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Method Development for Thermal Analyses Testing on Reillex HPQ Resin using the Advanced Reactive System Screening Tool (ARSST)

David R. Best

March 2016

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EXECUTIVE SUMMARY

Reillex™ HPQ resin was developed by Los Alamos Laboratory and Reilly Industries Inc. in an effort to increase safety and process efficiency during the recovery and purification of plutonium. Ionac™ A-641, another strong base macroporous anion exchange resin used in the nuclear industry, was known to undergo a runaway reaction in hot nitric acid solutions. Because of this, an extensive amount of thermal analyses testing on the Reillex™ HPQ resin in SRNL was performed in 1999-2001 prior to use. A report on the thermal stability qualification of the Reillex™ HPQ resin in 8M (35%) and 12M (53%) HNO_3 was reported in 2000.[1] In 2001, the reactivity of Reillex™ HPQ resin in 14.4M (64%) HNO_3 was evaluated.[2] In January of 2001, thermal stability scoping tests were performed on irradiated Reillex™ HPQ resin in 14.4M (64%) HNO_3 (as a worst case scenario) and the results sent to Fauske and Associates to calculate a rupture disk size for the HB-Line resin column.[3] A technical report by Fauske and Associates[4] was issued in February 2001 recommending a 2.0” vent line with a rupture disk set pressure of 60 psig. This calculation was based on ARSST thermal analyses scoping tests at SRNL in which 4 grams of dried resin and 6.0 grams of 64% nitric acid in a 10 gram test cell, produced a maximum pressure rate (dP/dt) of 720 psi/min (12 psi/sec) and a maximum temperature of 250 °C.

In 2015, a new batch of Reillex™ HPQ resin was manufactured by Vertellus Industries. A test sample of the resin was sent to SRNL to perform acceptance and qualification thermal stability testing using the ARSST. During these tests, method development was performed to ensure that a representative resin to acid ratios were used while running the tests in the ARSST. Fauske and Associates recommended to either use a full test cell representative of the HB-Line column or a 10 gram sample in the test cell that was representative of the ratios of resin to nitric acid in the actual HB-Line column. An observation was made during method development testing that the 4 grams of resin to 6 grams of 64% acid ratio used in 2001 to determine the rupture disk size did not entirely wet the resin and was not representative of the actual HB-Line column.

The results of this study raised questions as to whether the ratio of 4 grams of resin to 6 grams of 64% nitric acid recommended by Fauske and Associates in 2001 was the correct ratio. Method development showed that 2.4 grams of resin to 7.6 grams of 64% nitric acid completely wet the resin and allowed for a small volume of acid above the resin. After running ARSST tests with the new 2.4g:7.6g ratio, the maximum pressure rate was significantly higher (dP/dt = 1870, 1434, 3350 and 1810 psi/min) than that observed with the 4g:6g ratio (dP/dt = 720 psi/min) in 2001. The result raised concerns on the recommendation of 64% nitric acid (14.4M) being truly the maximum acid safety limit acceptable for the current 2” vent line on the HB-Line column .

Additional ARSST thermal analyses tests in this report using 53% (12M) nitric acid produced maximum pressure rates of dP/dt = 182 and 162 psi/min. These pressure rates are less than the maximum pressure rate dP/dt = 720 psi/min that was used to calculate the HB-Line relief valve size. Therefore, SRNL concludes that the current 2” rupture disk set at 60 psig provides adequate pressure protection for the unlikely event of a runaway reaction between Reillex™ HPQ resin and nitric acid for acid concentrations up to 12M.

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LIST OF ABBREVIATIONS

ARSST	Advanced Reactive System Screening Tool
SRNL	Savannah River National Laboratory
HTE	High Temperature Exotherm
dP/dt	Rate of pressure change with respect to time

1.0 Introduction

Reillex™ HPQ resin is a strong-base macroporous anion exchange resin composed of a copolymer backbone of 1-methyl-4-vinylpyridine (70%) and divinylbenzene (30%). It currently is used in the HB-Line facility for the purification of plutonium. The plutonium (Pu) is loaded onto the resin by forming the anionic complex $Pu(NO_3)_6^{2-}$ with nitric acid (>6M). The loaded column is then washed with nitric acid (~8M) to remove impurities and then the Pu is eluted with a dilute nitric acid (<0.5M).

The Reillex™ HPQ resin was developed by Los Alamos National Laboratory and Reilly Industries Inc. in an effort to increase safety and process efficiency during the recovery and purification of plutonium. Ionac™ A-641, another strong base macroporous anion exchange resin used in the nuclear industry, was known to undergo a runaway reaction in hot nitric acid solutions. Because of this, an extensive amount of thermal analyses testing on the Reillex™ HPQ resin was performed in 1999-2001 prior to use. A report on the thermal stability qualification of the Reillex™ HPQ resin in 8M (35%) and 12M (53%) HNO_3 was issued in 2000.[1] In 2001, the reactivity of Reillex™ HPQ resin in 14.4M (64%) acid was evaluated.[2] The tests in the 2001 report evaluated the thermal behavior and reactivity of irradiated and unirradiated resin after long term exposure to acid. The conclusion was that 8M (35%) and 14.4M (64%) HNO_3 showed similar reactivity to the resin. Irradiated resin showed lower reactivity than unirradiated. The 2001 report also showed that aged resin in acid at 50º C did not have a runaway reaction. However, the ratios of acid to resin used in the 2001 tests were 2.5 grams of resin to 10 grams of acid. This ratio has a significant excess of acid and is not representative of what is in the HB-Line column during production. In January of 2001, thermal stability scoping tests were run on irradiated Reillex™ HPQ resin in 14.4M (64%) nitric acid (as a worst case scenario) and the results were sent to Fauske and Associates to calculate a rupture disk size for the HB-Line resin column.[3] A technical report by Fauske and Associates[4] was issued in February 2001 recommending a 2.0” vent line with a rupture disk set pressure of 60 psig. This recommendation was based on ARSST thermal analyses scoping tests at SRNL using 4.0 grams of dried resin and 6.0 grams of 14.4M (64%) nitric acid in a 10 gram test cell. Thermal tests produced a maximum pressure rate (dP/dt) of 720 psi/min (12 psi/sec) and a maximum temperature of 250 °C. These values were used in Fauske’s equation to determine vent size requirements.

In 2015, a new batch of Reillex™ HPQ resin was manufactured by Vertellus Industries. A test sample of the resin was sent to SRNL to perform acceptance and qualification thermal stability testing using the ARSST.

2.0 Experimental Procedure

2.1 Experimental Procedure

Bench-scale adiabatic calorimeters are used to test and evaluate runaway reaction data to determine rupture disk sizing for full-scale processes. In the case of the HB-Line Reillex™ HPQ resin column, an Advanced Reactive System Screening Tool (ARSST) from Fauske and Associates, was used for the thermal analyses testing to qualify the initial Reilly Reillex™ HPQ resin[1] in 2001 and a new test batch of Vertellus Reillex™ HPQ resin in 2015.

Thermal analyses using the ARSST for acceptance testing of the Vertellus Reillex™ HPQ resin[6] and method development for the qualification of the resin were performed. A typical ARSST set up is as follows. A 10 ml test cell is prepared by adding dried resin and acid to the test cell along with a small stir bar. Then, a thin heater is attached to the test cell with a heater belt, and the whole test cell is wrapped in aluminum foil. Test cells are then placed in an aluminum sheath packed with insulation around the entire test cell. An extension tube is placed on top of the test cell and a thermocouple is inserted through the tube into the test cell, where it makes contact with the sample. The thermocouple is checked for accuracy against a calibrated thermocouple prior to use. The insulation sheath containing the test cell is then placed in the calorimeter. The leads to the heater and thermocouple are then attached to the heater and thermocouple glands. A pressure transducer is connected from an outlet of the calorimeter to measure pressure.

Figure 2-1. ARRST Test Set Up

The calorimeter is placed on a stir plate and the calorimeter cap secured tightly on the calorimeter. A tube connected to a nitrogen cylinder is attached to the calorimeter and 400 psig of nitrogen is loaded into the calorimeter. The 400 psig of nitrogen is used to help reduce vapor saturation (boiling) during testing. The 400 psig of nitrogen is checked with a calibrated pressure valve.

