min)
#115	250	569	233	166	257
#135	249	580	236	86	291
#137	247	568	248	105	250
#143	248	563	251	110	272
#191	248	572	234	58	298
Average	248	570	240	105	274
Std. Dev.	1	6	8	40	21

Table 4. **Effect of Pressure on the Reillex**f **HPQ and Nitric Acid Reaction**

RSST Test Number	**All tests Were done in 8 M HNO_3**	**Time to Max. Rate (DT/Dt) (min)**	**Max. T (°C)**	**Max Rate: DT/Dt: (°C/min)**	**Max. P (psi)**	**Max Rate: DP/Dt (psi/min)**
#159	Reillex**f** HPQ, 400 psig	125	87	3	425	0.4
		222	250	110	580	120
#161	Reillex**f** HPQ, 200 psig	122	82	0.2	212	0.4
		187	217	114	298	40
#163	Reillex**f** HPQ, 0 psig	103	87	0.2	0	0
		Not observed*****	---	---	---	---

*****At 0 psig, no high-temperature exotherm was observed, the solvent had evaporated, and cell contents were dry.

The differences in the RSST tests run under 200 and 400 psig are attributed differences in the rates of solvent loss. Solvent loss (as water evaporation) results in an increase nitric acid concentration of the reactant solution. Higher backpressure minimizes solvent stripping so that less solvent is lost under 400 psig than 200 psig as a function of time. This change in the composition of reactants, which creates a more reactive system, is an artifact of the RSST. Figure 6 shows the intensity of the exothermic reaction (self-heating rate) as a function of temperature. Note that the low-temperature exotherm is observed in all cases, and is not affected by the backpressure. However, for the high-temperature runaway reaction, as the backpressure is increased, the maximum self-heating rate occurs at a higher temperature.

Due to the observed effects of solvent stripping on the reactivity of the resin mixtures, routine RSST tests were run under nominally 410 psig to suppress solvent loss, and to maintain the original reactant composition.

5.3. Comparison of Nitric Acid-Resins Reaction Profiles

The RSST reaction profiles of Ionac**f** A-641, Reillex**f** HPQ, and irradiated Reillex**f** HPQ resins were compared in nitric acid solution in the presence and absence of cerium (IV). Tables 5-7 summarize the pressure-temperature-time characteristics.

5.3.1. Resins in 8 M and 12 M HNO_3.

The reaction profiles are shown for 8 and 12 molar nitric acid mixtures in Figures 7-10 and Figures 11-14, respectively. Thermal effects were observed in two general regions: the low-temperature Region I (< 100 ^{o}C), high-temperature Region II (> 100 ^{o}C). The exotherms in Region I can be attributed to a small amount of an easily-oxidized material, whereas the exotherms in Region II may be attributed to general oxidative degradation of aromatic-alkyl cross-linking groups of the resin.[6]

The time-temperature profile in Figure 7 shows the high-temperature excursion for all three resins, but only shows a low-temperature exotherm for *unirradiated* Reillex**f** HPQ. The absence of the low-temperature exotherm for *irradiated* Reillex**f** HPQ suggests that the irradiation treatment (100 MRad) eliminated the low temperature exotherm. In other words, the low-temperature exothermic reaction occurred as a result of irradiation. This implies that gas and heat will be evolved due to an irradiation-initiated exotherm. The amounts of gas and heat evolved during the irradiation were not determined.

Figure 8 shows the pressure-time profiles, with the low-temperature pressure excursion barely discernable. Figures 9 and 10 show the self-heating rate-temperature and pressure rate-temperature profiles. Below 100 ^{o}C, only Reillex**f** HPQ showed self-heating and pressure rate increases. Just above 100 ^{o}C, the self-heating rates and pressure rates are erratic as the runaway reactions initiate, followed by steady exponential increases as the runaway reactions self-accelerate. The maximum self-heating rates are comparable for all three resins, although Ionac**f** A-641 has an additional local maximum at 140 ^{o}C.

Table 5. Characterization of the Reaction of Ionacf A-641 and Nitric Acid Solutions [Imposed Heating Rate = 0.5 ^{o}C/min, 400 psi].

RSST Test Number	Recipe	Time to DP/Dt Max. Rate (min)	Max. T (^{o}C)	Max Rate: DT/Dt: (^{o}C/min)	Max. P (psi)	Max Rate: DP/Dt (psi/min)
#113	8 M HNO_3	243	242	110	515	113
#111	12 M HNO_3	227	225	104	515	30
#133	8 M HNO_3, 24g/L Ce	243	236	132	522	120
#131	12 M HNO_3, 24g/L Ce	252	235	53	530	100

Table 6. Characterization of the Reaction of Reillexf HPQ and Nitric Acid Solutions [Imposed Heating Rate = 0.5 ^{o}C/min, 400 psi].

RSST Test Number	Recipe	Time to Max. Rate DP/Dt (min)	Local Or Max. T (^{o}C)	Max Rate: DT/Dt: (^{o}C/min)	Local Or Max. P (psig)	Max. Rate: DP/Dt (psi/min)
Avg. Table 2	8 M HNO_3	125	82	2	419	0.3
Avg. Table 3		242	248	117	570	268
#117	12 M HNO_3	95	75	1	420	0.2
		163	250	104	590	134
#123	8 M HNO_3, 24g/L Ce	105	72	2	418	0.2
		172	250	103	573	110
#125	12 M HNO_3, 24g/L Ce	105	71	2	418	0.2
		217	247	105	568	131

Table 7. Characterization of the Reaction of *Irradiated* Reillexf HPQ and Nitric Acid Solutions [Imposed Heating Rate = 0.5 ^{o}C/min, 400 psi].

RSST Test Number	**Recipe**	**Time to Max. Rate DP/Dt (min)**	**Local Or Max. T (^{o}C)**	**Max Rate: DT/Dt: (^{o}C/min)**	**Local or Max. P (psig)**	**Max. Rate: DP/Dt (psi/min)**
#119	8 M HNO_3	Low-temperature exotherm was not observed				
		256	246	105	548	131
#121	12 M HNO_3	Low-temperature exotherm was not observed				
		179	247	84	565	124
#127	8 M HNO_3, 24g/L Ce	Low-temperature exotherm was not observed				
		268	245	120	545	110
#129	12 M HNO_3, 24g/L Ce	Low-temperature exotherm was not observed				
		273	240	102	545	103

Above 100 ^{o}C, these results indicate that Reillex**f** HPQ is comparable to Ionac**f** A-641 with respect to chemical reactivity. The *irradiated* form has a more erratic self-heating rate than the *unirradiated* form. However, the runaway behaviors are comparable in intensity and the temperature at which they occur. Below 100 ^{o}C, a low-intensity exotherm is observed only for Reillex**f** HPQ. A small amount of easily-oxidized material may be reacting at approximately 80 ^{o}C. Additional testing of the low-temperature exothermic reaction was required to identify its origin and to evaluate its significance with respect to pressure generation.

The easily-oxidized material was may be a residual additive used in processing (methanol, acetone, or methyl benzoate), unreacted cross-linking agent (styrene), a phase change or swelling, or an easily-oxidized resin component. These possibilities are discussed in SECTION 5.4.

The low temperature exotherm was not unique to this batch of Reillex**f** HPQ resin, but was also observed in RSST tests with Reillex**f** HPQ from a 1999 production run, and with polyvinylpyridine (25% cross-linked) sold by Aldrich Chemical Company but also produced by Reilly Industries.

5.3.2. Resins in Cerium(IV)-Nitric Acid Solutions.

5.3.2.1. The Effect of Cerium(IV) on Each Resin. The effect of 0.174 molar cerium (IV) on each resin/nitric acid reaction was evaluated for each resin. The RSST profiles are presented in Figures 15-32. The cerium-laden mixture might increase the reactivity of the resins by increasing the local concentration of nitrate or by catalytic pathways.

For Ionac**f** A-641 resin, Figure 15 shows that cerium had no effect on the time to maximum rates. Figures 16 and 17 show self-heating and pressure generation initiating after 100 ^{o}C for both mixtures. From 100 to 160 ^{o}C, the cerium-resin mixture has lower self-heating and pressure rates. At higher temperatures, these self-heating and pressure rates are similar. The same comparisons in 12 molar nitric acid mixtures are given in Figures 18-20. The cerium test had a longer TMR (Figure 18). However, this finding may not be significant. The time difference may be attributed to differences in heat capacities of the mixtures that result in different imposed heating rates. Figures 19 and 20 show comparable self-heating and pressure rates, although above 150 ^{o}C, these rates are higher with the cerium-laden mixture.

For Reillex® HPQ resin, Figure 21 shows that the presence of cerium(IV) in 8 molar nitric acid results in a difference in the TMR. In this case, the cerium-laden mixture reached maximum rate in a shorter time than the cerium-free mixture, but this difference may again be attributed to differences in heat capacities. An important finding, which is shown in Figures 22 and 23, is that the presence of cerium(IV) in 8 molar nitric acid results in a continuous increase in pressure and self-heating rates from the low-temperature exotherm to the high-temperature exotherm. In contrast, in the absence of cerium(IV), the self-heating and pressure rates return to baseline values after the low-temperature exotherm, and initiate runaway behavior at 105^{o}C. In 12 molar nitric acid solution, the effect of cerium(IV) is less noticeable. Figures 24 show differences in the TMR, however the reactivity characterization in Figures 25 and 26 show comparable behavior; for both tests a continuous increase in pressure and self-heating rates from the low-temperature exotherm to the high-temperature exotherm is observed.

For irradiated Reillex® HPQ resin, for which no low-temperature exothermic reaction was observed (Section 5.4.1), the RSST tests in 8 and 12 molar nitric acid in the presence and absence of cerium(IV) are almost identical (Figures 27-32). The pressure and self-heating rates do not increase until a temperature of 100 ^{o}C is exceeded.

This latter result for *irradiated* Reillex® HPQ highlights the influence of the low-temperature exothermic reaction on the reactivity of the *unirradiated* resin. For *unirradiated* Reillex® HPQ resin in 8 molar nitric acid (with cerium) or in 12 molar nitric acid (with or without cerium), the low and high-temperature exothermic reactions occur simultaneously between about 90 and 100 ^{o}C. This "peak overlap" observed in the RSST reaction profiles suggests that the low-temperature exothermic reaction may have the capacity to supply energy to initiate the high-temperature reaction. To address this issue, the reactivities of Reillex® HPQ and Ionac® A-641 in 8 molar nitric acid solutions were compared (Figure 33) at 101^{o}C (± 2) over 8 hours in the RSST. For Ionac® A-641, no reaction was observed even after the sample went dry. For Reillex® HPQ, the low-temperature reaction was observed (onset at 73 ^{o}C) but the high-temperature reaction was not observed until 8.7 hours (held at temperature). The observance of the high-temperature exothermic reaction is an artifact due to the solvent stripping that occurs during the RSST test. At 8.7 hours, most of the nitric acid solvent had been stripped from the test cell, resulting in more concentrated nitric acid solution, and thus, a more reactive system. This test showed that the low temperature exothermic reaction of Reillex® HPQ did not initiate the high-temperature exothermic reaction, and that the high-temperature reaction only occurred after cell contents went dry.

In summary, for Ionac® A-641 and for irradiated Reillex® HPQ, no increase in reactivity was observed in the presence of cerium(IV) in 8 and 12 molar nitric acid. For Reillex® HPQ, both cerium(IV)-laden and 12 molar nitric acid solutions produced low intensity pressure rates and self-heating rates that were continuous between the low- and high-temperature exothermic reactions. Finally, in 8 molar nitric acid, the energy released from the low-temperature exothermic reaction was not sufficient to activate the high-temperature exothermic reaction.

5.3.2.2. Comparison of the Effect of Cerium(IV) for Each Resin. The self-heating rate profiles of the different resins in the presence of cerium(IV) in 8 and 12 molar nitric acid are compared in Figures 34 and 35, respectively. An interesting feature is scatter in the Reillex® HPQ plots (in which the low-temperature exotherm is observed) that is noticeably absent in the other tests (in which the low-temperature exotherm is absent). For all three resins in cerium(IV)- nitric acid solution, the self-heating rates show two distinct high-temperature exotherms at 150 and 215 ^{o}C.

5.4. Low-temperature Exothermic Reaction of Reillex® HPQ

The origin of the low-temperature exotherm of Reillex® HPQ was investigated. Clearly, a reactive material is generating small amounts of heat and gas. Some of the possible reactive materials that were considered are a residual additive used in processing (methanol, acetone, or methyl benzoate), unreacted cross-linking agent (styrene), a phase change or swelling, and an easily-oxidized resin component.

5.4.1. Evaluation of Resin Alone.

First, the possibility the low-temperature exotherm was due to the resin alone was investigated. Reillex® HPQ (nitrate form) was heated using typical vacuum pump oil as the solvent. No nitric acid was present. Figure 36 shows that no low-temperature exothermic reaction in the inert reaction medium, pump oil. This result is evidence that the low-temperature exothermic reaction for Reillex® HPQ involves nitric acid, and eliminates the possibilities of phase change, swelling, and heat induced reaction of cross-linking agent.

5.4.2. Pre-Treatments to Remove Residual Chemicals.

Next, the presence of residual chemicals from the resin production was evaluated. First, experiments were performed to determine if a reactive material could be removed from the resin by washing it with water (hot), methanol, or acetone. Figure 37 shows that the low-temperature exotherm is still present after all three washes. A subsequent treatment, which involved boiling Reillex® HPQ in 12 molar nitric acid, did remove the exotherm (Figure 38), however, visual inspection showed that this latter treatment transformed the spherical resin beads into a large distribution of small fragments. Judging from the change in particle size, it is likely that this treated resin will result in undesirably large pressure changes (“pressure drop”) for flow across a column bed.

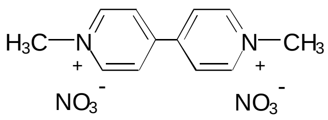
Also, a dry-resin heat treatment was also used to try to eliminate the low-temperature exotherm. The resin turned from white to brown upon heating at 105 ^{o}C for 16 hours. However, the low-temperature exotherm in 8 molar nitric acid was still observed as shown in Figure 39.

