^{238}Pu Anion Exchange Column Safety during Flow Interruptions




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SAVANNAH RIVER NATIONAL LABORATORY

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Outline

- Historical Context
- Theory
- Controls
- Modeled System & Assumptions
- Calculated Results
- Incident at Mayak Russian
- Conclusions

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Historical Context

- Hazards recognized in 1950’s by DuPont
- At least 7 accidents in Literature 1962-68
- Lead to controls on temperature, acid, flow interruption time, resins used and venting

- Early tests on effects of radiation damage on capacity
- Dried Resins recognized as risk

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Theory

- Resin bed has low Heat Capacity and thermal conductivity resulting in near adiabatic column center
- Liquid Flow removes heat generated by radioactive decay and chemical reaction
- No flow condition allows heat to accumulate in bed and temperature to rise
- Reaction rate exponential function of temperature

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Theory (continued)

"Well Vented" Column

- T limited by solution boiling pt (100-120 °C)
- T rises until evaporative cooling removes heat generated
- Sufficient venting necessary to remove all gaseous reaction products and evaporation
- Insufficient venting will allow pressure rise resulting in temperature increase and runaway reaction

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Controls

10^8 rad Dose to resin
Max 60 °C - operated ambient
15 min flow interruption
9 M HNO_3 Max
Thermal testing of resins

"Ever Open" Vents on columns
"Ever Wet" resin bed

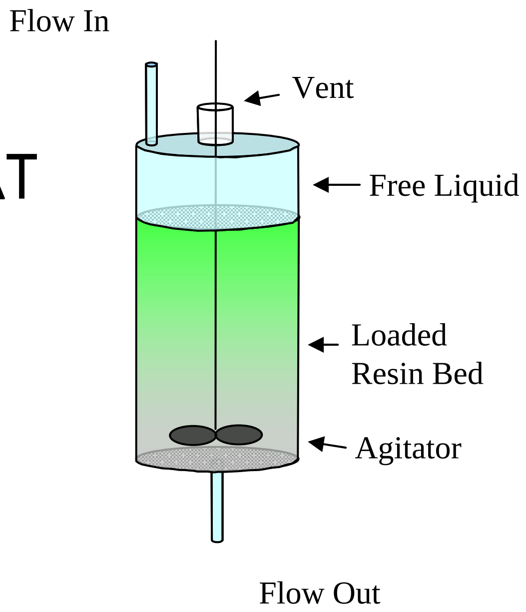
Modeled System

$$Q_{total} = Q_{radiolytic} + Q_{rxn} - Q_{Heat\ Transfer}$$

$$= \rho_{resin\text{-}bed}\, C_p\, \Delta T$$

$$= (\rho_{dry\text{-}resin}\, C_{p\ dry\text{-}resin} + \rho_{solution}\, C_{p\ solution})\, \Delta T$$

$$Q_{rxn} = Q_o \exp(E_a/RT)$$



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Assumptions

- 800 g ^{238}Pu (100% isotopic)
- 85L resin with 42L of 8M HNO_3 above resin bed
- 45 g/L max Pu resin loading
- Pu loaded on upper resin bed only
- No mixing of resin/liquid within resin bed (below boiling pt)
- 50 °C initial column temperature
- No axial heat transfer
- Agitator in resin bed OSS (out of service)

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Resin Testing

- Accelerating Rate Calorimeter (ARC) data on MSA-1/Dowex 21K
  - T,P profiles high phi test cell
  - Used to establish kinetic parameters on reaction rates
  - Temperature, Pressure rates (also venting requirements)
- RSST/ARSST/VSP2 data on Reillex HPQ™
  - T,P profiles low phi test cell
  - Used to determine venting requirements and size pressure relief devices
  - Screening to compare reactivity various resins/treatments

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“Well-Vented” Column Assumption

- Calculation to test assumption of adequate venting
  - Test cell for ARC/ARRST is sealed
  - Calculated moles of gas as f(t) from P(t),T(t) data
  - $n(t) = n_O (1/P\ \delta P/\delta t - 1/T\ \delta T/\delta t)$, assuming Z=1
  - Heat source 800 g ^{238}Pu
  - Assume chemical reaction energy @90 °C = radiolytic decay heat and doubles for each 10 °C rise
  - Estimate offgas rate from column at various temperatures from both reaction gases and evaporation
- Offgas rate rises from 46 L/min to 472 L/min as T increases from 90 °C to 130 °C
- Existing 3” vent estimated @ ~500 L/min with ~0.01” w.c. ΔP

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“Well-Vented” Column Assumption

T,C	Reaction	Evaporation	Total	
	L/min	L/min	L/min	kg /hr
91	5	41	46	1
101	9	64	73	2
111	19	109	128	4
121	40	202	242	7
130	82	390	472	13

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Measured Parameters

- $E_a/R = 12771$ /K
- $Q_o = 3.35e\text{-}12$ J/s/cc
- $\Delta H_{rxn} = 619$ J/g
- $\rho_{\text{resin-bed}} = 1.2$ g/cc
- $C_{p\ \text{resin-bed}} = 0.71$ cal/cc/K
- 0.56 watts/g ^{238}Pu