A reduction in vapor saturation can eliminate some of the interferences seen with the exotherm reaction as the water and acid are being stripped from the test cell. A reduction in vapor saturation allows for the reaction to be considered a gassy system versus a tempered system. In that, a gassy system allows the high temperature exotherm to reach maximum pressure. The total pressure in the reactor is equal to the gas pressure. The principal parameter determining the vent size in a gassy system is the maximum rate of pressure rise (dP/dt). In a tempered system, the heat of reaction is removed by the latent heat of vaporization and the principal parameter determining vent size is the maximum rate of temperature rise (dT/dt).[5] It should be noted that the system, even under a blanket of 400 psig nitrogen, still has some tempering effects and, as noted by Crooks[1] "vapor saturation creates differences in the tempering rate". These differences affect the cell contents at the time of the exotherm and contribute to variations in measured self-heating and pressure rates.

All thermal analysis tests on the resin in acid were performed by heating the sample from room temperature to 225 °C at a controlled rate (1 °C/min). Temperature was recorded with a thermocouple and the pressure with a pressure transducer attached to the calorimeter. The controlled heating was performed using a polynomial temperature calibration. Running in polynomial mode allows the control software to maintain a constant heating rate. In order to do this, the control software will add or subtract power to the heater as needed to maintain the constant heating rate of the sample. As a result, when the exotherm begins producing heat, the control box will send less and less power to the heater in order to lower the heating rate. The polynomial calibration was performed using 7.8 g of pentadecane and ramping at 1 ºC/min @ 400 psig to a temperature of 225 ºC. Auto shutoff criteria were set at 700 °C, 400 minutes and 800 psig for all tests. In the ARSST, a nearly adiabatic calorimeter, some heat is lost due to the sample holder or test cell. The heat loss is assessed using the phi-factor. In determining how much material to place in the test cell for thermal analyses, one needs to ensure that the phi-factor is low (close to 1) and that conditions are similar to the fill ratio of the full scale process, in this case the HB-Line resin column. The phi-factor is calculated as phi-factor = 1+ (mass of test cell * heat capacity of test cell)/(mass of sample * heat capacity of sample).

The Fauske and Associates screening equation for vent sizing contains two constants. A 10 gram sample to ensure the phi-factor is near 1 and a freeboard volume of 350 ml. These both are already factored into the screening equation when rupture disk sizing is evaluated. In the screening tests performed in 2001 for the rupture disk evaluation for the HB-Line Reillex™ HPQ resin column, a 10 gram sample of resin and acid was used and the maximum pressure rates (dP/dt) and maximum temperature (dT/dt) evaluated. In these screening tests, 4 grams of dried resin and 6 grams of 14.4M (64%) nitric acid were used. A maximum pressure rate of 720 psi/min or 12 psi/sec and maximum temperature of 250 ºC (523K) were observed and used for the vent size calculation by Fauske and Associates.

2.2 Quality Assurance

Requirements for performing reviews of technical reports and the extent of review are established in manual E7 2.60. SRNL documents the extent and type of review using the SRNL Technical Report Design Checklist contained in WSRC-IM-2002-00011, Rev. 2.

3.0 Results and Discussion

3.1 Acceptance Testing

Acceptance testing for the new Vertellus Reillex™ HPQ resin showed that when the identical amounts of resin to 8M HNO_3 (2.8 g resin:9.5 g acid) were used in Crooks report[1], maximum temperature, pressure, time to maximum rate, self-heating rate and pressure rates all compared within 10%.[6] A maximum pressure rate of 720 psi/min was not exceeded (maximum 322 psi/min) in acceptance testing and a maximum temperature of 250 ºC was observed. The results provided sufficient data to allow acceptance of the new batch of resin based on the thermal analyses. Acceptance testing was only performed with resin and 8M HNO_3 (currently HB-Line nominal operating conditions).

3.2 Thermal Testing – Full Test Cell

During method development, an observation was made that the scoping test ratio of 4 grams of resin to 6 grams of 14.4M (64%) nitric acid used to do the vent size calculation in 2001 did not "wet" the entire sample. In the HB-Line Reillex™ HPQ resin column, the column is fully loaded with resin (13 kg) and the entire sample is "wet" with ~8M HNO_3. A small layer of acid would be at the top and bottom of the column whether the acid is being fed in an upward or downward flow.

Fauske and Associates was contacted to suggest recommendations on proper test cell loading of resin and acid for method development testing of Reillex™ HPQ resin. Fauske and Associates recommended loading as much material as possible to the test cell to lower the phi-factor and to duplicate process conditions or using a 10 gram sample which is the amount factored into Dr. Fauske's screening equation. A fully loaded test cell methodology was chosen in the first set of tests. For a > 10 gram sample, a correction in the pressure rate is made. A full test cell is shown in Figure 3-1. A corrected pressure rate is calculated as follows. Pressure Rate (psi/min) x 10(g)/Total Mass(g) = Corrected Pressure Rate (psi/min)

Figure 3-1. Full Test Cell with Resin and Nitric Acid (Shown with Heater and Belt)

Prior to testing, the unirradiated, nitrate form Reilly Reillex™ HPQ resin was dried at 60ºC for 72 hours under vacuum. ARSST tests on full test cells were performed using the dried resin and concentrations of

12M, 14.4M and 15.8M acid. Test cells were filled with ~4 grams of resin and ~12 grams of acid. Results of these tests are in Table 3-1. As stated in Crooks report, "maximum pressure and temperatures have relatively high precision and can be viewed more quantitatively than maximum pressure rates, which have much less precision and should be looked at qualitatively"[1]. The correction factor for a full test cell was factored into the final pressure rate (dP/dt).

Table 3-1. ARRST Full Test Cell Runs

Full Test Cells	Max Pressure	Max Temperature	dP/dt (psi/min)
53% HNO3 (12M)			
Test 1 – (4.5g:12.0g)	**658**	**392**	**529**
Test 2 – (4.5g:11.1g)	**659**	**310**	**398**
64% HNO3 (14.4M)			
Test 1 (4.5g:12.6g)	**708**	**311**	**609**
Test 2 (4.5g:12.9g)	**713**	**348**	**1570**
Test 3 (4.5g:13.0g)	**671**	**325**	**4450**
70% HNO3 (15.8M)			
Test 1 (4.0g:12.5g)	**675**	**397**	**3142**
Test 2 (4.0g:12.5g)	**726**	**445**	**2560**

The current rupture disk size calculation by Fauske and Associates was based on ARSST results from runs with 14.4M (64%) HNO_3 and therefore the initial expectation was that acid concentrations up to 14.4M are safe. However, of concern during method development was that for tests above 12M HNO_3 (14.4M and 15.8M), the majority of those tests produced pressure rates well above the 720 psi/min value seen in the scoping runs in 2001. For full test cells using 12M HNO_3 during method development testing, pressure rates on the ARSST were below the 720 psi/min value used to size the current rupture disk in HB-Line.

Another observation in each run with a full test cell was that a good bit of resin was observed on the outside of the insulation sheath after a test, as shown in Figure 3-2. The resin outside the insulation caused concern because this resin would not attain the exothermic reaction temperature and therefore was not oxidized in the reaction.

