Actinide Chemistry and Repository Science Program in support of the Waste Isolation Pilot Plant (WIPP)

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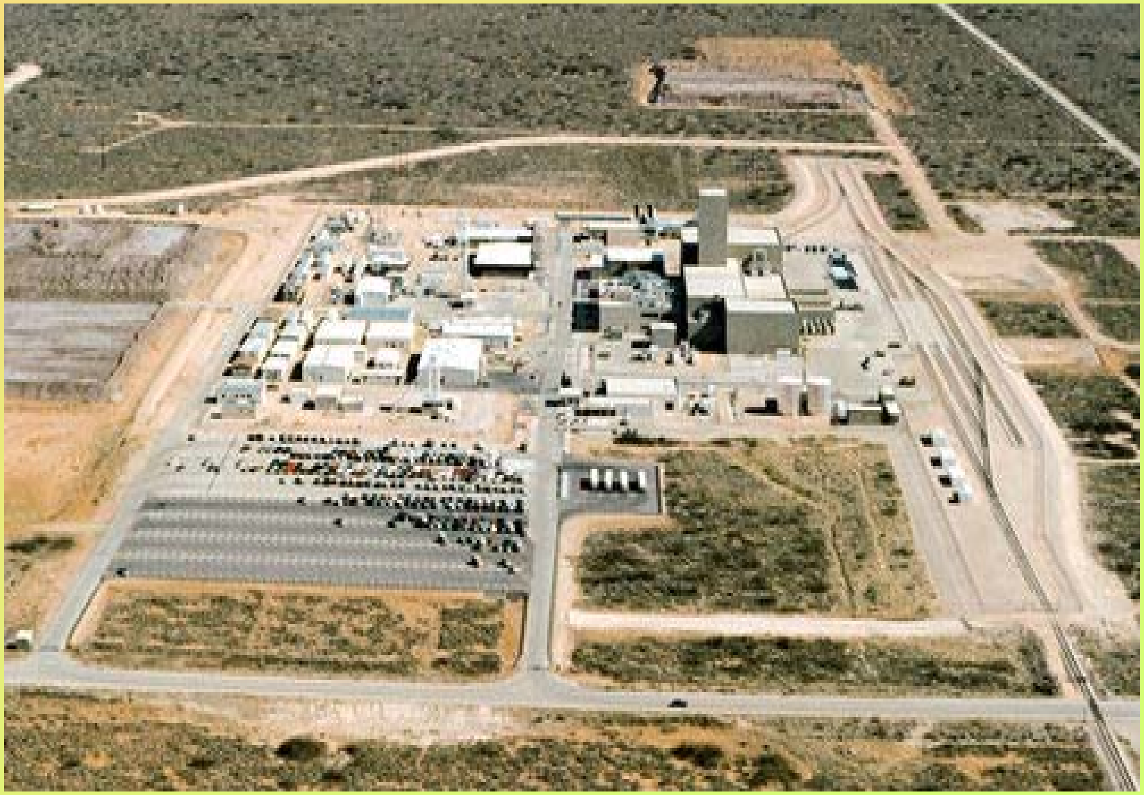
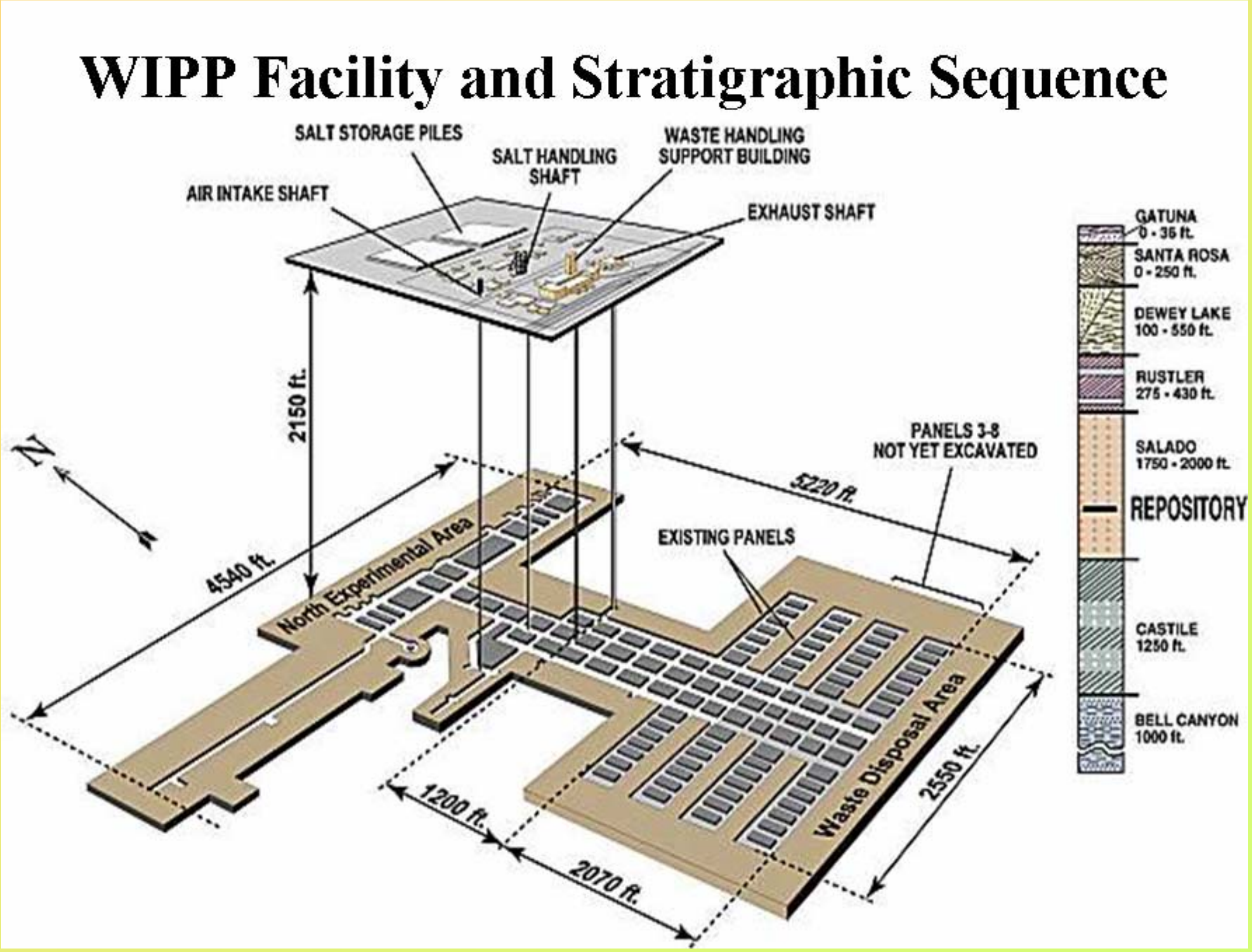
The Waste Isolation Pilot Plant, WIPP, a cornerstone of the DOE' s cleanup effort, is designed to permanently dispose of defense-generated transuranic radioactive waste from research and production activities in the