5.4.3. Nitric Acid Reactions of Methanol and Methyl Benzoate.

Another possibility is that residual materials are entrained within the Reillex**f** HPQ resin beads. Reilly Industries Inc. has indicated that methanol and an aromatic methyl ester were during the production of Reillex**f** HPQ. Therefore, the reaction profiles of methanol and methyl benzoate (an aromatic methyl ester) in 8 molar nitric acid in the RSST were determined and compared to the low-temperature exotherm. Figure 40 shows a series of spikes with various quantities of methanol in 8 molar nitric acid (with no resin present). The methanol-nitric acid exothermic reaction has peak self-heating rates between 105 and 117 ^{o}C. Methyl benzoate was spiked into a Reillex**f** HPQ-8 molar nitric acid mixture to see if the intensity of the low-temperature exotherm increased (Figure 41). A peak self-heating rate at about 104 ^{o}C is consistent with the nitric acid reaction of methanol, generated *in situ* by the acid catalyzed hydrolysis of methyl benzoate. These RSST reaction profiles eliminate the possibility that methanol or methyl benzoate is entrained in the resin beads. This conclusion is supported by GC-MS analysis of organic extracts of Reillex**f** HPQ that showed only trace quantities of volatile organic compounds.

5.4.4. Evaluation of the Reactivity of Reillexf HPQ Resin Components.

The general Reillex**f** HPQ resin structure **2** identifies the repeating polymeric subunits. The reactivity of repeating subunits was evaluated using model compounds. The pyridine ring was expected to be especially chemically inert. First, the N-methyl functional group on the pyridine repeating unit was oxidizing using the bis-N-methylpyridine **7**. No reaction was observed in 8 molar nitric acid at 90 oC, evidence the N-methylpyridine groups in Reillex**f** HPQ are not responsible for the low-temperature exotherm. In addition, the pyridine groups were shown to be unreactive with nitric acid, as expected.



7

To evaluate the reactivity of the unreacted cross-linking agent, divinylbenzene, the styrene reaction with 8 molar nitric acid was studied in the RSST (Figure 42). A peak self-heating rates occurred at about 107 ^{o}C for the reaction with styrene, significantly higher that the low-temperature exotherm.

The reactivity of the ethylbenzene pendant group (a polymeric subunit) was evaluated. These ethylbenzene functional groups were introduced into the resin structure as an impurity during production. According to Reilly Industries Inc., the cross-linking agent, divinylbenzene, used in Reillex**f** HPQ production actually contains about 20-25% ethylvinylbenzene. Only one end of the ethylvinylbenzene molecule polymerizes during the cross-linking process, creating the ethylbenzene pendant groups in Reillex**f** HPQ. Diethylbenzene was used as a model compound for the ethylbenzene pendant group. RSST tests with biphasic mixtures (liquid-liquid) of diethylbenzene and 8 molar nitric acid are shown in Figure 43. A low-temperature exothermic reaction is observed that varies as a function of concentration. If ethylbenzene pendant groups are responsible for the low-temperature exotherm, we would expect the reaction to occur at higher temperatures for a solid-liquid (resin-nitric acid) reaction than the liquid-liquid reaction (diethylbenzene-nitric acid). In the solid state, the reactive ethyl groups have less surface area exposed to the solvent, leading to fewer molecular collisions. For the solid-liquid reaction, a higher temperature is required to achieve comparable reaction rate to an analogous liquid-liquid reaction. At higher temperatures, the frequency of molecular collisions increases, leading to a greater probability of achieving the energy of activation.

To evaluate whether ethylbenzene pendant groups are responsible for the low-temperature exotherm, the off-gas reaction products and the solid resin residue were analyzed. GC-MS analysis of the off-gas showed nitric oxide (NO) gas and carbon dioxide (CO_2) were the predominant products. Due to a limitation of the analytical method, nitrogen dioxide (NO_2) could not be detected, but was visibly observed as a brown gas. The FTIR of the solid resin residue showed a carbonyl stretching frequency at 1700 cm^{-1}, which was absent in the unreacted resin. This finding is consistent with literature precedents that report the oxidation of ethylbenzene to benzoic acid with variety of oxidizing agents.[8, 9, 10, 11, 12, 13, 14] However, the oxidative degradation of the polymeric backbone of the resin would also result in similar reaction products.

5.4.5. Estimation of the Volume of Gas Generated and Average Gas Generation Rate in a 20-Liter Column of Reillexf HPQ Resin and 8 Molar Nitric Acid.

The balanced chemical equations for two plausible nitric acid reactions are given in equations (1) and (2) below. Both reactions are exothermic and produce gaseous products. In the calculation of the volume of gas generated, we assume all reaction is due to reaction 1 or reaction 2.

---

[8] S. Yamazaki, "Nickel-catalyzed benzylic oxidation of NaOCl", Synthetic Communications (1999), 29(13), 2211-2216.

[9] R.L. Holliday, B. Jong, Y.M. Brenton, J.W. Kolis, "Organic Synthesis in subcritical water. Oxidation of alkyl aromatics, Journal of Supercritical Fluids (1998), 12(3), 255-260.

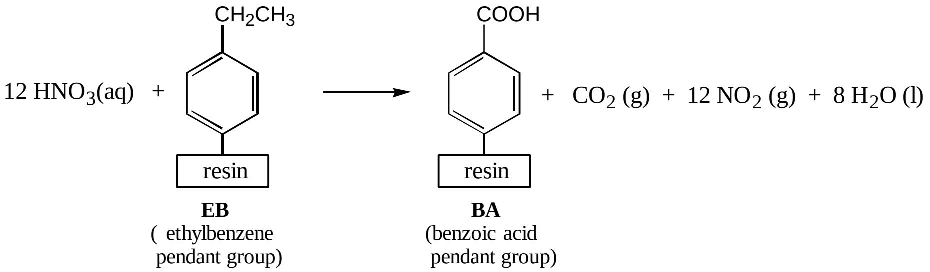
[10] E. Ganin, I. Amer, "Cerium-catalyzed selective oxidation of alkylbenzenes with bromate salts", Synthetic Communications (1995) 25(20), 3149-54.

[11] P. Guiton, S. Menager, O. Lafont, "Permanganic oxidation of ethylbenzene in the presence of quaternary ammonium", Fr. Ann. Pharm. Fr. (1986) Volume Date 1985 43(4), 373-7.

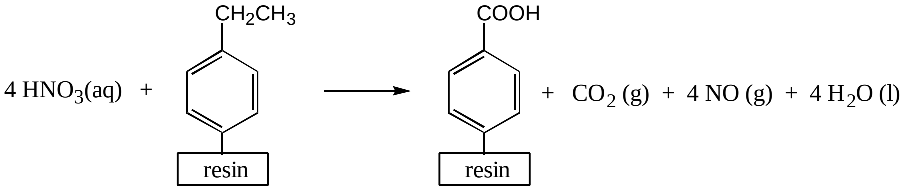
[12] Y.C. Sun, J.M. Winterbottom (Dow Chemical Company), "Oxidation of ethylbenzenes", US Patent (1973) 72-268824 19720703.

[13] H. Chafwtz, W.D. Blackley, K.L. Kreuz (Texaco Inc.), "Hydrocarbon oxidation with nitric oxide and oxygen", US Patent (1972) 69-818837 19690423.

[14] J.P. Harris (Marathon Oil Corp), "Acetophenone and benzoic acid from ethylbenzene", US Patent (1966) 19640702.



(1)



(2)

A rough calculation was made to predict the theoretical volume of gas evolved and volumetric gas rates assuming a 20-L volume of resin in nitric acid were heated to initiate the low-temperature exotherm (see equations (3) and (4) in Table 11). This calculation is based on the thermal inertia (Φ), the enthalpy of reaction (ΔH_{rxn}), the weighted-average heat capacity of the resin/nitric acid mixture ($C_{v,mix}$), and the adiabatic temperature rise (ATR) during the RSST test.

First, the thermal inertia was calculated for Reillex**f** HPQ in 8 molar nitric acid mixtures used in the RSST. The parameters, equations, and result, $\Phi = 1.03$, are shown in Table 8. Second, the ΔH_{rxn} values for the ethylbenzene oxidation reactions (1) and (2) were calculated from enthalpies of formation and are shown in Tables 9 and 10, respectively. This calculation indicates that equation 2 (with the NO product) is 4 times more exothermic than equation 1 (with the NO_2 product). Third, the mass of ethylbenzene reacted (m_{EB}) in 20 liters of Reillex**f** HPQ as a result of the low-temperature exothermic reaction was calculated as described in Table 11, and the results are presented in Tables 12 and 13. Finally, the mass of ethylbenzene undergoing reaction was converted into volume of gaseous products (298 K, 1 atm), and the volumetric gas generation rate was calculated.

This ATR-based calculation of gas volumes and gas generation rates results in extremely large values. For equation 1 (NO_2 product), the calculated maximum volume of gases is about 600 L ± 200 and the average gas generation rate of 26 L/min ± 14. Assuming the more exothermic reaction 2 (NO product) is the only reaction occurring, the calculated maximum volume of gases is about 53 L ± 14 and the average gas generation rate of 2 L/min ± 1. If another more exothermic chemical reaction were occurring, the calculated values for the gas volume and rate would be corresponding smaller.

In contrast, an attempt was made to determine the gas volumes from the experimental pressure change by heating Reillex**f** HPQ resin in 8 molar nitric acid in the RSST (#138). The low-temperature exotherm was observed. However, after the sealed Parr bomb returned to room temperature, no net increase in pressure was observed. This ΔP-based calculation predicts no net gas volume generated. One explanation for the absence of a net pressure change is that the gaseous products generated (NO, NO_2, CO_2, and H_2O) recondensed, even under a low backpressure of 11 psig. Another explanation is that the NO generated reacts with nominal O_2 in the air present in the RSST, balancing gas generation with gas consumption. Although this experiment to determine a pressure change failed to demonstrate a net pressure increase, off-gas was *visually observed* during a 60-gram-scale pre-treatment experiment (see Section 5.4.6).

5.4.6. Pre-treatment of Reillexf HPQ to Eliminate the Low-temperature Exothermic Reaction.

When 50 grams of Reillexf HPQ resin and 200 grams of 8 molar nitric acid (b.p. about 120 ^oC) were heated to 85 ^oC for 30 minutes at ambient pressure in a vacuum oven with a Plexiglas™ viewing window, the reaction mixture bubbled steadily, and orange NO_x gases were evolved. The resin changed from the original white to a pale orange-yellow color. After the 30-minute heating period, determined to be sufficient to eliminate the low-temperature exotherm based on small-scale tests, the resin/acid mixture was diluted with water, filtered, washed with water until the eluent possessed a neutral pH, and air-dried for 3 days. An additional sample of Reillexf HPQ resin was pretreated for a 45-minute heating period following the sample procedure. A sample of both pretreated resins was tested in the RSST, and the low-temperature exotherm was absent (Figure 44). Most importantly, Figure 45 shows that there was no significant pressure increase below 100 ^oC.

Microscopic analysis showed the pretreated resin beads retained their size and shape, although the color changed from white to pale-yellow. The retention of bead size after the pretreatment was confirmed by comparing the particle size distribution for the untreated and treated Reillexf HPQ as shown in Figure 46. . The performance testing of the treated resin showed that plutonium loading results are comparable to untreated resin, and are described in an another report.

6. Conclusions

Resin/nitric acid mixtures were heated in the RSST and the temperature-pressure responses were determined as a function of resin type, nitric acid concentration, cerium(IV) loading, and damage caused by previous irradiation of the resin. Above 100 ^oC, Reillexf HPQ, irradiated Reillexf HPQ, and Ionacf A-641 showed similar reaction profiles as a function of temperature. Reillexf HPQ showed no obvious inertness to chemical degradation relative to Ionacf A-641. In the *irradiated* form of Reillexf HPQ, the self-heating rate is a little more erratic than the *unirradiated* form; however, the runaway behaviors are comparable in intensity and the temperature at which they occur. Below 100 ^oC, a low intensity, low-temperature exotherm (80 ^oC, 2 ^oC/min) was observed only for Reillexf HPQ, suggesting the presence of a small amount of easily-oxidized material.

The effect of cerium(IV) on the resin/nitric acid reactions was evaluated. For Ionacf A - 641 and for irradiated Reillexf HPQ, no increase in reactivity was observed in the presence of cerium(IV) in 8 and 12 molar nitric acid solutions. For Reillexf HPQ, both cerium(IV)/8 molar nitric acid and 12 molar nitric acid solution produced low intensity pressure rates and self-heating rates that were continuous between the low and high-temperature exothermic reactions, however, the energy released from the low-temperature exothermic reaction is not sufficient to activate the low-temperature reaction.

Additional testing focused on identifying the origin of the low-temperature exothermic reaction and evaluating its significance with respect to pressure generation. The off-gas products were identified as NO, CO_2, and NO_2. An FTIR analysis of the resin residue identified a carbonyl stretching frequency at 1700 cm^{-1}, evidence for the presence of a carboxylic acid. To evaluate the possibility that the ethylbenzene pendant groups of the Reillexf HPQ resin are associated with the exotherm, diethylbenzene, used as a model compound, was heated with nitric acid in the RSST. Indeed, the diethylbenzene-8 molar nitric acid reaction showed a low-temperature exotherm, and generated NO, CO_2, NO_2, and a mixture of mono- and dicarboxylic acids as reaction products. Furthermore, literature precedents have reported the oxidation of ethylbenzene with various oxidizing agents.

An estimate of the maximum gas volume and gas generation rate was made assuming the low-temperature exotherm occurred on a 20-liter process-scale. While these calculated gas volumes and gas generation rates are extremely large, the experiment showed that after the sealed reaction vessel returned to room temperature, no increase in pressure was observed. However, in a separate experiment, off-gassing of NO_x was observe during the heating. The large estimates for the gas volumes generated and the experimental observation of NO_x off-gassing suggest large quantities of gas may be liberated if the ion exchange column temperature approaches 70 to 80 ^oC.

