Chemistry Aspects of the WTP Criticality Safety Analysis

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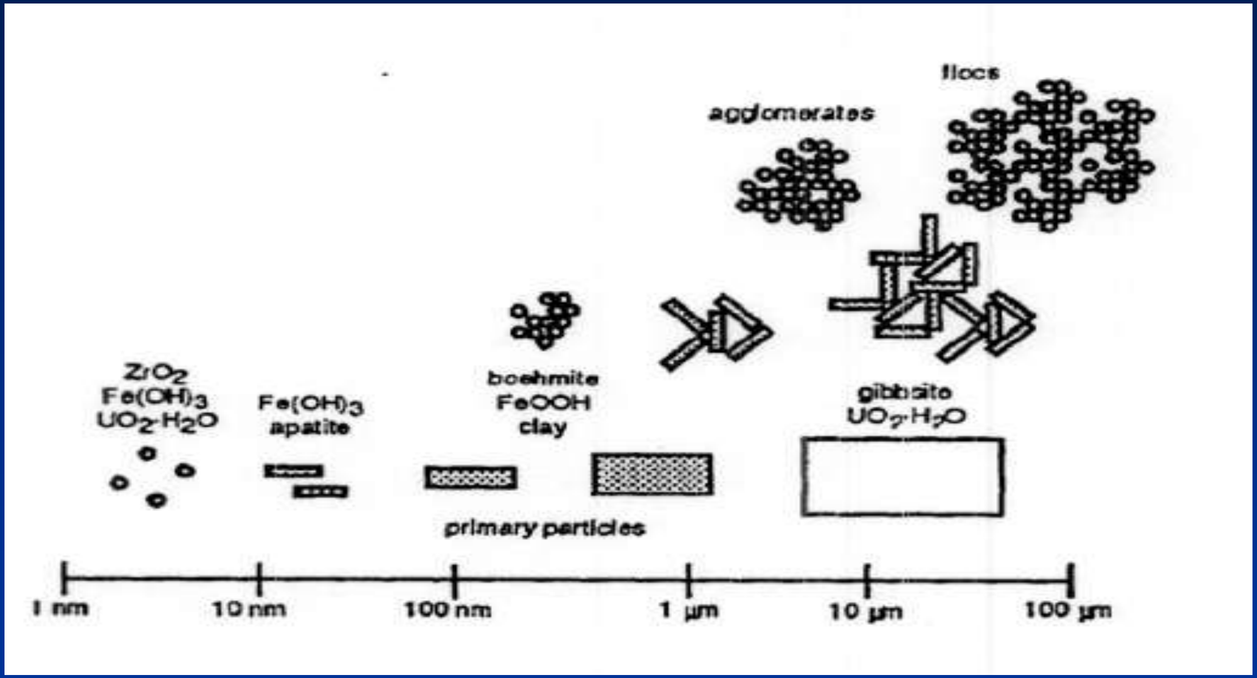
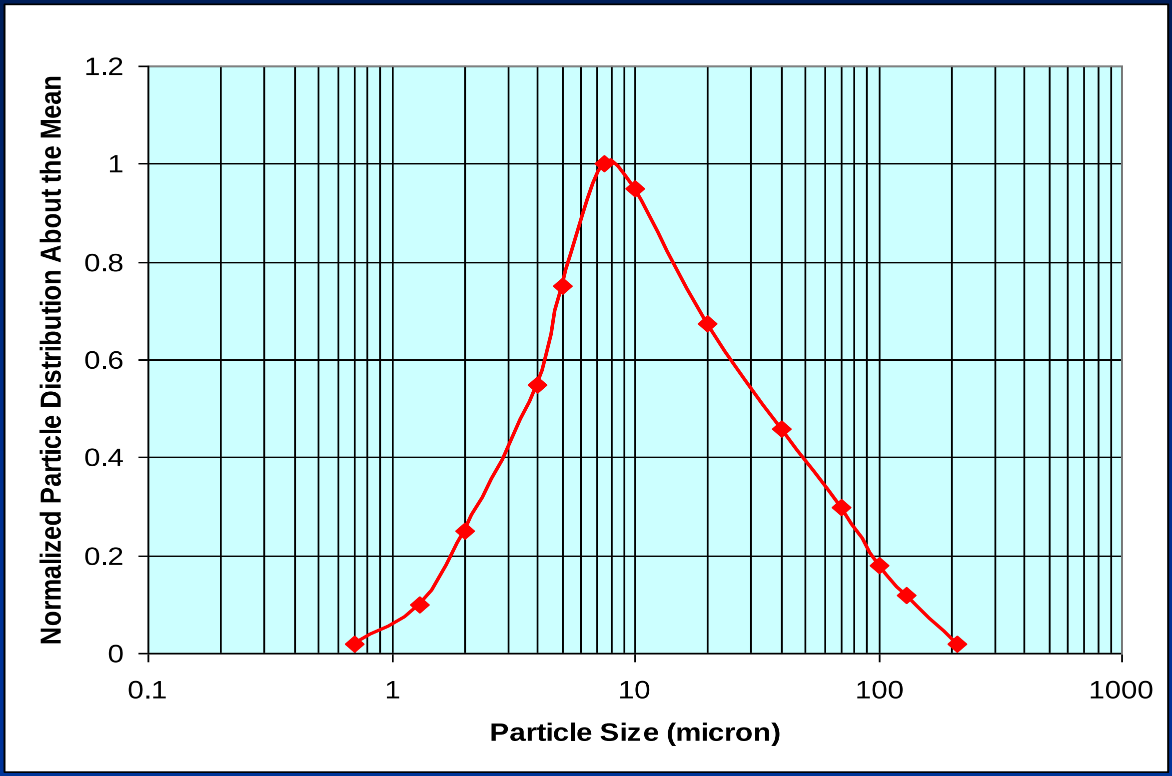
Characteristics of the WTP Waste