DOE weapons complex. The WIPP is located in southeastern New Mexico, 26 miles east of Carlsbad.

Waste disposal operations began on March 26, 1999.



Transuranic waste is shipped to the WIPP from many generator and storage sites such as Savannah River Site, Oak Ridge, Argonne, Rocky Flat, Idaho, Nevada Test Site, Livermore and Los Alamos. All shipments are done using specially designed TRUPAC-II containers.



Disposal rooms are excavated in an ancient, stable salt formation 2,150 feet (almost one-half mile) underground. Transuranic waste, which consists of clothing, tools, rags, debris and other disposable items contaminated with radioactive elements, mostly plutonium, are emplaced in 55 gallon steel drums for permanent disposal.

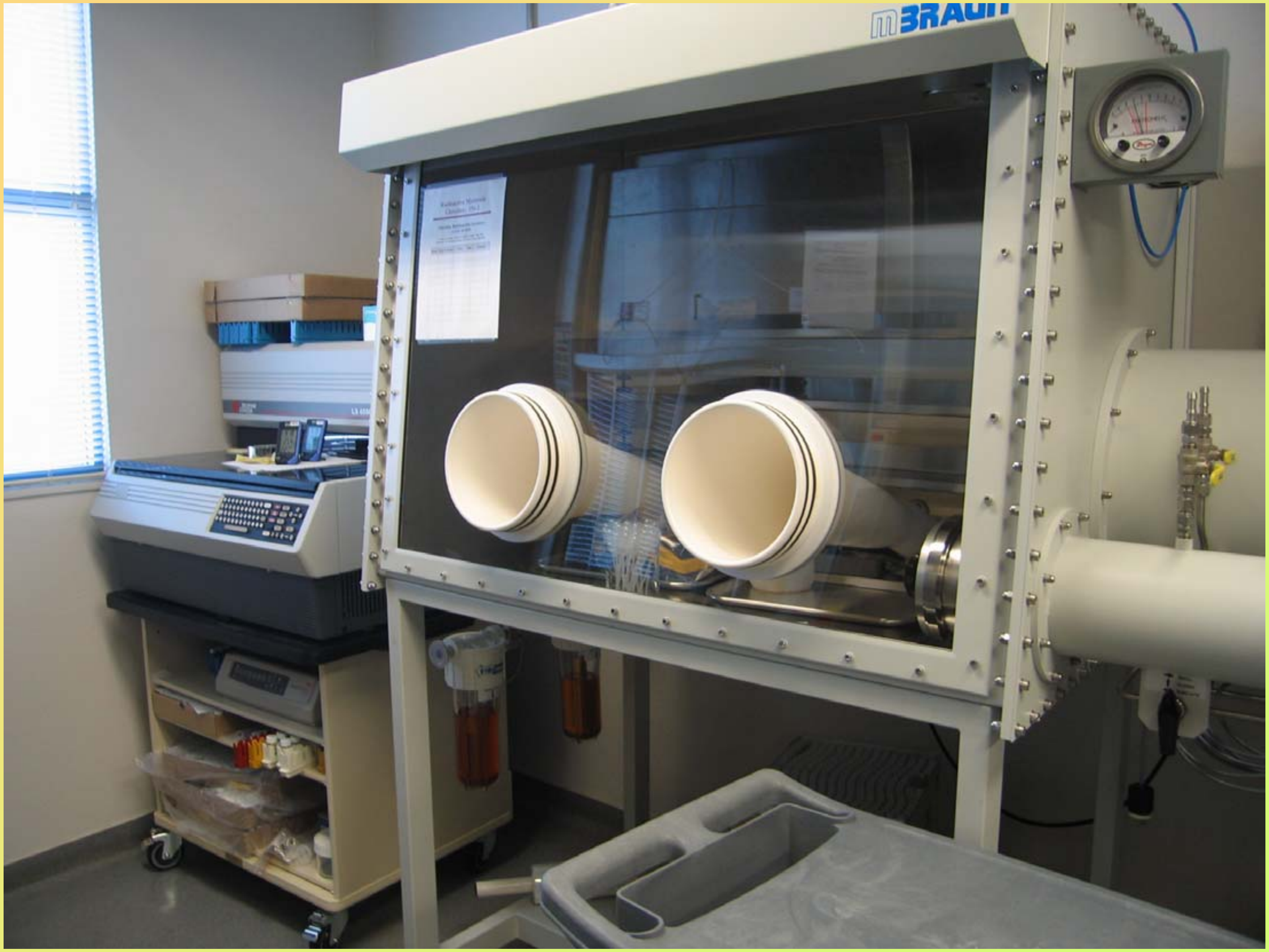
Waste and magnesium oxide are placed in a WIPP Disposal Room. On March 23, 2006 the amount of 76,156 containers are disposed in the underground.