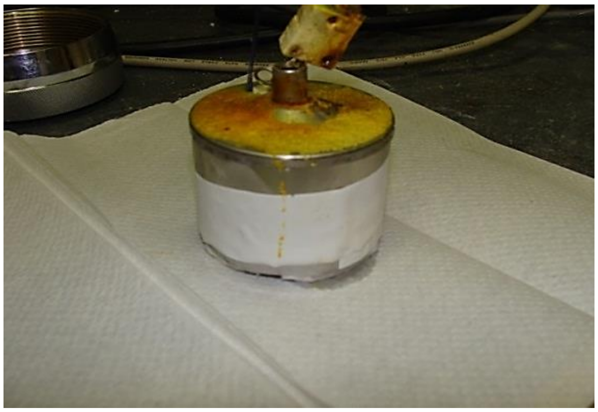

Figure 3-2. Resin Outside Insulation Sheath

A suggestion by E. Kyser was to perform an ARSST test by heating the test cell to a temperature just below where the high temperature exotherm (HTE) occurs and then observe the insulation sheath to see if resin and acid had discharged out of the test cell. From previous thermal runs, data continuously showed that the HTE occurred near 140 °C. So, a ramp temperature to 130 °C was chosen. Two runs were performed. One test cell was fully loaded with 4.0 g of dry resin to 12 g of 8M HNO_3 acid and the other was loaded with a 10 gram sample containing 2.9 g of resin and 7.1 g of 8M HNO_3 acid. In each test, the temperature increased at 1 ºC/min to 130 °C and then was allowed to cool to room temperature. As seen in Figure 3-3, the full test vessel lost a considerable amount of resin and acid after increasing the temperature to 130 °C and then cooling down. This result clearly showed that the discharge occurs prior to the HTE and could cause errors in pressure and temperature rates. In the 10 gram sample test, no resin or acid was observed on the insulation sheath housing after heating to 130 °C and allowing the test cell to cool down. It was apparent that some acid had evaporated from the 10 gram cell prior to the HTE, but the resin was still wet. Pressurization of the calorimeter to 400 psig of nitrogen assists in limiting evaporation in the ARSST but does not totally eliminate it. If the HB-Line column were to heat, the open vent line would produce some evaporation but it is unknown if it would be at the rate in which it occurs in the ARSST. Crooks reported that a HTE occurs only when the cell content is dry. "This test showed that the low-temperature exothermic reaction of Reillex™ HPQ did not initiate the high-temperature exothermic reaction, and the high-temperature reaction only occurred after the cell contents were dry"[1]. This may be why Crooks chose a 4g:6g ratio of resin to acid for his scoping studies. However, in the test to 130 °C using the representative ratio of 2.9 g resin to 7.1 g acid, the resin remained wet. Therefore, 10 gram samples were used for all additional method development tests that include the representative ratios covered in section 3-3.

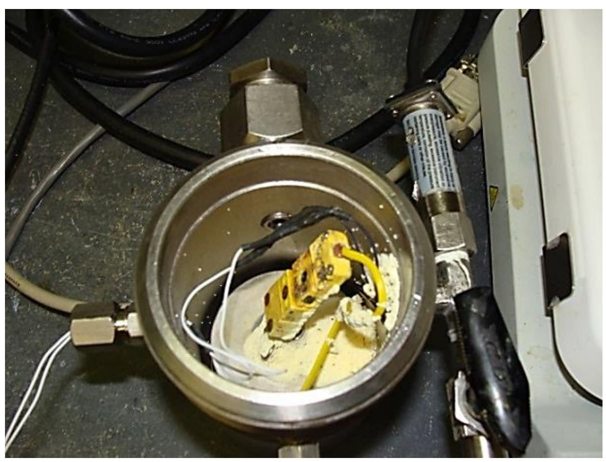

Figure 3-3. Full test cell heated to 130 ºC.

3.3 <u>Thermal Testing – 10 gram Tests</u>

To determine the correct 10 gram ratio of resin to acid for testing, bench scale tests were performed in which 1.3 g of dry resin (simulating 13 kg of resin in the HB-Line column) were added to a graduated cylinder. Nitric acid was then added drop wise until the resin was "wet" with a small layer of acid on top. The mass of acid was recorded. From this data, the ratios in Table 3-2 were established to provide the 10 gram sample ratios for thermal runs. As shown in Table 3-2, since the density of nitric acid increases with concentration, the more concentrated acid solutions require a higher mass percent of acid to maintain the same liquid level.

Table 3-2. Resin:Acid Ratios

Percent Nitric Acid	Grams of Resin (g)	Grams of Acid (g)	% Resin	% Acid	Test Cell (g) of Resin	Test Cell (g) of Acid
35%	1.3086	3.2471	29%	71%	2.90	7.10
53%	1.3032	3.8765	25%	75%	2.50	7.50
64%	1.3025	4.1354	24%	76%	2.40	7.60
70%	1.3000	4.2168	23.5%	76.5%	2.35	7.65

Additional thermal analyses tests with 10 gram sample mixtures, using the ratios in Table 3-2, were performed using dried (unirradiated) Reilly Reillex™ HPQ resin. Concentrations of 8M, 12M, 14.4M and 15.8M HNO_3 were used to determine the maximum pressure, maximum temperature and maximum pressure rates obtained under these conditions. These tests were performed as method development in preparation for the qualification of the new batch of Vertellus Reillex™ HPQ resin after irradiation.

Test results for 8M (35%) HNO_3 and 12M (53%) HNO_3 are summarized in Table 3-3 and Figures 3-4 through 3-9. Each of these tests provided data showing that a high temperature exotherm occurred at around 150-170ºC, reaching maximum pressures of 557 psig @ 8M and 544 and 552 psig @ 12M, maximum temperatures of 266 ºC @ 8M and 274 and 341 ºC @ 12M and pressure rates well below the 720 psi/min maximum used to size the existing 2" rupture disk in HB-Line (which is larger than the ~1.5" value required for a full column and a pressure rate of 720 psi/min).

Pressure rates are determined using Fauske's reduction of data equation in which the derivative is determined over a specified number of data points. The difference of pressure (dP) and time (dt) spanned over the number of data points specified is calculated and dP/dt calculated. With 8M and 12M ARSST runs, the standard five point smoothing was chosen to determine pressure rates during the exothermic reaction and maximum values are shown in Table 3-3.

Table 3-3. 8M, 12M – Reilly Reillex™ HPQ resin and HNO_3 (10g sample)

HNO_3 Concentration	Maximum Pressure	Maximum Temperature	Maximum Pressure Rate
Resin(g):Acid (g)	(psig)	(ºC)	(dP/dt)
35% (8M) 2.9g:7.1g	557	266	198
53% (12M) 2.5g:7.5g	544	274	183
53% (12M) 2.5g:7.5g	552	341	163