- Most sludge consist of 1 to 10 µm agglomerates of submicron primary particles that will readily break apart when exposed to pump and pulse jet mixer (PJM) action
- Smaller particles tend to Fe hydroxides
- Larger particles tend to be Al hydroxides
- Most of the Pu co-precipitated with Fe, Ni, and Mn when the tank farm waste was made caustic.
- Al particles are not known to contain Pu

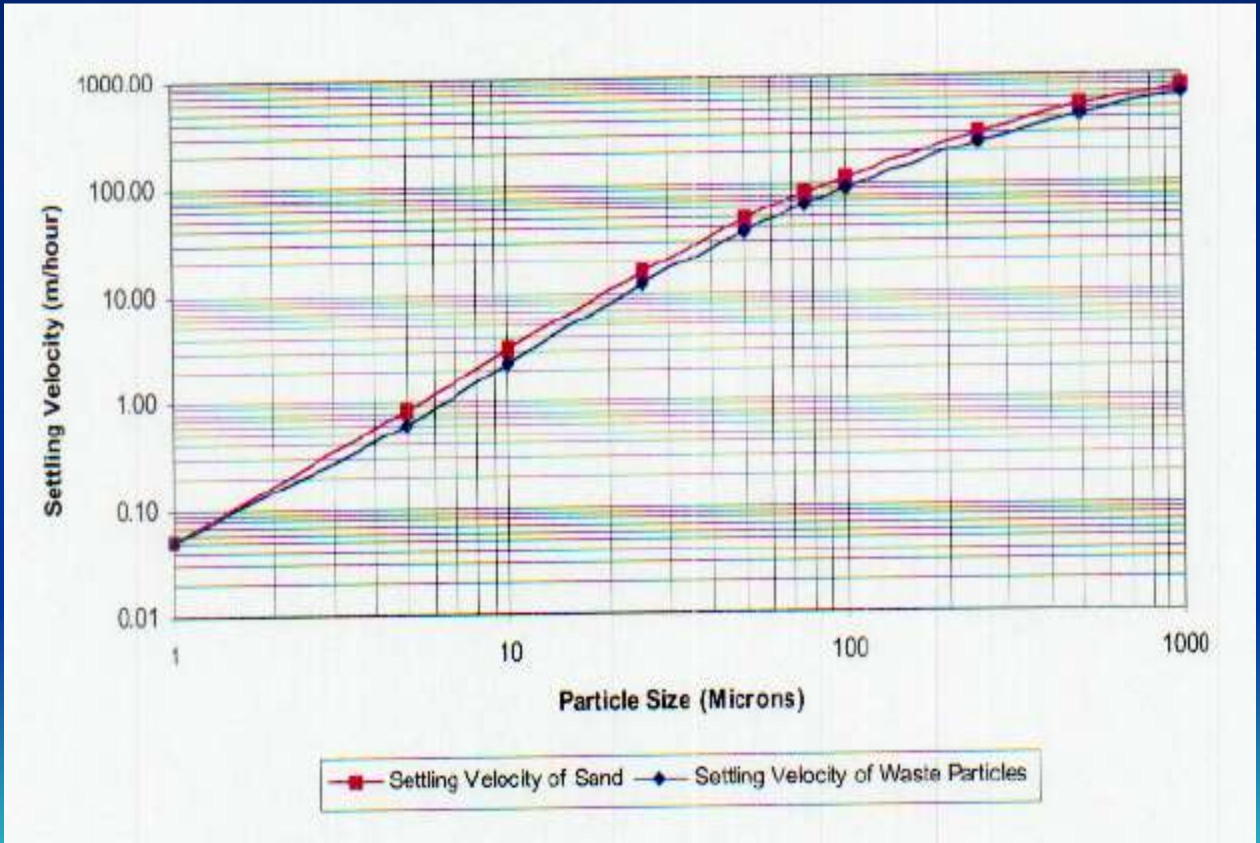
Particle Size Distribution of Hanford Tank Farm Waste