The Actinide Chemistry and Repository Science Program (ACRSP) is part of a larger multi-disciplinary Los Alamos group (EES-12) working in Carlsbad. We conduct our laboratory research programs at the Carlsbad Environmental Monitoring and Research

Center, an institute that is operated by New Mexico State University. Our most important purpose is to provide laboratory research and program support on actinide-related issues to the DOE Carlsbad Field Office (CBFO) to maintain the certification of the WIPP. Additionally, we have the capability to conduct research programs in actinide environmental chemistry for other sponsors.

Glove boxes with controlled atmosphere

Glove box for high radioactivity operation and LCS (behind)



Hoods for work with low radioactivity samples

ICP-MS and Dr. Mike Richmann as operator

Lab Capability:

- ICP-MS designated for Pu and Am
- Photo-acoustic spectroscopy with powerful laser
- XRD (x-ray diffraction)
- Spectroscopy (Cary 500)
- Ion Chromatography
- CO_2 analysis (down to ppb level)
- Liquid Scintillation Counting
- Glove boxes with controlled atmosphere (<0.1 ppm O_2)

The Actinide Chemistry and Repository Science Program (ACRSP) is conducted according to five Test Plans approved by CBFO:

- Solubility/Stability of Uranium (VI) in WIPP
  - Solubility of U(VI) in WIPP brine
  - Redox stability of U(VI) in WIPP brine
  - Effect of radiolytic products on uranium speciation
- Plutonium (VI) Reduction by Iron
  - Limited scope - confirmatory study on effect of various form of iron, iron oxide on plutonium redox reaction

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Neodymium (III) Solubility in WIPP Brine

- Solubility of Nd(III) in WIPP brine, an analog for Am(III) and Pu(III), studied as a function of pC_{H+} and carbonate concentration and measured from over-saturation and under-saturation

Americium Solubility/Stability in WIPP Brine

- Solubility of Am(III) in WIPP brine
- Effect of radiolytic products and repository components on americium oxidation and stability/solubility of Am higher oxidation states at the repository conditions

- Plutonium Speciation and Solubility in the WIPP
  - Technical assessment of the current WIPP Database on Pu
  - Relevance of Pu(III) in the WIPP
  - Solubility of Pu(IV) in the WIPP
  - Reduction of Pu(V0 and Pu(VI) in the WIPP
  - Speciation of plutonium in the WIPP

Two major programmatic groups can be distinguished:

1. Effect of radiolytic products of brine, microbial activity and repository components on redox speciation of plutonium, americium and uranium.