Finally, a pre-treatment was developed to remove the low-temperature exotherm. The method involves digesting the resin for 45 minutes at 85 ^oC at ambient pressure. The low-temperature exotherm was eliminated without changing the size or shape of the resin beads. The performance testing of the treated resin showed that plutonium loading results are comparable to untreated resin, and are described in an another report.

Table 8. Calculation of the thermal inertia, F ,for Reillexf HPQ and 8 molar nitric acid mixtures

Test Parameter	Definitions
m_r	Mass of resin in an RSST test
m_a	Mass of 8 molar nitric acid solution in an RSST test
m_{mix}	Mass of resin/8 molar nitric acid mixture in RSST test
m_s	Mass of borosilicate glass RSST test cell
m_{HNO3}	Molality of nitric acid solution
C^o	Specific heat of the pure solvent (water)
C_a	Specific heat for 8 molar nitric acid
C_r	Specific heat for resin (assumed)
$C_{v,mix}$	Weighted average heat capacity of resin/nitric acid mixture
C_s	Specific heat of borosilicate glass test cell
$\Phi_{c,\ HNO3}$	Apparent molal heat capacity of the HNO_3 in water
Φ	Thermal inertia for RSST test

Test Parameter	Equations
$C_{v,mix}$	$[m_a/(m_a+m_r)]*C_a+[m_r/(m_a+m_r)]*C_r$
Φ	$(m_s*C_s+m_b*C_b)/(m_s*C_s)$

Test Parameter	Values	Units	Reference
m_r	2.87	Grams	
m_a	7.35	Grams	
$[HNO_3]$	8	Molar	
m_{HNO3}	6.5	Moles/kg	
$\Phi_{c,\ HNO3}$	11.40	cal/(g°C)	15
C^o	1.00	cal/(g°C)	
MW_{HNO3}	63	g/mole	
C_a	1.00	cal/(g°C)	
C_r	0.50	cal/(g°C)	
$C_{v,mix}$	0.86	cal/(g°C)	
m_{mix}	10.22	Grams	
m_s	1.40	Grams	
C_s	0.19	cal/(g°C)	16
Φ	1.03		

---

[15] Handbook of Chemistry and Physics, 65th Edition, 1984-85, R.C. West, ed., Chemical Rubber Company Press Inc, Boca Raton, Florida, D-123.

[16] Perry's Chemical Engineers' Handbook, 6th Edition, 1984, R.H. Perry and D.W. Green, McGraw-Hill Company, Section 23, page 52.

Table 9. Calculation of the enthalpy of reaction ($DH_{rxn,1}$) for equation 1 (NO_2 as product)

	Stoich. Coeff.	**DH_f^*** kcal/mol	**Calc'd DH_f** KJ/mol
Reactants:			
Ethylbenzene (l)	1	-3.0	-12.5
HNO_3 (dil. aq)	12	-49.6	-207.4
$\Sigma \Delta H_f$ (reactants)		**-598**	**-2501**
Products:			
Benzoic Acid (cr)	1	-92.0	-385.1
CO_2 (g)	1	-94.1	-393.5
NO_2 (g)	12	7.9	33.2
H_2O (l)	8	-68.3	-285.8
$\Sigma \Delta H_f$ (products)		**-637**	**-2667**
DH_{rxn} =		**-40**	**-166**

Table 10. Calculation of the enthalpy of reaction ($DH_{rxn,2}$) for equation 2 (NO as product)

	Stoich. Coeff.	**DH_f^*** kcal/mol	**Calc'd DH_f** KJ/mol
Reactants:			
Ethylbenzene (l)	1	-3.0	-12.5
HNO_3 (dil. aq)	4	-49.6	-207.4
$\Sigma \Delta H_f$ (reactants)		**-201**	**-842**
Products:			
Benzoic Acid (cr)	1	-92.0	-385.1
CO_2 (g)	1	-94.1	-393.5
NO (g)	4	21.6	90.2
H_2O (l)	4	-68.3	-285.8
$\Sigma \Delta H_f$ (products)		**-373**	**-1561**
DH_{rxn} =		**-172**	**-719**

Table 11. Calculation of the mass of ethylbenzene reacted (m_{EB}) in 20 liters of Reillexf HPQ as a result of the low-temperature exothermic reaction.

$$DH_{rxn} = -F\, C_v(ATR)(MW_{EB})/(m_{EB}/m_p) \qquad (3)$$

or

$$(m_{EB}/m_p) = -F\, C_v(ATR)(MW_{EB})/DH_{rxn} \qquad (4)$$

Parameter	Value	Units	Description	Equation/Comment
F	1.02	Unitless	Thermal inertia	$(m_s*C_s+m_b*C_b)/(m_s*C_s)$
C_v	0.86	Cal/(g/°C)	Wt-avg Heat capacity of sample mixture	$[m_a/(m_a+m_r)]*C_a+[m_r/(m_a+m_r)]*C_r$
$DH_{rxn,1}$	-40	Kcal/mole	Enthalpy of reaction *per mole of EB* **for (1)**	$\Sigma(\Delta H_{f,products} - \Delta H_{f,reactants})$
$DH_{rxn,2}$	-172	Kcal/mole	Enthalpy of reaction *per mole of EB* **for (2)**	$\Sigma(\Delta H_{f,products} - \Delta H_{f,reactants})$
MW_{EB}	105	G/mole	MW for ethylbenzene pendant group	Calculated for C_8H_9
ATR	cal'd	°C	Adiabatic temperature rise	ΔT - (IHR)*(Δt)
C_r	0.50	Cal/(g°C)	Heat capacity of Reillex**f** HPQ resin	Assumed
C_a	0.9997	Cal/(g°C)	Heat capacity of 8M nitric acid solution	Literature value
m_r	2.87	g	Mass of resin in RSST test cell	Experimental
m_a	7.35	g	Mass of 8M HNO_3 in RSST test cell	Experimental
m_p	22.3	kg	Mass of reactants for process-scale	$V_{p*}\rho_{resin}$
IHR	0.5	°C/min	Imposed heating rate	Experimental
LTE			Low-temperature exotherm	Definition
T_{max}	Exp'tal	°C	Maximum temperature of LTE	Experimental
$T_{baseline}$	Exp'tal	°C	Temperature at which LTE initiates	Experimental
ΔT	Exp'tal	°C	Experimental temperature change	Local T_{max} - Local $T_{baseline}$
t	Exp'tal	min	Time	Experimental
Δt	Exp'tal	min	Experimental time change	Time $_{local\ T,max}$ - Time$_{local\ T,\ baseline}$
V_p	20	L	Volume of reactants for process-scale	Assumed
ρ_{resin}	1.1151	g/mL	Density of resin/nitric acid mixture	Experimental - E. Kyser
(m_{EB}/m_p)	cal'd	Unitless	Ratio of "EB reacted" to process mass	**$-F\, C_v(ATR)(MW_{EB})/DH_{rxn}$**
m_{EB}	cal'd	g	Mass of resin/nitric acid mixture that reacts	$(m_{EB}/m_p)*(m_p)$

Table 12. Results of the calculation of the mass of ethylbenzene reacted (m_{EB}) according to equation 1 (NO_2 as product)

Record Reference Page No.	**T_{max} °C**	***at* T min.**	**$T_{baseline}$ °C**	***at* t min.**	**DT_{exp} °C**	**Dt_{exp} min.**	Ratio: **m_{EB} / m_p**	**m_{EB} grams**
#115	77.6	119.9	68.6	111.5	9.0	8.4	1.1%	244
#135	77.0	121.4	68.9	110.8	8.1	10.6	0.6%	145
#137	78.9	122.8	68.8	109.5	10.1	13.3	0.8%	178
#143	82.9	124.5	70.8	110.3	12.1	14.3	1.2%	257
#191	76.9	136.7	67.2	123.1	9.8	13.6	0.7%	153
Average	**79**	**125**	**69**	**113**	**10**	**12**	**0.9%**	**195**
Std. Dev .	**3**	**7**	**1**	**6**	**2**	**2**	**0.2%**	**52**
Relative Error	3%	5%	2%	5%	15%	20%	27%	---

95% confidence interval: 195 g EB ± 65

Table 13. Results of the calculation of the mass of ethylbenzene reacted (m_{EB}) according to equation 2 (NO as product)

Record Reference Page No.	**T_{max} °C**	***at* t min.**	**$T_{baseline}$ °C**	***at* t min.**	**DT_{exp} °C**	**Dt_{exp} min.**	Ratio: **m_{EB} / m_p**	**m_{EB} grams**
#115	77.6	119.9	68.6	111.5	9.0	8.4	0.3%	57
#135	77.0	121.4	68.9	110.8	8.1	10.6	0.2%	34
#137	78.9	122.8	68.8	109.5	10.1	13.3	0.2%	41
#143	82.9	124.5	70.8	110.3	12.1	14.3	0.3%	60
#191	76.9	136.7	67.2	123.1	9.8	13.6	0.2%	36
Average =	**79**	**125**	**69**	**113**	**10**	**12**	**0.2%**	**45**
Std. Dev =	**3**	**7**	**1**	**6**	**2**	**2**	**0.1%**	**12**
Rel. Err. =	3%	5%	2%	5%	15%	20%	27%	---

95% confidence interval: 45 g EB ± 15

Table 14. Estimation of the volume of gas generated and average gas generation rate in a 20-liter column of Reillexf HPQ and 8 molar nitric acid.

$$1\ \mathrm{EB\ (s)} + 12\ \mathrm{HNO_3\ (aq)} = 1\ \mathrm{BA\ (s)} + 1\ \mathrm{CO_2\ (g)} + 12\ \mathrm{NO_2\ (g)} + 8\ \mathrm{H_2O\ (l)} \quad \mathbf{(1)}$$

$$1\ \mathrm{EB\ (s)} + 4\ \mathrm{HNO_3\ (aq)} = 1\ \mathrm{BA\ (s)} + 1\ \mathrm{CO_2\ (g)} + 4\ \mathrm{NO\ (g)} + 4\ \mathrm{H_2O\ (l)} \quad \mathbf{(2)}$$

Parameter	**Value**	**Units**	**Description**	**Equation or comment**
MW_{EB}	105	G/mole	MW for ethylbenzene pendant group	Calculated for C_8H_9
$N_{gas,1}$	13	Unitless	Moles gas produced per mole EB reacted [1 mole CO_2 plus 12 moles NO_2]	From balanced chemical equation 1.
$N_{gas,2}$	5	Unitless	Moles gas produced per mole EB reacted [1 mole CO_2 plus 4 moles NO_2]	From balanced chemical equation 2.
R	0.0821	L·atm/(K·mol)	Universal gas constant	
T	298	K	Temperature for gas volume calculation	
P	1	Atm	Pressure for gas volume calculation	
m_{EB}	cal'd	g	Mass of ethylbenzene reacting	
n_{EB}	cal'd	Moles	Moles of ethylbenzene present in resin	$m_{EB}/(MW_{EB})$
n_{gas}	cal'd	Moles	Maximum moles of NO_2 generated	$n_{EB}*N_{gas,\,x}$, where x = 1 or 2
V_{gas}	cal'd	L	Maximum volume of gas generated Under ambient conditions: 298K, 1 atm	$n_{gas}\cdot R\cdot T/P$

Calculation according to equation 1.

Record Reference Page No.	**m_{EB} g**	**n_{EB} mol**	**m_{gas} mol**	**Process-scale V_{gas} L**	**Rxn Period, Dt (min)**	**Avg. DV/DT L/min**
#115	244	2.3	30	740	15	49
#135	145	1.4	18	438	27	16
#137	178	1.7	22	538	25	21
#143	257	2.4	32	777	30	26
#191	153	1.5	19	462	30	15
Avg.	195	1.9	24	**591**	25	**26**
Std. Dev.	52	0.5	6	**158**	6	**14**

95% Confidence Interval: 591 L ± 196 26 L/min ± 17

Calculation according to equation 2.

Record Reference Page No.	**m_{EB} g**	**n_{EB} mol**	**m_{gas} mol**	**Process-scale V_{gas} L**	**Rxn Period, Dt (min)**	**Avg. DV/DT L/min**
#115	57	0.5	2.7	66	15	4.4
#135	34	0.3	1.6	39	27	1.5
#137	41	0.4	2.0	48	25	1.9
#143	60	0.6	2.8	69	30	2.4
#191	36	0.3	1.7	41	30	1.4
Avg.	45	0.4	2.2	**53**	25	**2.3**
Std. Dev.	12	0.1	0.6	**14**	6	**1.2**

95% Confidence Interval: 53 L ± 17 2.3 L/min ± 1.5

7. Figures

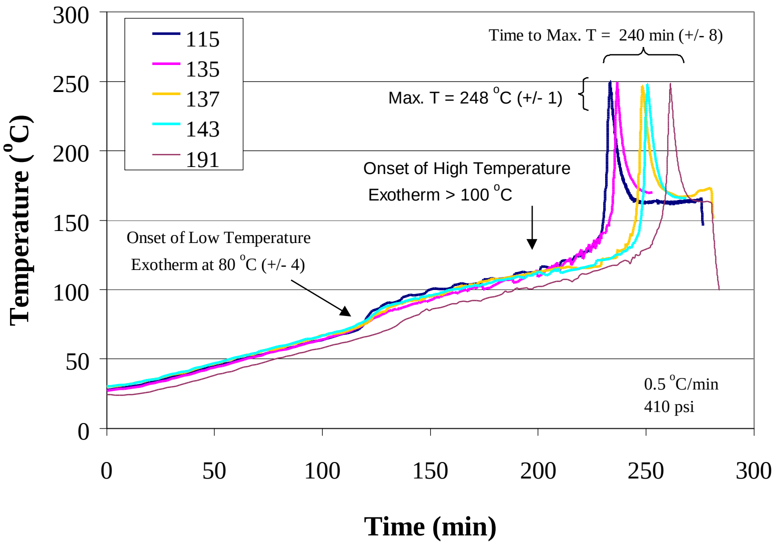


Figure 1. RSST Reproducibility Tests of Reillex f HPQ in 8 M HNO_3: Temperature (^oC) vs. Time (min)

