Labile U(VI) and Progress Toward a Generalized Surface Complexation Model

J. A. Davis, D. L. Bond, and P. Fox

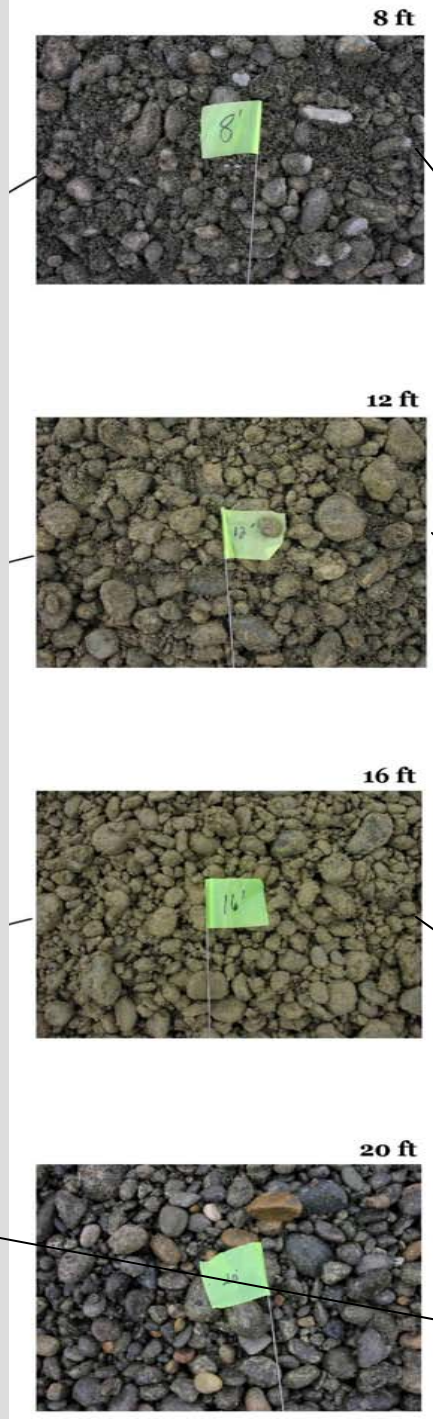
EMSL, May 2004

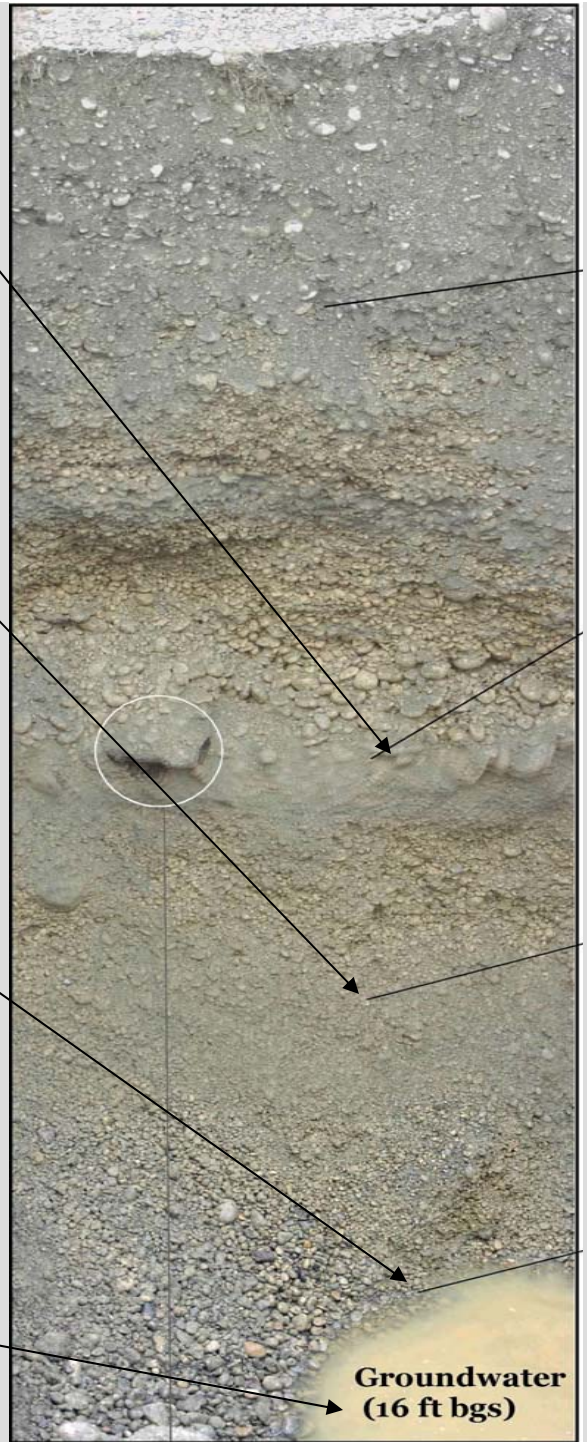
NPP Pit #1

Samples studied:
<2 mm size fraction of sediments 8, 12, 16, and 20 ft below ground surface and fines suspended in the groundwater

Surface areas of <2 mm samples:
8 ft – 19.9 m^2/g
12 ft – 27.2 m^2/g
** 16 ft – 27.2 m^2/g
20 ft – 17.5 m^2/g
Fines – 46.9 m^2/g

Photos from Bruce Bjornstad, PNNL



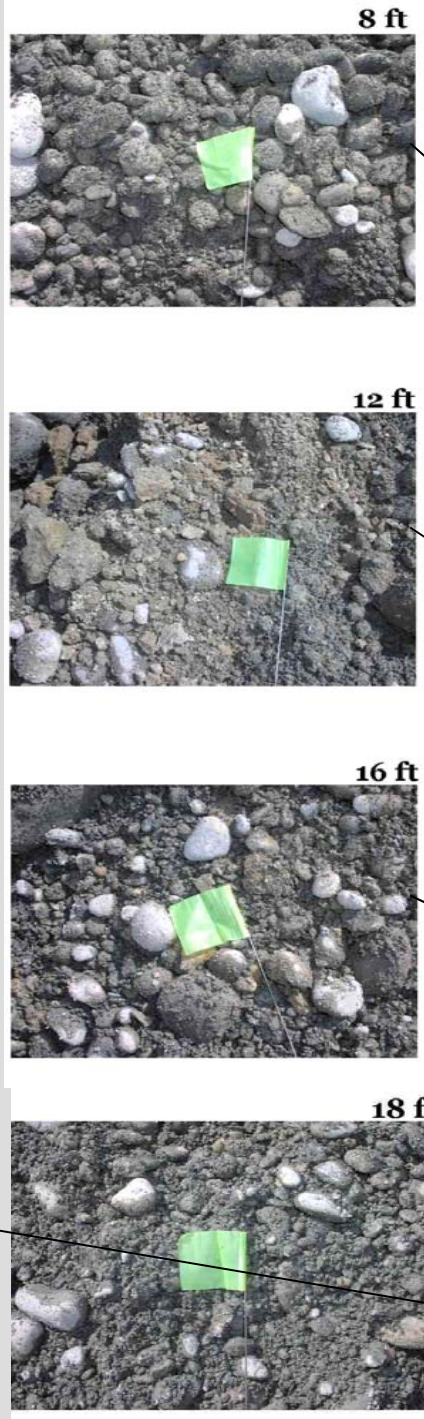


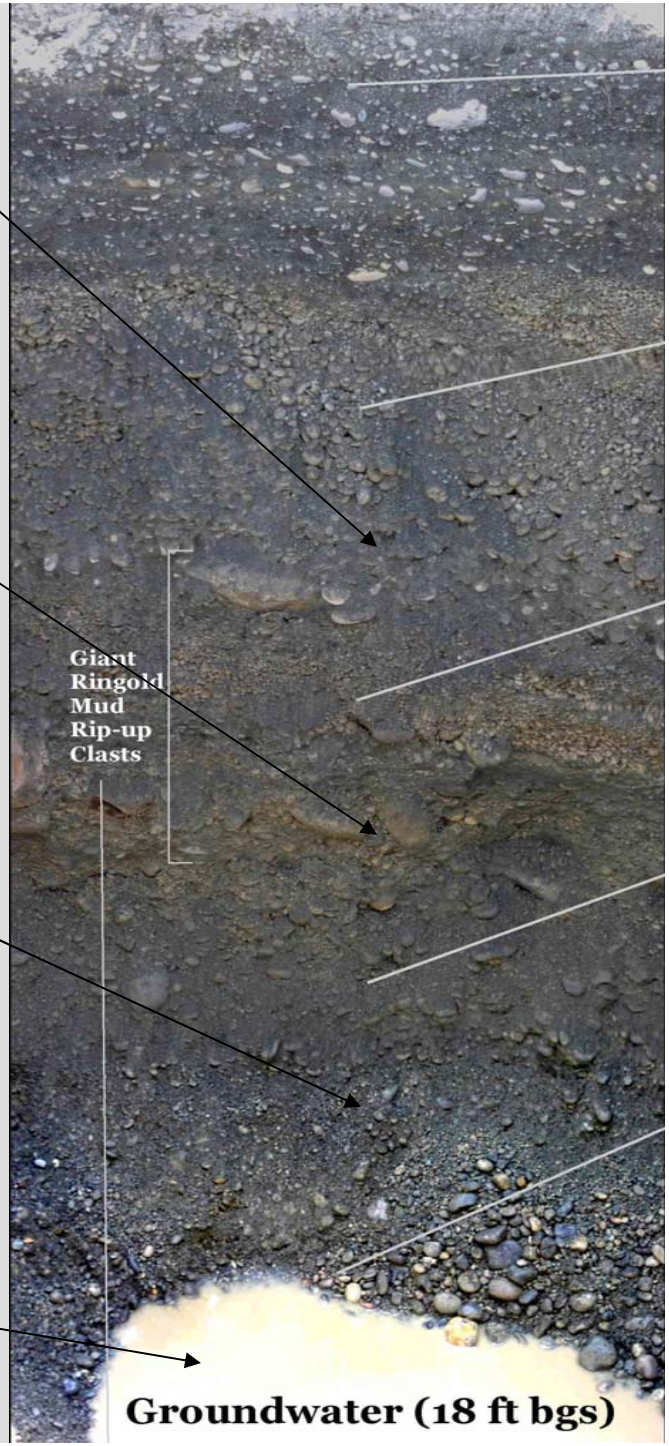
SPP Pit #2

Samples studied:
<2 mm size fraction of sediments 8, 12, 16, and 18 ft below ground surface and fines suspended in the groundwater

Surface areas of <2 mm samples:
8 ft – 17.7 m^2/g
12 ft – 15.9 m^2/g
16 ft – 15.5 m^2/g
**18 ft – 15.3 m^2/g
Fines – 40.5 m^2/g

Photos from Bruce Bjornstad, PNNL





NPP Pit #2

Samples studied:
<2 mm size fraction of sediments 2, 4, 8, and 12 ft below ground surface and fines suspended in the groundwater

SPP Pit #1

Samples studied:
<2 mm size fraction of sediments 16, 18, and 22 ft below ground surface and fines suspended in the groundwater

Total of 19 sediment samples studied

Total Uranium in the NPP and SPP sediment samples studied

Sample (<2 mm or fines)	Total U by ^{234}Th gamma counting (ppm)*	Total U by XRF (PNNL) (ppm)
NPP-1-8 ft	10.5	12.9
NPP-1-12 ft	14.0	20.5
NPP-1-16 ft	9.6	11.1
NPP-1-20 ft	6.3	11.2
NPP-1-GW fines	21.2	33.3
NPP-2-2 ft	106	89.2
NPP-2-4 ft	100	139
NPP-2-8 ft	39.8	44.7
NPP-2-12 ft	14.2	15.2
NPP-2-GW fines	157	200
SPP-1-16 ft	7.3	13.6
SPP-1-18 ft	7.4	12.5
SPP-1-22 ft	7.9	6.2
SPP-1-GW fines	31.3	35.0
SPP-2-8 ft	10.8	11.0
SPP-2-12 ft	8.0	12.2
SPP-2-16 ft	3.8	< 5.3
SPP-2-18 ft	2.9	< 5.4
SPP-2-GW fines	13.3	12.7

* U^{238} was determined from measurement of the Th^{234} daughter 63 KeV gamma ray emission line assuming secular equilibrium.

Extractable Uranium in the NPP and SPP sediment samples

*** Carbonate extraction:**
0.014M $NaHCO_3$
0.003M Na_2CO_3
Initial pH 9.45
1000 hours

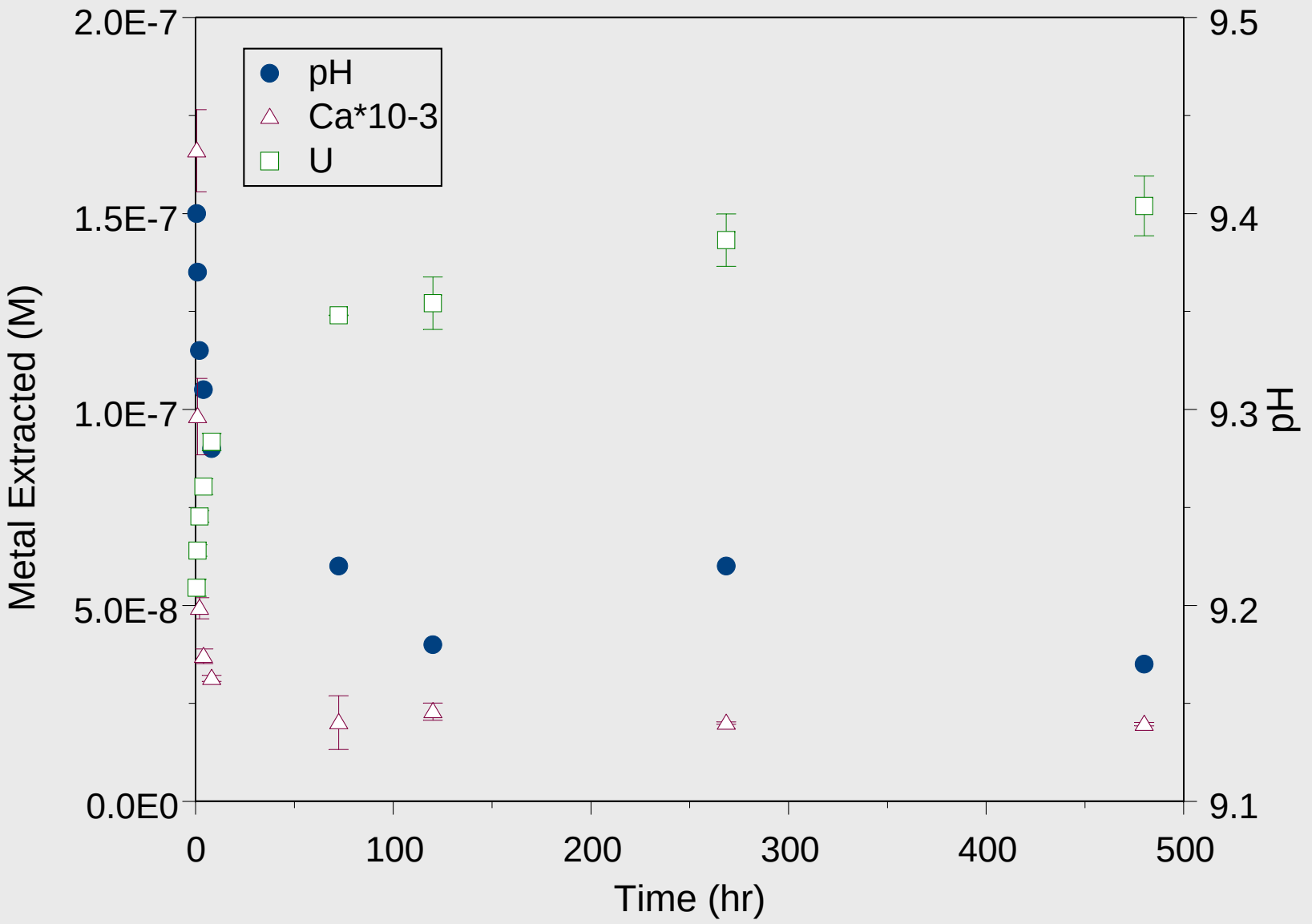
Defined as labile U(VI)