- Fe hydroxide particles which carry most of the Pu is expected to be among the smaller particles < 5 microns.

Fe hydroxides containing most of the Pu has slow settling velocities

~ 0.5 m/hr or 1 inch per minute



Expected Average Composition of Waste Received at WTP

Molecular Formula	Mass (%)	Molecular Formula	Mass (%)
$Al(OH)_3$	56.4	$Mn(OH)_2$	0.68
$NaAlSiO_4$	11.1	$Mn_3(PO_4)_2$	0.26
FeOOH	8.2	$MnCO_3$	0.086
$NaAlCO_3(OH)_2$	7.8	SiO2	0.61
$Na_2U_2O_7$	3	$Ni(OH)_2$	0.74
CrOOH	2.7	NiC_2O_4	0.023
Bi_2O_3	2.2	$Ni_3(PO_4)_2$	0.01
ZrO_2	2.1	$Pu(OH)_4$	0.0058
$Ca_5OH(PO_4)_3$	2	Total	97.91
		Pu/metal	0.5

- This data shows that there are many absorbers that are mixed with WTP waste that can be used to control the reactivity of fissile Pu and U.
- Wash/leach removes a large fraction of the Al, Na, and Cr
- Wash/leach has little effect on Fe, Mn, Ni, Cd, and Pu
- A typical density of the liquid phase is 1.35 g/cc (indicating large amounts of dissolved ions)

The CSER relies upon Pu/metal ratios for criticality safety of the WTP waste

- Mass, geometry, volume, moderation, reflection are not practical because of the presence of large vessels.
- Fissile uranium/U-238 mass ratio is used to ensure safety of fissile uranium.
- CSL 1 Pu/{Fe + 1.66*Ni} < 6.2 g/kg (solids)
- CSL 2 Pu/{Fe + 1.66*Ni +5.4*Mn + 153*Cd} < 6.2 g/kg) (liquids)
- The values of 1.66, 5.4, and 153 are multipliers to adjust the absorbers of Ni, Mn, and Cd to an Fe equivalent mass.
- The presence of other absorbers such as Al and Zr hydroxides provide defense in depth through absorption and by ensuring a high Pu/H atom ratio even under dry out conditions.

