Recovery of purified nickel from material contaminated with Tc^{99}

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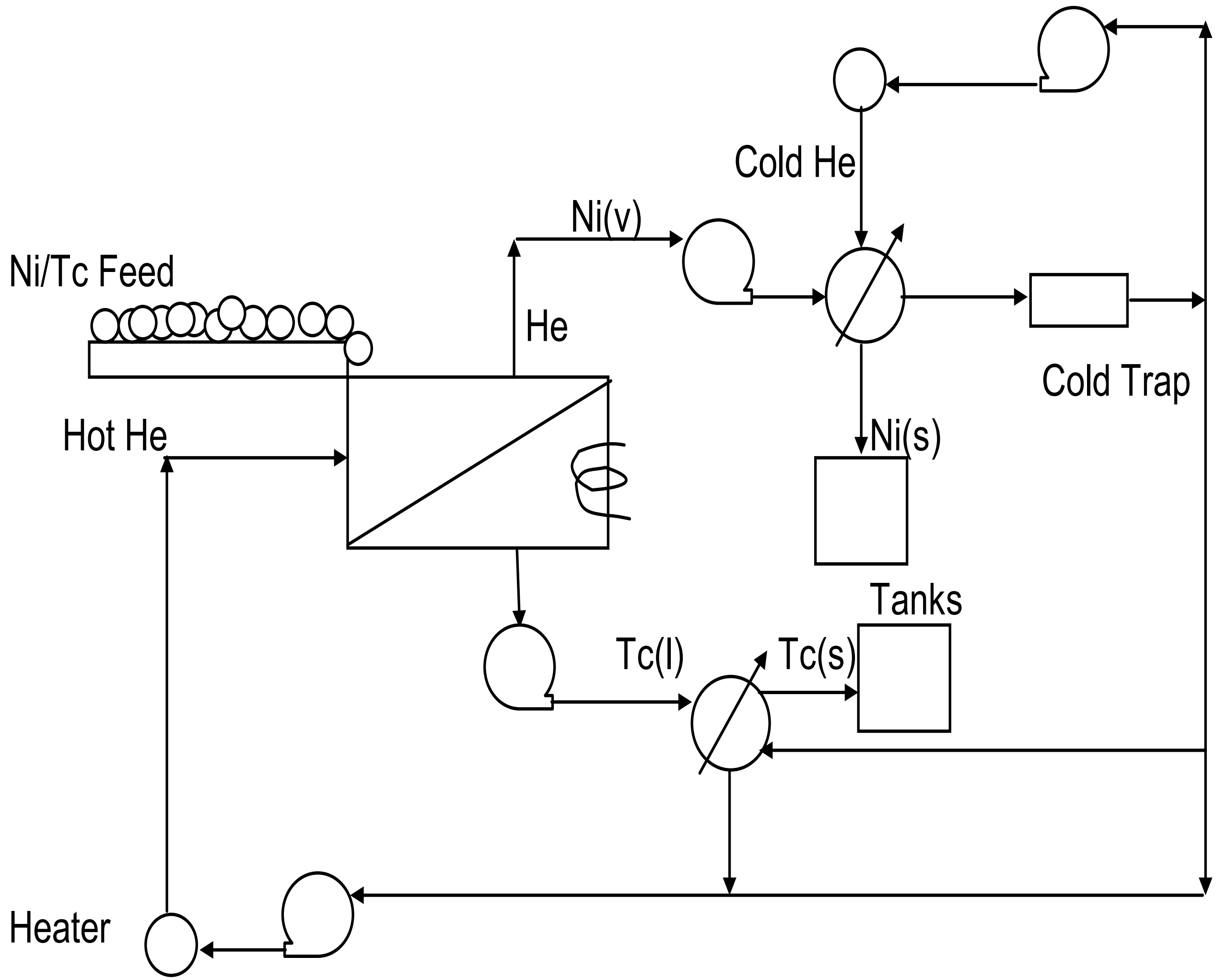
Research objectives

1. analyze the feasibility of separation of Ni-Tc system by thermodynamic modeling
2. design and build an high-T effusion cell mass spectrometer for studying thermodynamic properties of contaminant-metal systems such as Ni-Re and Ni-Tc.
3. Measure the activity coefficients and pure component saturated vapor pressures of the Ni-Tc system (phase diagram construction if appropriate)
4. Evaluate a model system for clarifying feasibility to reduce Tc from 0.1% to below 1 ppb in metal
5. To model and understand the vaporization-condensation kinetics and the effects of materials variables

Task schedule

Task	Status	Comment
1. feasibility	Completed F 05	
2. Design & build high temperature effusion cell	MS portion designed and received, W 06. Knudsen cell received Aug. 06	Numerous design iterations. Construction, calibration to be completed this term
3. Measure vapor pressure, activity coef.	After 2	Estimates are being used to design process
4. Evaluate Re-Ni system, 5. thermo model		May be removed as not essential
6. Process design + economics	Batch distillation options identified	PFD shows critical path needs

1st process concept. Feb. 2005



Crude cost estimate. 1st process concept

	Price($)/kg	mass (kg)	Price ($)
Ni Price/Kg	14.61944	9,699,960	141,807,980
Tc Price/Kg	50,000	40	2,011,780
Ni / Tc		9700000	143,819,760

	Cost($)/kg	Cost($)/Prod	Profit	Savings *	Savings *
Electrolysis					
Ni (1Bq)	**5.61**	**54,417,000**	**87,390,980**	**121,961,780**	**127,43**
Sold Ni & Tc			**89,402,760**	**123,973,560**	**129,44**
Nevada (disposal)	3.564	34,570,800			
Envirocare	4.128	40,041,600			
Our Process					
Ni (>> 1Bq)	**1.14**	**11,021,260**	**130,786,720**	**165,357,520**	**170,82**
Sold Ni & Tc			**132,798,500**	**167,369,300**	**172,84**

* Disposal at Nevada
** Disposal at Envirocare

Metal distillation

- First reported in 1935
- Prior art available; applications include magnesium alloys

Batch or differential distillation.