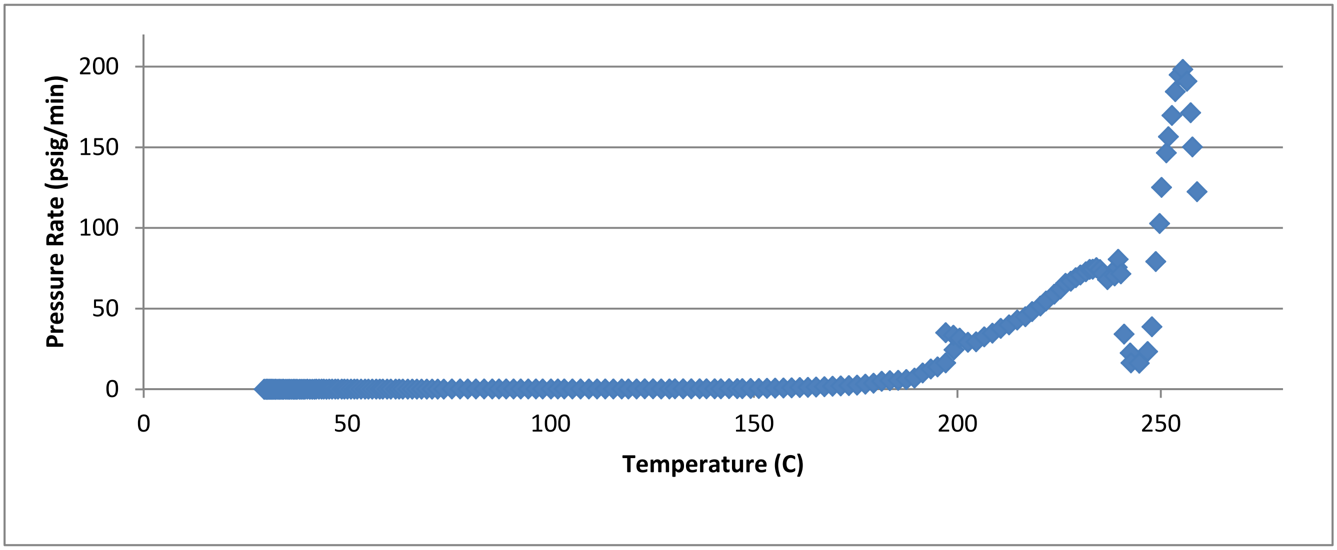

Figure 3-4. Reillex™ HPQ Resin in 8M HNO_3: Pressure Rate versus Temperature

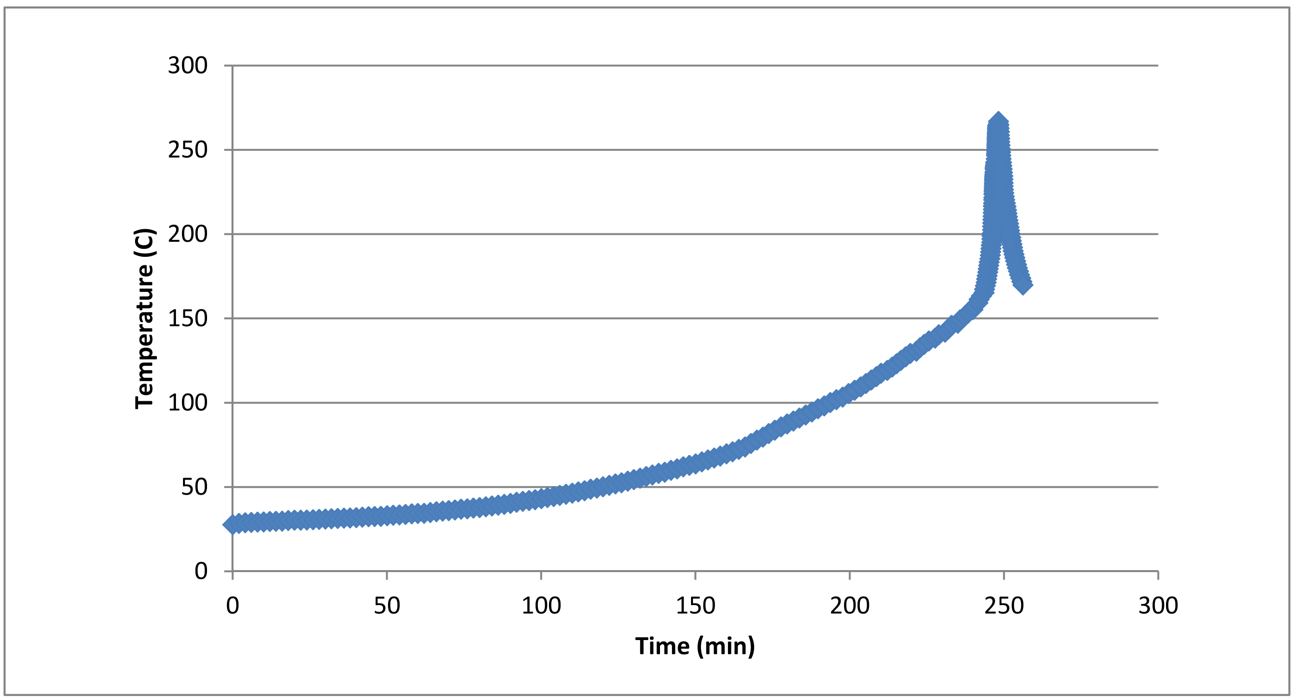

Figure 3-5. Reillex™ HPQ Resin in 8M HNO_3: Temperature versus Time (8M HNO_3)