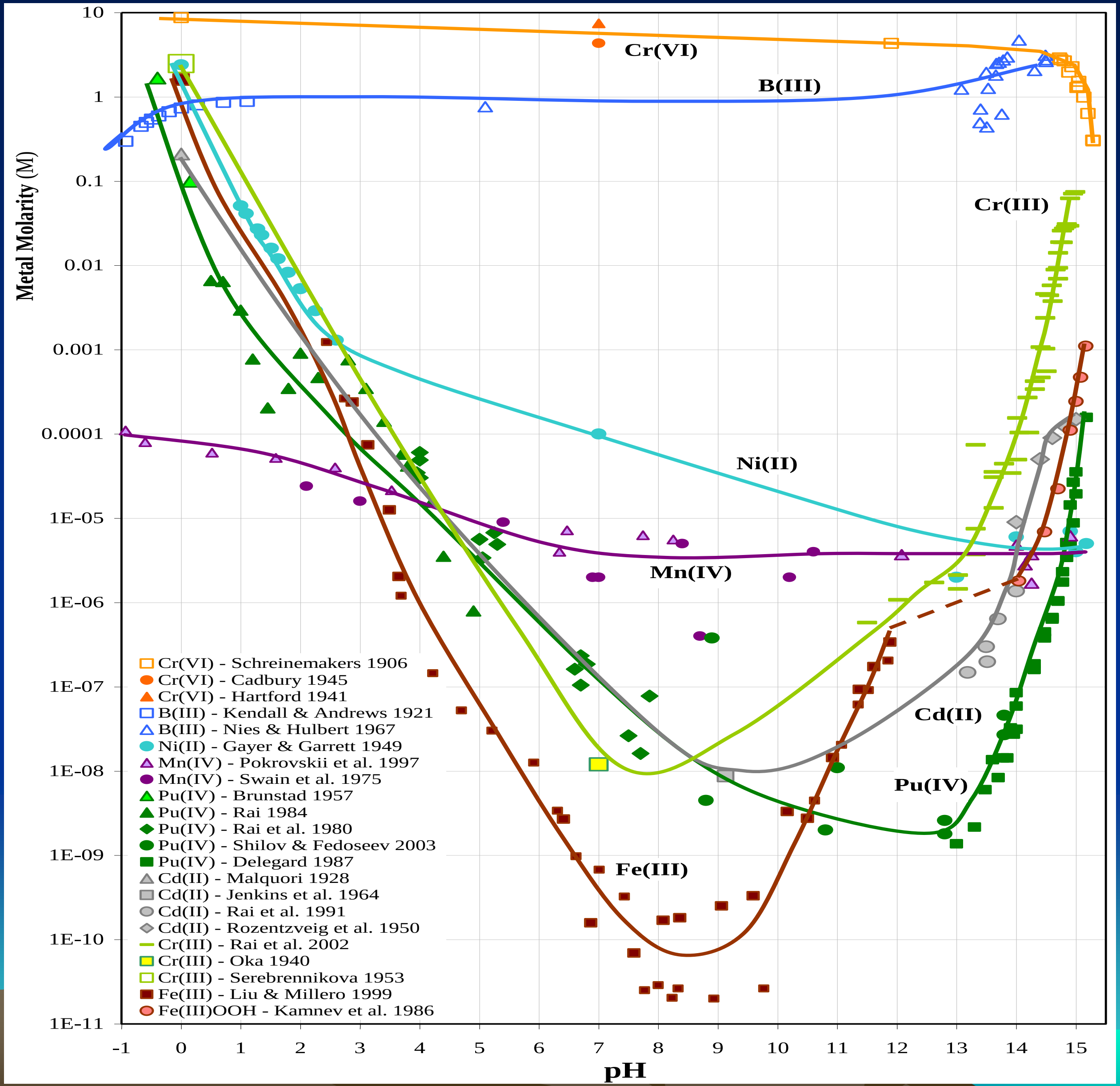
A concern identified through a hazard analysis was the potential for transitions that could change the Pu/metal ratios (solid/liquid and liquid/solid).

Four processes were identified to have this potential

- Carbonate addition
- Caustic wash/leach
- Oxidative wash leach
- Acid addition

These Transitions Were Evaluated by:

- Research into the scientific literature
- Collecting solubility data for Pu and the absorbers of interest.
- Applying the solubility data to determine the effect of solubility vs. pH on compliance with the CSLs
- Solubility data is illustrated in the following figure