**** Hydroxylamine Hydrochloride acid extraction, 72 hours**

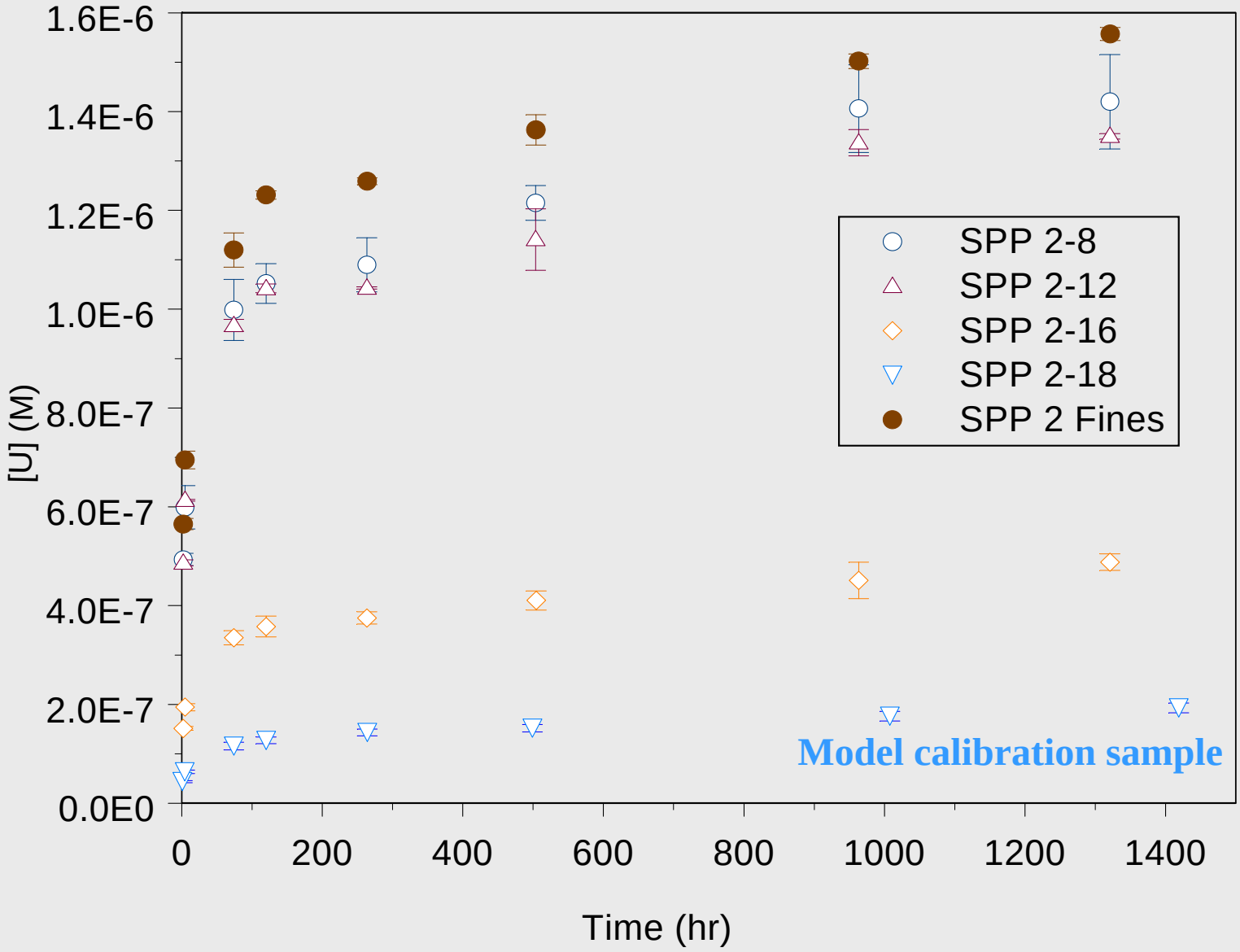
Sample (<2 mm or fines)	Carbonate extractable U (ppm)*	% of total U	HH extractable U (ppm)**	% of total U	Total U (ppm)
NPP-1-8 ft	6.9	66			10.5
NPP-1-12 ft	8.3	60			14.0
NPP-1-16 ft	4.7	49	8.7	91	9.6
NPP-1-20 ft	2.7	43			6.3
NPP1-GW fines	10	47	20.5	97	21.2
NPP-2-2 ft	46	43			106
NPP-2-4 ft	38	38			100
NPP-2-8 ft	21	53			39.8
NPP-2-12 ft	10.7	75			14.2
NPP2-GW fines	54	34	171	90-100	157
SPP-1-16 ft	5.3	73			7.3
SPP-1-18 ft	3.7	50			7.4
SPP-1-22 ft	3.6	46			7.9
SPP1-GW fines	19	61	28.6	91	31.3
SPP-2-8 ft	6.5	60			10.8
SPP-2-12 ft	6.2	78			8.0
SPP-2-16 ft	2.1	55			3.8
SPP-2-18 ft	0.78	27	1.8	62	2.9
SPP2-GW fines	6.8	51	12.1	91	13.3

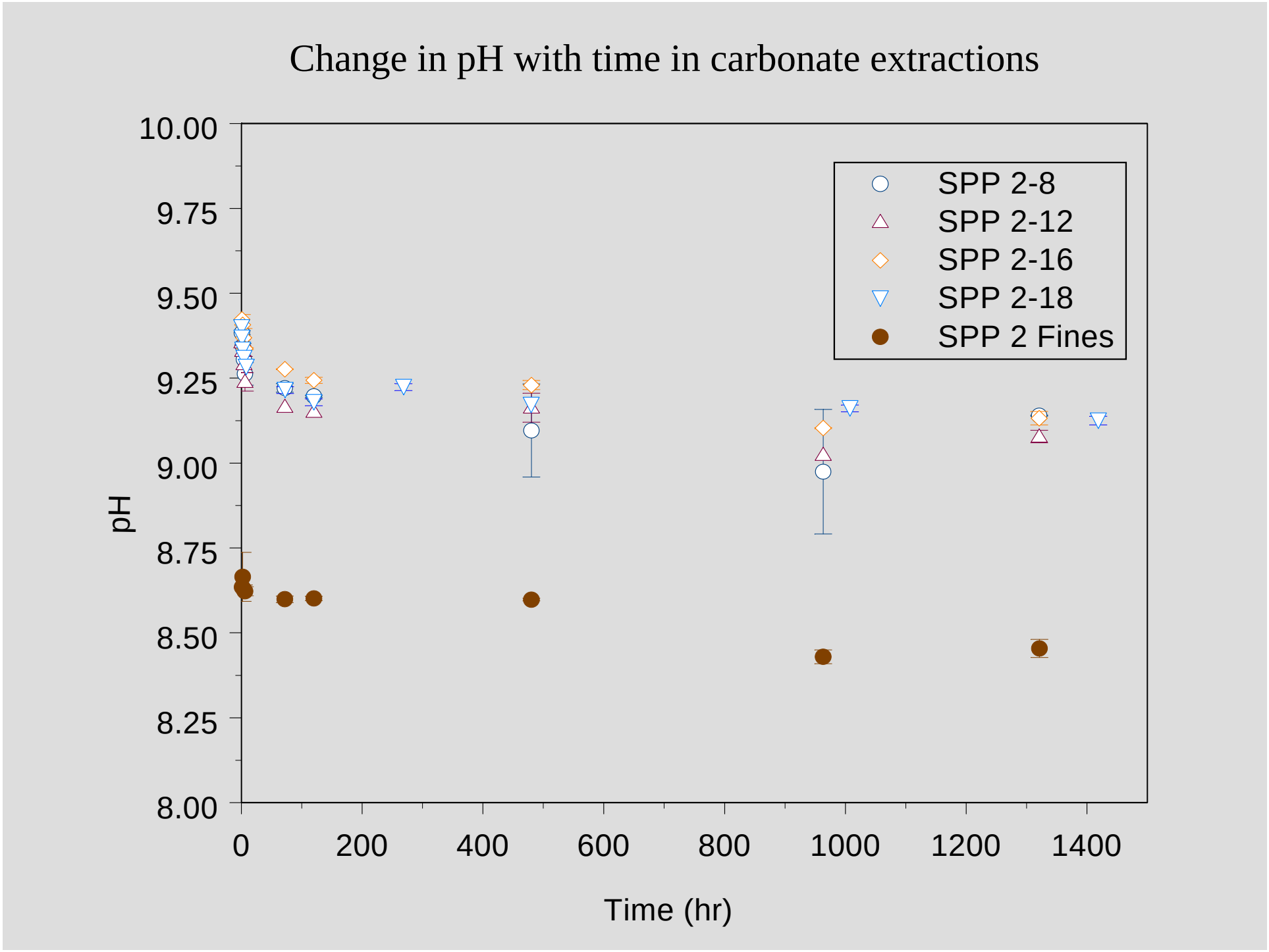
Change in pH, dissolved U, and Ca with time in carbonate extractions

Sample SPP-2-18



Change in dissolved U with time in carbonate extractions




Change in pH with time in carbonate extractions
10.00
9.75
9.50
9.25
9.00
8.75
8.50
8.25
8.00
pH
0
200
400
600
800
1000
1200
1400
Time (hr)
SPP 2-8
SPP 2-12
SPP 2-16
SPP 2-18
SPP 2 Fines

Extractable Uranium in the NPP and SPP sediment samples

*** Carbonate extraction:**
0.014M $NaHCO_3$
0.003M Na_2CO_3
Initial pH 9.45
1000 hours

Defined as labile U(VI)

**** Hydroxylamine Hydrochloride acid extraction, 72 hours**

Sample (<2 mm or fines)	Carbonate extractable U (ppm)*	% of total U	HH extractable U (ppm)**	% of total U	Total U (ppm)
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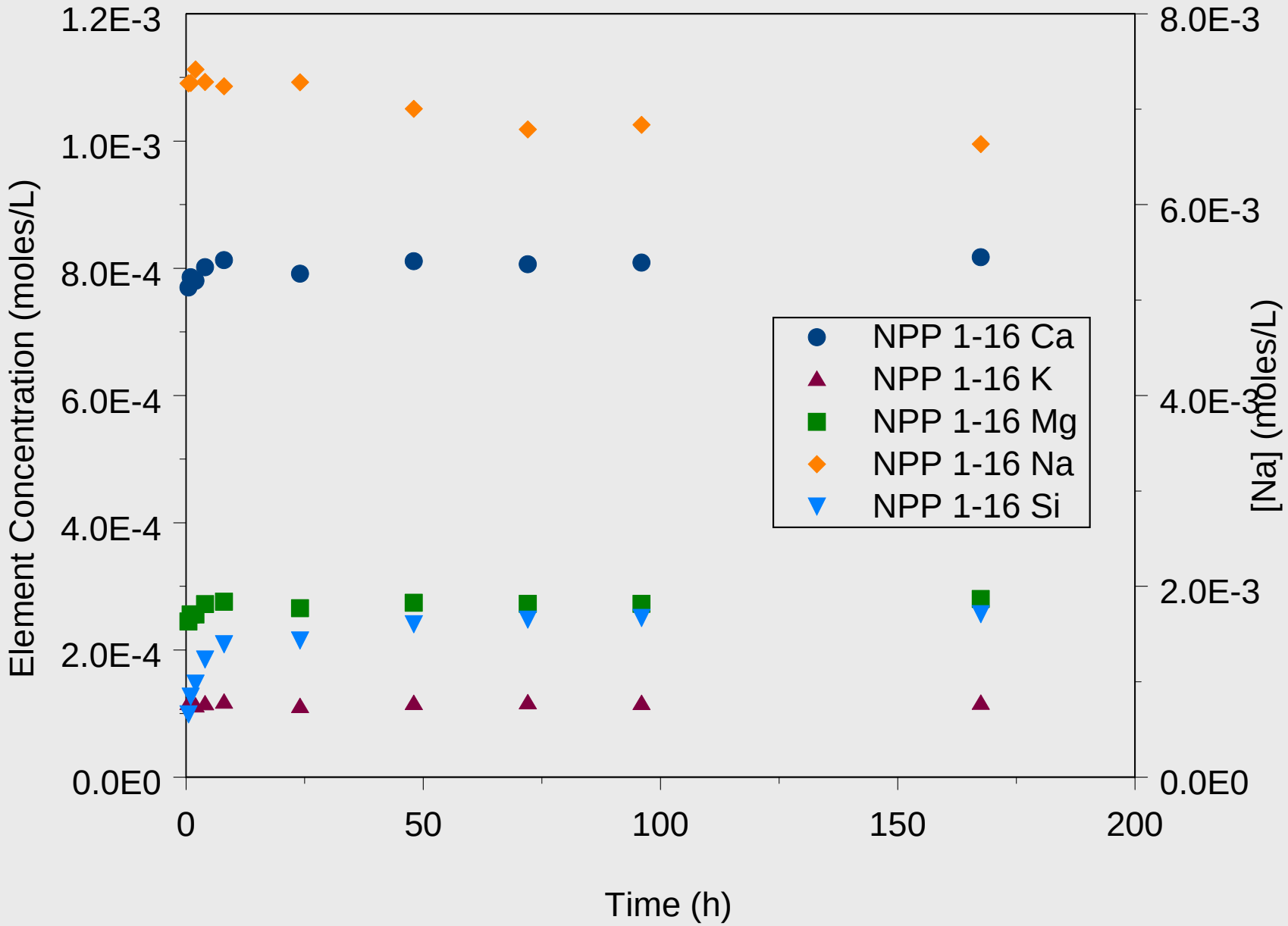
NPP-1-12 ft	8.3	60			14.0
NPP-1-16 ft	4.7	49	8.7	91	9.6
NPP-1-20 ft	2.7	43			6.3
NPP1-GW fines	10	47	20.5	97	21.2
NPP-2-2 ft	46	43			106
NPP-2-4 ft	38	38			100
NPP-2-8 ft	21	53			39.8
NPP-2-12 ft	10.7	75			14.2
NPP2-GW fines	54	34	171	90-100	157
SPP-1-16 ft	5.3	73			7.3
SPP-1-18 ft	3.7	50			7.4
SPP-1-22 ft	3.6	46			7.9
SPP1-GW fines	19	61	28.6	91	31.3
SPP-2-8 ft	6.5	60			10.8
SPP-2-12 ft	6.2	78			8.0
SPP-2-16 ft	2.1	55			3.8
SPP-2-18 ft	0.78	27	1.8	62	2.9
SPP2-GW fines	6.8	51	12.1	91	13.3

Methods for Desorption and Adsorption Studies

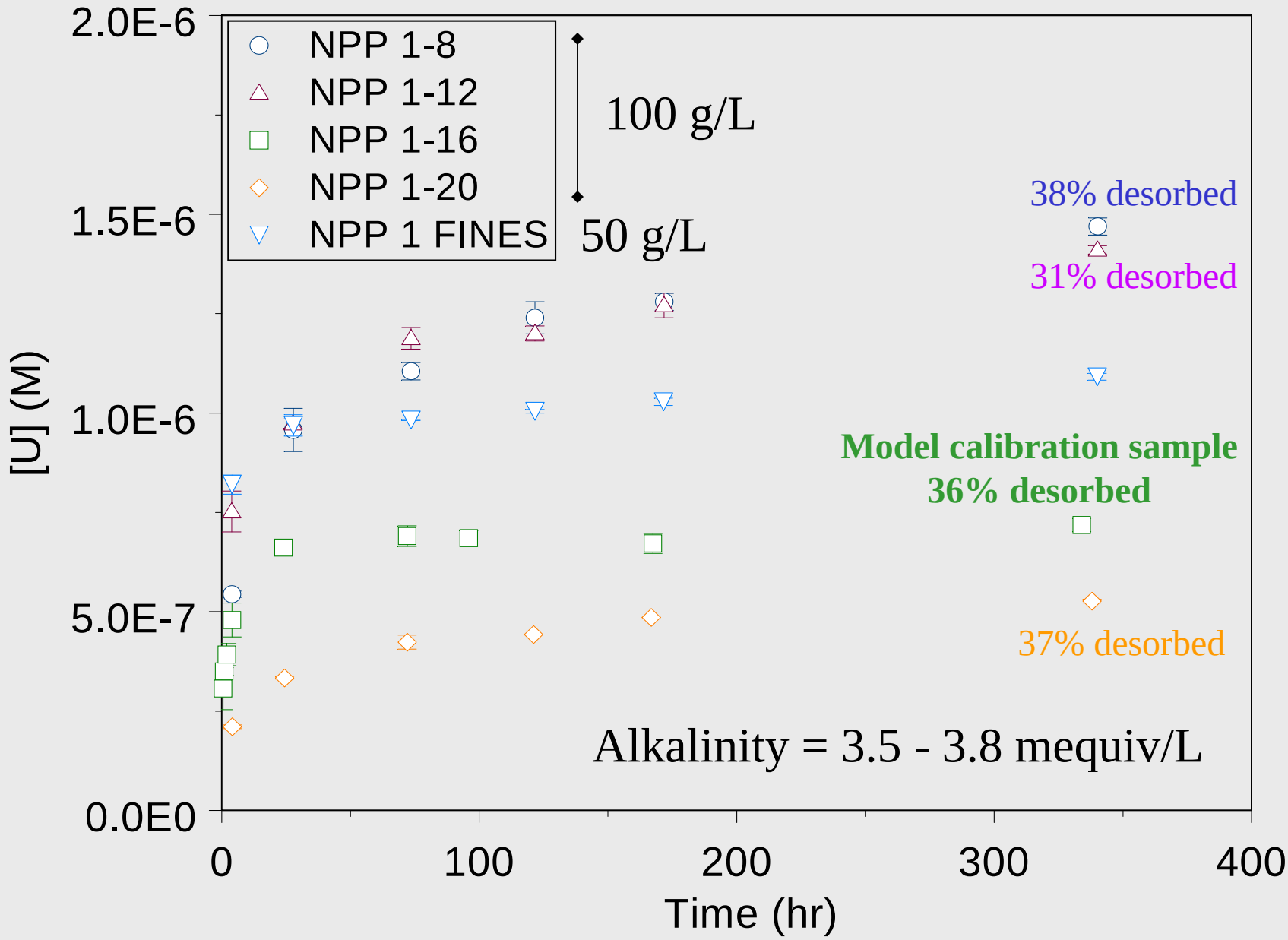
Sediments reacted with artificial groundwaters of varying initial composition (alkalinity, ionic strength, Ca concentration). No pre-equilibration of sediments with the artificial groundwaters. Initial pH values of the artificial groundwaters ranged from 7.9-8.7. For adsorption experiments, U(VI) was added with the artificial groundwater.