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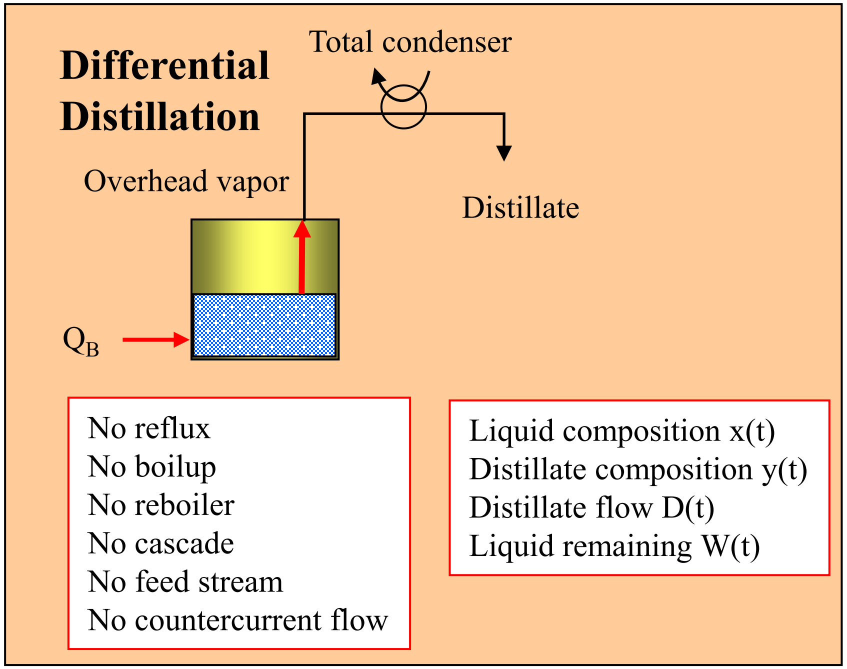


Batch distillation for metal separations

Reason	**Application to metal separations**
Small capacity does not merit continuous operation	Small materials lots, variable contamination levels, simple apparatus; expensive materials of construction; delicate equipment (ceramics)
Separation is needed occasionally	Work-away of samples with different levels of contamination
Separation produces a new product	Each purified batch can be certified for Tc level
Upstream operations are batchwise or feedstocks vary	If solids are loaded directly, batch operation is required; premelt can be loaded directly

Operation of a batch still

- Material is charged and brought to separation conditions
- Material may be liquid or solid
- Vapor is generated continuously and collected
- Metals may be condensed on plates in the vapor stream (prior art, old patents)
- Reboiler and overheads compositions change continuously – not a steady-state operation

Batch still design

Design basis and constraints

Design equations

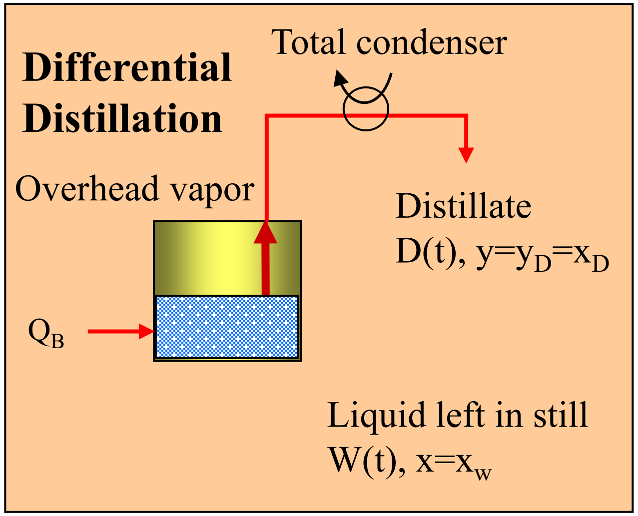
The rate of depletion of the liquid is equal to the rate of distillate output

$$-\frac{d}{dt}\left(Wx_W\right) = -W\frac{dx_W}{dt} - x_W\frac{dW}{dt}$$

Change in total amount of that component in the liquid

Change in composition in the liquid

Change in the total amount of the liquid



The distillate composition and liquid composition are related through an equilibrium equation (y=kx). Integrating:

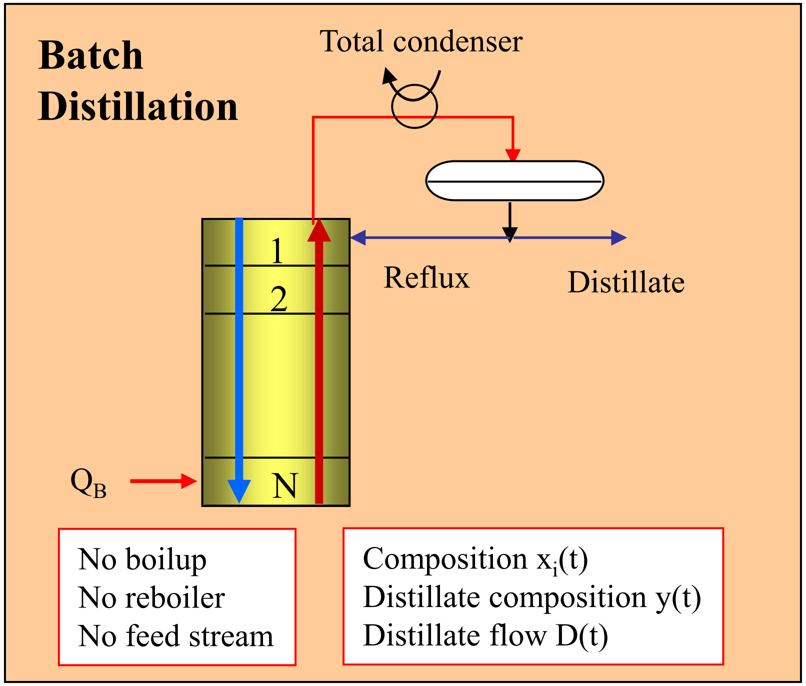
$$\frac{1}{(\alpha-1)}\left[\ln\frac{x_0}{x} + \alpha\ln\frac{(1-x)}{(1-x_0)}\right] = \ln\frac{w_0}{w}$$

Batch still with reflux

Two alternative batch designs for higher purity products:

•Batch rectification with constant reflux - distillate composition has higher purity but still varies with time

•Batch rectification with variable reflux – reflux conditions are varied continuously to achieve constant composition distillate



The second technique, variable reflux, would be preferred as a product with constant Tc^{99} levels could be produced. However, the need for liquid condensation and recycle imposes complexity and equipment costs that probably are not needed now.