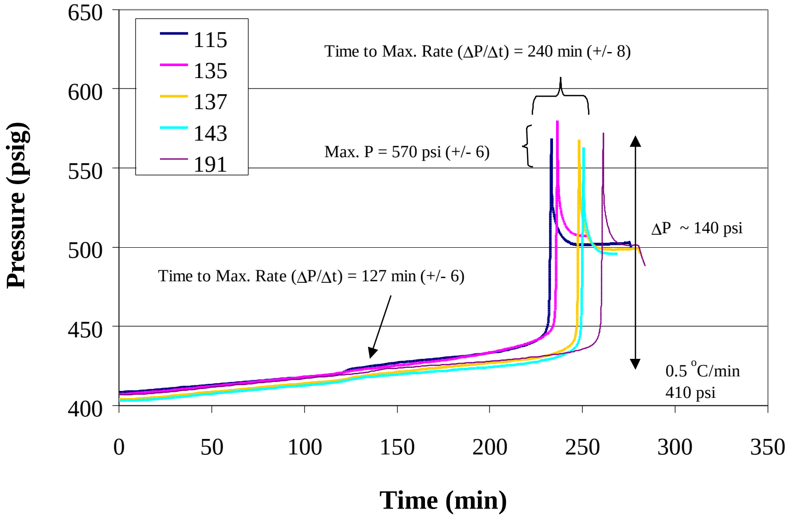


Figure 2. RSST Reproducibility Tests of Reillex f HPQ in 8 M HNO_3: Pressure (psig) vs. Time (min)

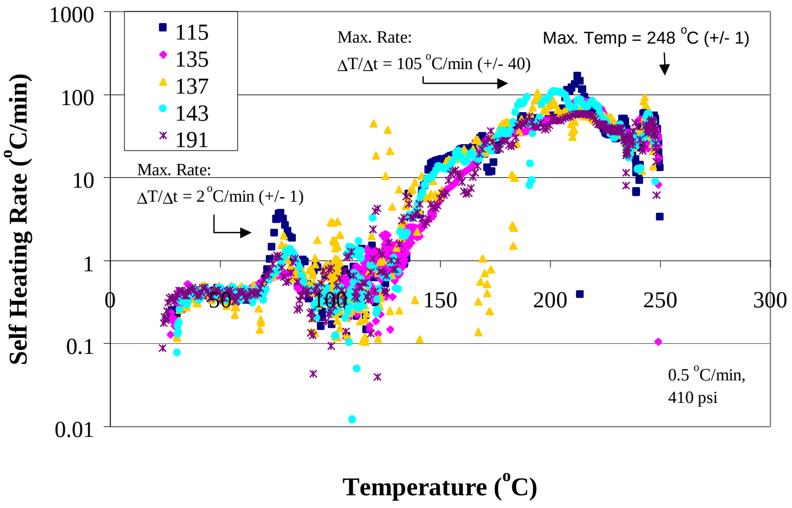


Figure 3. RSST Reproducibility Tests of Reillexf HPQ in 8 M HNO$_3$: Self-Heating Rate (°C/min) vs Temperature (°C)

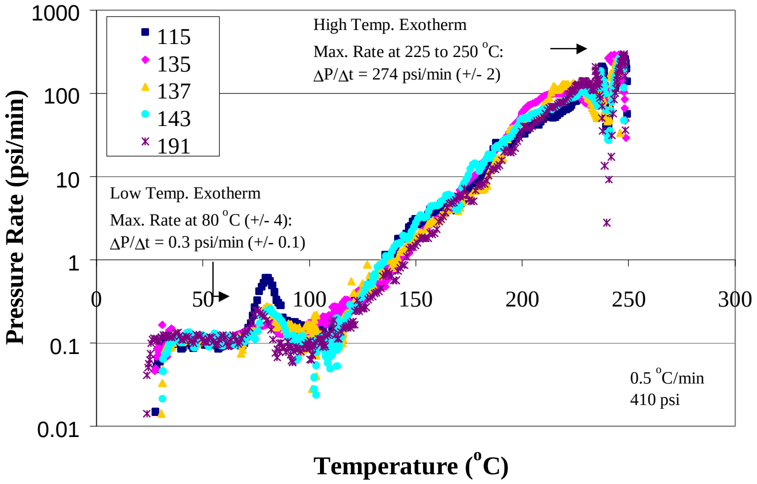


Figure 4. RSST Reproducibility Tests of Reillexf HPQ in 8 M HNO$_3$: Pressure Rate (psig/min) vs. Temperature (°C)

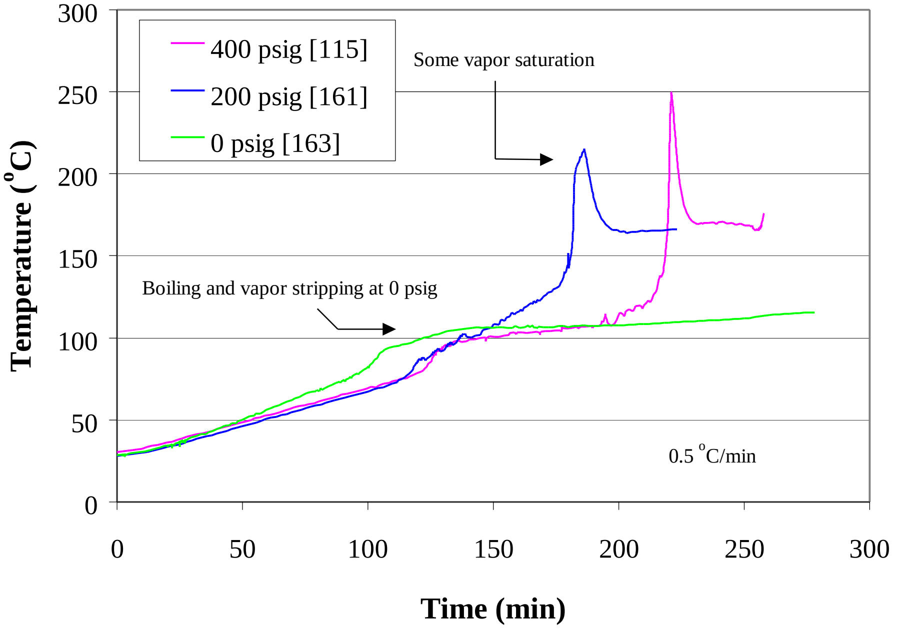


Figure 5. RSST Backpressure Variation Test of Reillex f Resin in 8 M HNO_3: Temperature (°C) vs. Time (min)

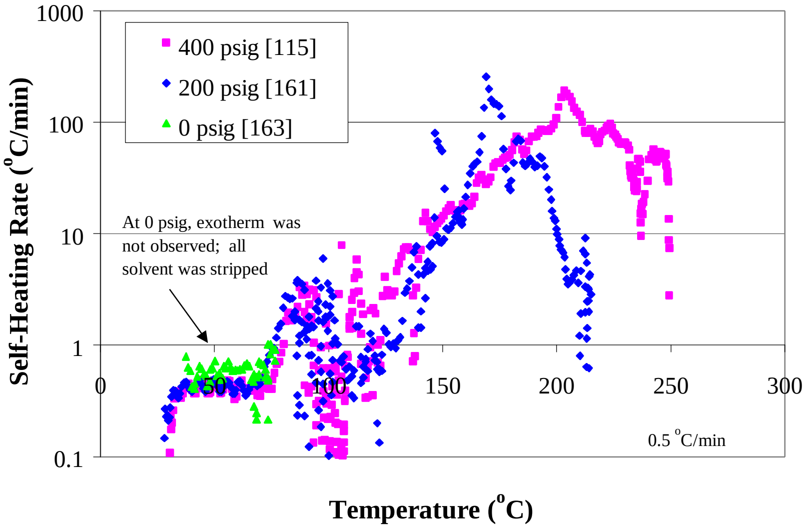


Figure 6. RSST Backpressure Variation Test of Reillex f Resin in 8 M HNO_3: Self-Heating Rate (°C/min) vs. Temperature (°C)

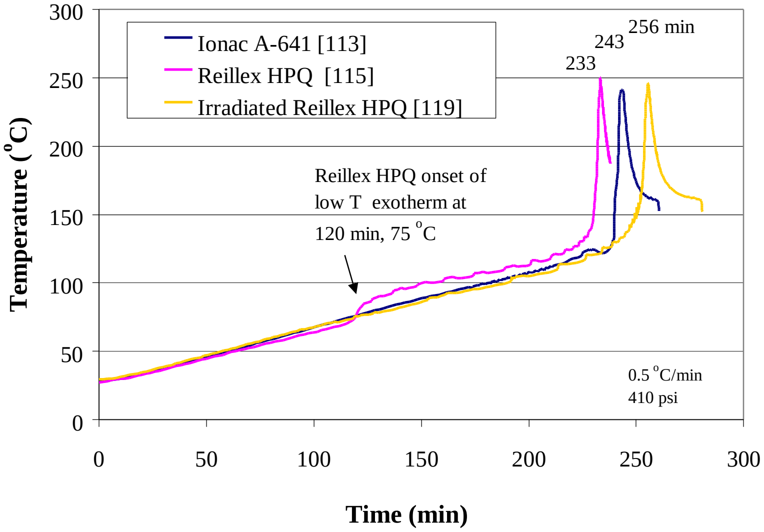


Figure 7. RSST Resin Comparison Tests in 8 M HNO_3: Temperature (^oC) vs. Time (min)

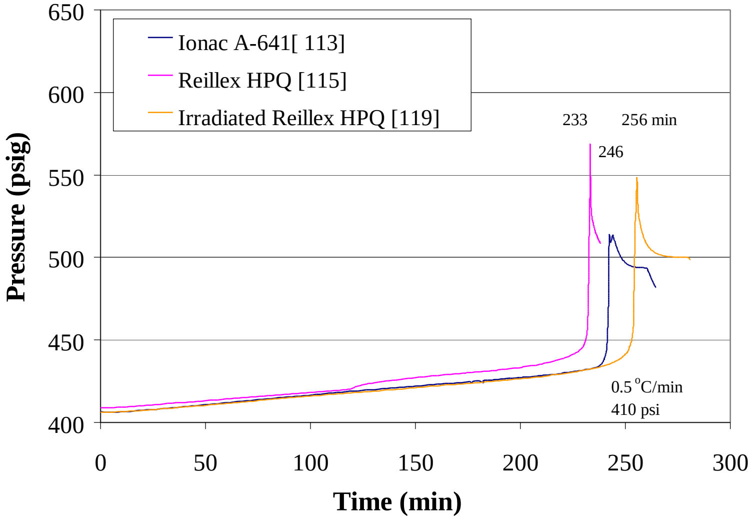


Figure 8. RSST Resin Comparison Tests in 8 M HNO_3: Pressure (psig) vs. Time (min)

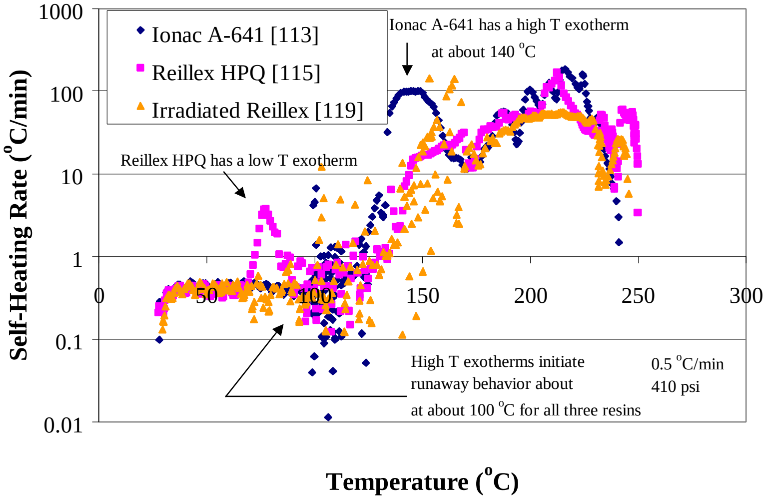


Figure 9. RSST Resin Comparison Tests in 8 M HNO_3: Self-heating rate (°C/min) vs. Temperature (°C)

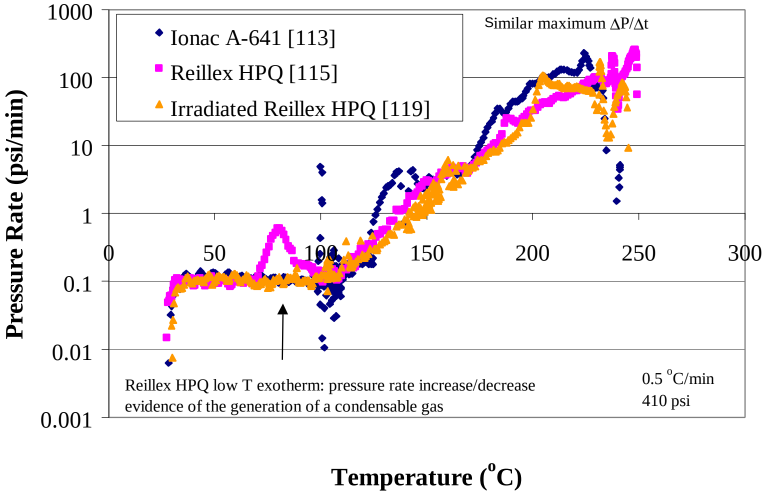


Figure 10. RSST Resin Comparison Tests in 8 M HNO_3: Pressure Rate (psi/min) vs. Temperature (°C)

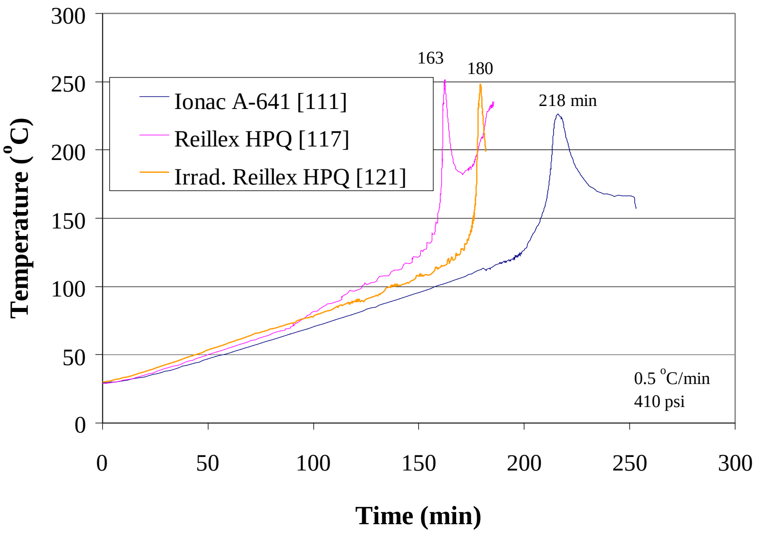


Figure 11. RSST Resin Comparison Tests in 12 M HNO_3: Temperature (^{o}C) vs. Time (min)