Metal Molarity (M)
10
1
0.1
0.01
0.001
0.0001
1E-05
1E-06
1E-07
1E-08
1E-09
1E-10
1E-11
pH
-1
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Cr(VI)
B(III)
Cr(III)
Ni(II)
Mn(IV)
Cd(II)
Pu(IV)
Fe(III)
Cr(VI) - Schreinemakers 1906
Cr(VI) - Cadbury 1945
Cr(VI) - Hartford 1941
B(III) - Kendall & Andrews 1921
B(III) - Nies & Hulbert 1967
Ni(II) - Gayer & Garrett 1949
Mn(IV) - Pokrovskii et al. 1997
Mn(IV) - Swain et al. 1975
Pu(IV) - Brunstad 1957
Pu(IV) - Rai 1984
Pu(IV) - Rai et al. 1980
Pu(IV) - Shilov & Fedoseev 2003
Pu(IV) - Delegard 1987
Cd(II) - Malquori 1928
Cd(II) - Jenkins et al. 1964
Cd(II) - Rai et al. 1991
Cd(II) - Rozentzveig et al. 1950
Cr(III) - Rai et al. 2002
Cr(III) - Oka 1940
Cr(III) - Serebrennikova 1953
Fe(III) - Liu & Millero 1999
Fe(III)OOH - Kamnev et al. 1986

Solubility data help one to understand the effects of processes such as caustic leach or acid addition.

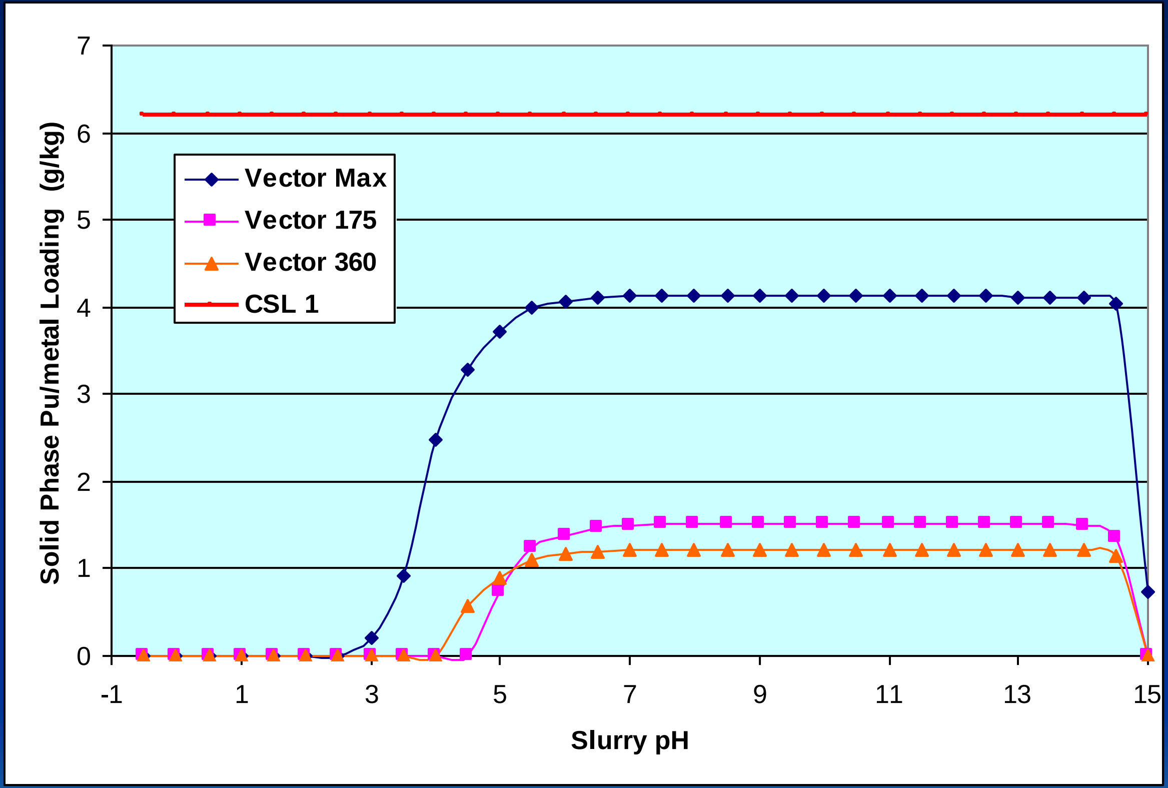
- Carbonate addition - reduces pH
- Caustic wash/leach - increases pH
- Oxidative wash leach - Pu(IV) to Pu(V)
- Acid addition - lowers pH
- Solubility can be used to predict compliance with CSL 1 and CSL 2 over a wide range of pH values.