Design Basis

- Feed: 10 ppm Tc^{99} in nickel
- Regular solution theory for metal solutions
- For this problem, the activity coefficient for nickel is one, and that of Tc^{99} is assumed to be 5.

$$y_i \cdot P = p_i = \gamma_i \cdot x_i \cdot P_i^{sat}$$

$$P = p_{Ni} + p_{Tc}$$

$$\alpha_{Ni,Tc} = \frac{\gamma_{Ni}}{\gamma_{Tc}} \cdot \frac{P_{Ni}^{sat}}{P_{Tc}^{sat}}$$

$$\lim \alpha_{Ni,Tc}\, x \longrightarrow 0 = \frac{\gamma_{Ni}^{\infty} \cdot P_{Ni}^{sat}}{P_{Tc}^{sat}}$$

$$\lim \alpha_{Ni,Tc}\, x \longrightarrow 1 = \frac{P_{Ni}^{sat}}{\gamma_{Tc}^{\infty} \cdot P_{Tc}^{sat}}$$

Design basis, cont'd.

Component	Tm, K	Tb, K
Nickel	1728	2415
Technetium	2430	5000

Operate the process in the range between the melting and boiling point of nickel

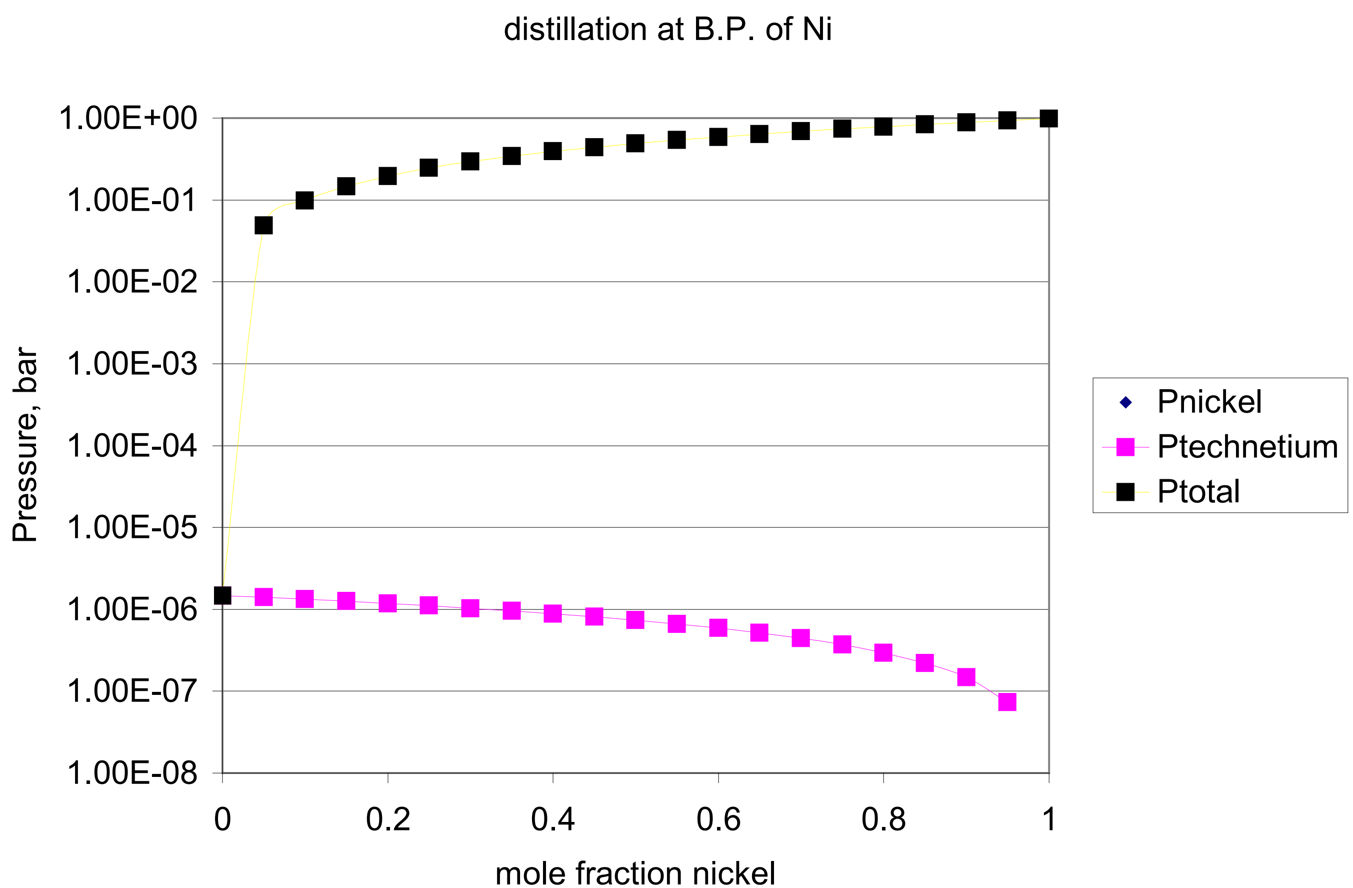
The relative volatility can be taken as constant, near that of pure nickel (x_{Ni} goes to 1). Initial design done for T = 2415 K.