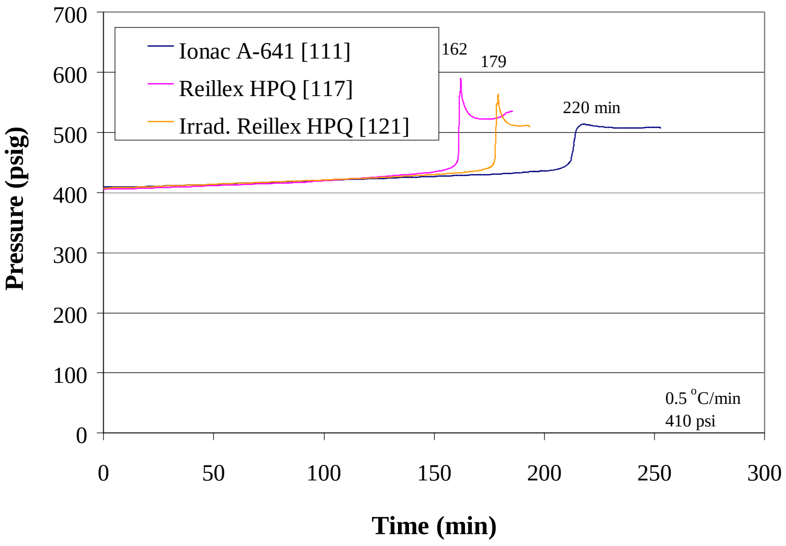


Figure 12. RSST Resin Comparison Tests in 12 M HNO_3: Pressure (psig) vs. Time (min)

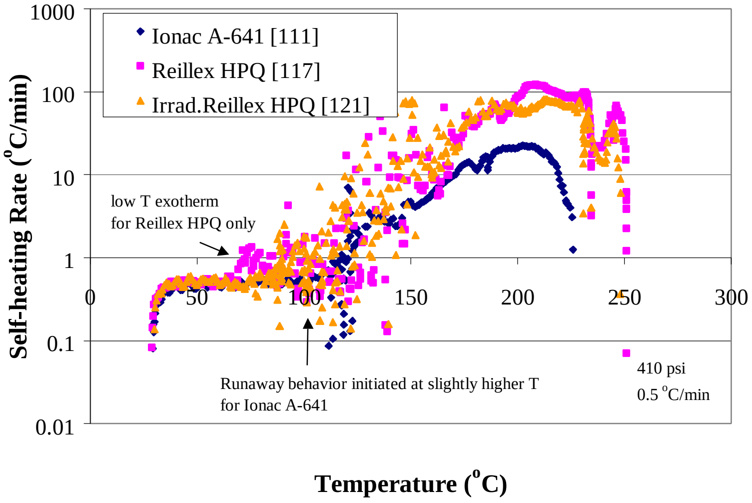


Figure 13. RSST Resin Comparison Tests in 12 M HNO_3: Self-heating rate (°C/min) vs. Temperature (°C)

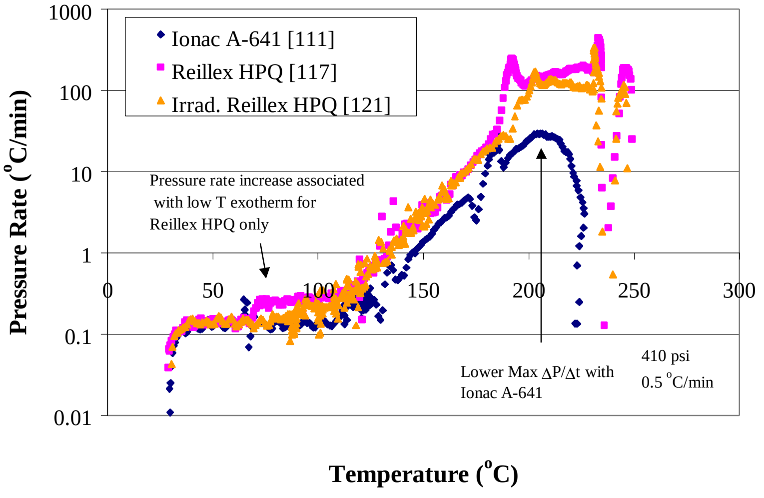


Figure 14. RSST Resin Comparison Tests in 12 M HNO_3: Pressure Rate (psi/min) vs. Temperature (°C)

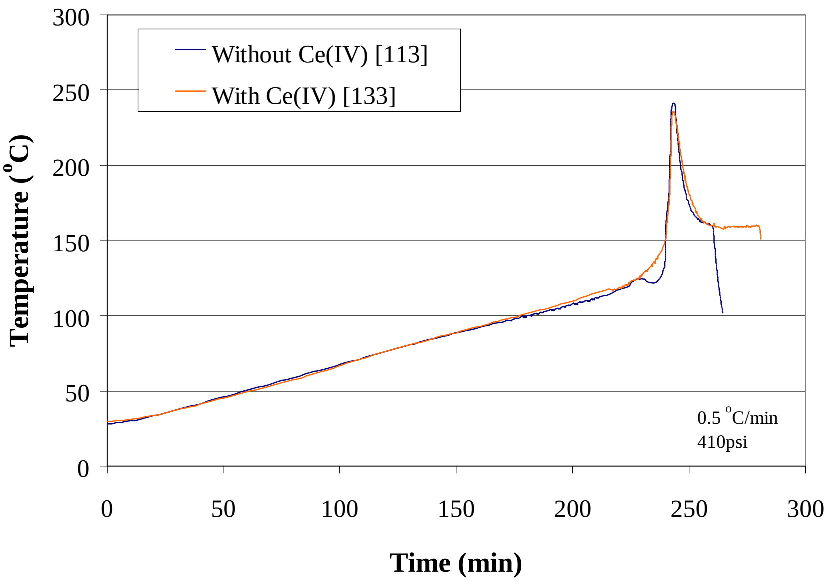


Figure 15. RSST Test of the Effect of Ce(IV) on Ionacf A-641 in 8 M HNO_3: Temperature (°C) vs. Time (min)

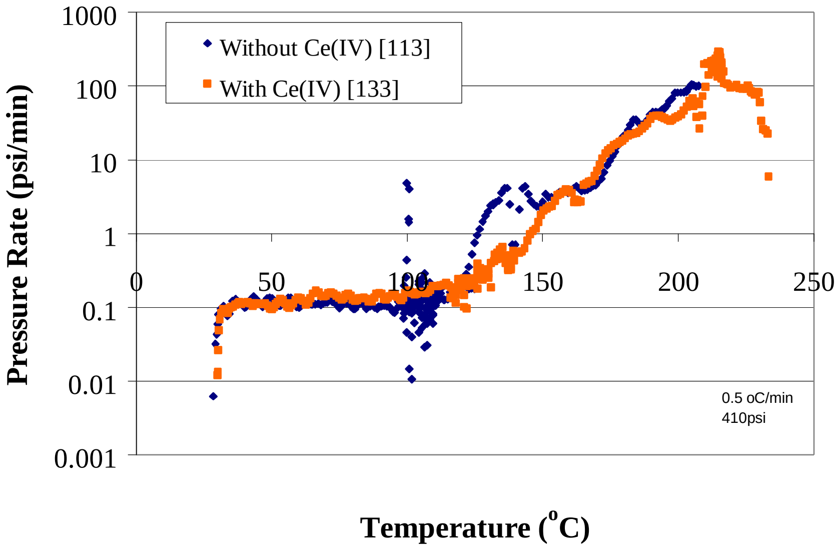


Figure 16. RSST Test of the Effect of Ce(IV) on Ionacf A-641 in 8 M HNO_3: Pressure Rate (°C/min) vs. Temperature (°C)

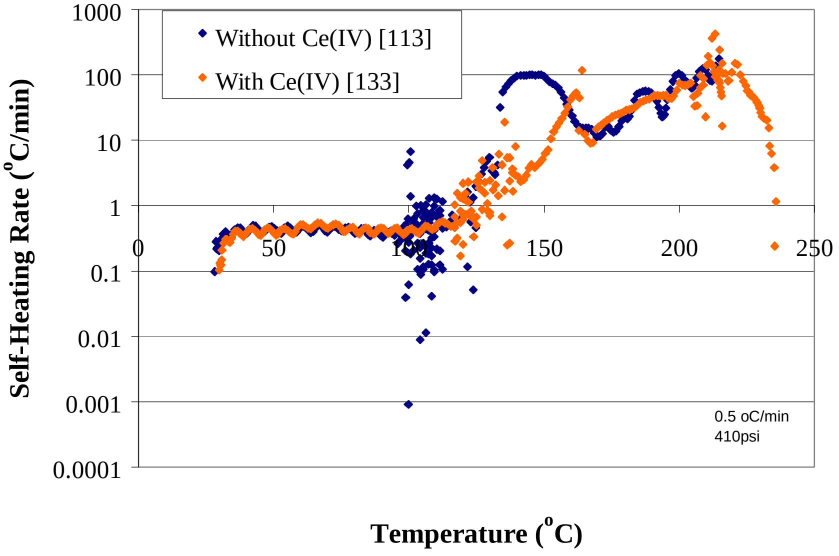


Figure 17. RSST Test of the Effect of Ce(IV) on Ionac f A-641 in 8 M HNO_3: Self-heating Rate (°C/min) vs. Temperature (°C)

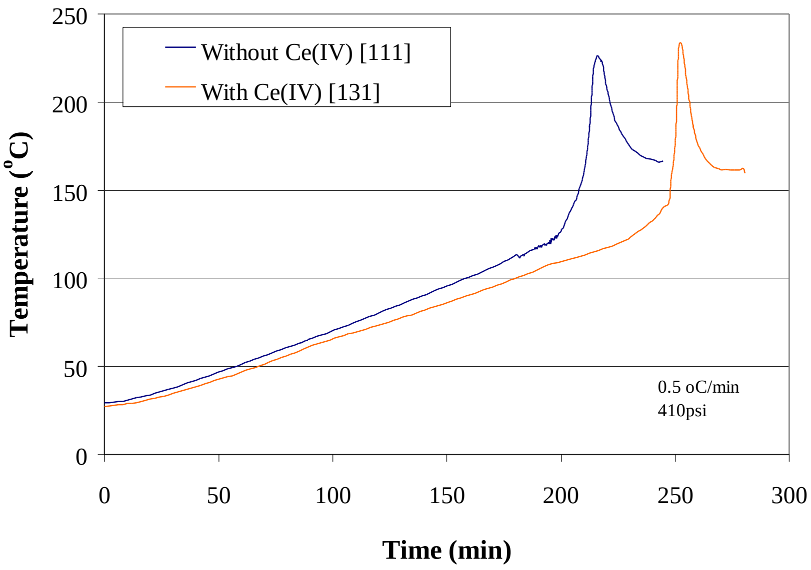


Figure 18. RSST Test of the Effect of Ce(IV) Test on Ionac f A-641 in 12 M HNO_3: Temperature (°C) vs. Time (min)

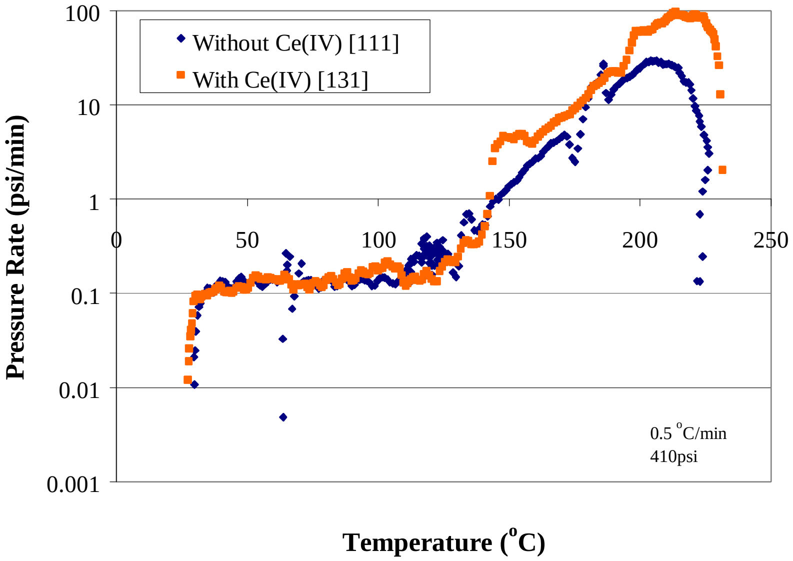


Figure 19. RSST Test of the Effect of Ce(IV) on Ionac f A-641 in 12 M HNO_3: Pressure Rate (psi/min) vs. Temperature (°C)

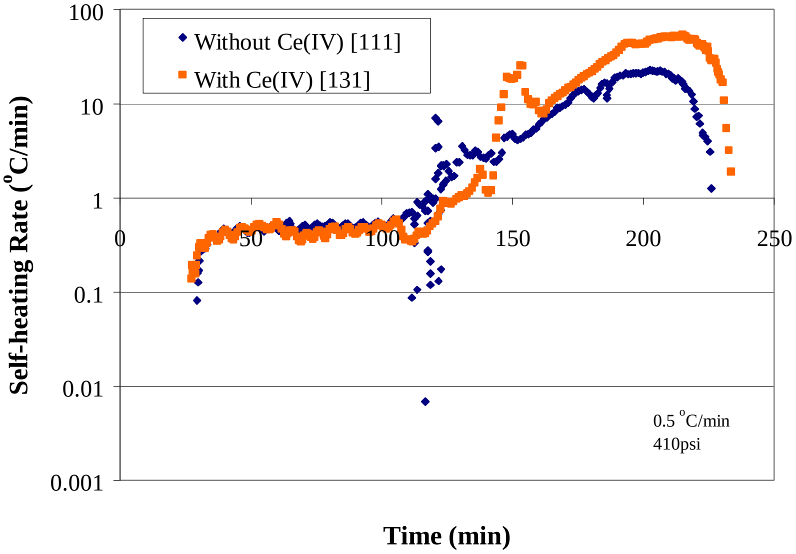


Figure 20. RSST Test of the Effect of Ce(IV) on Ionac f A-641 in 12 M HNO_3: Self-heating Rate (°C/min) vs. Temp (°C)