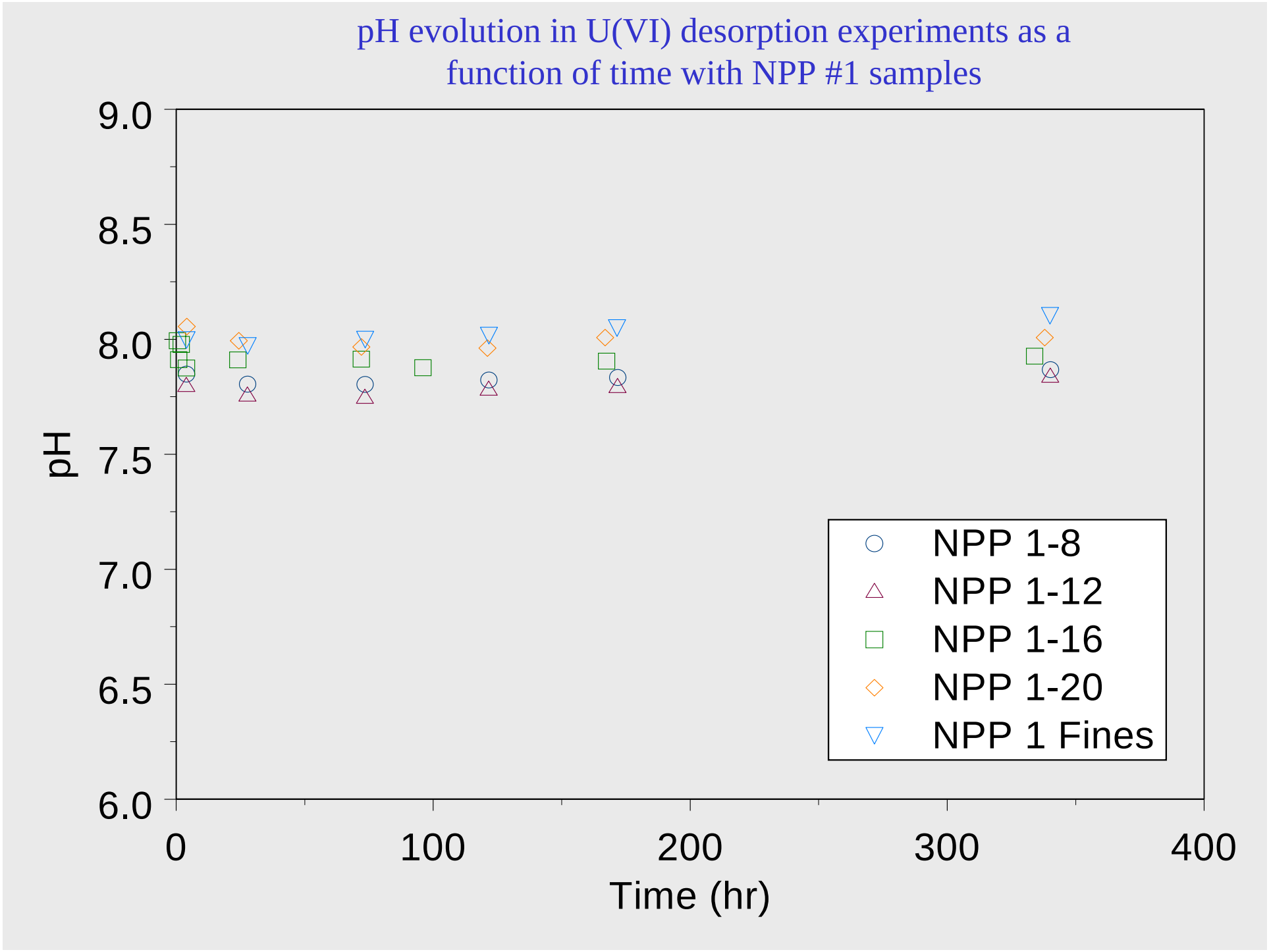
Dissolved U(VI), pH, alkalinity, and major ion composition measured as a function of time.

Evolution of major ion concentrations in U(VI) desorption experiments as a function of time with NPP #1 samples

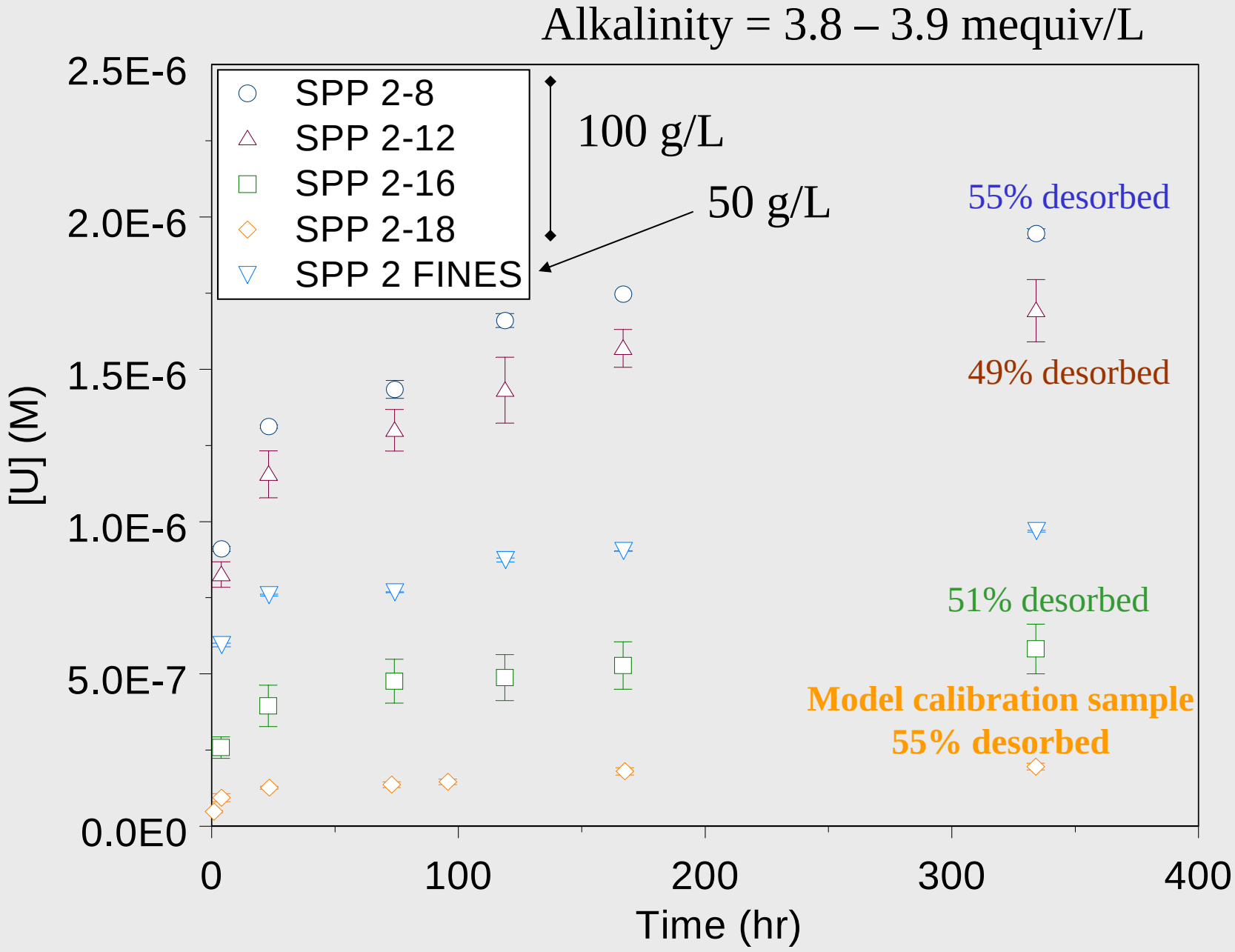


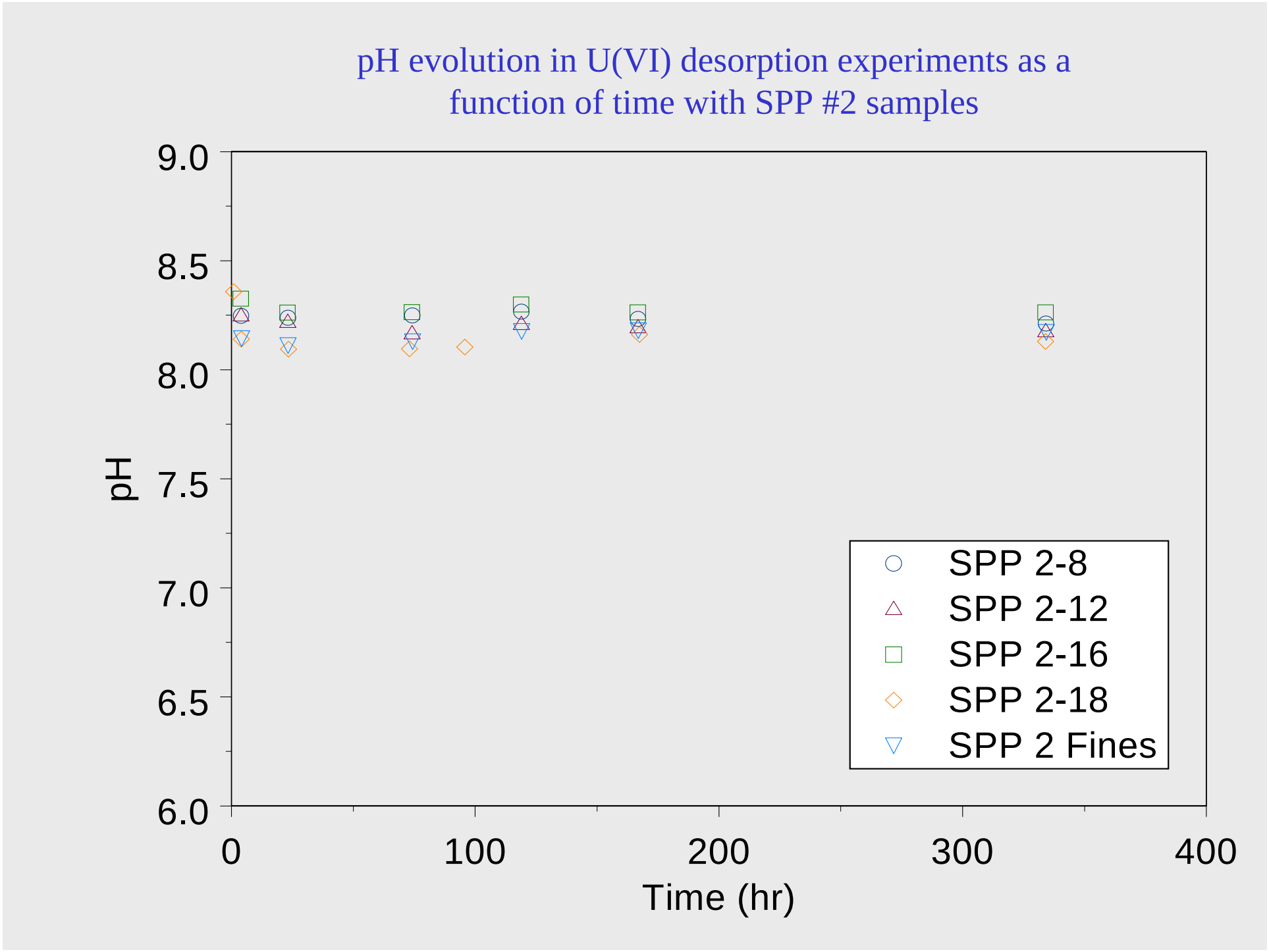
Desorption of U(VI) as a function of time from NPP #1 samples



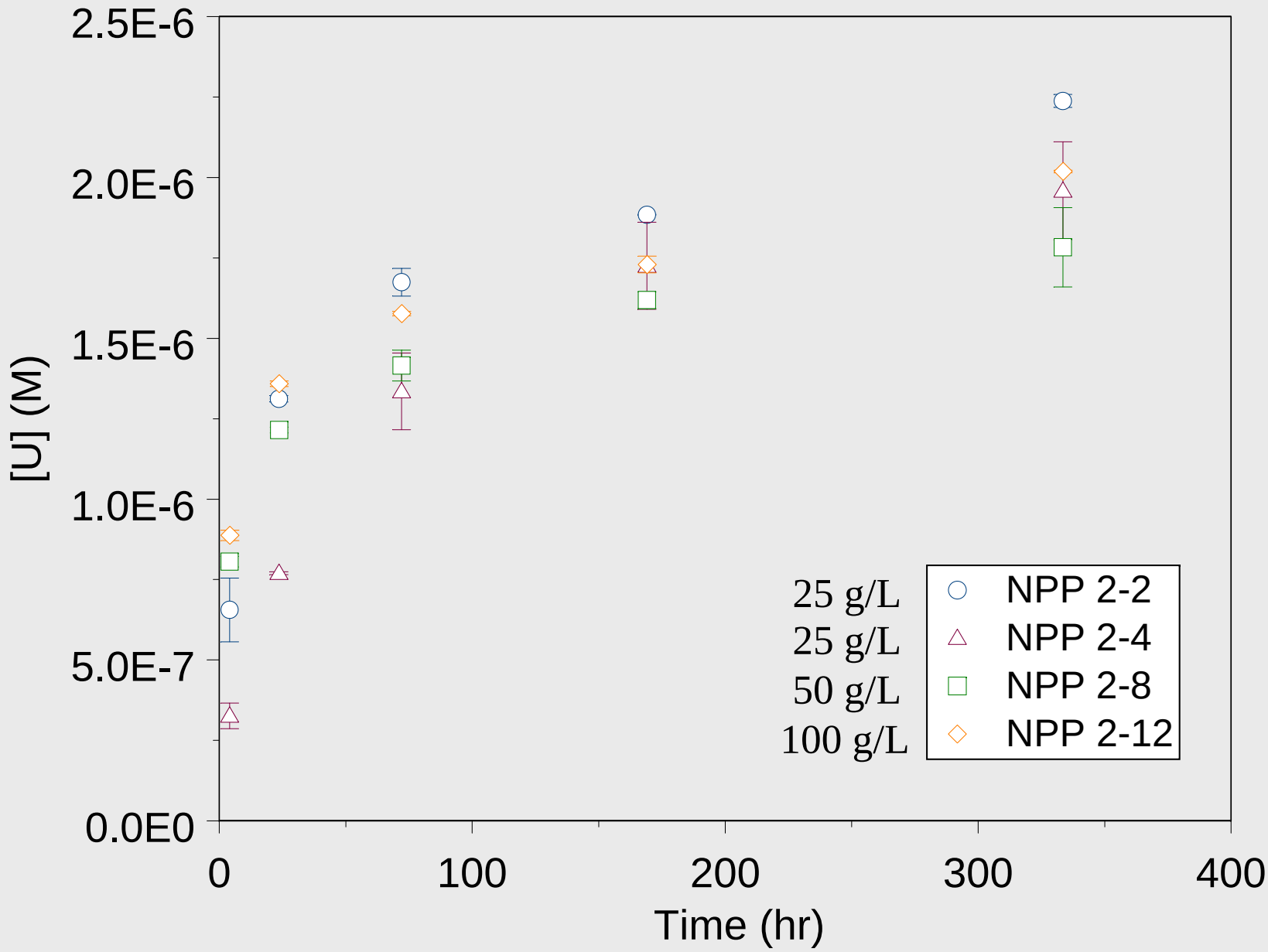

pH evolution in U(VI) desorption experiments as a function of time with NPP #1 samples
9.0
8.5
8.0
7.5
7.0
6.5
6.0
pH
0
100
200
300
400
Time (hr)
NPP 1-8
NPP 1-12
NPP 1-16
NPP 1-20
NPP 1 Fines