2. Solubility of transuranium elements in WIPP brine (effect of pC_{H+}, carbonate, organic ligands, etc.)

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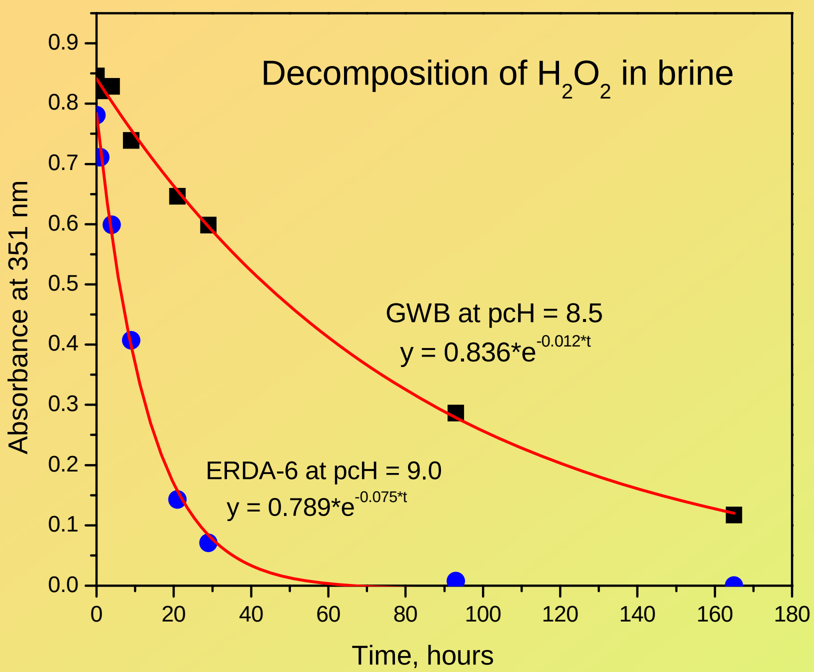
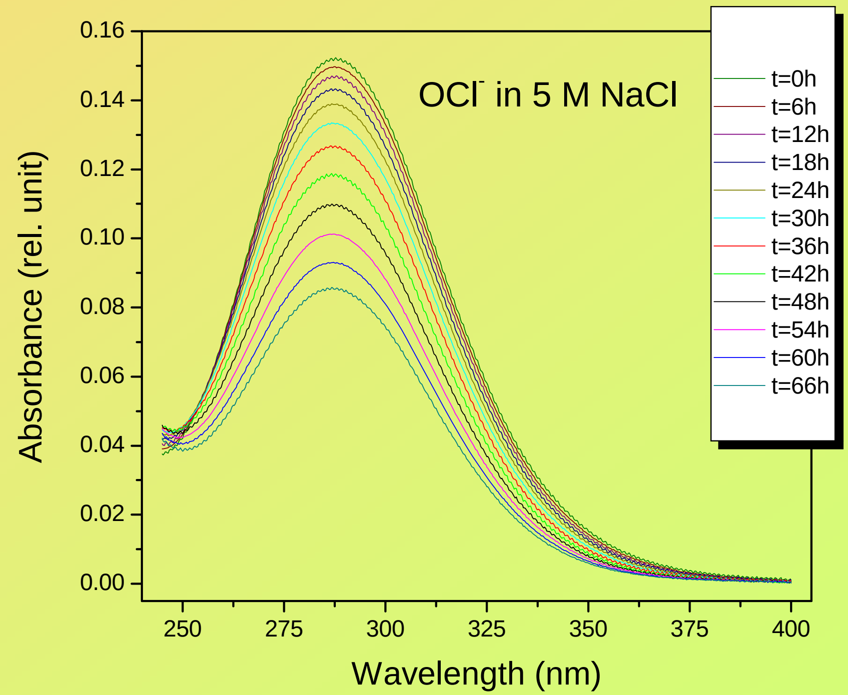
Brine Composition Used in Actinide Solubility Studies

	ERDA-6		GWB		$MgCl_2$ simplified		NaCl simplified	
Component	g/L	M/L	g/L	M/L	g/L	M/L	g/L	M/L
NaCl	248.6	4.254	167.8	2.874			292.2	5.0
$MgCl_2.6H_2O$	3.667	0.018	193.4	0.953	751.9	3.704		
Na_2SO_4	22.52	0.159	23.61	0.166				
NaBr	1.074	0.010	2.565	0.025				
$Na_2B_4O_7.10H_2O$	5.7	0.015	14.03	0.037				
KCl	6.869	0.092	32.57	0.437				
LiCl	-	-	0.174	0.004				
$CaCl_2.2H_2O$	1.672	0.011	1.896	0.013				
Ionic strength	4.965 M		6.839 M		11.1 M		5.0 M	
Density g/mL	1.183		1.216		1.252		1.185	

GWB - Generic Weep Brine
ERDA-6 - Energy Research and Development Administration Well 6