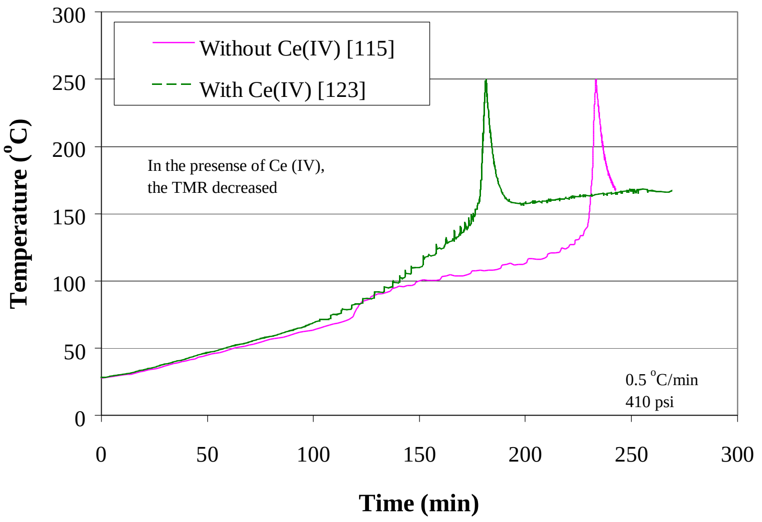


Figure 21. RSST Test of the Effect of Ce(IV) on Reillex f HPQ in 8 M HNO_3: Temperature (°C) vs. Time (min)

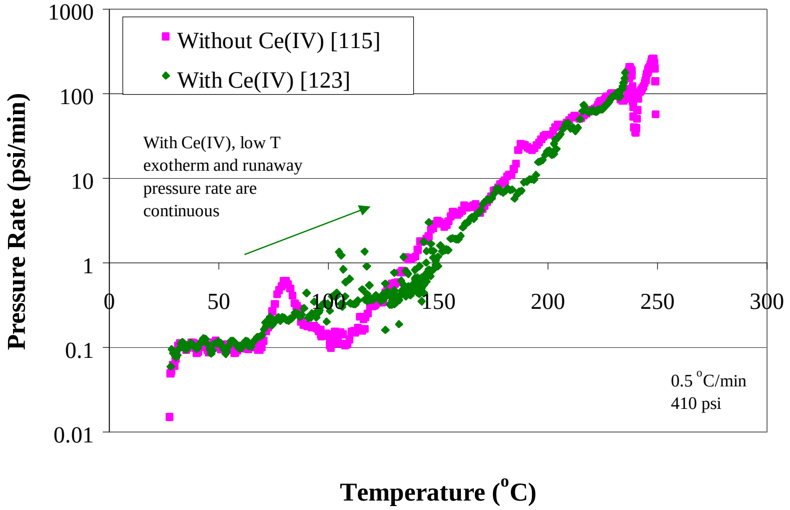


Figure 22. RSST Test of the Effect of Ce(IV) on Reillex f Resin in 8 M HNO_3: Pressure Rate (psi/min) vs. Temperature (°C)

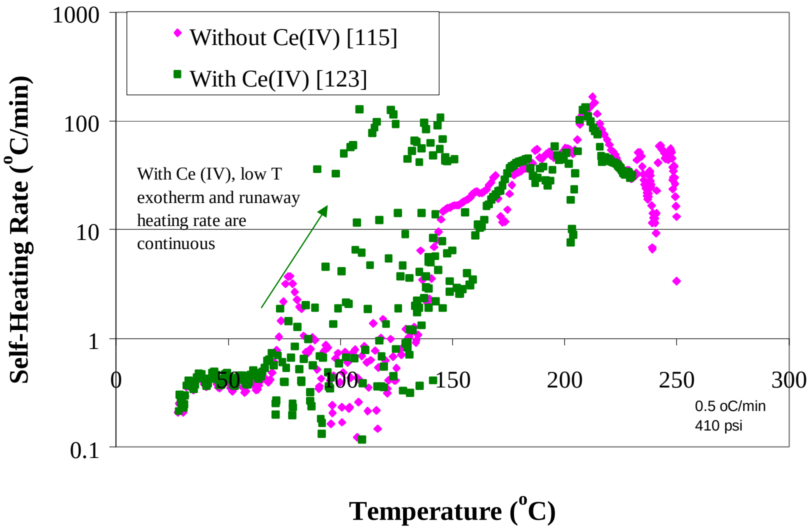


Figure 23. RSST Test of the Effect of Ce(IV) on Reillexf HPQ in 8 M HNO$_3$: Self-heating rate (°C/min) vs. Temperature (°C)

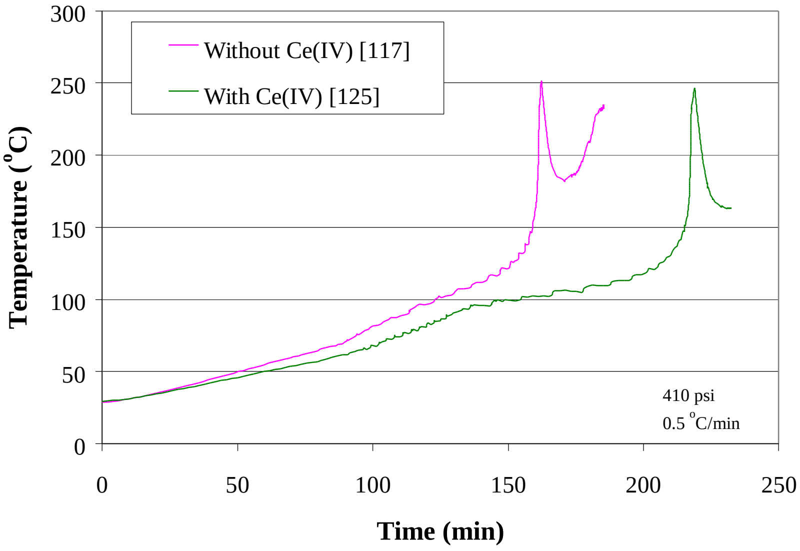


Figure 24. RSST Test of the Effect of Ce(IV) on Reillexf HPQ in 12 M HNO$_3$: Temperature (°C) vs. Time (min)

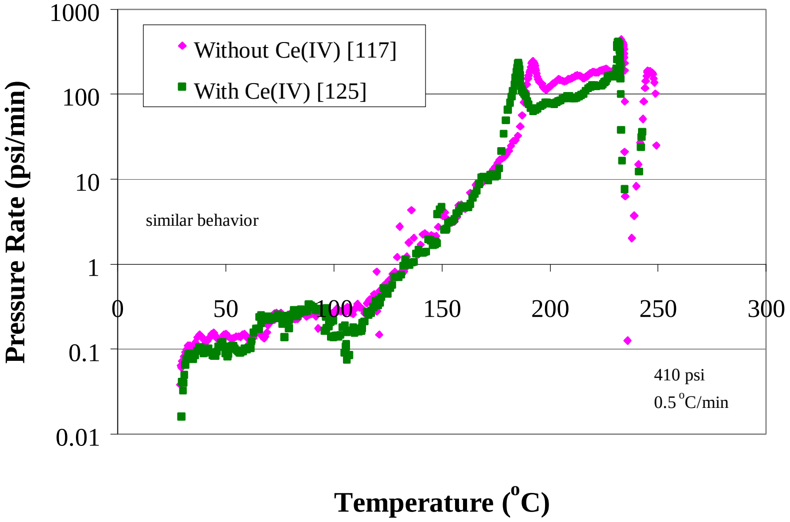


Figure 25. RSST Tests of the Effect of Ce(IV) on Reillexf HPQ in 12 M HNO_3: Pressure Rate (psi/min) vs. Temperature (°C)

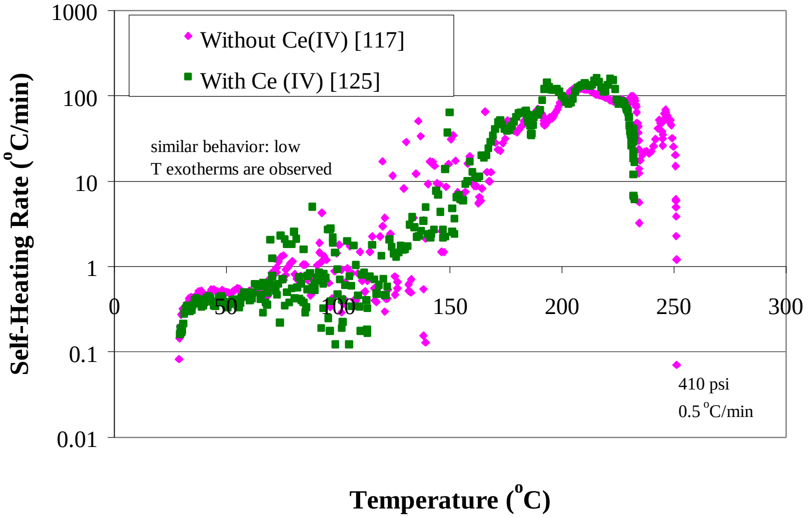


Figure 26. RSST Testsof the Effect of Ce(IV) on Reillexf HPQ in 12 M HNO_3: Self-heating Rate (°C/min) vs. Temperature (°C)

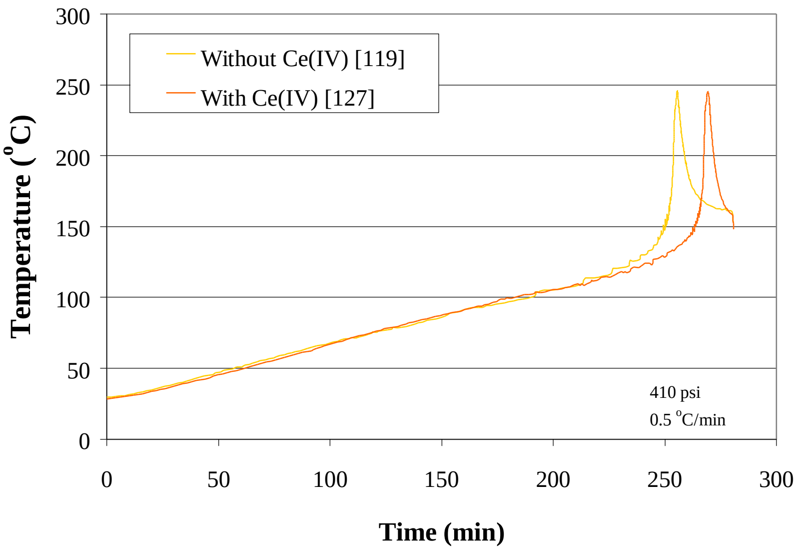


Figure 27. RSST Test of the Effect of Ce(IV) on Irradiated Reillexf HPQ in 8 M HNO_3: Temperature (°C) vs. Time (min)

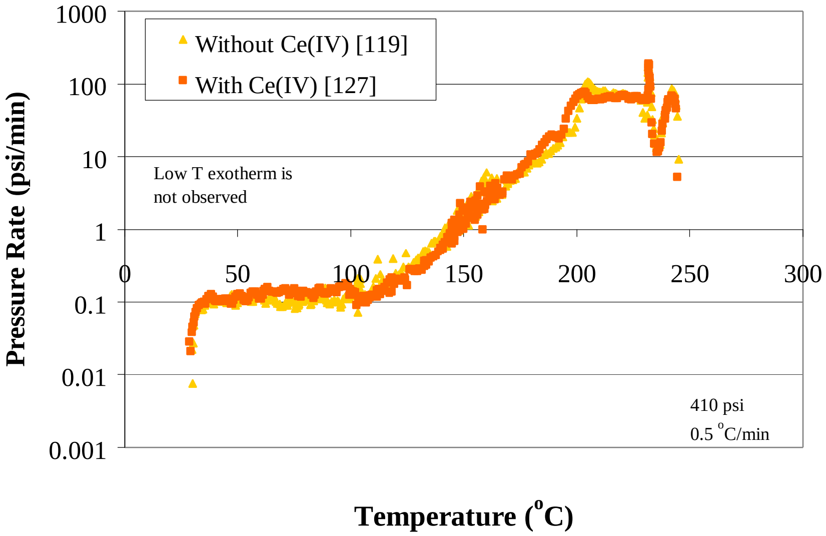


Figure 28. RSST Test of the Effect of Ce(IV) on Irradiated Reillexf HPQ in 8 M HNO_3: Pressure Rate (psi/min) vs. Temperature (°C)

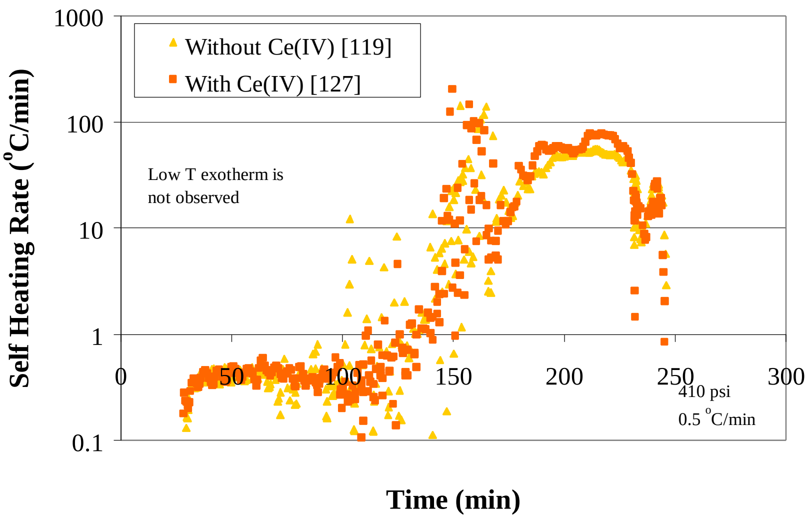


Figure 29. RSST Test of the Effect of Ce(IV) on Irradiated Reillexf HPQ in 8 M HNO$_3$: Self Heating Rate (^{o}C/min) vs. Temperature (^{o}C)