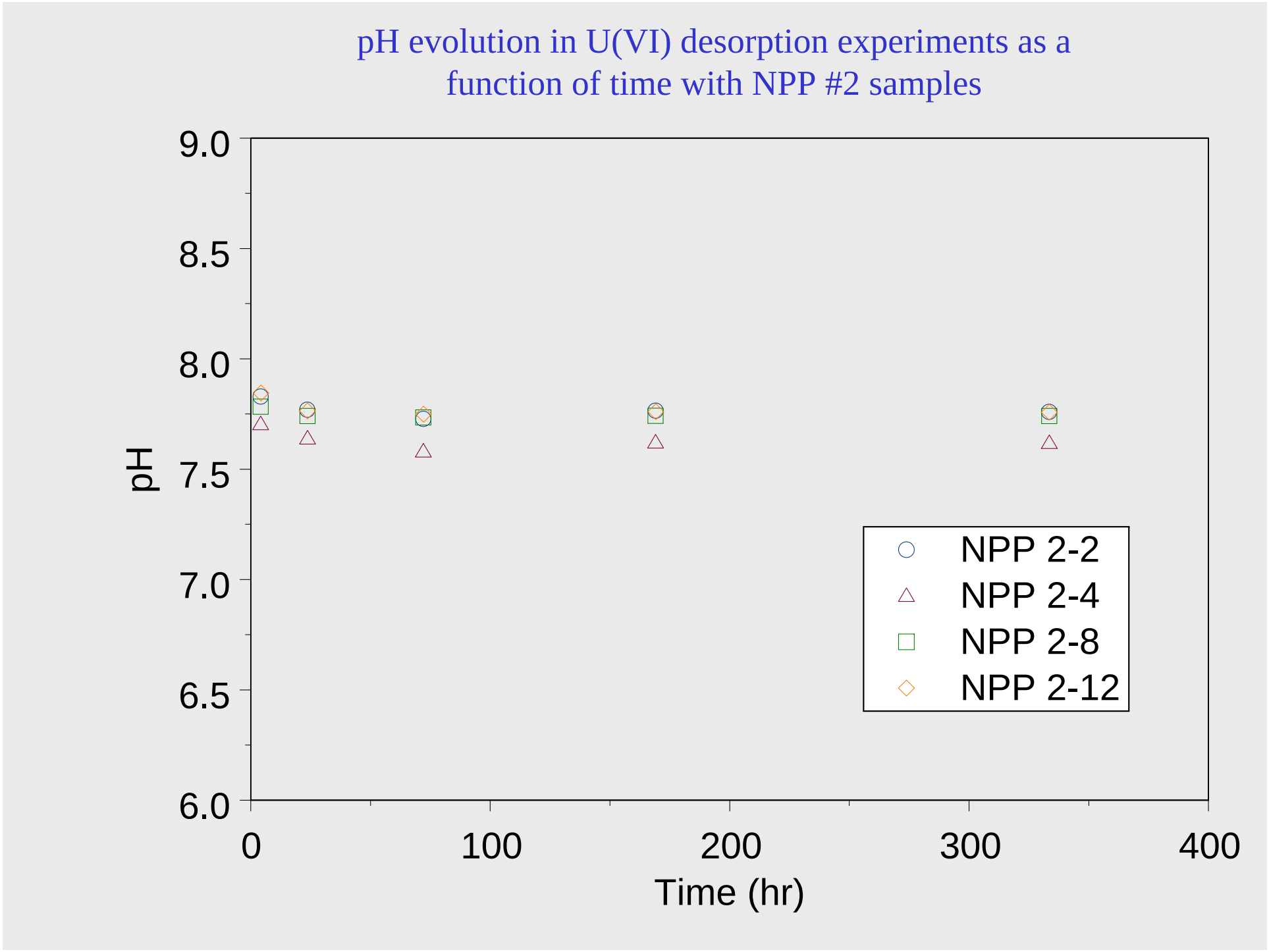
Desorption of U(VI) as a function of time from SPP #2 samples



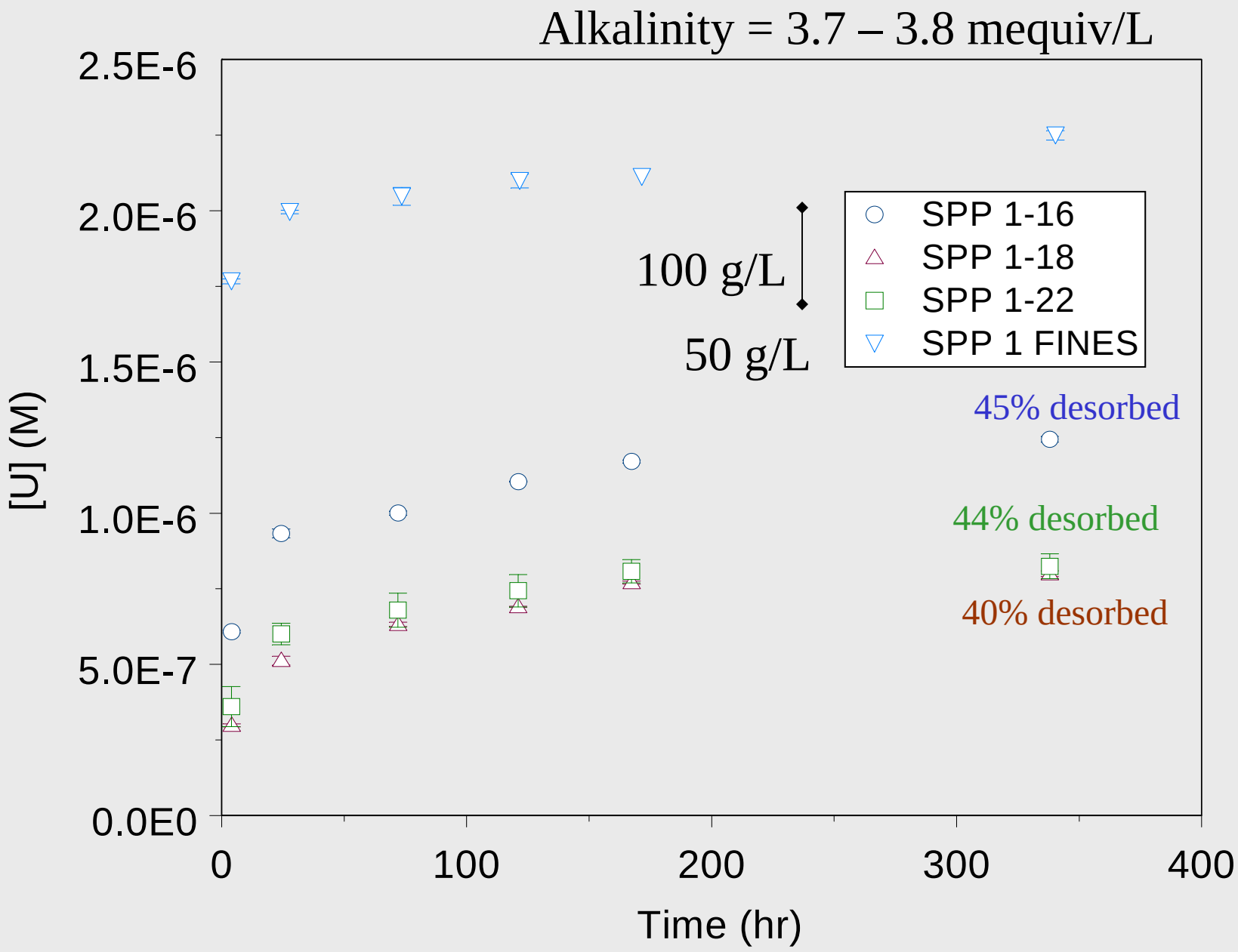

pH evolution in U(VI) desorption experiments as a function of time with SPP #2 samples
9.0
8.5
8.0
7.5
7.0
6.5
6.0
pH
0
100
200
300
400
Time (hr)
SPP 2-8
SPP 2-12
SPP 2-16
SPP 2-18
SPP 2 Fines

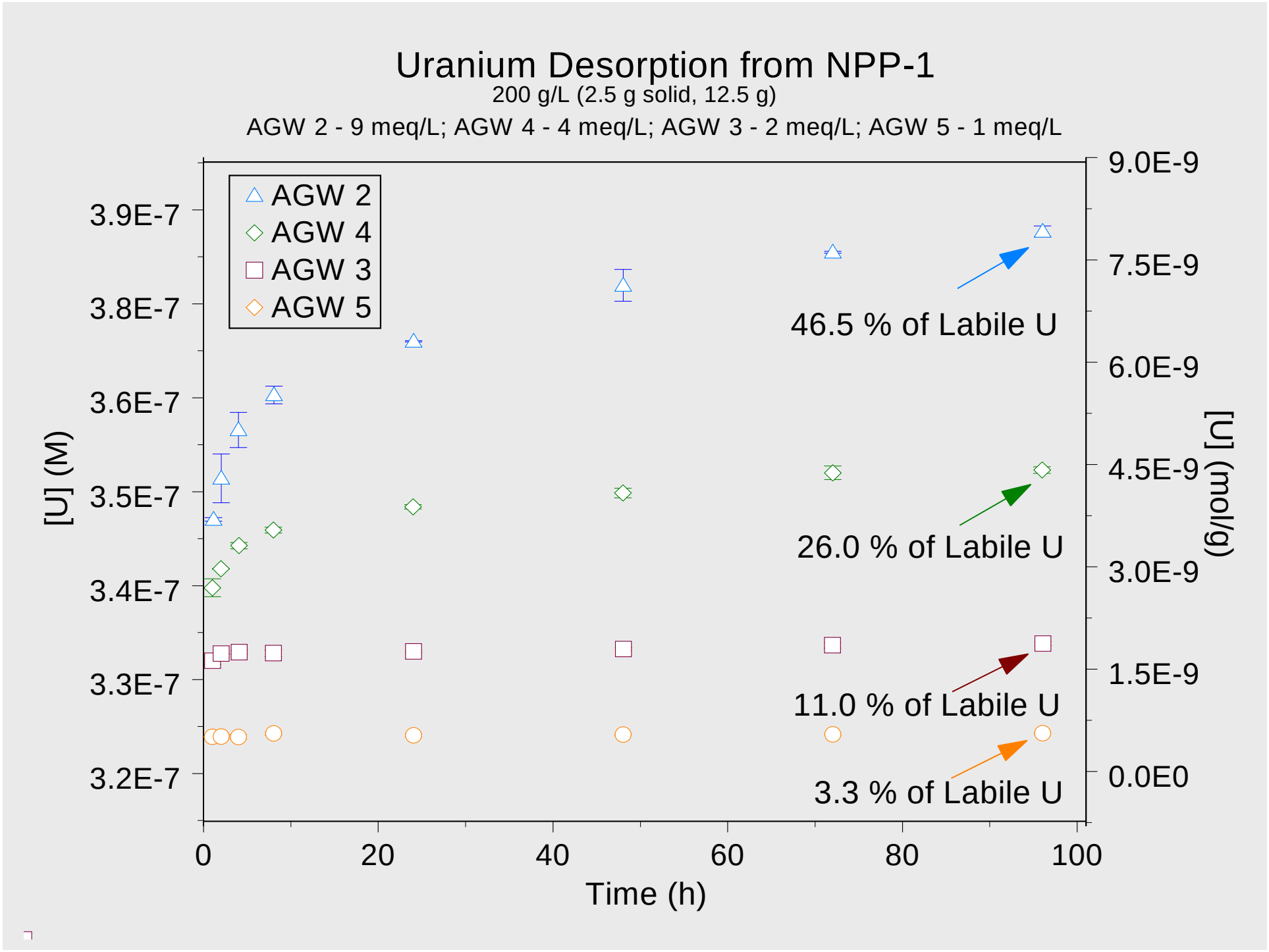
Desorption of U(VI) as a function of time from NPP #2 samples

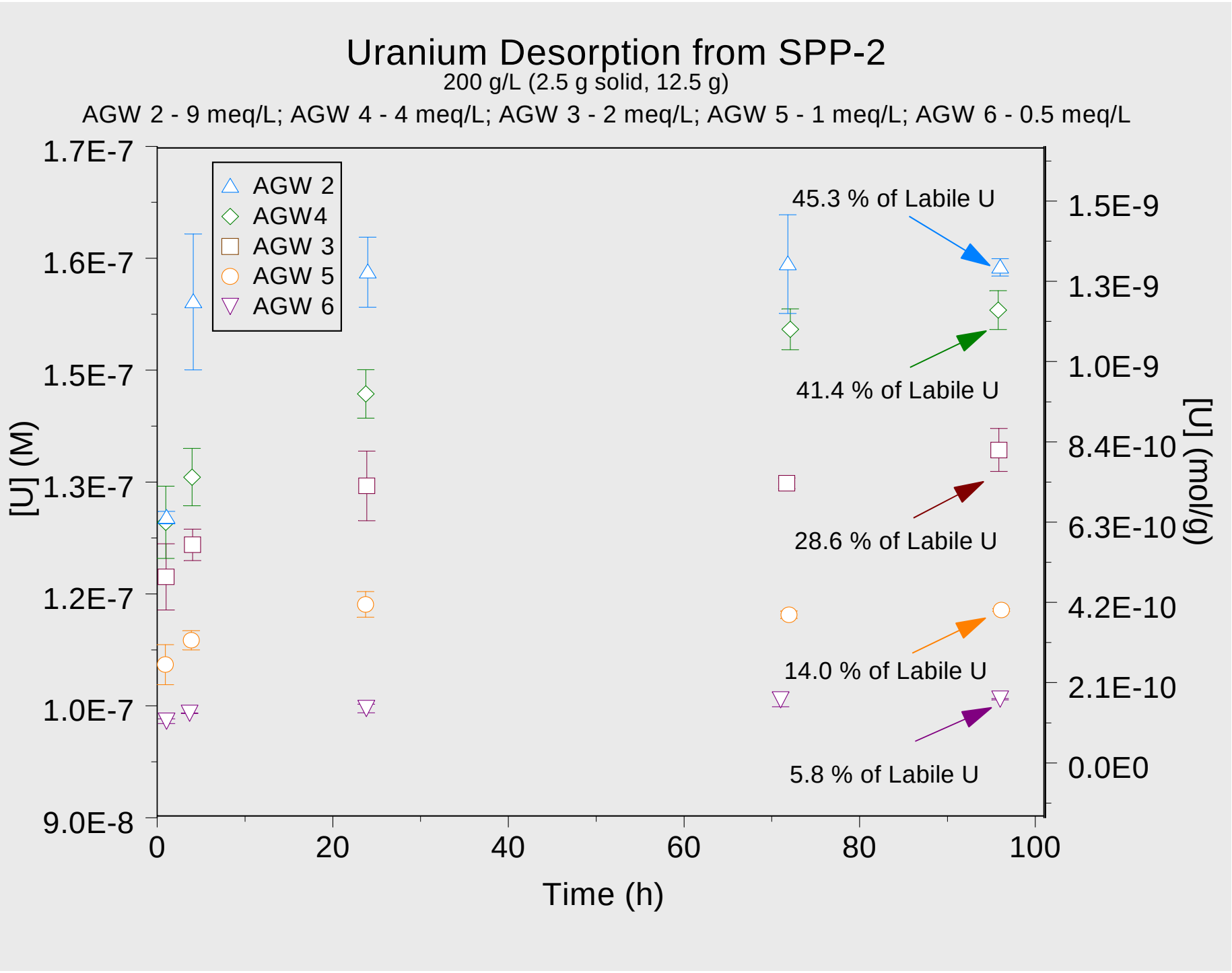



pH evolution in U(VI) desorption experiments as a function of time with NPP #2 samples
9.0
8.5
8.0
7.5
7.0
6.5
6.0
pH
0
100
200
300
400
Time (hr)
NPP 2-2
NPP 2-4
NPP 2-8
NPP 2-12