Relative volatility	1730 K	2415 K
x_{Ni} goes to 0	$2.7 * 10^9$	$3.3 * 10^6$
x_{Ni} goes to 1	$5.4 * 10^8$	$6.7 * 10^5$

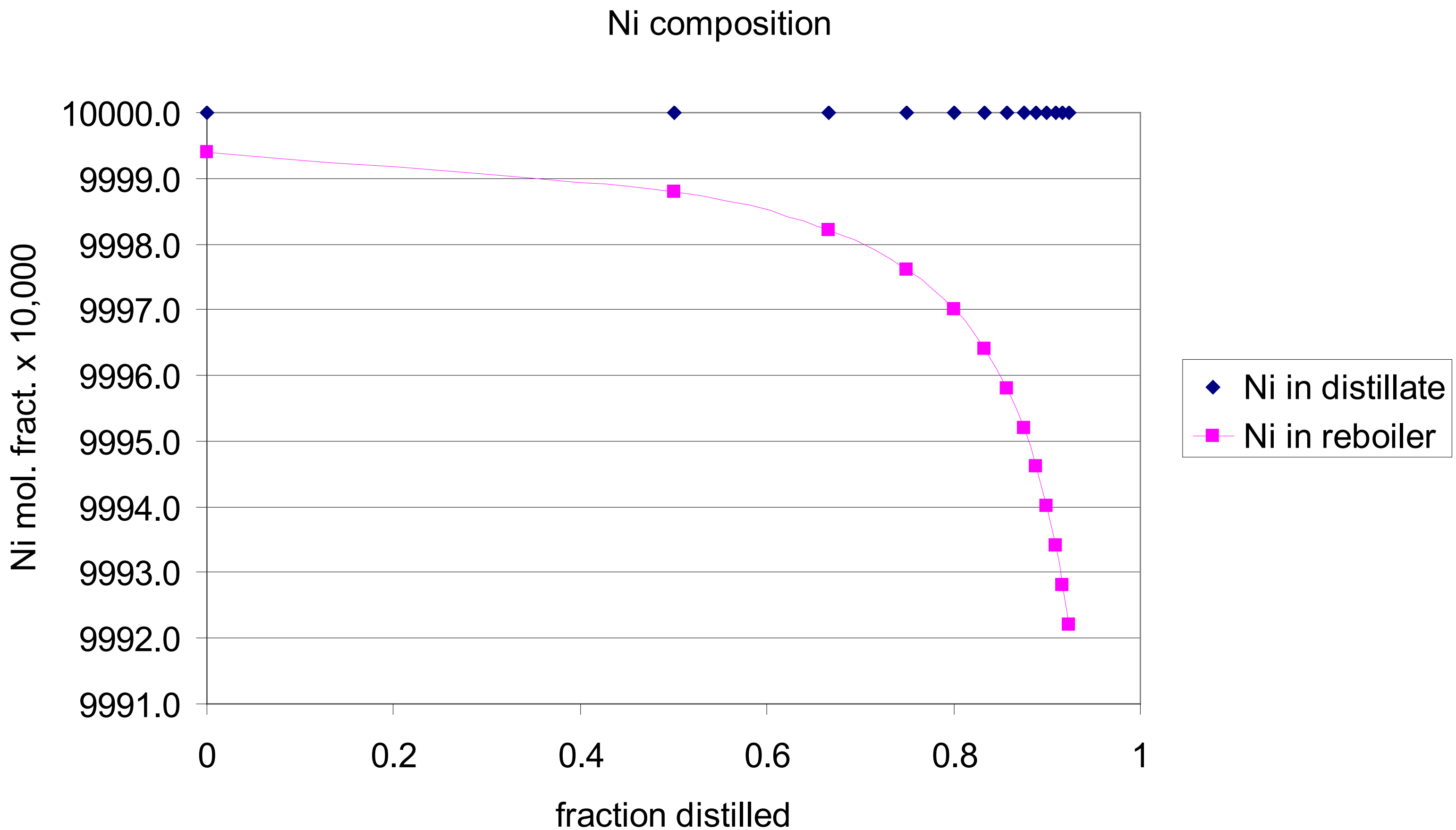
Batch distillation design

$T_{process}$ = 2415 K

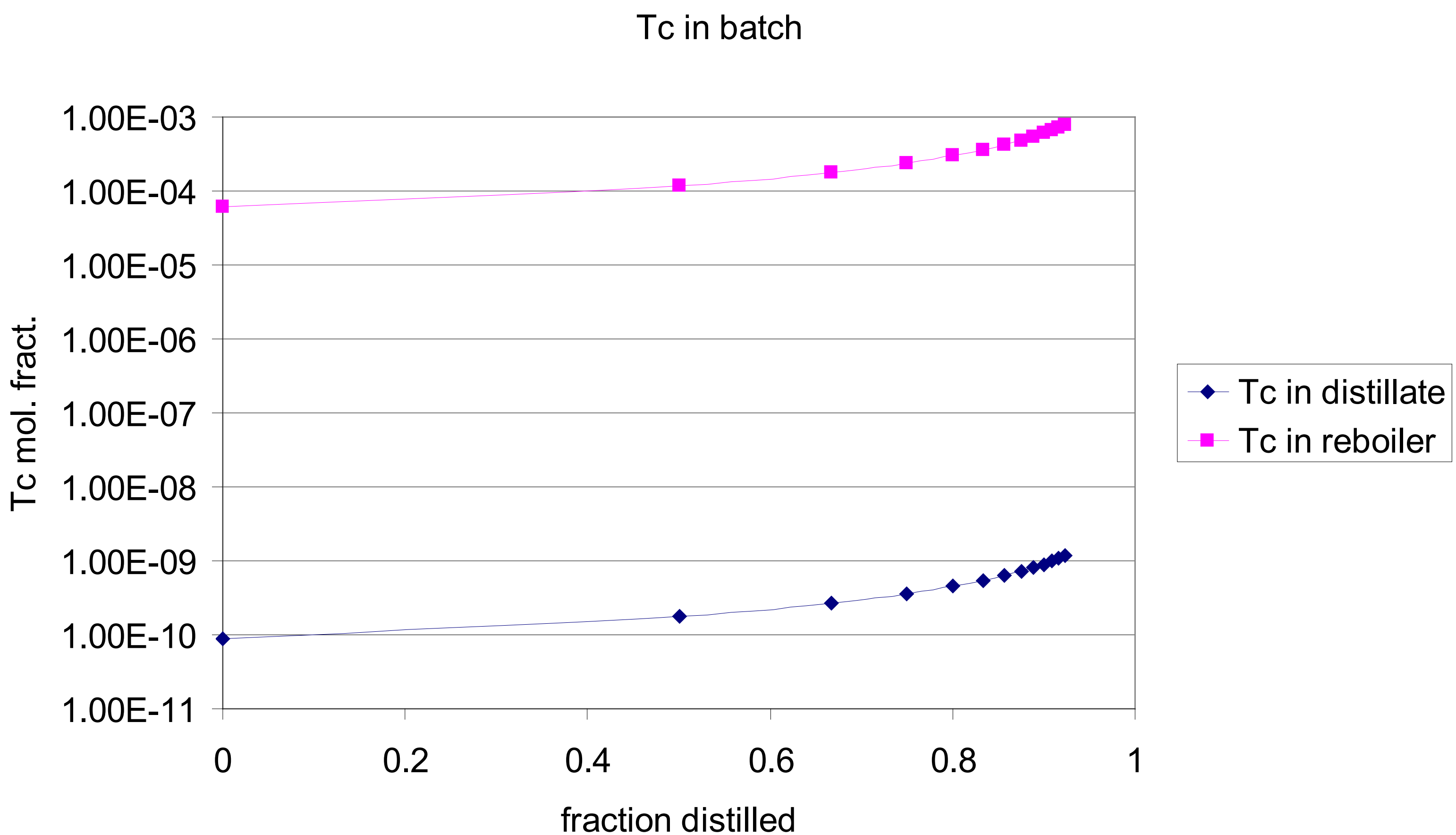
Total P


distillation at B.P. of Ni
Pressure, bar
1.00E+00
1.00E-01
1.00E-02
1.00E-03
1.00E-04
1.00E-05
1.00E-06
1.00E-07
1.00E-08
0
0.2
0.4
0.6
0.8
1
mole fraction nickel
Pnickel
Ptechnetium
Ptotal