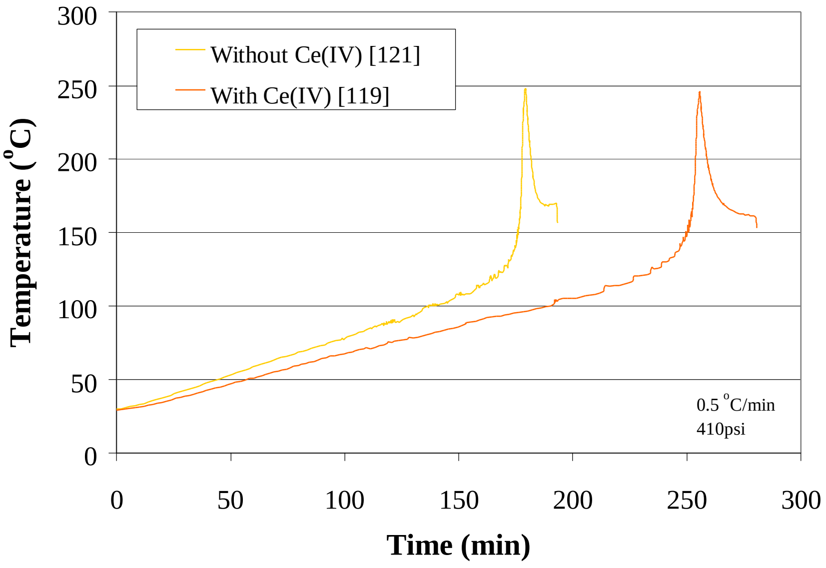


Figure 30. RSST Test of the Effect of Ce(IV) on Irradidated Reillexf HPQ in 12 M HNO$_3$: Temperature (^{o}C) vs. Time (min)

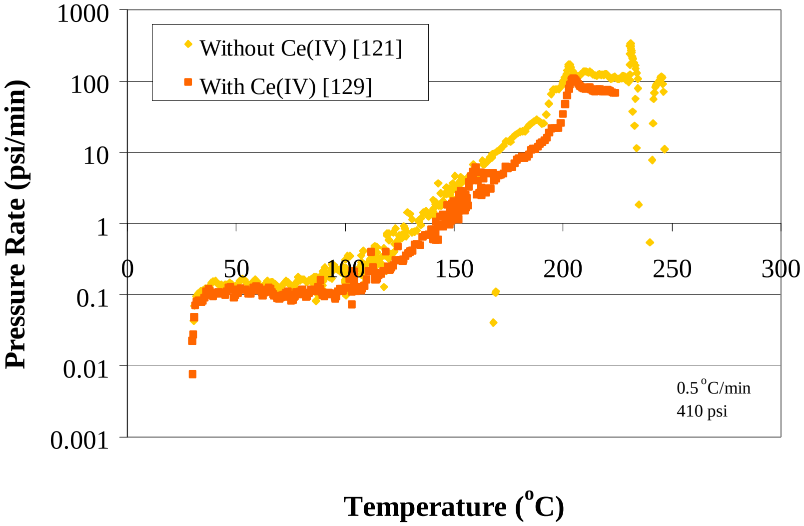


Figure 31. RSST Test of the Effect of Ce(IV) on Irradiated Reillex f in 12 M HNO_3: Presure Rate (°C/min) vs. Temperature (°C)

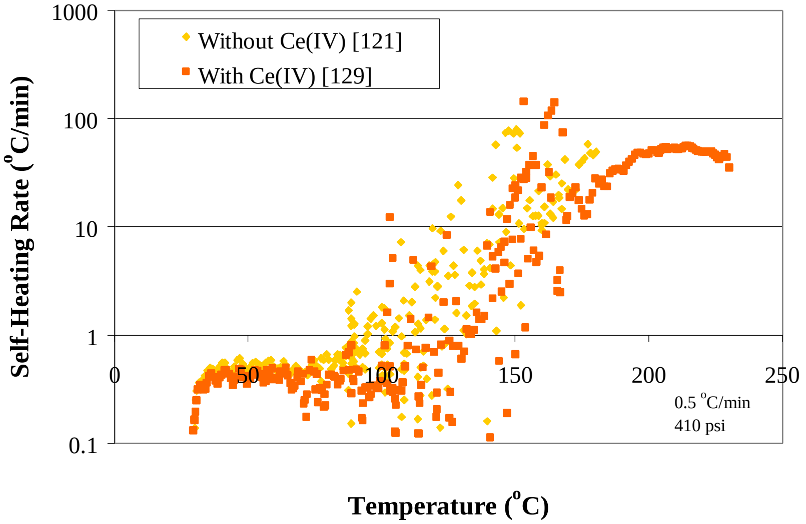


Figure 32. RSST Test of the Effect of Ce(IV) on Irradiated Reillex f in 12 M HNO_3: Self-heating Rate (°C/min) vs. Temperature (°C)

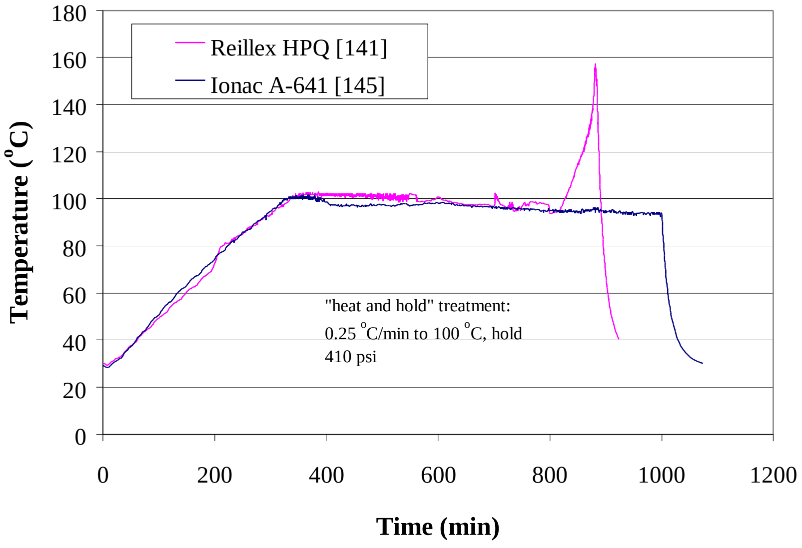


Figure 33. RSST Comparison Test of Resins in 8 M HNO_3 at 100 °C: Temperature (°C) vs Time (min)

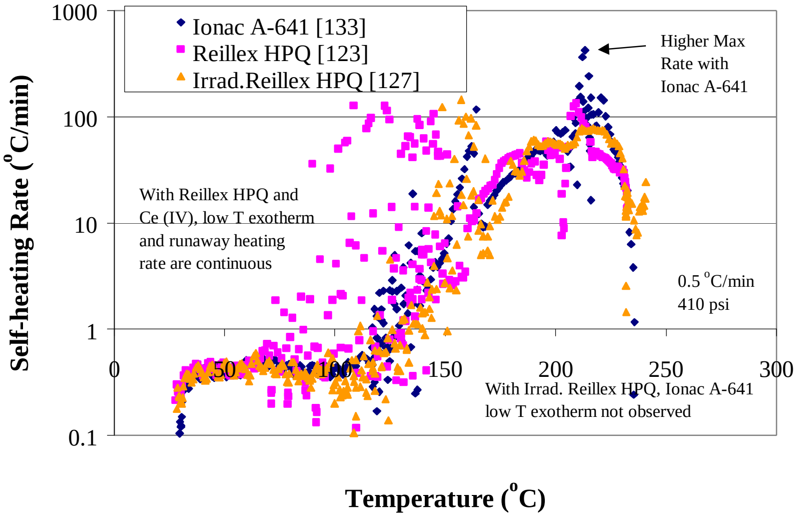


Figure 34. RSST Resin Comparison Test in 8 M HNO_3 with 24 g/L Ce (IV): Self-heating Rate (°C/min) vs. Temperature (°C)

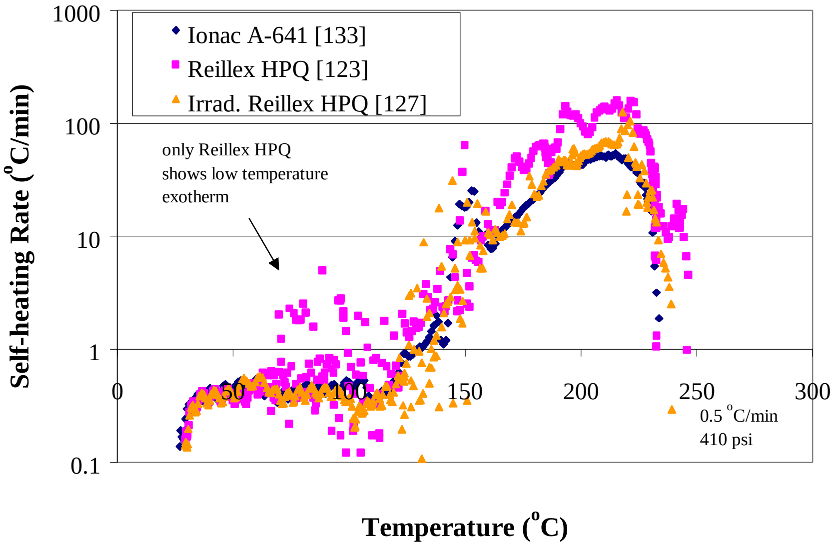


Figure 35. RSST Resin Comparison Test in 12 M HNO$_3$, 24 g/L Ce (IV): Self-heating Rate (°C/min) vs. Temperature (°C)

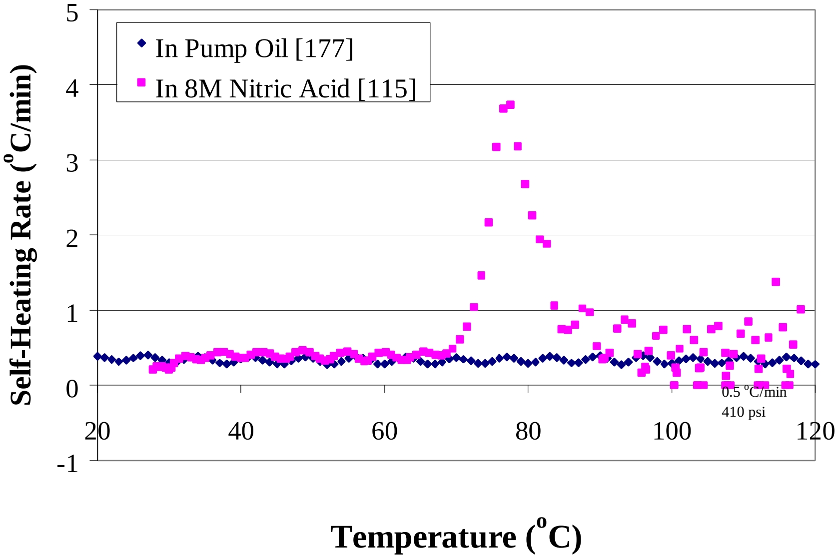


Figure 36. RSST Comparison Tests of Reillexf HPQ Resin in 8 M HNO$_3$ and in Pump Oil: Self-Heating Rate (°C/min) vs. Temperature (°C)

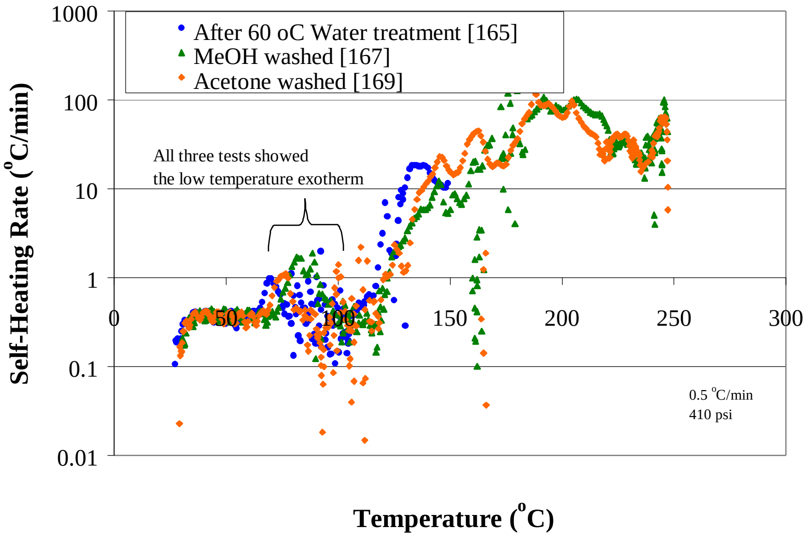


Figure 37. RSST Tests of Wash-Treated Reillex f HPQ in 8 M HNO_3: Self-Heating Rate (°C/min) vs. Temperature (°C)