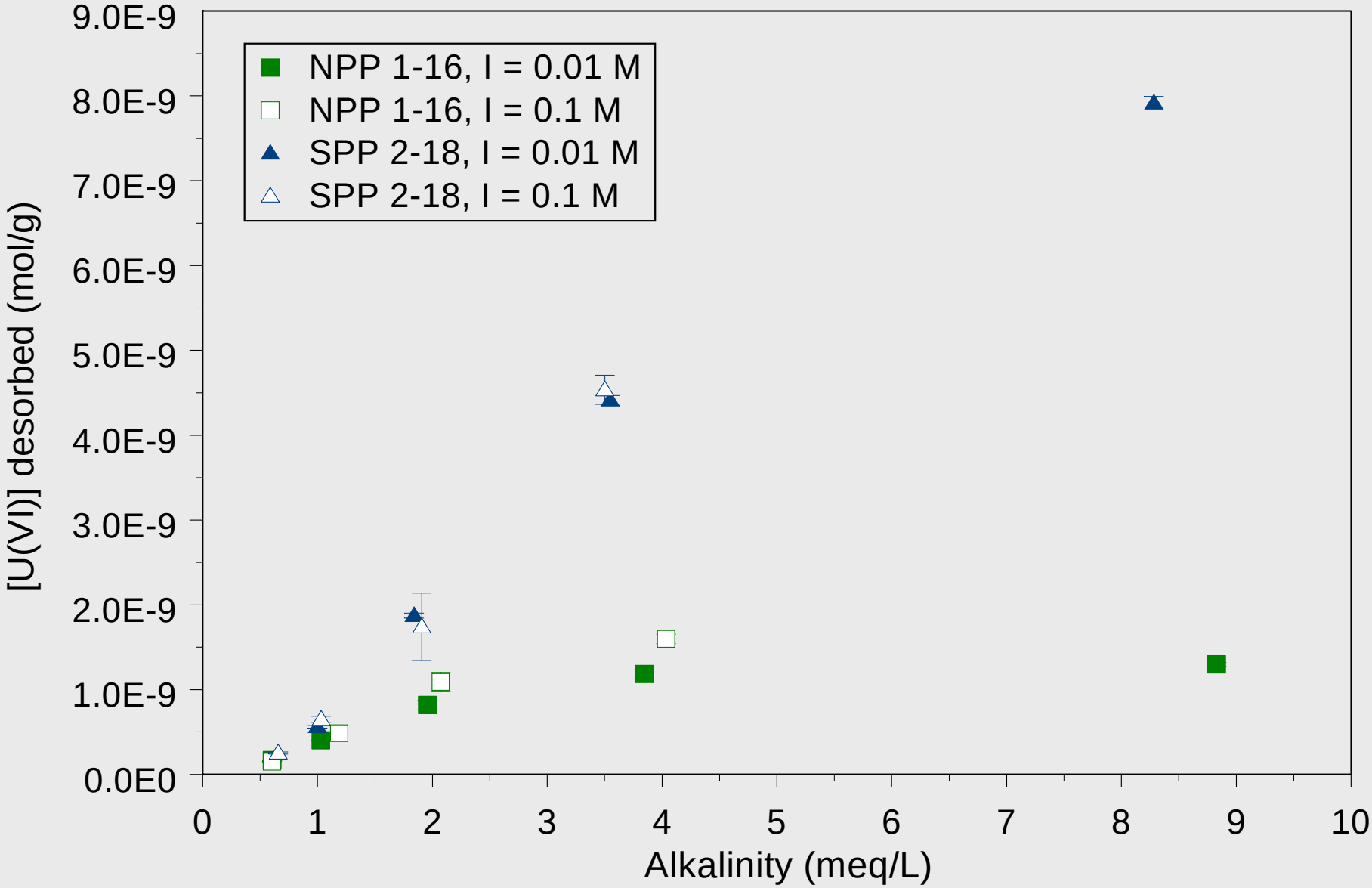
Desorption of U(VI) as a function of time from SPP #1 samples



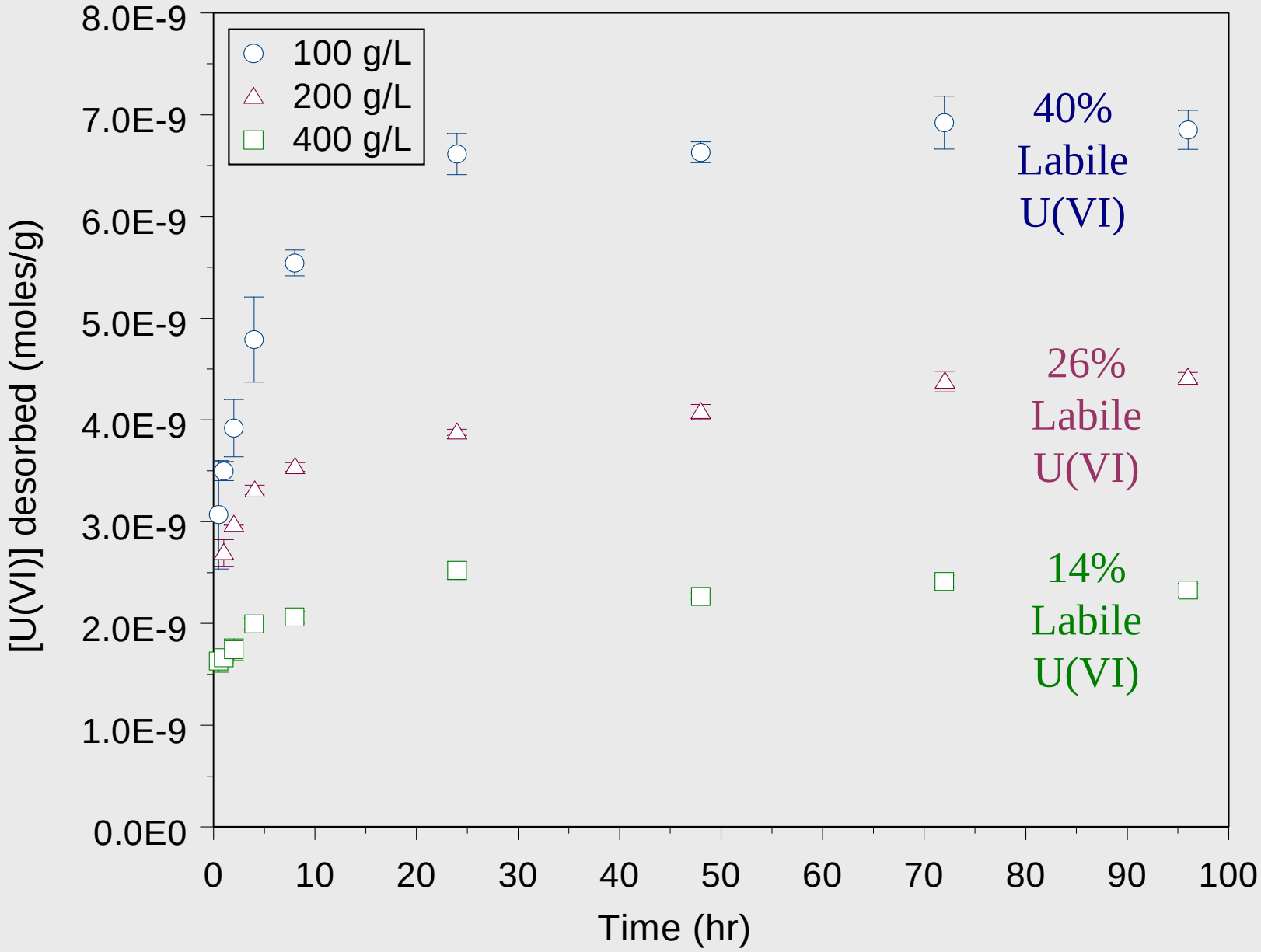

Uranium Desorption from NPP-1
200 g/L (2.5 g solid, 12.5 g)
AGW 2 - 9 meq/L; AGW 4 - 4 meq/L; AGW 3 - 2 meq/L; AGW 5 - 1 meq/L
AGW 2
AGW 4
AGW 3
AGW 5
46.5 % of Labile U
26.0 % of Labile U
11.0 % of Labile U
3.3 % of Labile U
[U] (M)
[U] (mol/g)
Time (h)
3.9E-7
3.8E-7
3.6E-7
3.5E-7
3.4E-7
3.3E-7
3.2E-7
9.0E-9
7.5E-9
6.0E-9
4.5E-9
3.0E-9
1.5E-9
0.0E0
0
20
40
60
80
100


Uranium Desorption from SPP-2
200 g/L (2.5 g solid, 12.5 g)
AGW 2 - 9 meq/L; AGW 4 - 4 meq/L; AGW 3 - 2 meq/L; AGW 5 - 1 meq/L; AGW 6 - 0.5 meq/L
AGW 2
AGW4
AGW 3
AGW 5
AGW 6
45.3 % of Labile U
41.4 % of Labile U
28.6 % of Labile U
14.0 % of Labile U
5.8 % of Labile U
[U] (M)
[U] (mol/g)
Time (h)
1.7E-7
1.6E-7
1.5E-7
1.3E-7
1.2E-7
1.0E-7
9.0E-8
1.5E-9
1.3E-9
1.0E-9
8.4E-10
6.3E-10
4.2E-10
2.1E-10
0.0E0
0
20
40
60
80
100

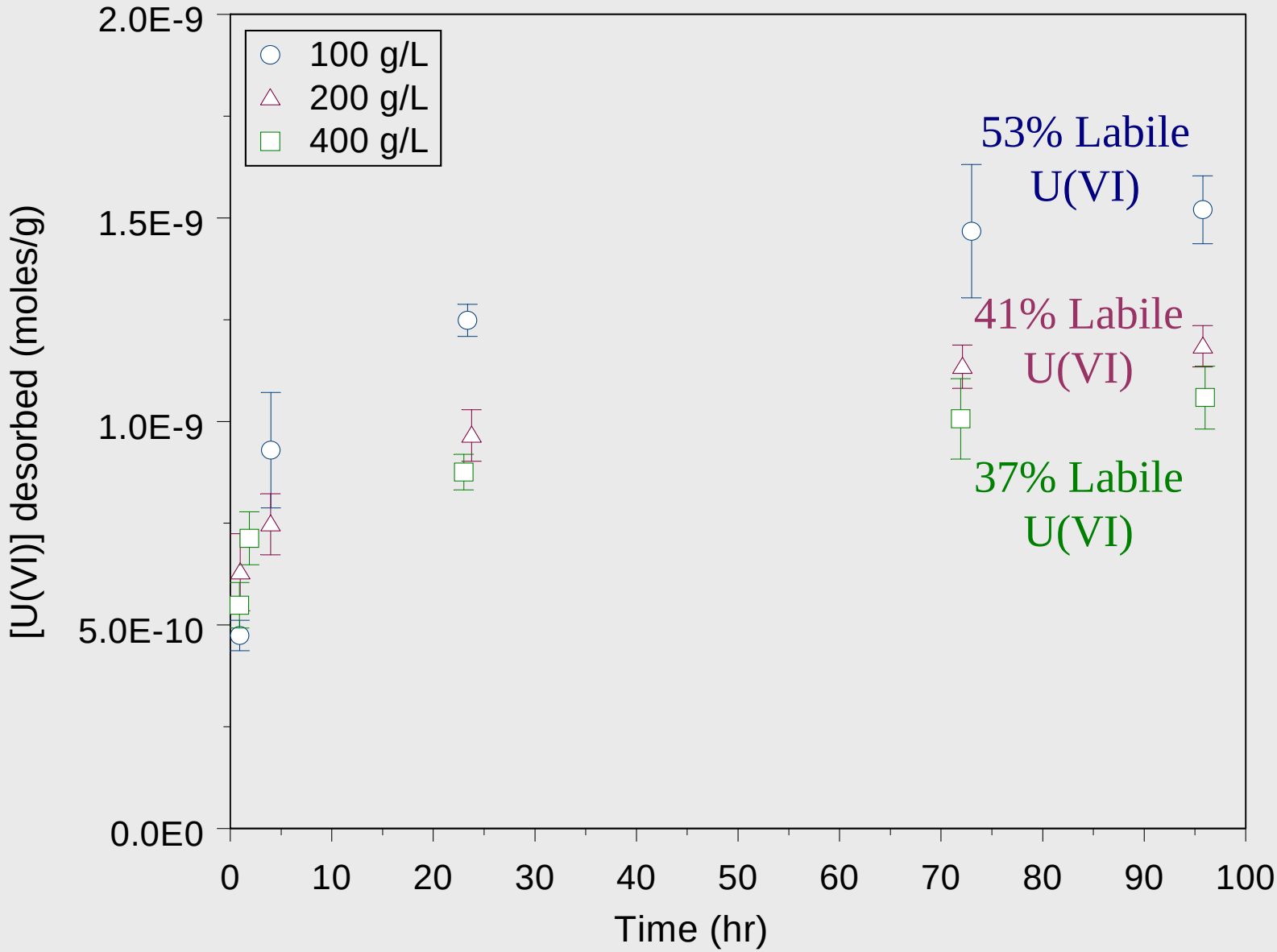
U(VI) desorption as a function of alkalinity and ionic strength