Compliance of the waste with the CSL limits depends on:

- Solubility vs. pH
- How the Pu is bound to other absorbers (conservative to assume Pu is not bound to absorbers)
- Total mass of Pu and absorbers in a waste batch (can’t dissolved a mass of absorbers greater than the inventory in the waste)

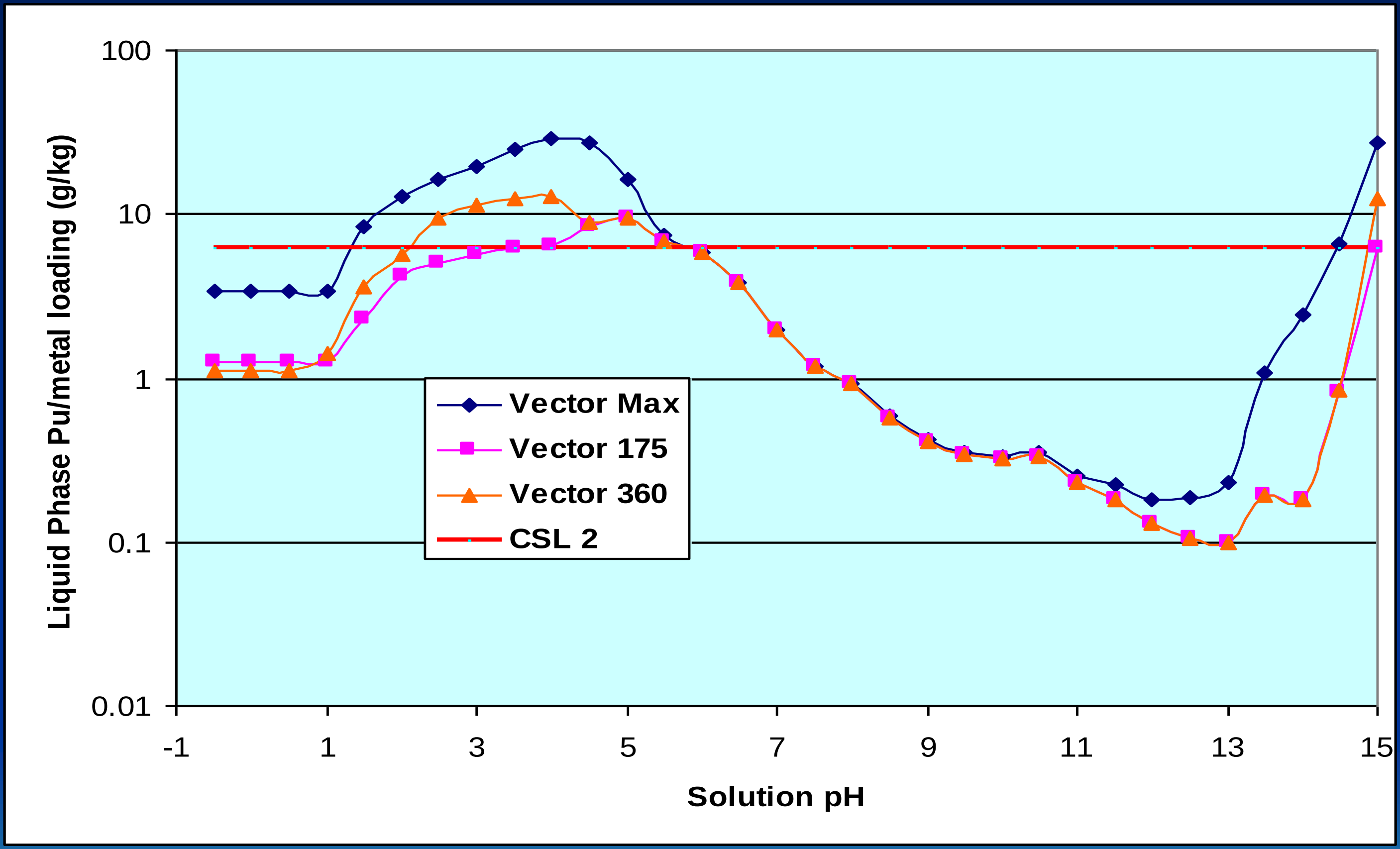
Using these constraints all of the WTP feed vectors have been evaluated over the full range of pH values to predict compliance with the CSL limits as a function of pH