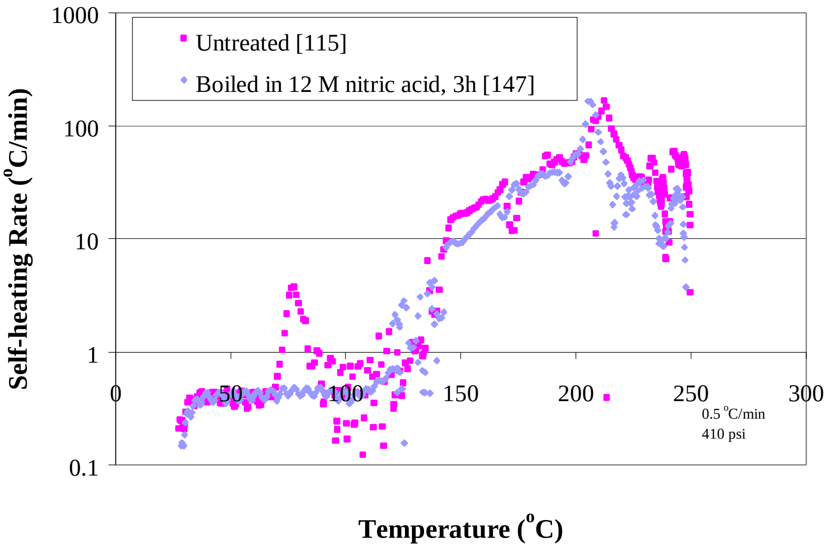


Figure 38. RSST Tests of 12 M HNO_3-Treated Reillex f HPQ in 8 M HNO_3: Self-heating Rate (°C/min) vs. Temperature (°C)

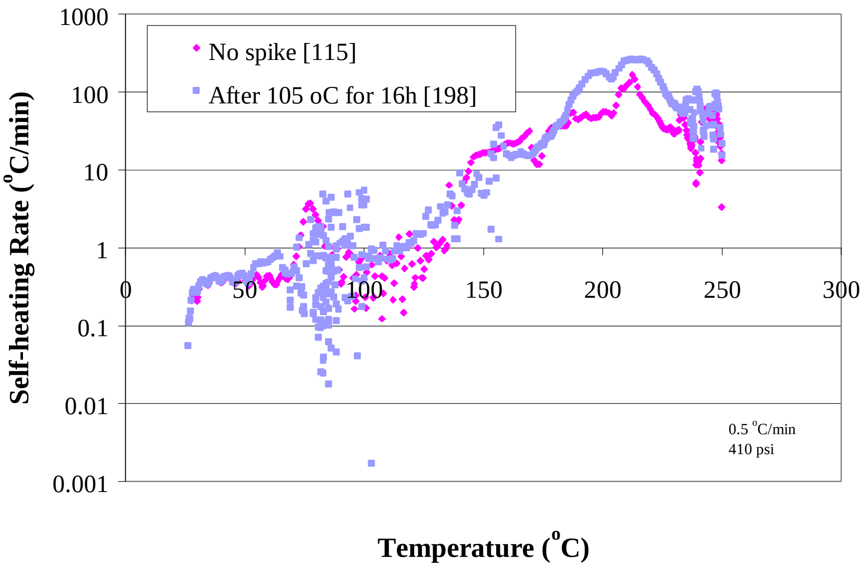


Figure 39. RSST Test of 12 M HNO_3-Treated Reillexf HPQ in 8 M HNO_3: Self-heating Rate (°C/min) vs. Temperature (°C)

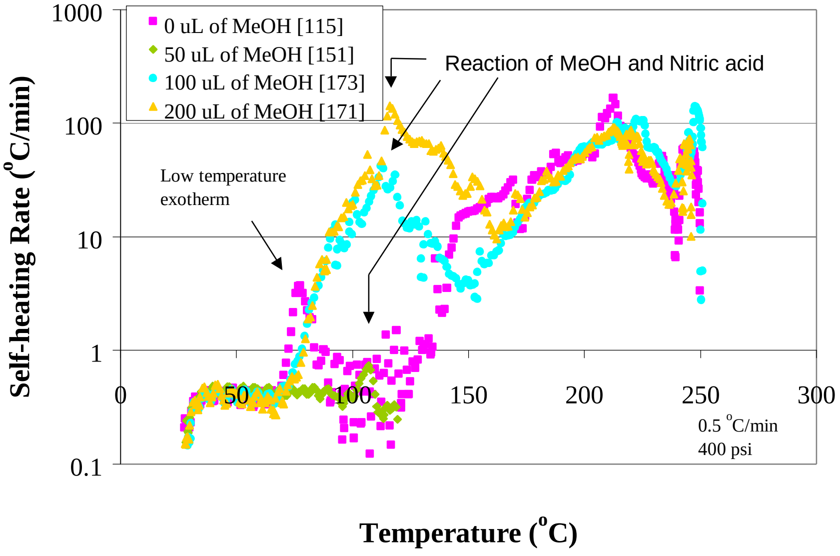


Figure 40. RSST Tests of Reillexf HPQ in 8 M HNO_3 Spiked with MeOH: Self-Heating Rate (°C/min) vs. Temperature (°C)

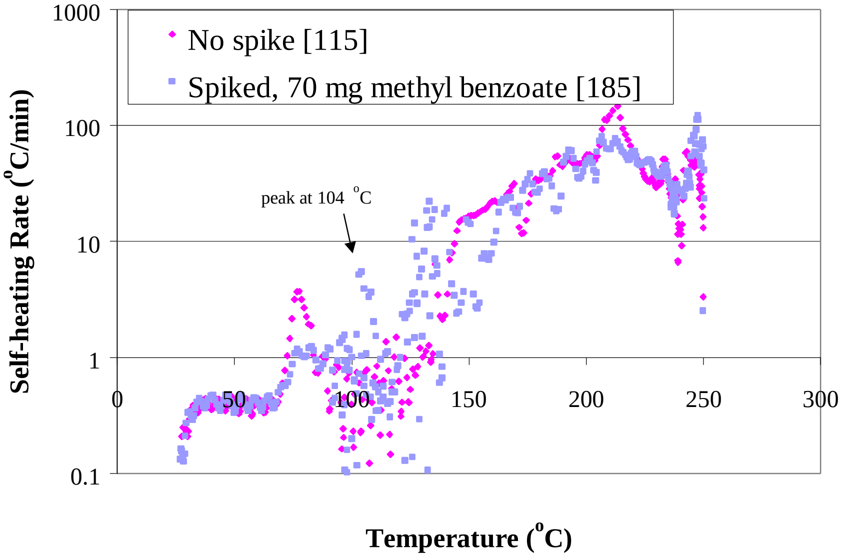


Figure 41. RSST Test of Reillexf HPQ in 8 M HNO_3 Spiked with Methyl Benzoate: Self-heating Rate (°C/min) vs. Temperature (°C)

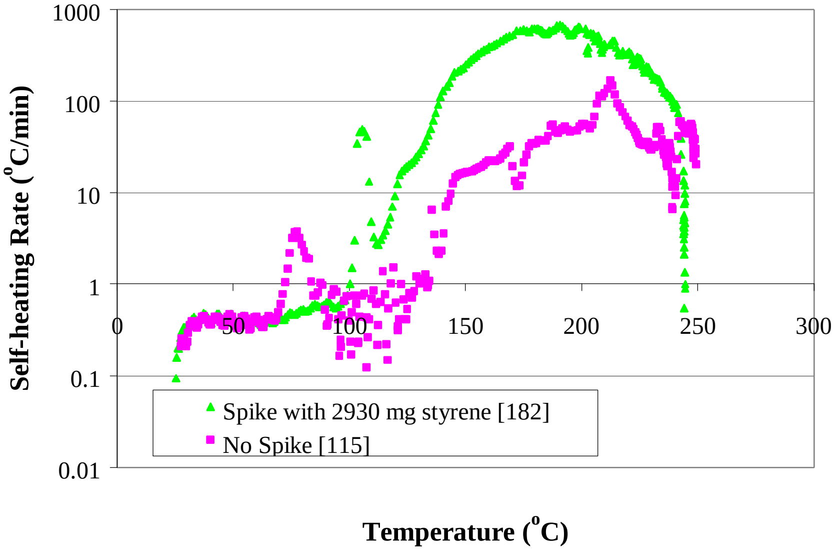


Figure 42. RSST Test of 8 M HNO_3 Spiked with Styrene (no resin): Self-heating Rate (°C/min) vs. Temperature (°C)

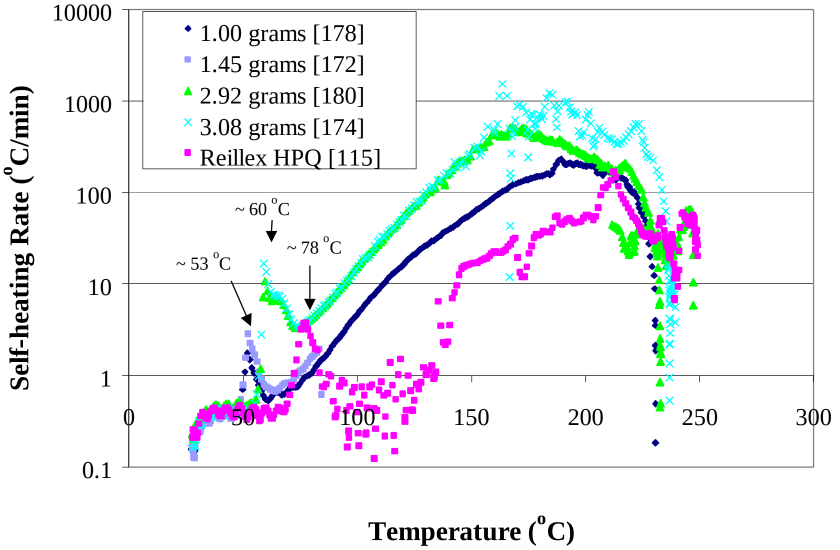


Figure 43. RSST Test of 8 M HNO_3 Spiked with Diethylbenzene (no resin): Self-heating Rate (°C/min) vs. Temperature (°C)

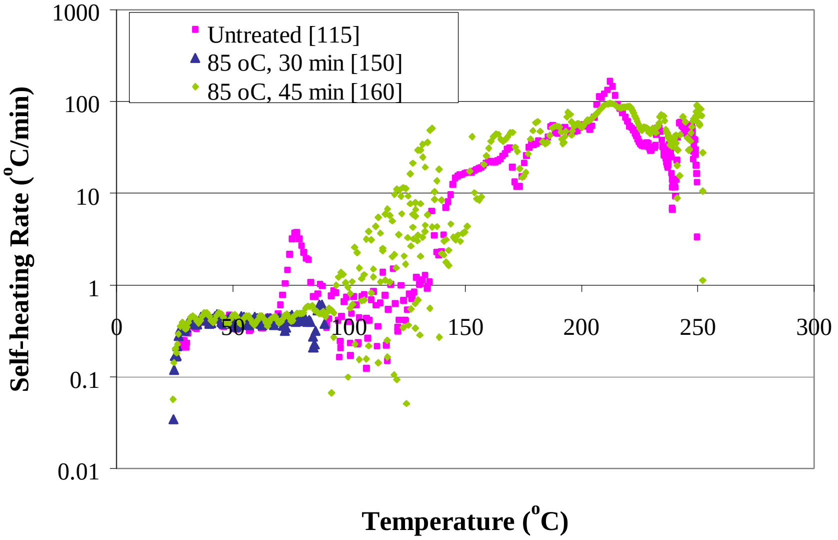


Figure 44. RSST Tests of 8 M HNO_3-Treated Reillex® HPQ in 8 M HNO_3: Self-heating Rate (°C/min) vs. Temperature (°C)

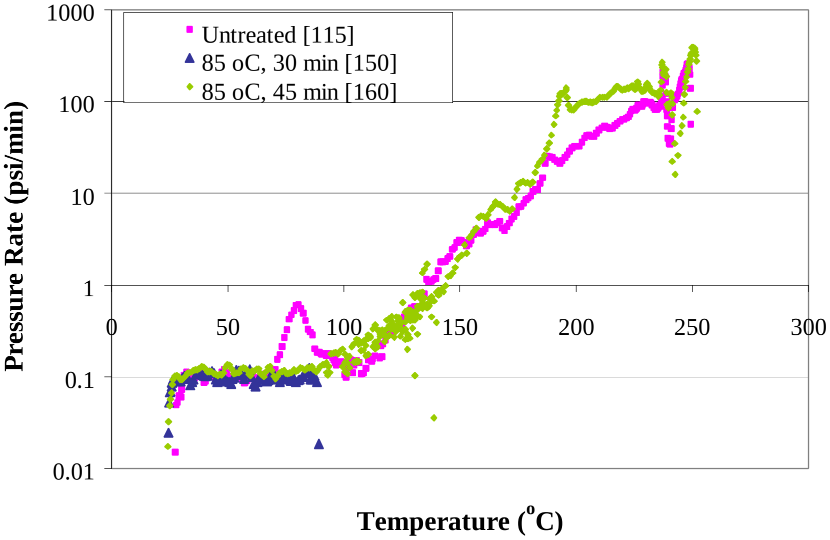


Figure 45. RSST Tests of 8 M HNO_3-Treated Reillexf HPQ in 8 M HNO_3: Pressure Rate (psi/min) vs. Temperature (°C)

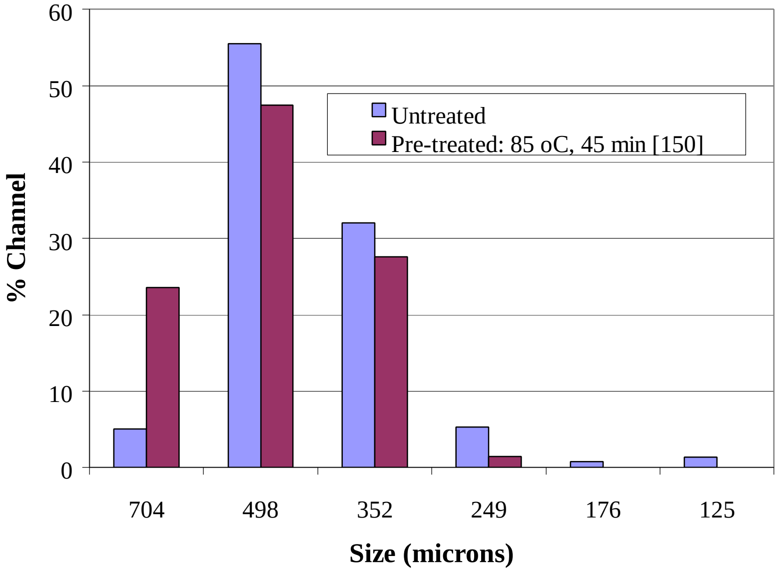


Figure 46. Particle Size Distribution of Reillexf HPQ: Untreated vs. 8 M HNO_3-Treated (45 min)