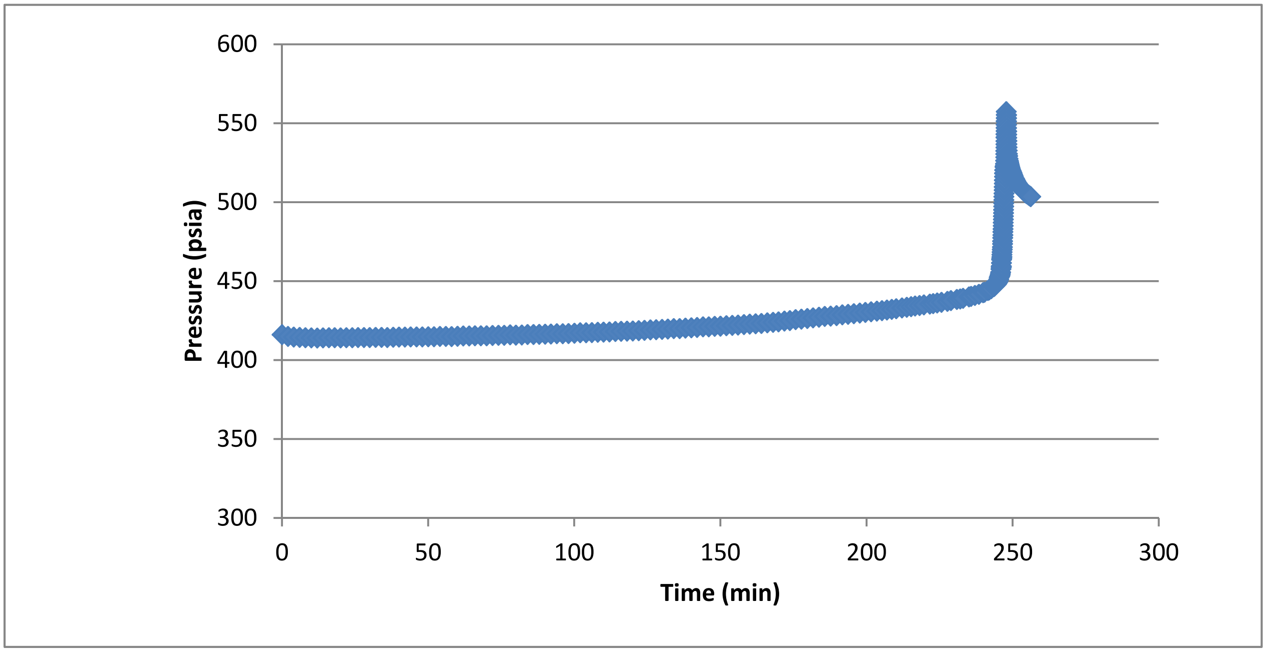

Figure 3-6. Reillex™ HPQ Resin in 8M HNO_3: Pressure versus Time

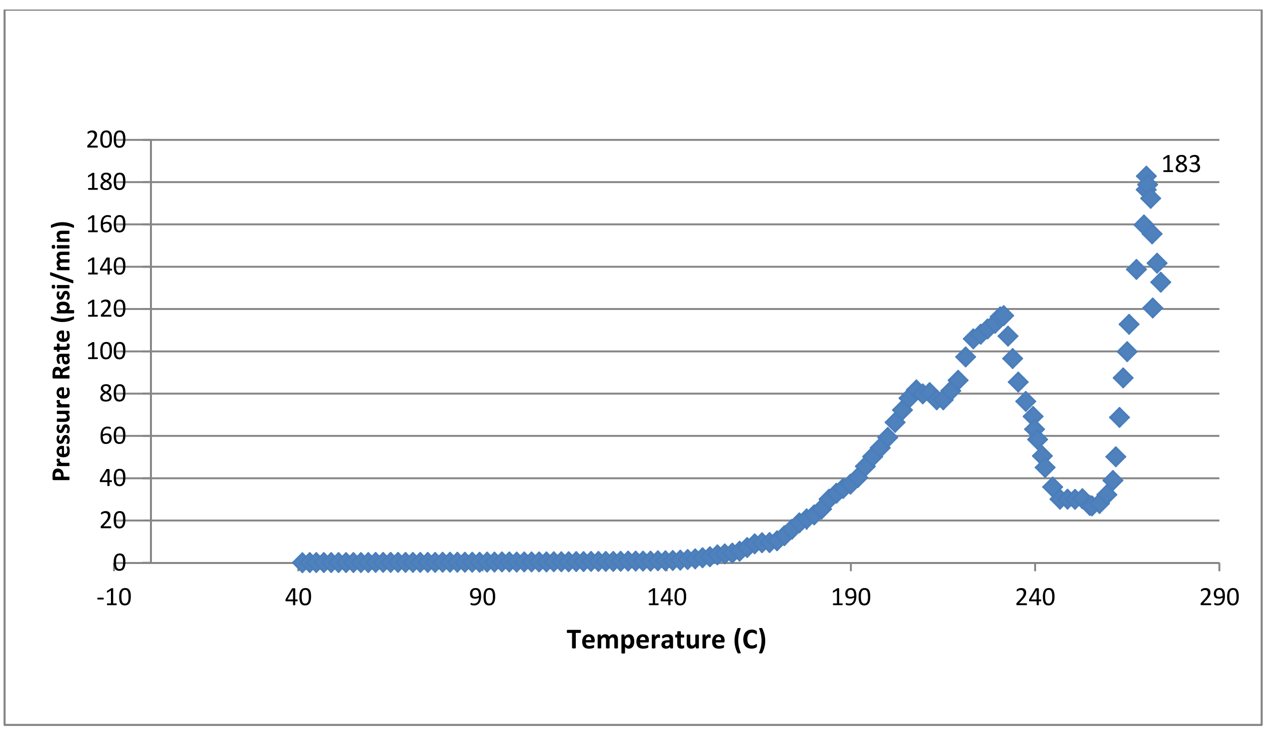

Figure 3-7. Reillex™ HPQ Resin in 12M HNO_3: Pressure Rate versus Temperature

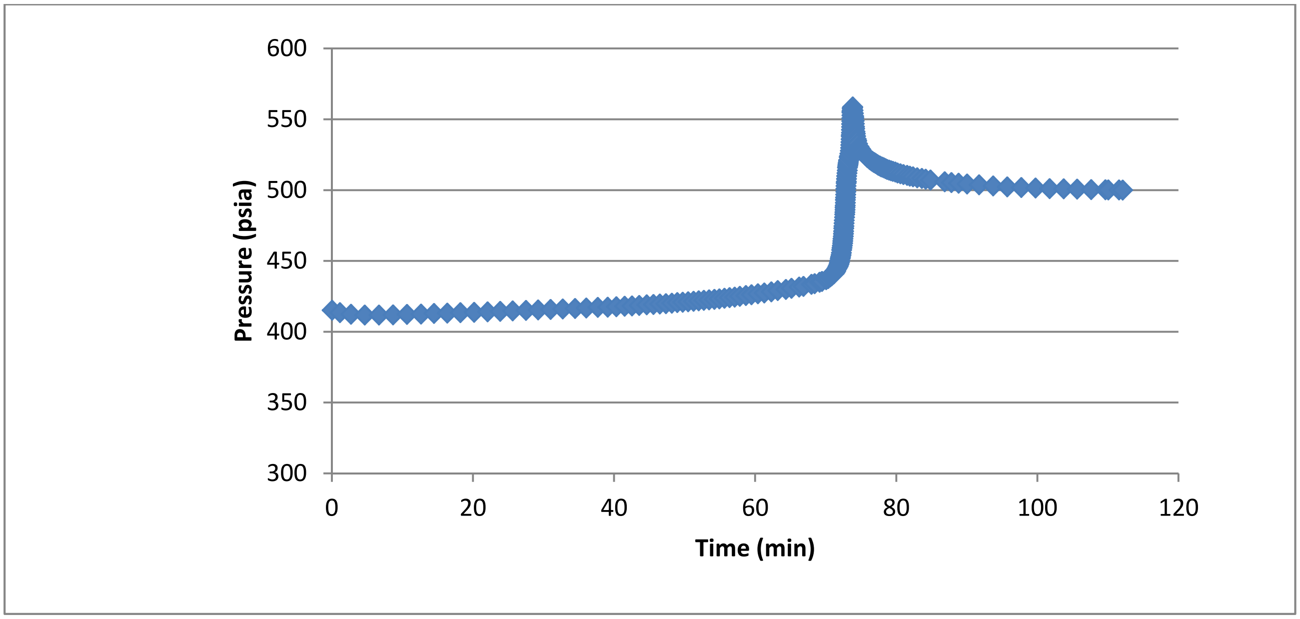

Figure 3-8. Reillex™ HPQ Resin in 12M HNO_3: Pressure versus Time

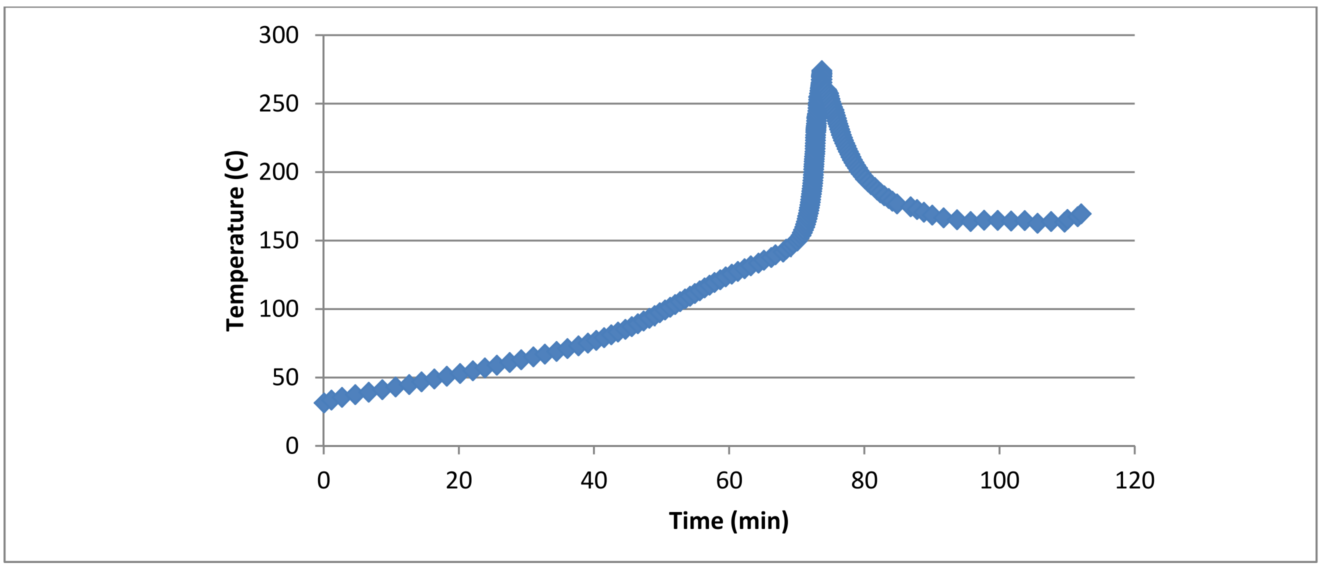

Figure 3-9. Reillex™ HPQ Resin in 12M HNO_3: Temperature versus Time

Additional tests were performed using higher acid concentrations of 14.4M HNO_3 (64%) and 15.8M HNO_3 (70%) using the more representative ratios in Table 3-2. An ARSST test was also performed on a ratio of 4.0 grams of resin to 6.0 grams of 64% HNO_3 to duplicate the scoping tests for rupture disk sizing in 2001. Results are in Table 3-4 and Figures 3-11 through 3-16.

Table 3-4. 14.4M and 15.8M - Reilly Reillex™ HPQ resin and HNO_3 (10g sample)

HNO_3 Concentration	Maximum Pressure (psig)	Maximum Temperature (°C)	Maximum Pressure Rate (dP/dt, psi/min)
64% (14.4M) – 4.0g:6.0g	582	297	337
64% (14.4M) – 2.4g:7.6g	587	294	1870
64% (14.4M) – 2.4g:7.6g	563	254	3350
64% (14.4M) – 2.4g:7.6g	571	318	1810
70% (15.8M) – 2.35g:7.65g	579	279	2382

When the ratio of 4.0g of resin to 6.0g of 14.4M (64%) HNO_3 was used, a pressure rate of 335 psi/min was observed. The HTE was similar to what was reported in Crooks' scoping test runs for the rupture disk sizing. However, as noted previously, prior to heat up only a portion of the resin was "wet" with the acid and a good portion of the resin was still dry.