Results for solids using current CSL limits



- Figure 2 Pu/metal loading in the solid (slurry) as a function of pH

Results for liquids using current CSL limits



- Figure 3 Pu/metal loading in the liquid as a function of pH

Issues associated with these results

- Liquid phase can exceed the CSL for pH values between 2 and 6 and >14.
- The predicted Pu/metal loading values for the solids are too high when the large uncertainties associated with HTF Best Basis Inventories is considered.

A possible solution is to credit more absorbers in the CSL limits.

Extend the list to Fe, Mn, Ni, Cd, B, and Cr and apply to both the solid and liquid phases.

Results of extension for the solids

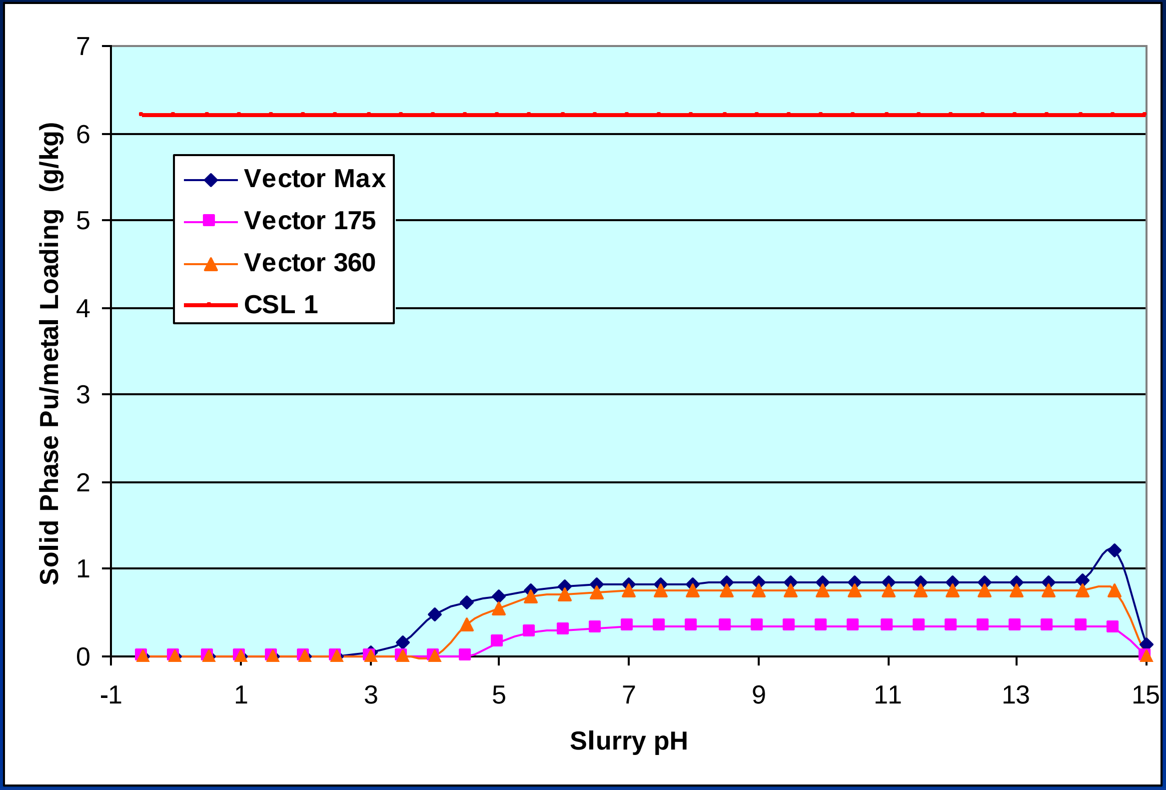


Figure 4 Pu/metal loading in the solids as a function of pH

(Absorbers credited are Fe, Mn, Ni, Cd, B, and Cr.)