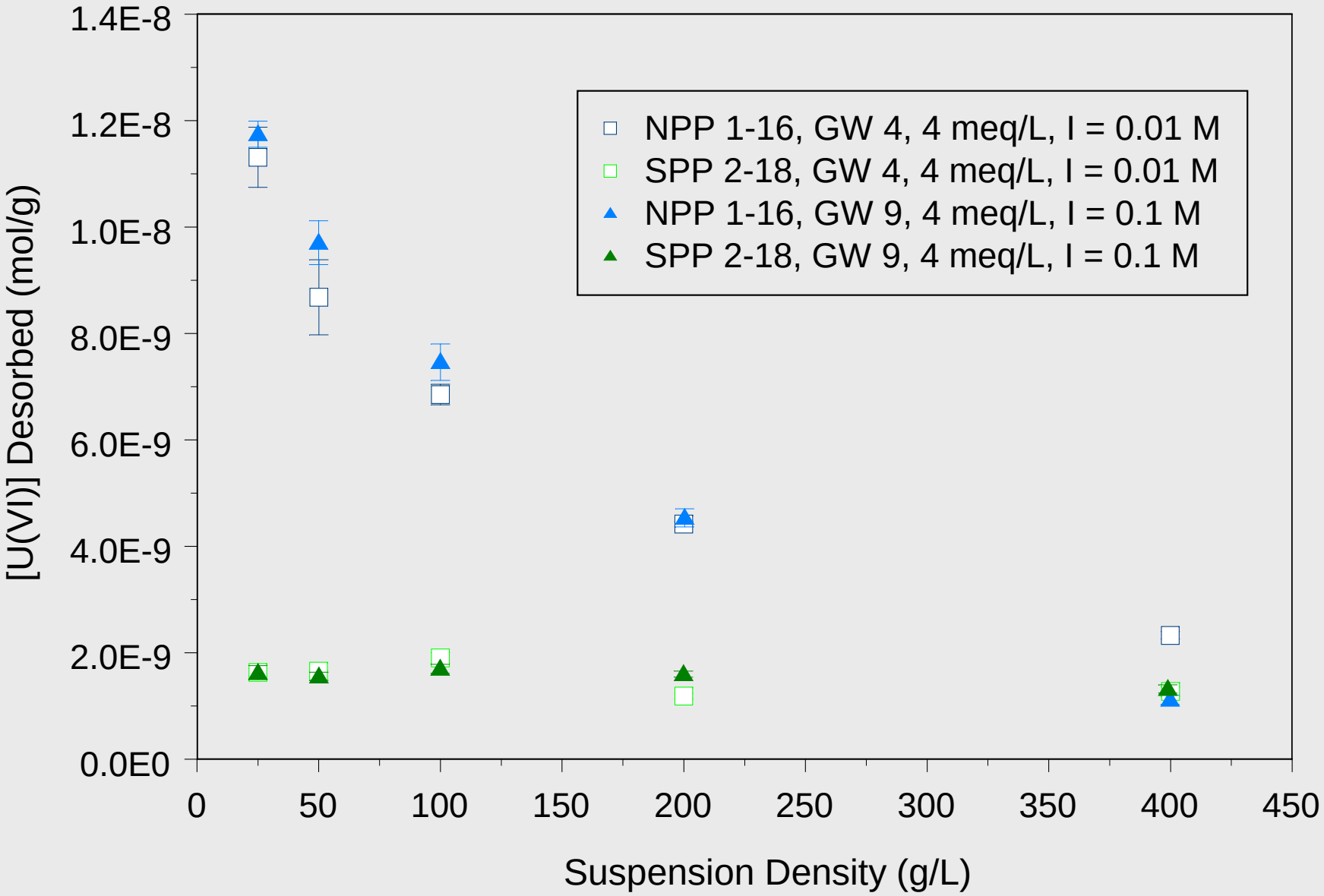
U(VI) desorption from NPP-1-16 as a function of suspension density



U(VI) desorption from SPP-2-18 as a function of suspension density

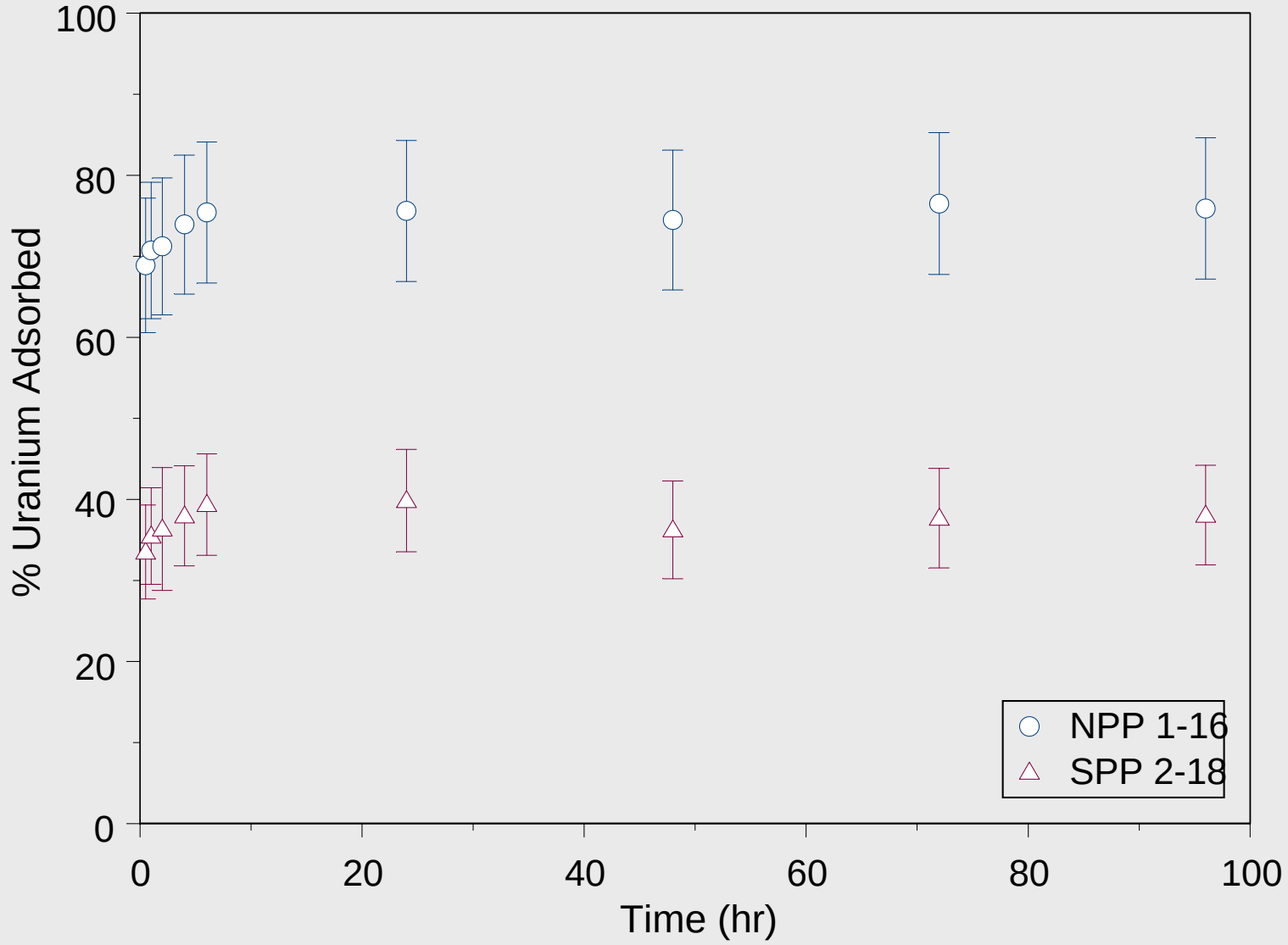


U(VI) desorption as a function of suspension density and ionic strength

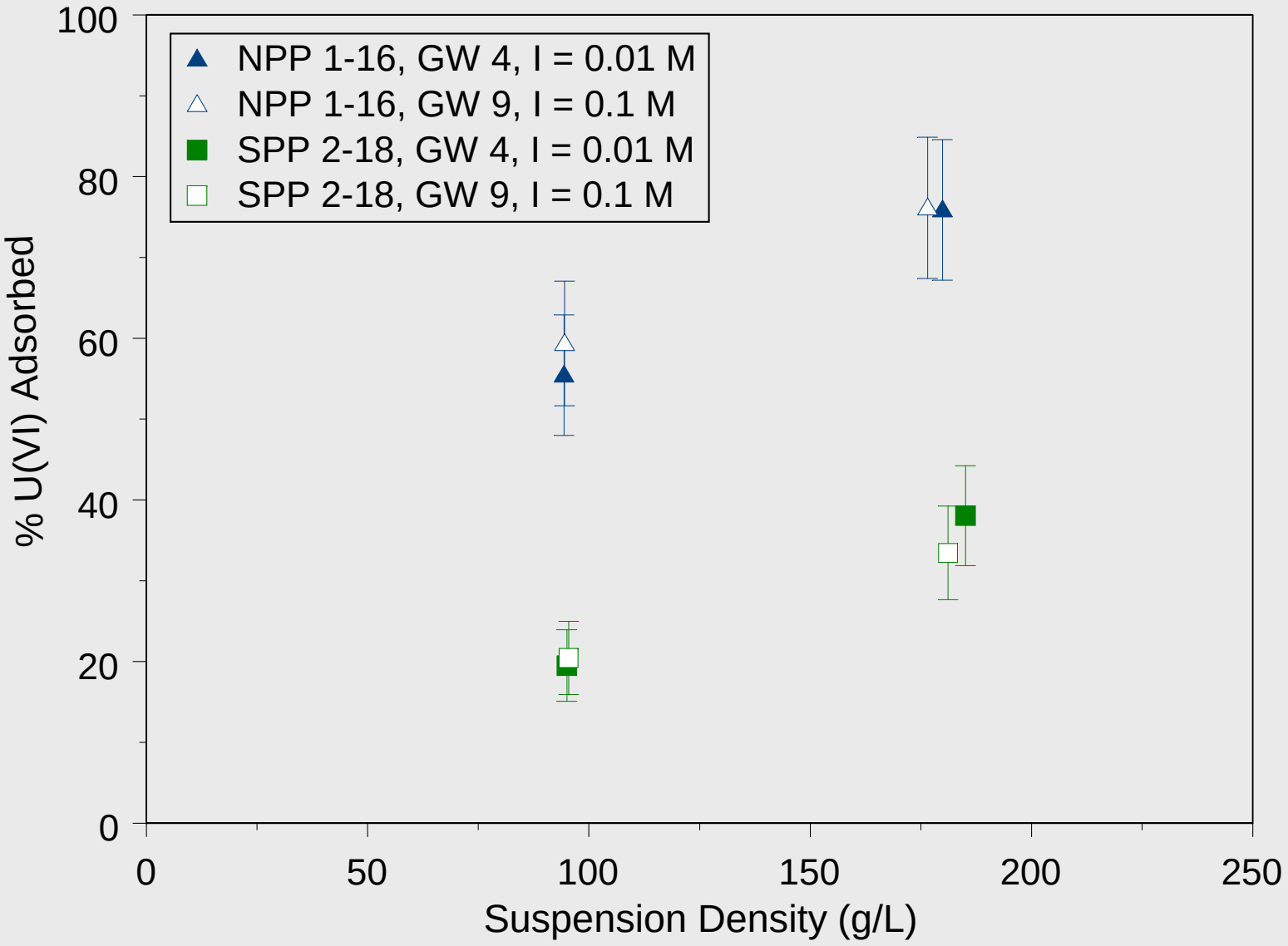


U(VI) adsorption kinetics on samples NPP-1-18 and SPP-2-18

Added U(VI) = 5 μM; 200 g/L sediment; alkalinity = 4 mequivalents/L



U(VI) adsorption on samples NPP-1-18 and SPP-2-18 as a function of suspension density and ionic strength



K_d values in U(VI) desorption experiments:

$$K_d = \frac{\text{adsorbed U(VI)}}{\text{dissolved U(VI)}} = \frac{1/x\ [\text{Labile U(VI)*} - \text{dissolved U(VI)}]}{\text{dissolved U(VI)}}$$

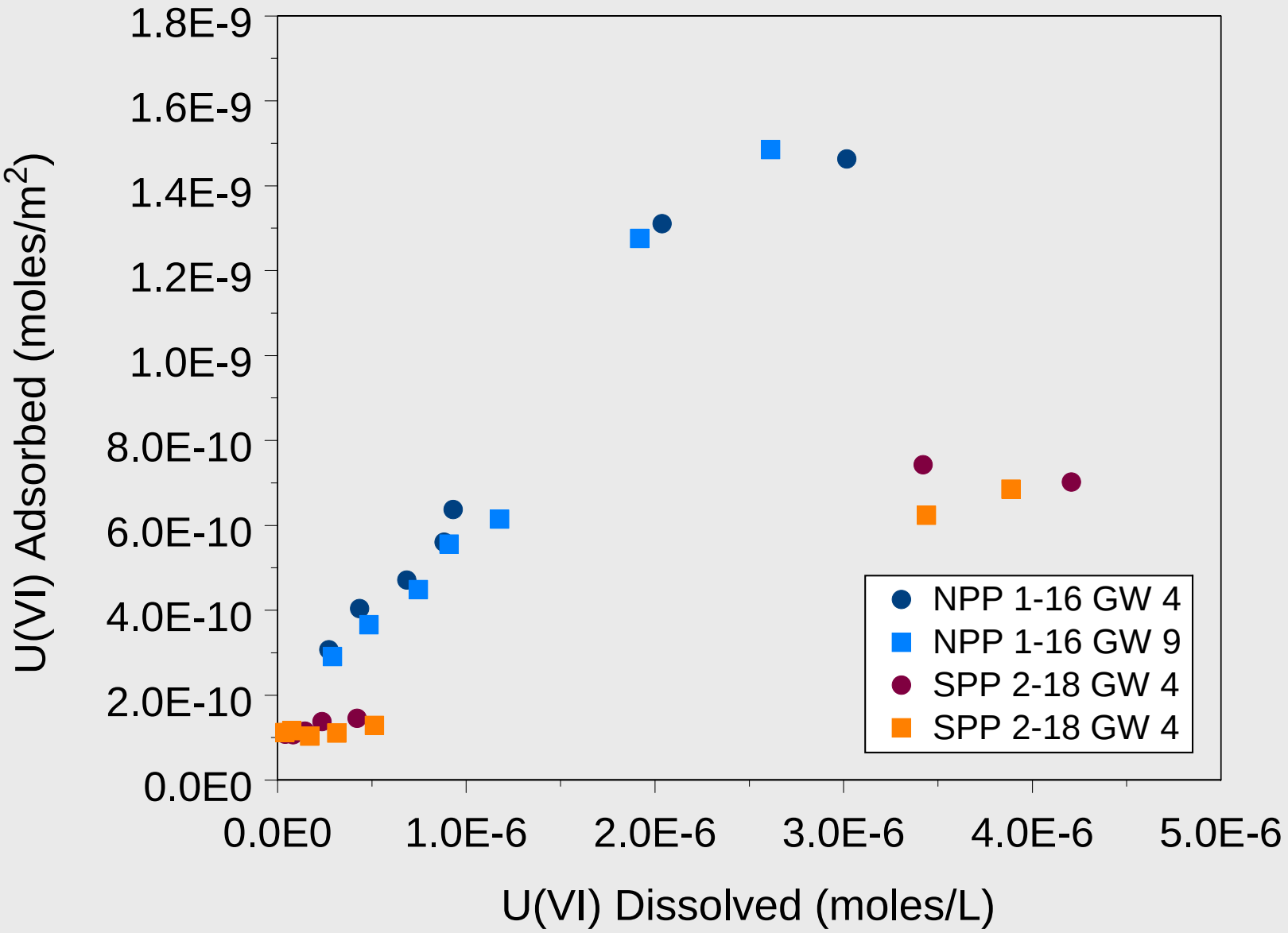
K_d values in U(VI) adsorption experiments:

$$K_d = \frac{1/x\ [\{\text{Added U(VI)} + \text{Labile U(VI)*}\} - \text{dissolved U(VI)}]}{\text{dissolved U(VI)}}$$