When the resin was loaded with the more representative ratio of acids at both 14.4M (64%) HNO_3 and 15.8M (70%) HNO_3, pressure rates exceeded the 720 psi/min limit that the current rupture disk is rated for. The maximum pressure and temperature were similar, but pressure rates were consistently higher. As stated earlier, maximum pressure rates also exceeded 720 psi/min with 14.4M (64%) and 15.8M (70%) HNO_3 in the full test cell run. Also, when reducing the raw data for maximum pressure rates in these runs, a larger amount of data points (15) had to be smoothed to eliminate the noise produced by the higher pressure exotherm (a suggestion by Fauske and Associates). Various factors indicated a more violent reaction with the higher acid runs, including the difficulty in smoothing the data due to the more violent thermal reaction and the smaller amount of charred resin remaining in the test vessel. See Figure 3-10. An increase in the moles of oxidant to moles of resin when using higher acid concentrations clearly produces a much higher pressure rate when the HTE occurs.

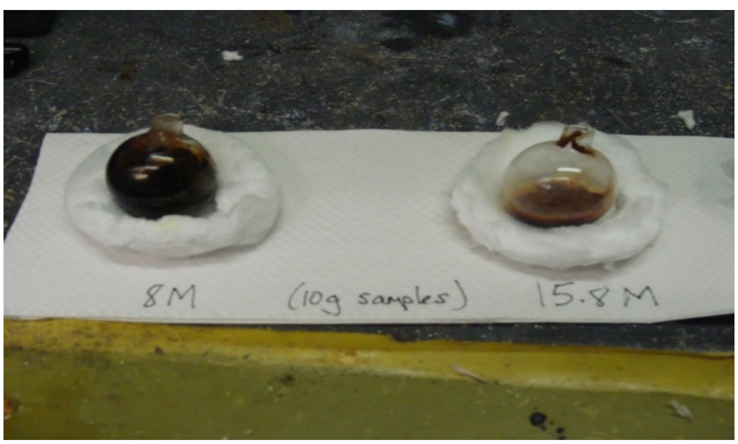

Figure 3-10. 8M and 15.8M Test Cells

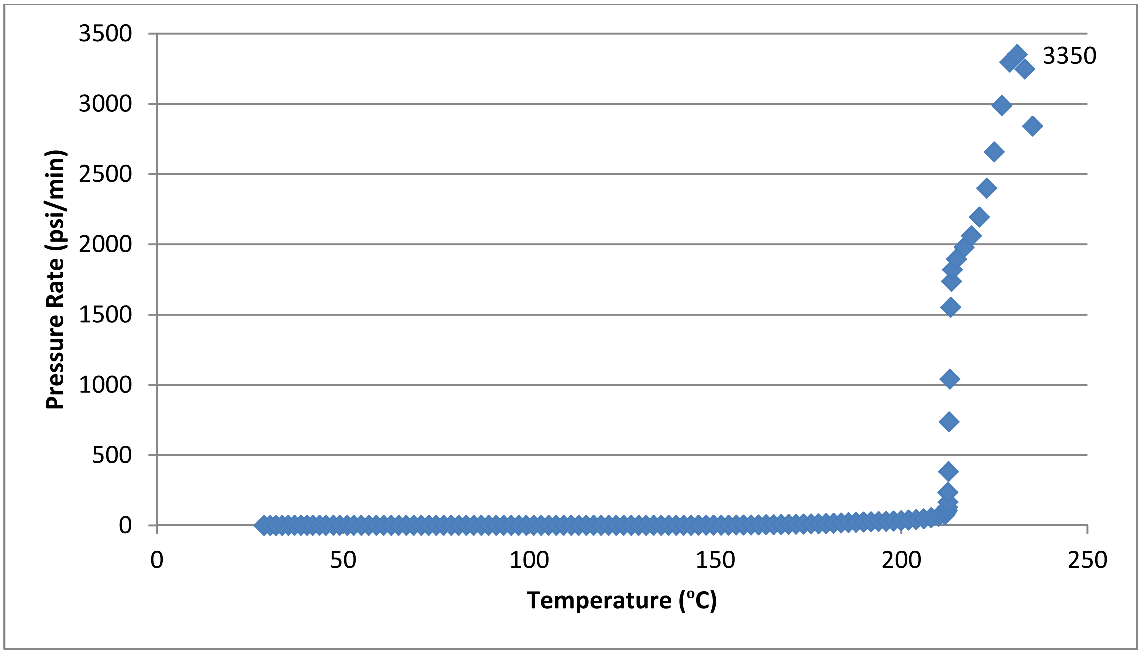

Figure 3-11. Reillex™ HPQ Resin in 14.4M HNO_3: Pressure Rate versus Temperature

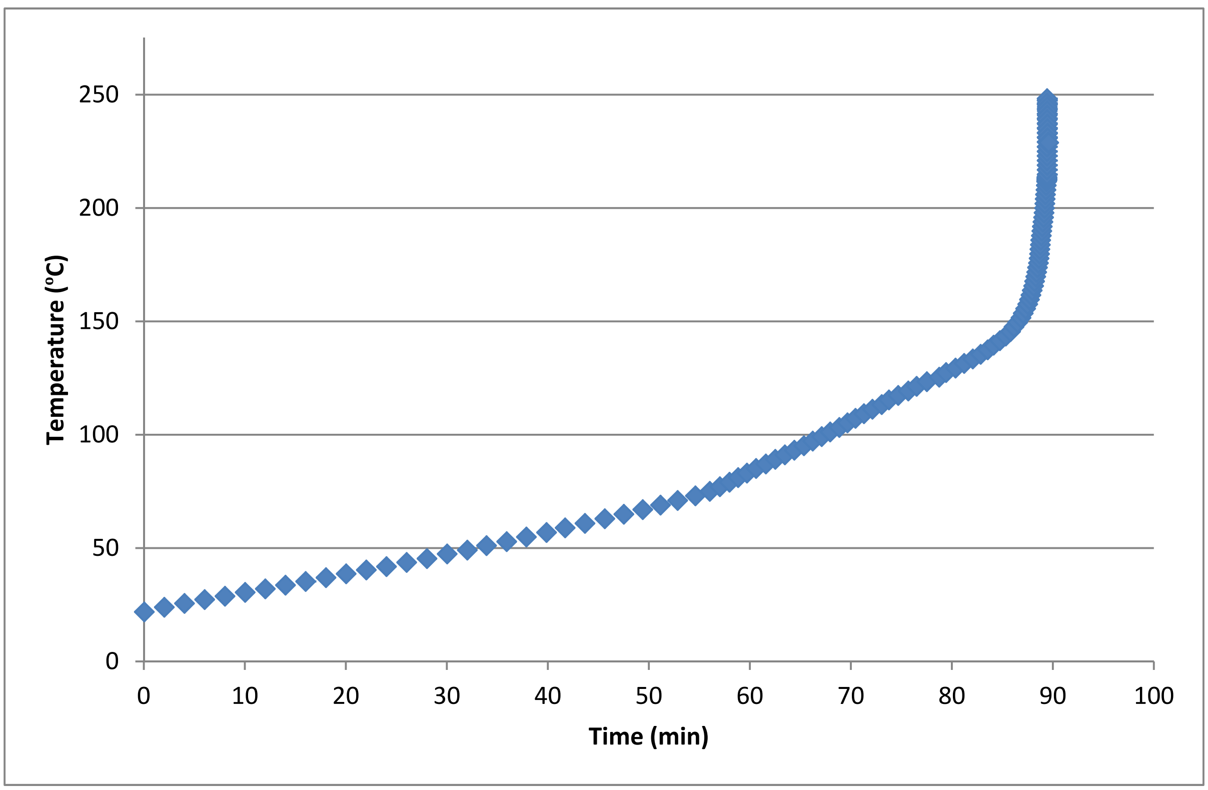

Figure 3-12. Reillex™ HPQ Resin in 14.4M HNO_3: Temperature versus Time

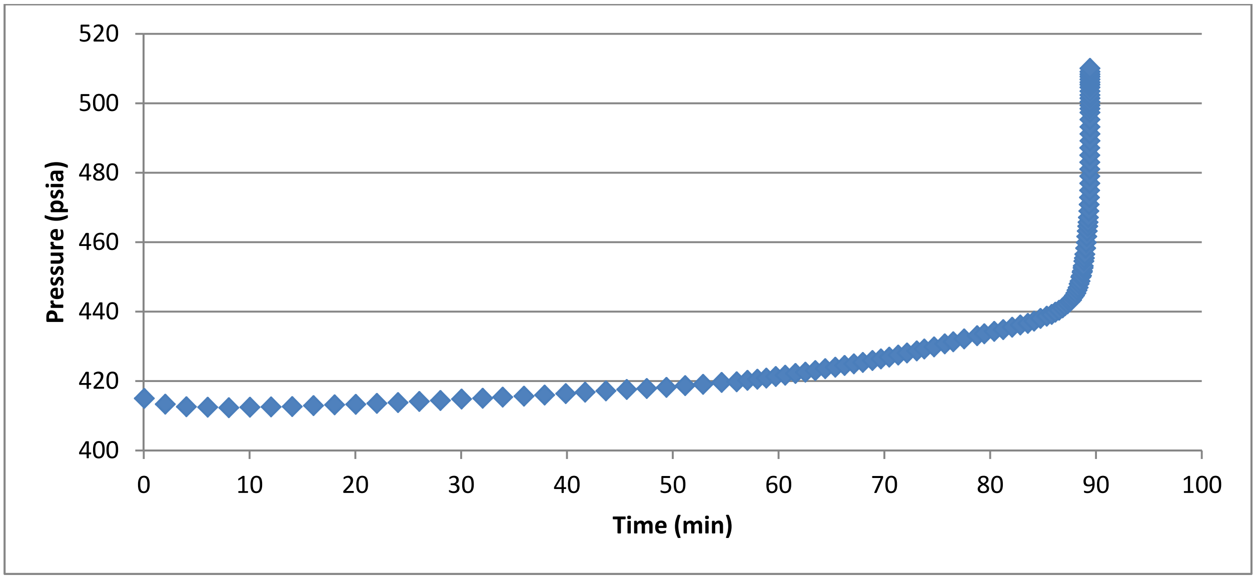

Figure 3-13. Reillex™ HPQ Resin in 14.4M HNO_3: Pressure versus Time

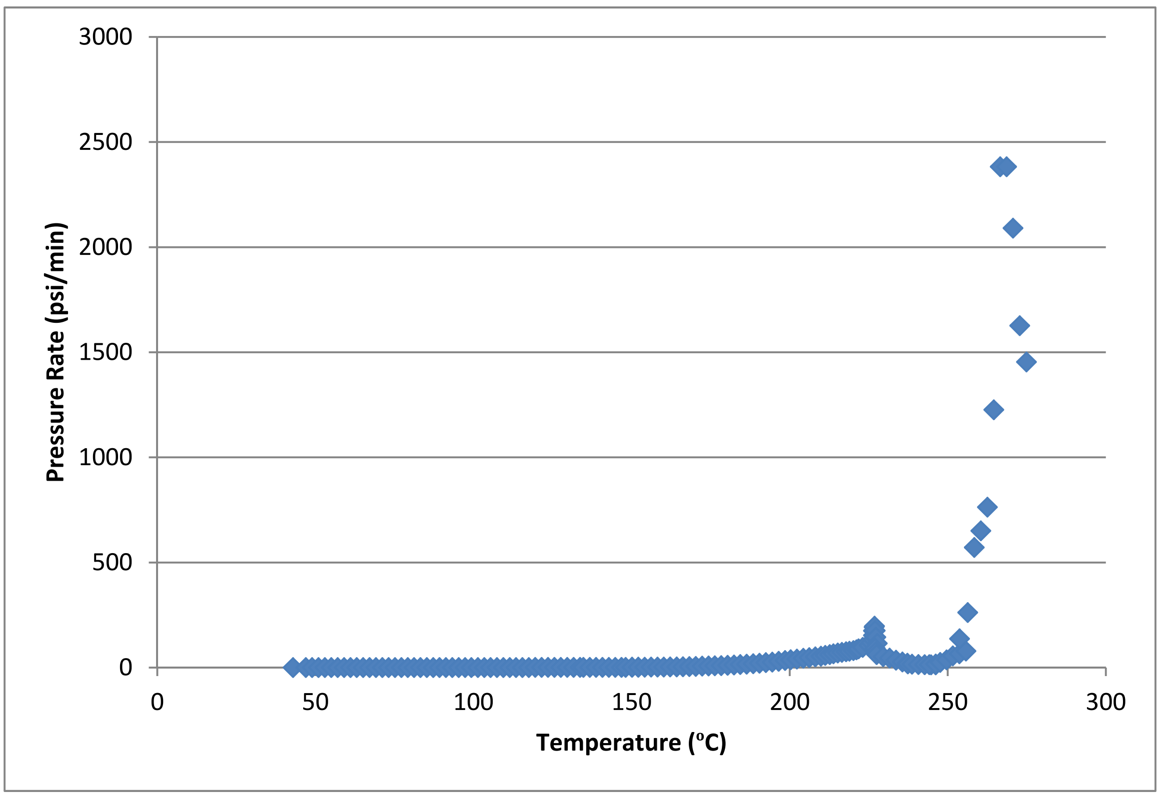

Figure 3-14. Reillex™ HPQ Resin in 15.8M HNO_3: Pressure Rate versus Temperature

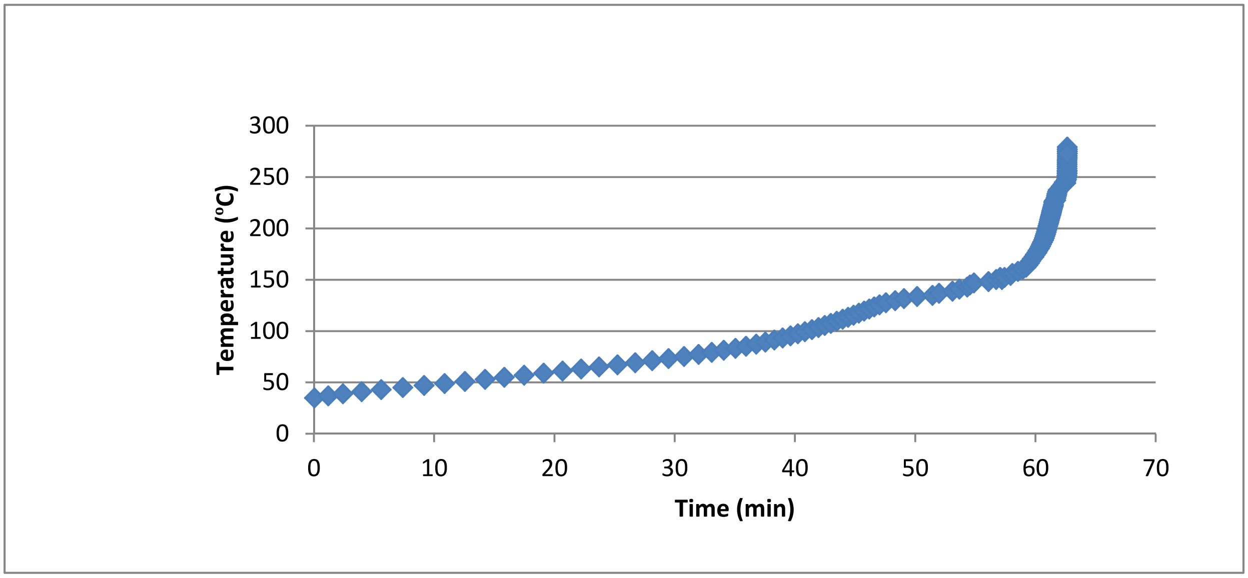

Figure 3-15. Reillex™ HPQ Resin in 15.8M HNO_3:Temperature versus Time

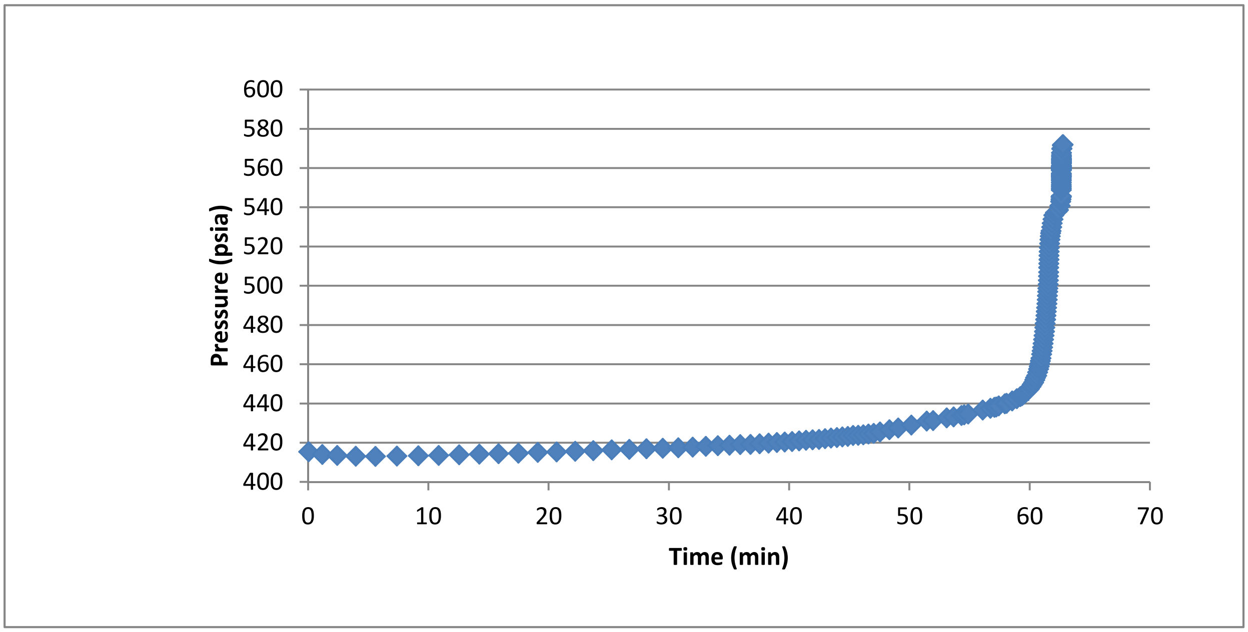

Figure 3-16. Reillex™ HPQ Resin in 15.8M HNO_3: Pressure versus Time

4.0 Conclusions