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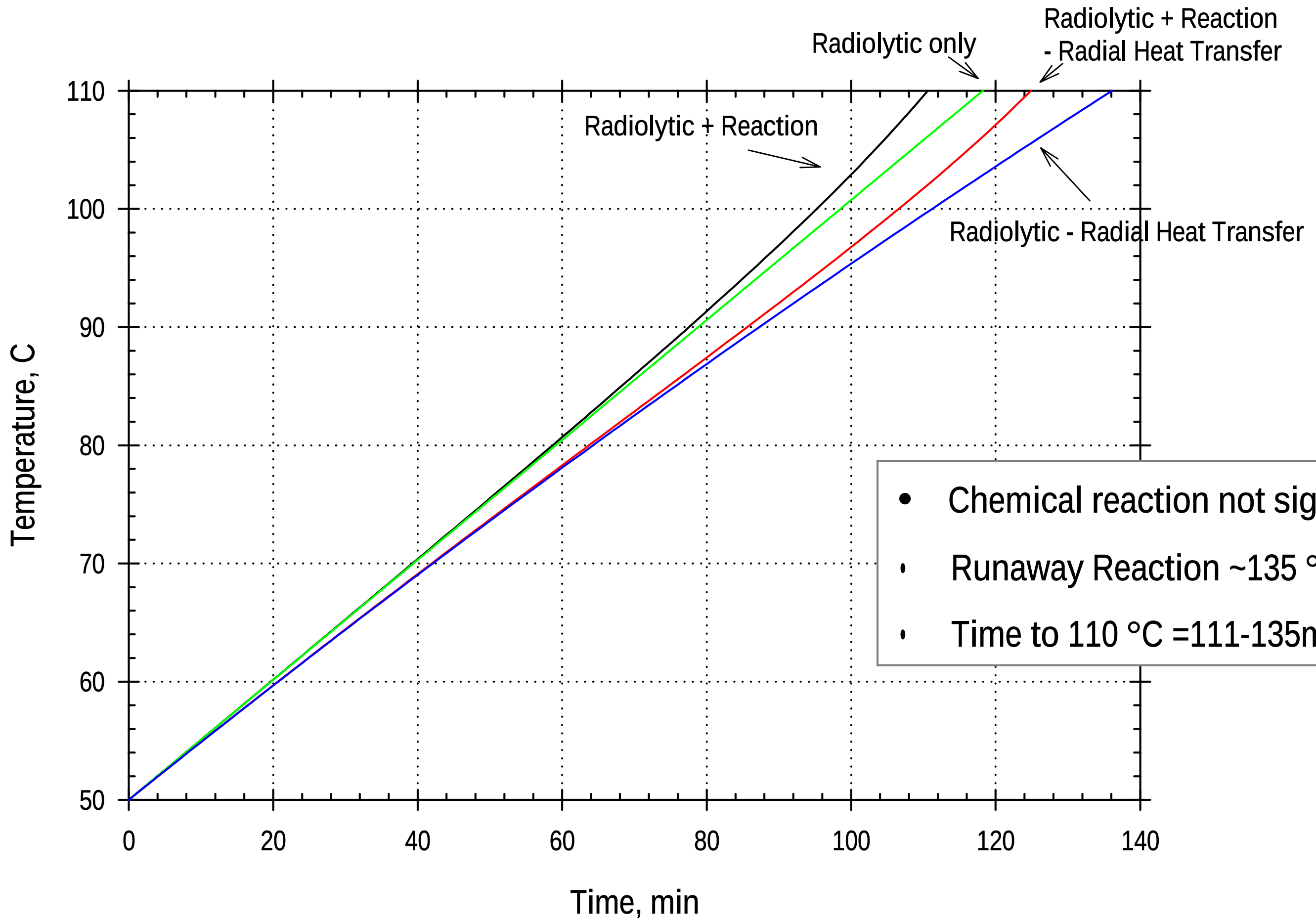
Calculated T(t) Profile



- Chemical reaction not significant < 90 °C
- Runaway Reaction ~135 °C
- Time to 110 °C =111-135min

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Mayak Incident

When: 7/17/93 14:15 Moscow Time

Where: Mayak Isotope Production Plant in Russia

What: Anion Column SN-04 with 374 g ^{238}Pu,

Loaded on sorbent VP-1AP (2,5-methyl vinylpyridine divinyl benzene copolymer)

Washed with 7M HNO_3, then allowed to stand with no-flow for 3 hours

Overpressurization, Vessel Rupture, resin ejected into cell, etc

Why:

Cooling Jacket? (incapable of removing all heat generated)

Valve Leakage? (possible loss of liquid on top of resin bed)

Increased batch size

Utilization of same tank for make-up of wash and elution acid (process delay)

Hazards not sufficiently analyzed

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Conclusions

- Wet ^{238}Pu column will heat up over an ~2 hour flow interruption
- "Well-Vented" Wet ^{238}Pu column would be expected to heat up and evaporate to dryness over a 4-10 hour period
- These calculations compare well with accident at Mayak
- Traditional 15 min flow interruption operating limit was shown to be adequate

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