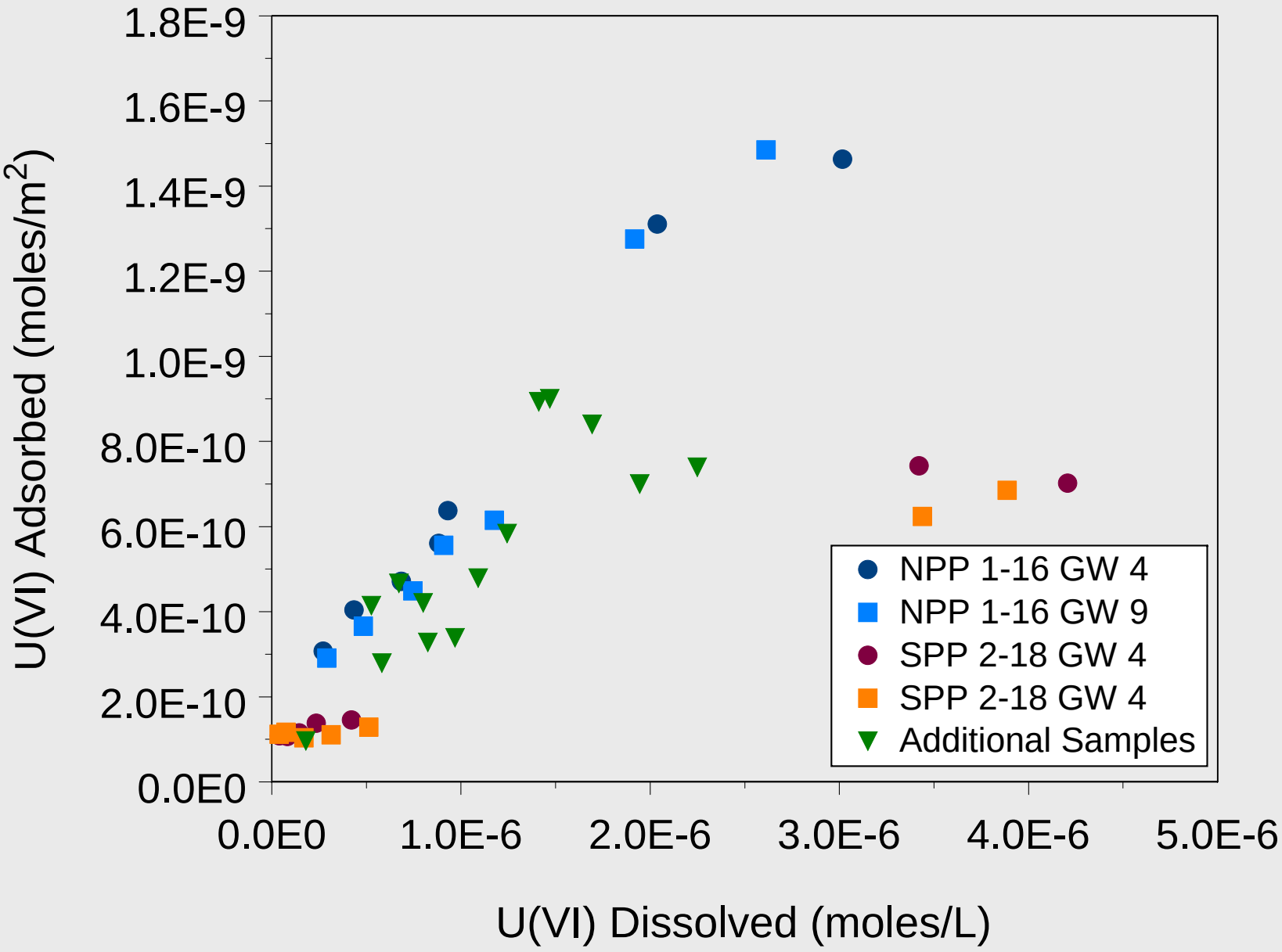
Labile U(VI) in moles/L* = Labile U(VI) in moles/kg * x

x = kg/L of sediment in the batch experiment

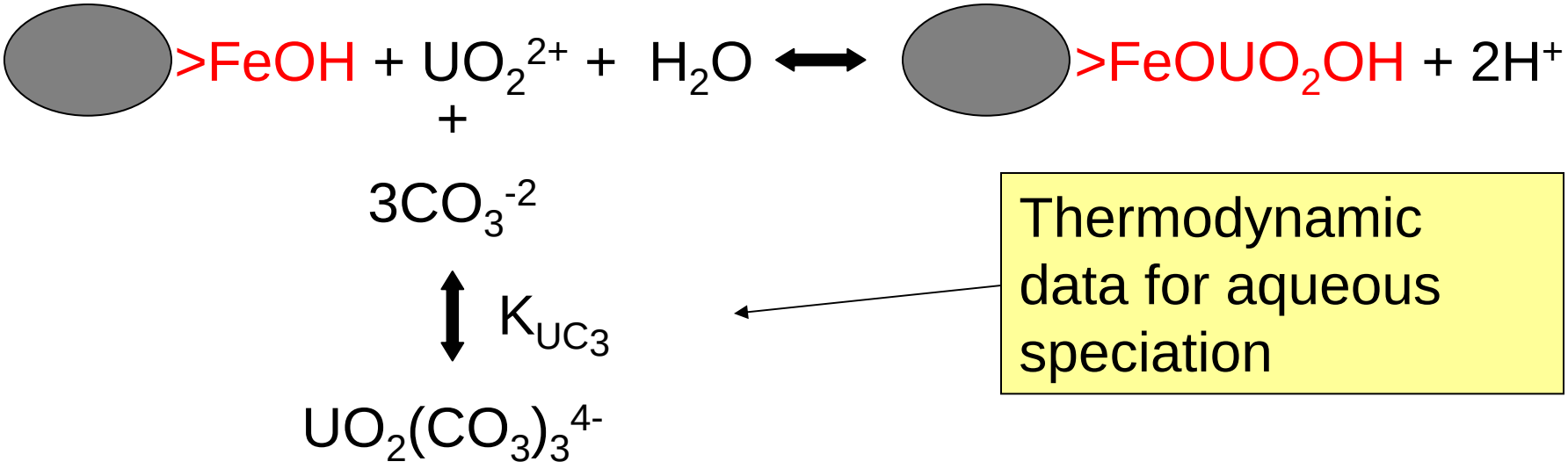
U(VI) adsorption “isotherms” for samples NPP-1-16 and SPP-2-18



U(VI) adsorption “isotherms” for all 300 area samples



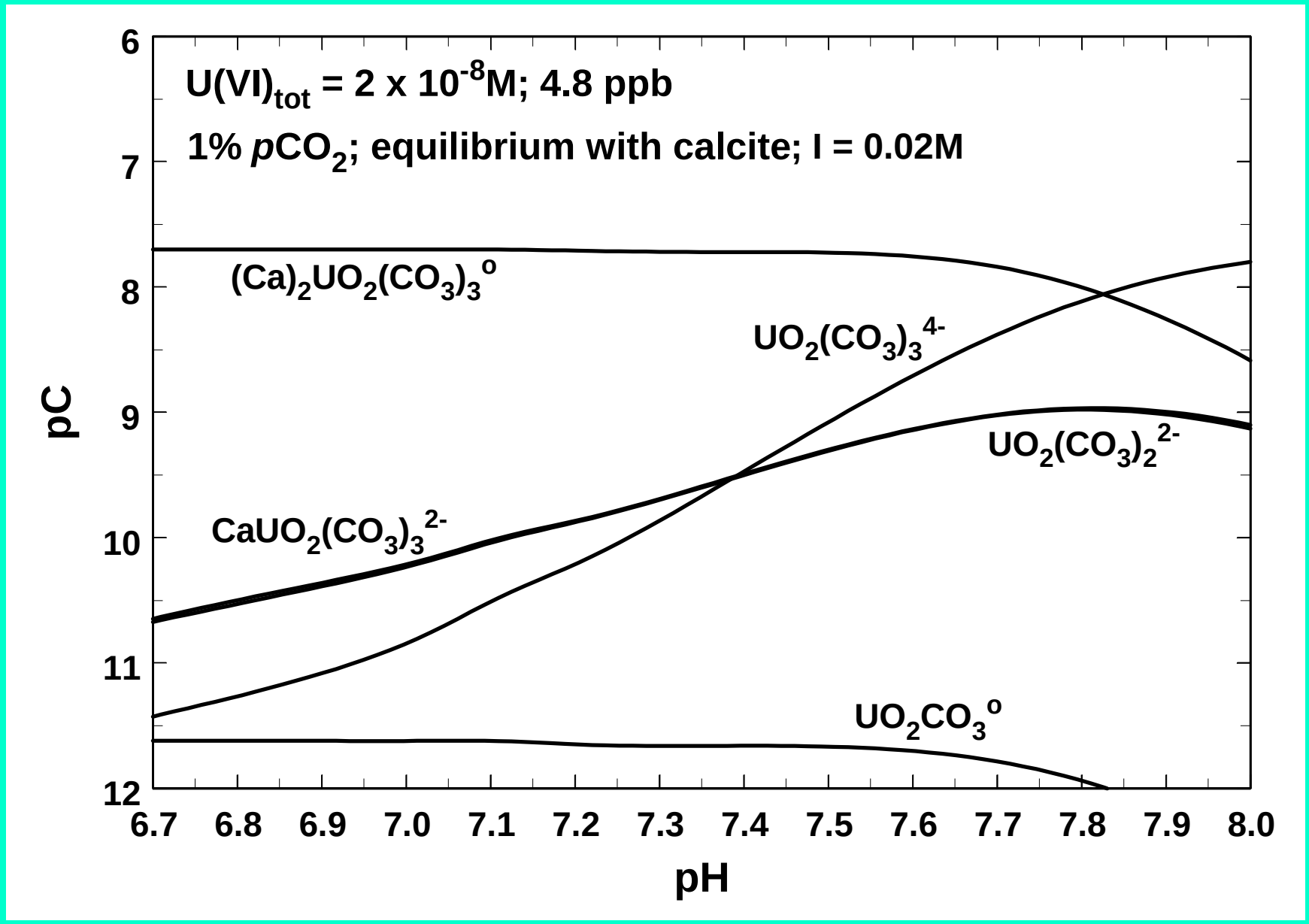
Surface and Aqueous Complexation Modeling



$$K_{ads} = \frac{[FeOUO_2OH](H^+)^2}{[FeOH](UO_2^{+2})}$$

$$K_d = \frac{\text{Adsorbed}}{\text{Aqueous}} = \frac{[FeOUO_2OH]}{[U(VI)]_{AQ}} = \frac{K_{ads} > FeOH_T}{K_{ads}\dfrac{[U(VI)]_{AQ}}{1 + K_{UC_3}(CO_3^{-2})^3} + H^2}$$

U(VI) aqueous speciation in carbonate-rich aquifers



Conceptual Models for Surface Complexation in Natural Systems

Forward Modeling Approach

- Quantify number of quartz, goethite, feldspar, clay, etc, sites
- Use published SCMs

Produces site specific predictive adsorption model

Inverse Modeling Approach

- Collect adsorption data relevant to field conditions
- Assume generic surface sites
- Use inverse models (eg FITEQL) to choose reactions and estimate parameters

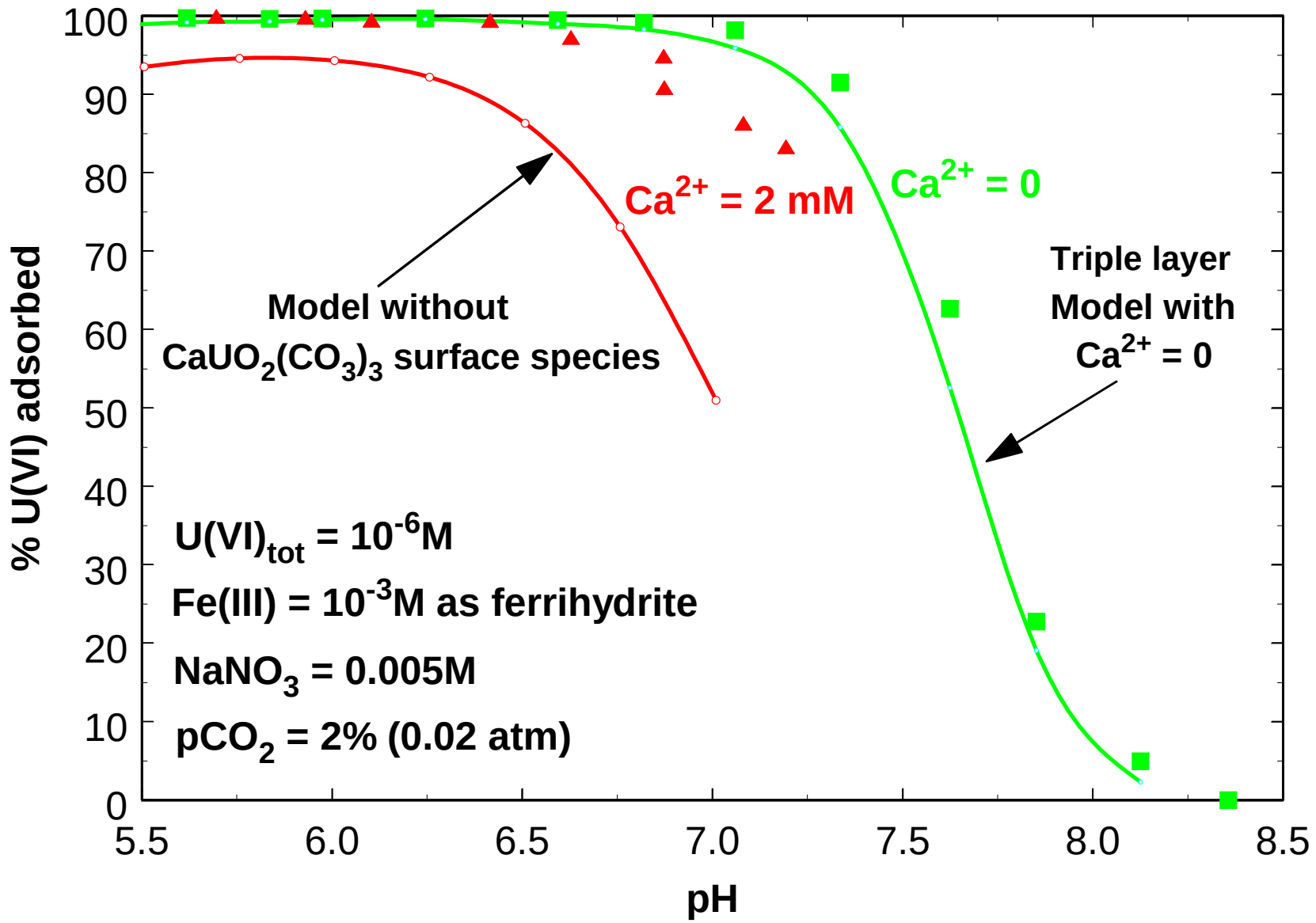
Produces site specific semi empirical adsorption model

Concept of Mineral Component Additivity (Honeyman, 1984)

Hanford 300 area sediments: quartz, feldspars, muscovite, hornblende, calcite, iron oxides, vermiculite, smectite, etc.

$$\text{Adsorbed U(VI)}_{\text{sediment}} = U_{\text{quartz}} + U_{\text{feldspars}} + U_{\text{calcite}} + U_{\text{iron oxides}} + U_{\text{clays}} + U_{\text{humics and bacterial surfaces}}$$

Surface complexation modeling databases for individual mineral phases (e.g., Dzombak and Morel; Sverjensky)


% U(VI) adsorbed
pH
100
90
80
70
60
50
40
30
20
10
0
5.5
6.0
6.5
7.0
7.5
8.0
8.5
Ca2+ = 2 mM
Ca2+ = 0
Model without
CaUO2(CO3)3 surface species
Triple layer
Model with
Ca2+ = 0
U(VI)tot = 10-6M
Fe(III) = 10-3M as ferrihydrite
NaNO3 = 0.005M
pCO2 = 2% (0.02 atm)

U(VI) surface reactions considered in semi-empirical SCM

Reaction
$SOH + UO_2^{2+} = SOUO_2^{+} + H^{+}$
$SOH + UO_2^{2+} + H_2O = SOUOOH + 2H^{+}$
$SOH + UO_2^{2+} + H_2CO_3 = SOUO_2HCO_3 + 2H^{+}$
$SOH + UO_2^{2+} + H_2CO_3 = SOUO_2CO_3^{-} + 3H^{+}$
$SOH + UO_2^{2+} + H_2CO_3 + H_2O = SOUO_2OHCO_3^{2-} + 4H^{+}$
$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(HCO_3)_2^{-} + 3H^{+}$
$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(CO_3HCO_3)^{2-} + 4H^{+}$
$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(CO_3)_2^{3-} + 5H^{+}$
$SOH + UO_2^{2+} + 2H_2CO_3 + H_2O = SOUO_2OH(CO_3)_2^{4-} + 6H^{+}$

Monodentate surface reactions shown for simplicity. Bidentate surface reactions used in the actual modeling. Model has no EDL terms or surface acidity constants.