The current relief valve sizing for the HB-Line resin column is a 2" vent line with a rupture disk set at 60 psig. The calculation by Fauske and Associates to determine the relief valve sizing was based on a pressure rate of dP/dt = 720 psi/min and a maximum temperature of 250 °C. The ARSST thermal test used to calculate the relief valve sizing was based on a 4 gram sample of dried irradiated Reilly Reillex™ HPQ resin and 6 grams of 14.4M (64%) HNO_3 to produce a 10 gram sample. However, during method development in preparation to run the new test batch of Vertellus Reillex™ HPQ resin, the 4g:6g ratio was found to not fully wet the resin with acid. This led to concern, because ARSST tests should duplicate process conditions and for the HB-Line resin column the resin is entirely wet with acid.

Additional ARSST tests were conducted during method development using more representative ratios of resin and acid concentrations to duplicate HB-Line process conditions (e.g. fully "wet" resin with acid). Thermal tests were conducted with 8M, 12M, 14.4M and 15.8M HNO_3. Although maximum temperatures were similar to those used in the relief valve sizing equation (250°C), maximum pressure rates were not. Maximum pressure rates were lower than 720 psi/min for runs conducted with 8M (35%) and 12M (53%) HNO_3. But, with 14.4M (64%) HNO_3, maximum pressure rates were significantly higher than 720 psi/min. See Figure 4.1, which shows the highest maximum pressure rates observed for each acid concentration.

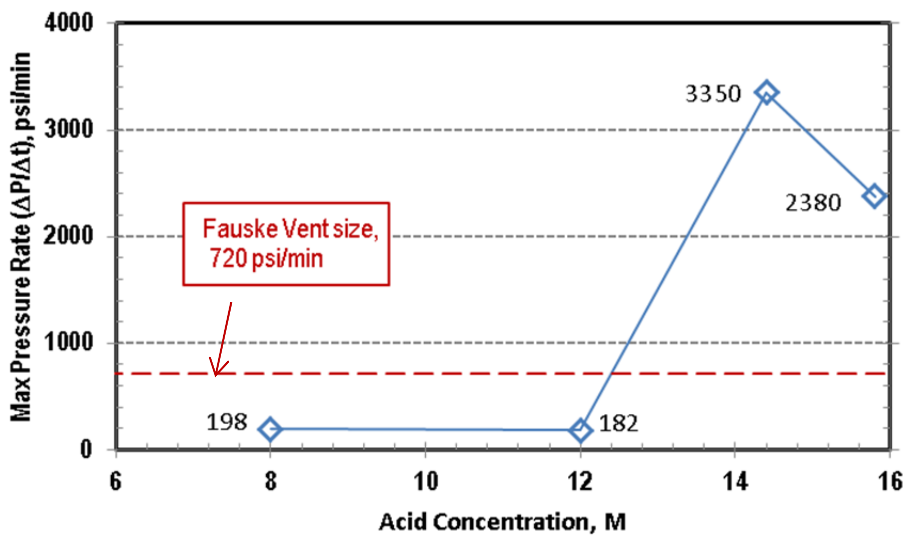

Figure 4-1. Maximum Pressure Rate per Acid Concentration with Fully Wetted Resin

This work shows that the relief valve sizing is sufficient for current operation of the HB-Line column at ~8M and up to 12M HNO_3. Maximum pressure rates with 12M HNO_3 (dP/dt = 182 psi/min, 162 psi/min) were less than the pressure rate (dP/dt = 720 psi/min) used to size the existing 2" vent line. The maximum temperatures of 274°C and 341°C @ 12M, although higher than 250 °C, result in a vent line requirement well below the existing 2" vent line when using these temperatures in Fauske's vent line screening equation.

5.0 Recommendations

There is a considerable history of violent thermal reactions with resin and acid that have resulted in fire, ruptures and explosions. A literature search was conducted and documented by Thompson and Shehee[7] showing numerous accidents over the years. A violent reaction and accident is always a potential with these materials under the right