Ni levels, reboiler & overheads



Tc^{99} levels, reboiler & overheads



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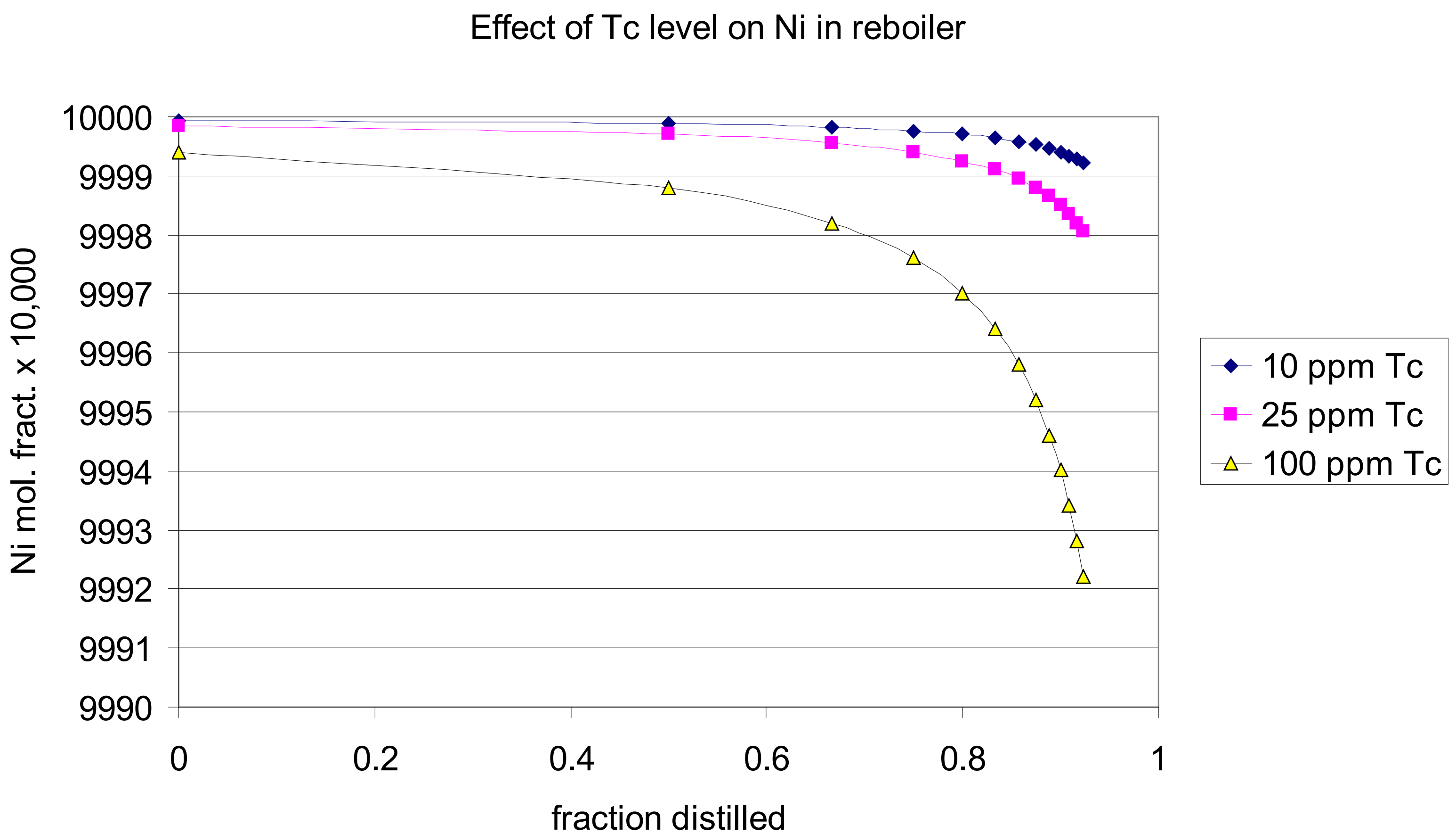
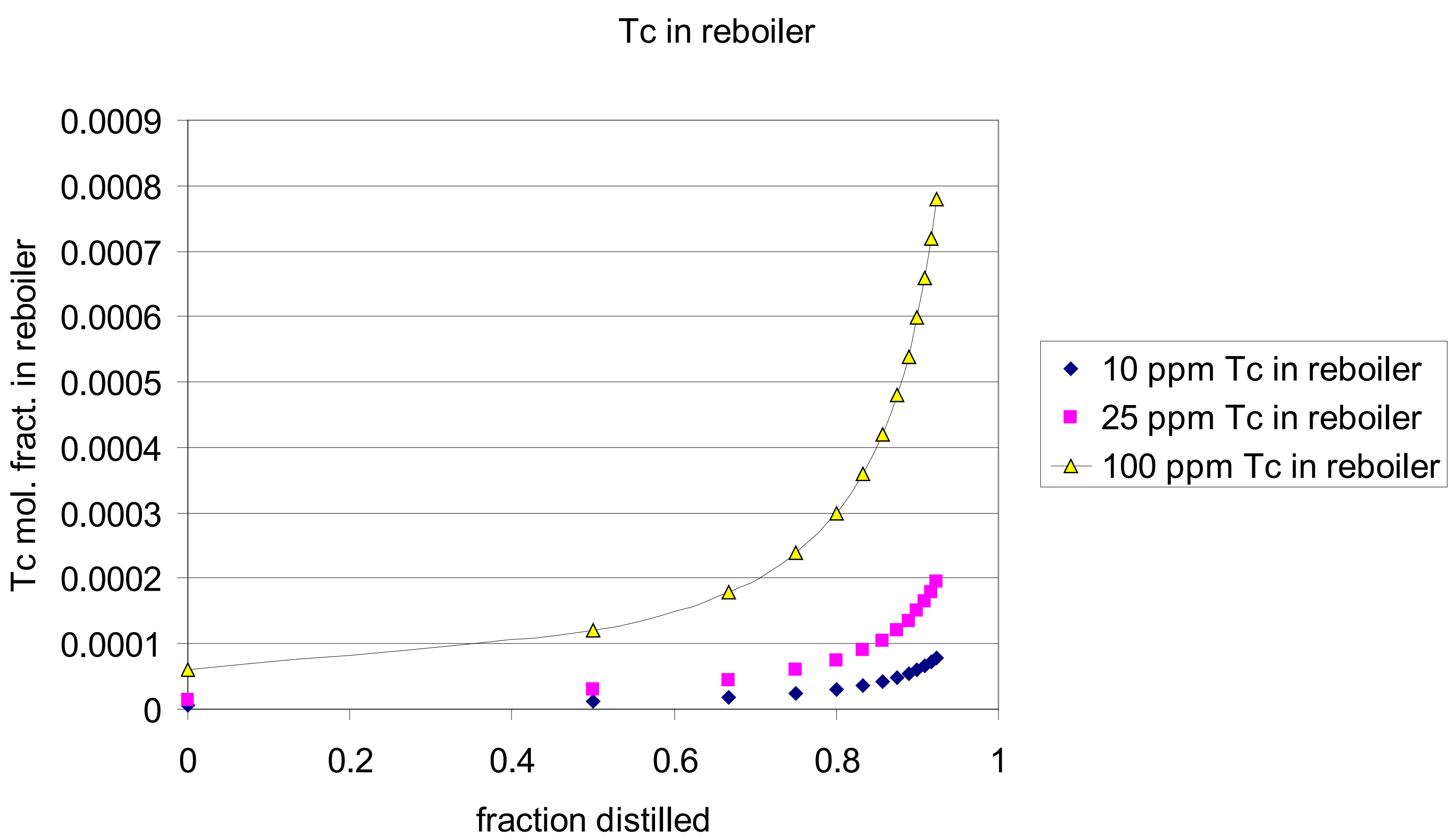
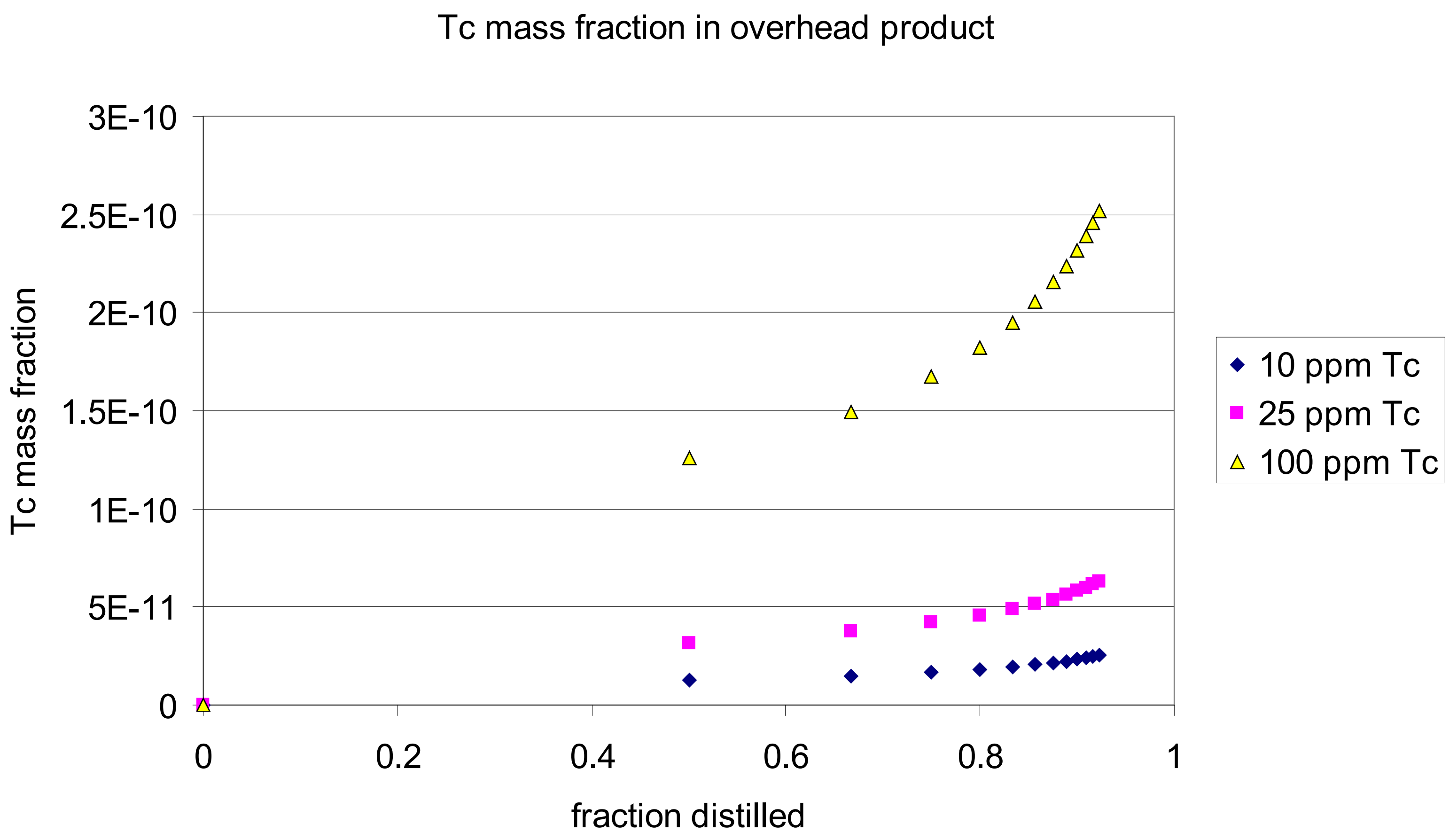
Ni in reboiler, various feeds