Results of extension for the liquids

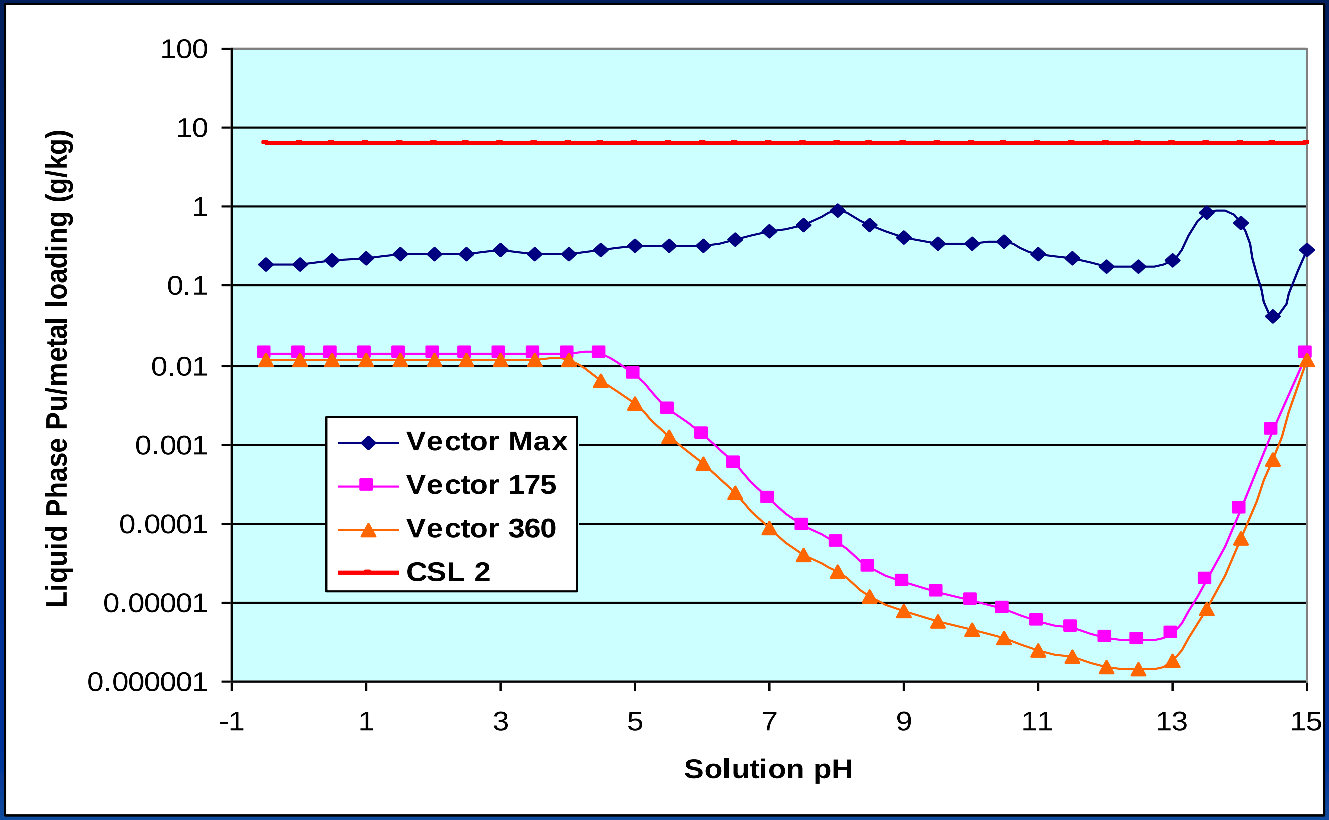


Figure 5 Liquid phase Pu/metal loading (g/kg)

(Absorbers credited are Fe, Mn, Ni, Cd, B, and Cr.)

Conclusions

- Margin of compliance with the solid phase CSL can be increased sufficiently to account for current uncertainty in BBI data.
- Margin of compliance for the liquid phase CSL is large and will be increased even more by oxidative leach which dissolves Cr.
- The Pu/metal loading for the solid phase is remarkably constant over a wide range of pH values.
- Other issues still remain such as possible settling of large Pu oxide particles on the bottom of WTP vessels. This will require more test and/or analysis of existing data.