conditions (e.g., high acid, high temperatures, lack of or improper vent size). ARSST tests in this report duplicate HB-Line resin conditions unlike the scoping studies performed in 2001[3]. The use of the proper ratio of resin to 14.4M (64%) HNO_3 in these tests have produced much higher maximum pressure rates than were used in the calculation to determine the proper relief vent sizing by Fauske[4]. Additional ARSST thermal analyses tests in this report using 12M (53%M) nitric acid produced maximum pressure rates (dP/dt) of = 182 and 162 psi/min. These pressure rates are less than the maximum pressure rate of 720 psi/min that was used to calculate the HB-Line relief valve size. Therefore, SRNL concludes that the current 2" rupture disk set at 60 psig provides adequate pressure protection for the unlikely event of a runaway reaction between Reillex™ HPQ resin and nitric acid for acid concentrations up to 12M.

5.1 Path Forward

ARSST tests will be performed on unirradiated and irradiated resin (100 MRad and possibly higher) using the new nitrate-converted Vertellus Reillex™ HPQ lot of resin for qualification. The proper ratio of dried resin to acid, and acid concentrations of 8M and 12M will be used in the ARSST. The maximum pressure rate of 720 psi/min, used in vent size calculations, will be used to guide the qualification of the new resin for use in the HB-Line resin column.

6.0 References

[1] W. J. Crooks, Qualification of Reillex™ HPQ Anion Exchange Resin for Use in SRS Processes", WSRC-TR-99-00317.

[2] W. J. Crooks, "Evaluation of the Reactivity of Reillex™ HPQ in 64% Nitric Acid", WSRC-TR-2001-00028.

[3] Scoping ARSST tests with 64% Nitric Acid for Fauske and Associates, WSRC-NB-99-00115, Pages 158-163.

[4] Fauske and Associates, LLC, "Relief Sizing for HB-Line Resin Column", FAI-01-15

[5] "Encyclopedia of Chemical Processing Design, 61", John J. McKetta, Guy E. Weismantel, 1997

[6] D. R. Best, "Thermal Stability Acceptance Testing for the Vertellus Reillex HPQ Resin", SRNL-L3100-2105-00137.

[7] T. C. Shehee and M. C. Thompson, "Change in Anion Exchange Nitric Acid Concentration Limit during Weapons Grade Plutonium Processing in HB-Line", SRNL-STI-2013-00455.