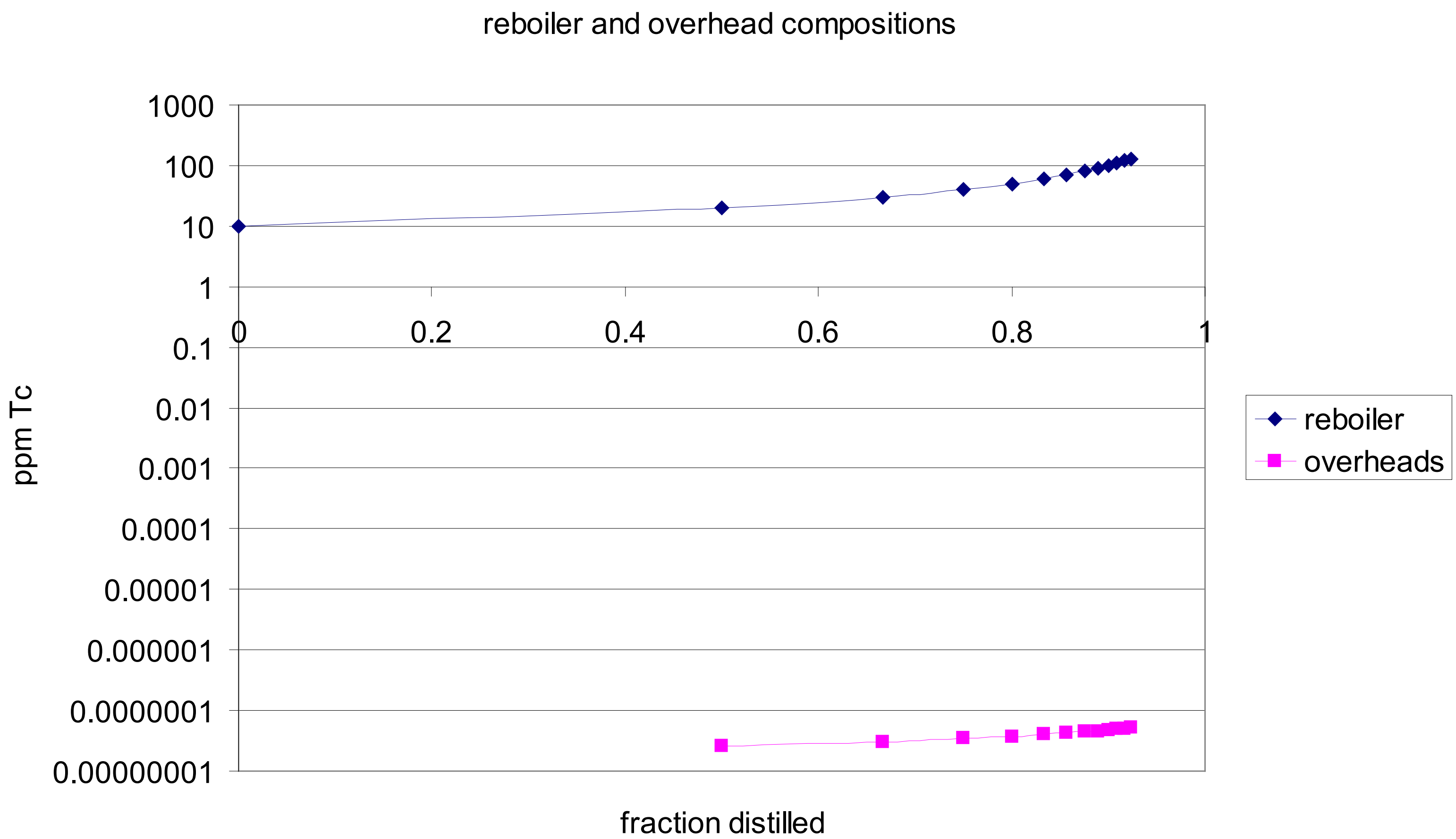
Tc^{99} in reboiler, various feeds



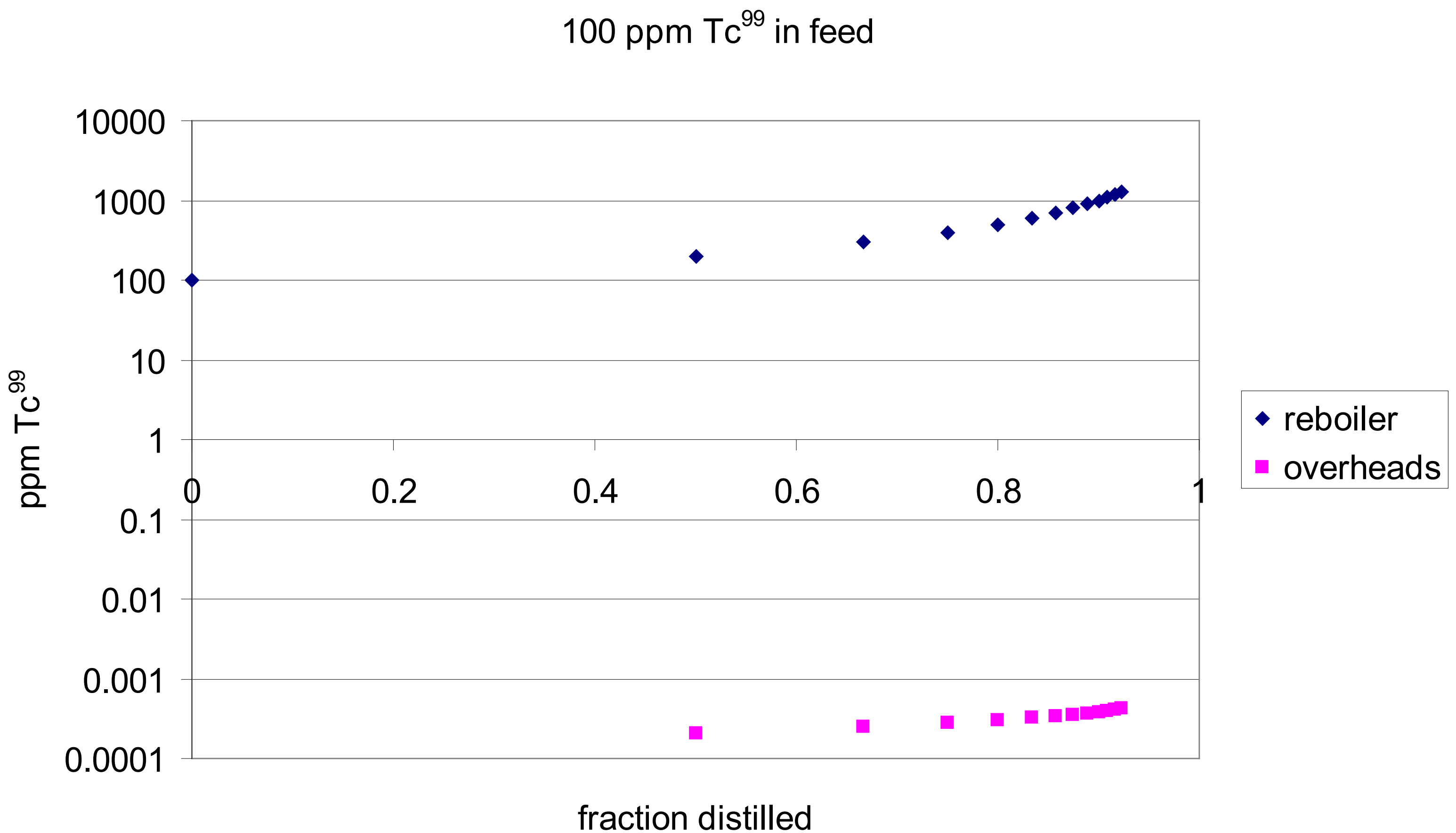
Tc^{99} in nickel product



10 ppm Tc^{99}, 2415 K



100 ppm Tc^{99}, 2415 K



Intermediate conclusions

- Separation should be excellent, even near the boiling point of nickel
- Lower temperatures would improve the separation significantly
- Large excursions in Tc^{99} levels in the feed should be managable
- Fluid flow must minimize droplet formation and carryover

Process options

T, K	P_{Ni}, bar	P_{Tc}, bar	P_{Ni} /P_{Tc}	
1700	0.0017	2.08E-12	8.17E+08	Air sweep?
1800	0.0057	2.60E-11	2.19E+08	
1900	0.017	2.50E-10	6.80E+07	High vacuum
2000	0.044	1.94E-09	2.27E+07	
2100	0.105	1.23E-08	8.54E+06	Inert gas sweep
2200	0.23	6.60E-08	3.48E+06	Low vacuum
2300	0.476	3.03E-07	1.57E+06	
2400	0.893	1.21E-06	7.38E+05	
2415	0.985	1.47E-06	6.70E+05	Atmospheric operation

Materials of construction: zirconia – to 2700 K; alumina to 2200 K; commercial alumina to 1900 K.

Process options, cont'd.

Method	T, K	Vapor Flow	Comments
1. Atmospheric distillation	2415	Pressure-driven flow from reboiler	Pure Tc melts at 2430 K; no vacuum or inert flow is needed; ZrO2 as material of construction?
2. Low vacuum distillation	2100	P_{Ni} = 0.23 bar	Inductor-type system used to generate low vacuum
3. High vacuum distillation	1900	P_{Ni} = 0.017 bar	Probably needs primary and secondary vacuum systems
4. Sweep gas	1730	P_{Ni} = 0.0025 bar	Nitrogen (recycled?), or possibly, air. Lowest possible temperature; assume that metal reaches 1/3 of its saturation pressure in the gas; lance or sweep over liquid surface; alumina materials of construction to 1750 C.
5. Continuous flash system with sweep gas	1730		Low liquid feed rate and removal; high gas sweep rate with condensation of nickel on nickel screens or plates in vapor effluent

Items in blue analyzed by batch distillation model

Experimental tasks, scale-up

- Key data is for vapor pressures and activity coefficients at low (1730 K) temperatures
- Process cost estimate
- Materials of construction are critical
- Equipment should be simple, including vacuum systems and valving; some prior art on vacuum distillation
- Process monitoring and control

Fall 06 schedule

- Assemble cell and get low temperature data
- Process designs
- Consult on materials of construction (Ceradyne, Precision Metals)
- IP submissions
- Prototype and proof of concept