Summary of Modeling Results and Parameters

Semi-empirical model calibrated with all 96-hour desorption and adsorption data for the NPP-1-16 and SPP-2-18 samples

Fitted parameters were one site density and the surface constants for three U(VI) surface reactions

Total site density assumed to be 3.84 μmoles/m^2 of BET surface area

Optimal strong site density determined with FITEQL to be 1.34 nmoles/m^2 of BET surface area

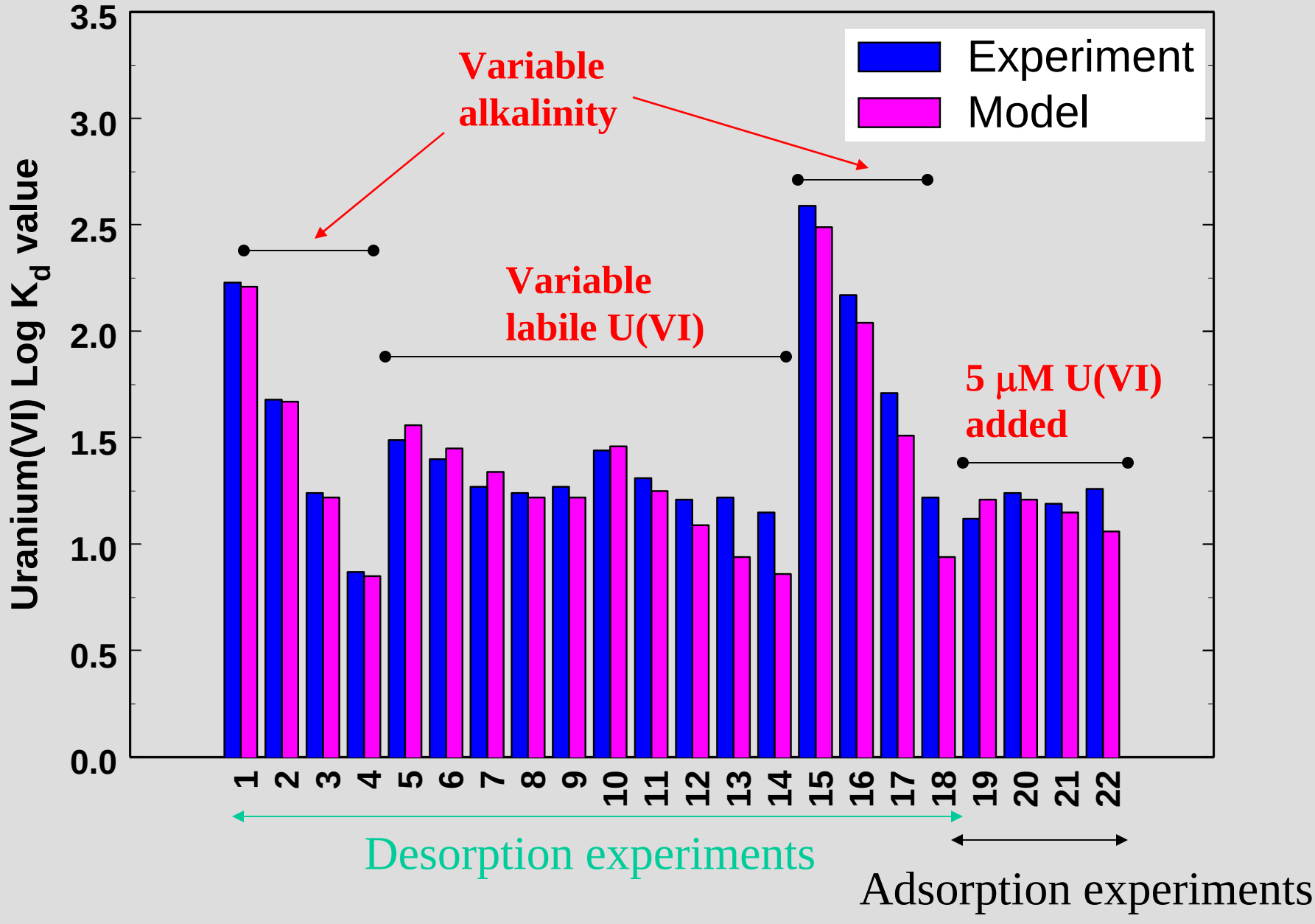
U(VI) surface reactions:

$$S(OH)_2 + UO_2^{2+} + 2H_2CO_3 = SO_2UO_2(HCO_3CO_3)^{3-} + 5H^+ \quad \text{Log K = -16.30}$$

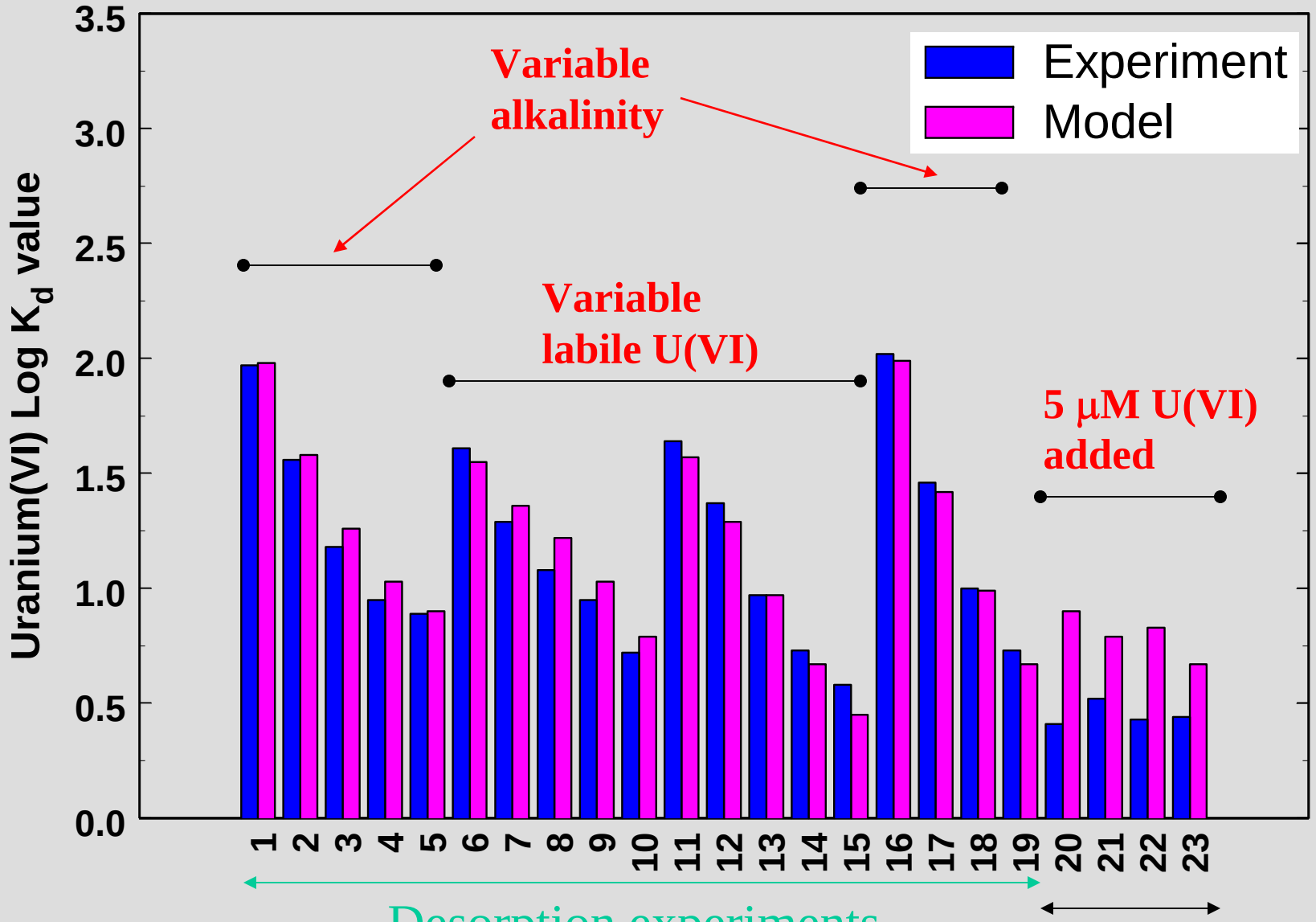
$$W(OH)_2 + UO_2^{2+} + 2H_2CO_3 = WO_2UO_2(HCO_3CO_3)^{3-} + 5H^+ \quad \text{Log K = -20.64}$$

$$W(OH)_2 + UO_2^{2+} + 2H_2CO_3 = WO_2UO_2(CO_3)^{4-} + 6H^+ \quad \text{Log K = -28.01}$$

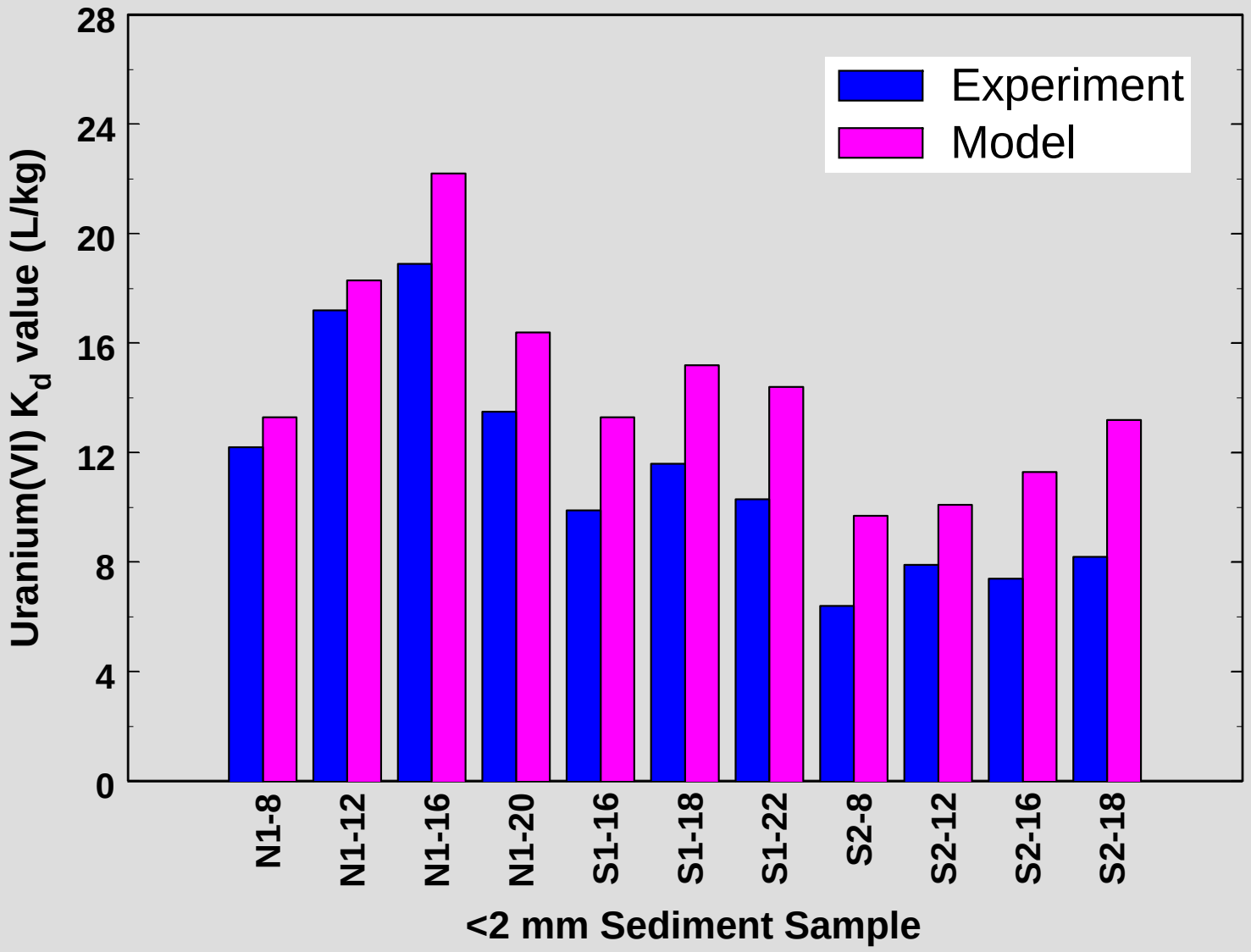
Model calibration – batch experiments with NPP-1-16 sample



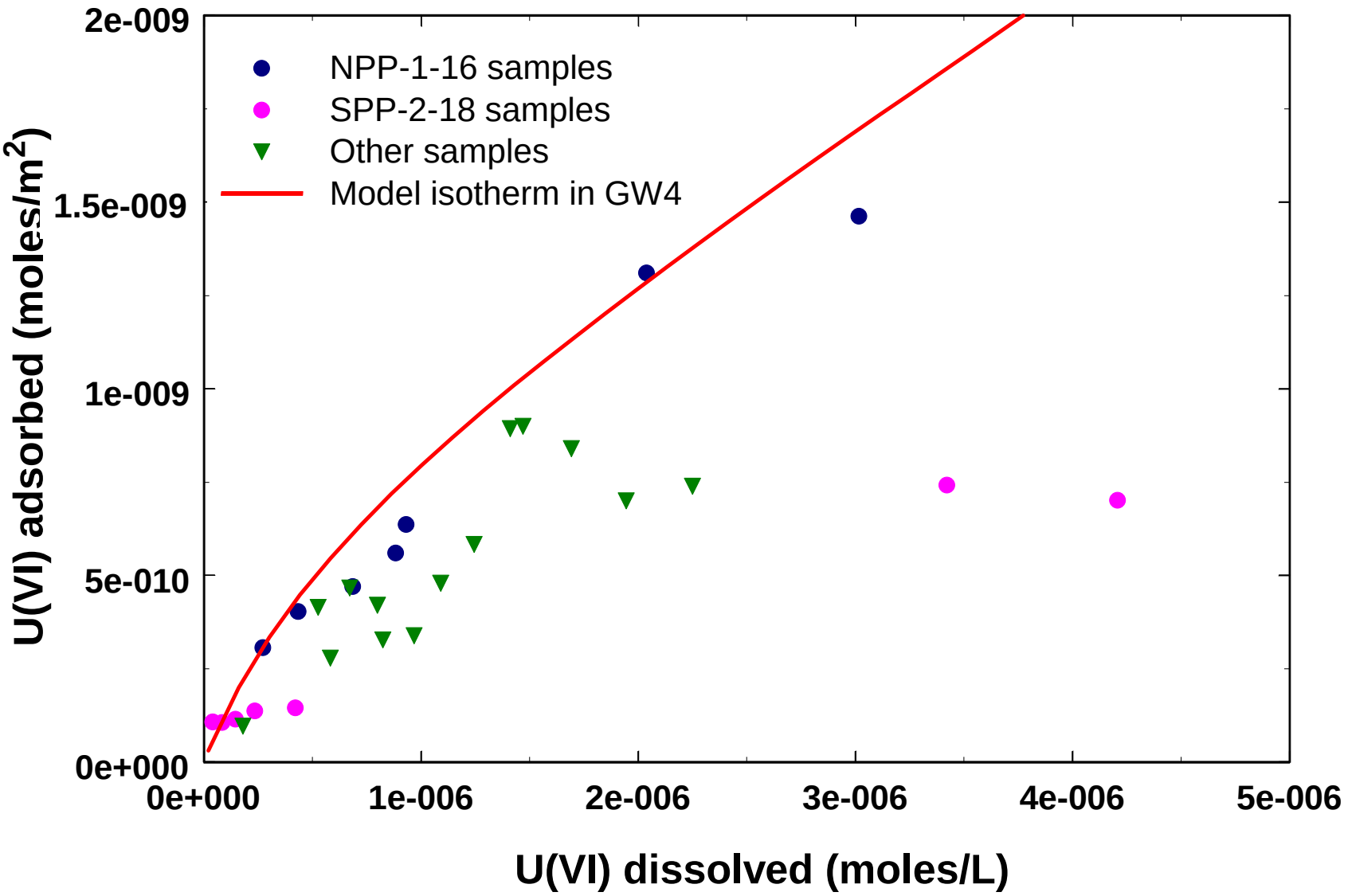
Model calibration – batch experiments with SPP-2-18 sample



Model prediction of Kd values for other NPP and SPP samples



Conditions: pH 7.9 – 8.3; alkalinity 3.5-3.9 mequiv/L; dissolved U(VI), 43-460 µg/L; 2 weeks equilibration; surface area 15.3-27.2 m^2/g; 2.9-14 ppm total U in sediments


NPP-1-16 samples
SPP-2-18 samples
Other samples
Model isotherm in GW4
U(VI) adsorbed (moles/m2)
U(VI) dissolved (moles/L)
2e-009
1.5e-009
1e-009
5e-010
0e+000
0e+000
1e-006
2e-006
3e-006
4e-006
5e-006

Conclusions thus far …….

1. U(VI) desorption sensitive to alkalinity changes

2. Contaminated sediment samples contain significant fractions of both adsorbed (labile) U(VI) and “co-precipitated” U(VI) (can be dissolved by hydroxylamine hydrochloride extractions)

3. Semi-empirical SCM describes the partitioning of the labile U(VI) fraction reasonably well, but likely needs further testing with other samples