Stability of H_2O_2 and OCl^- in brine

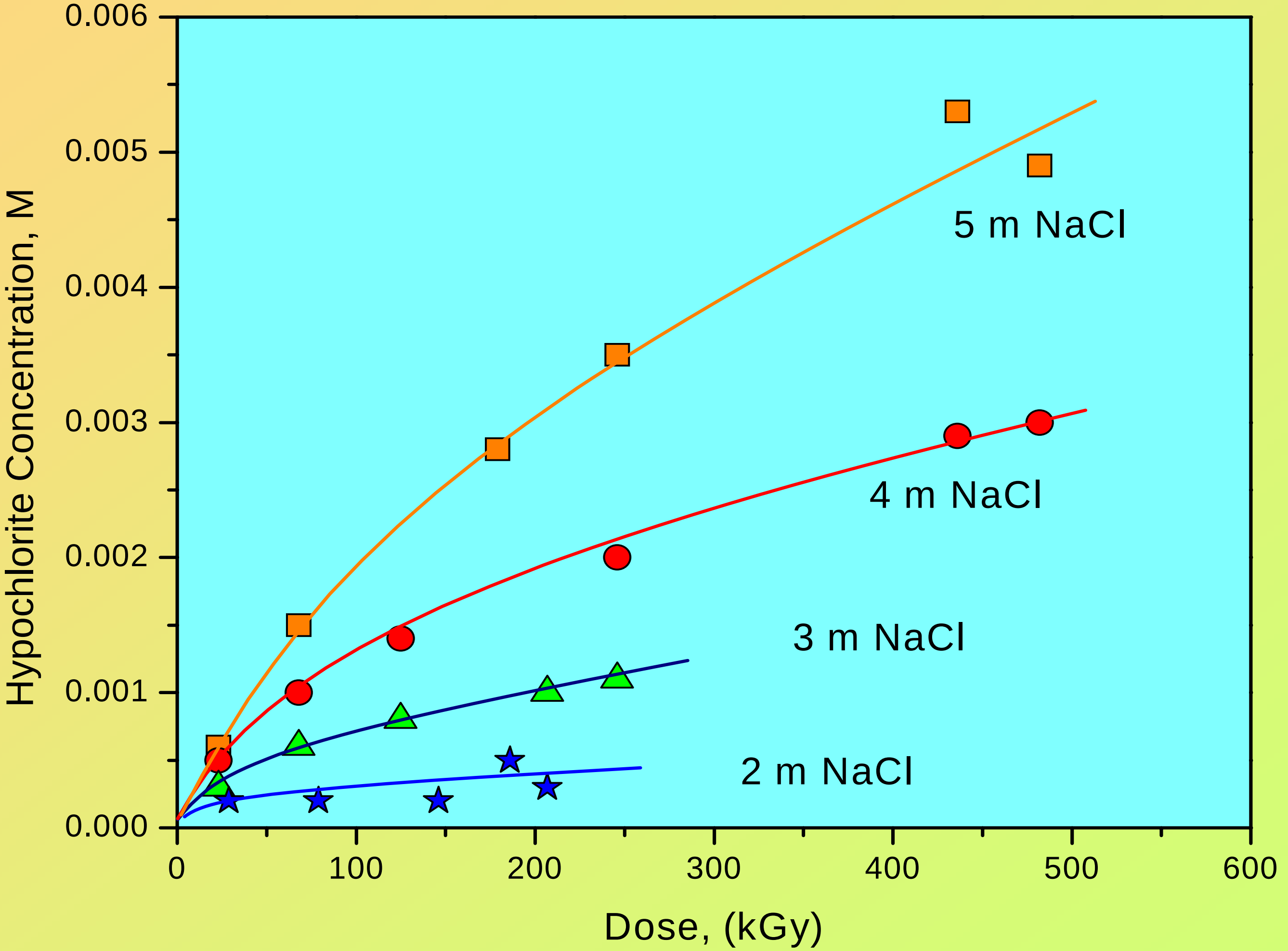




$$2\,OCl^- + H_2O_2 \leftrightarrows 2\,Cl^- + H_2O + O_2$$

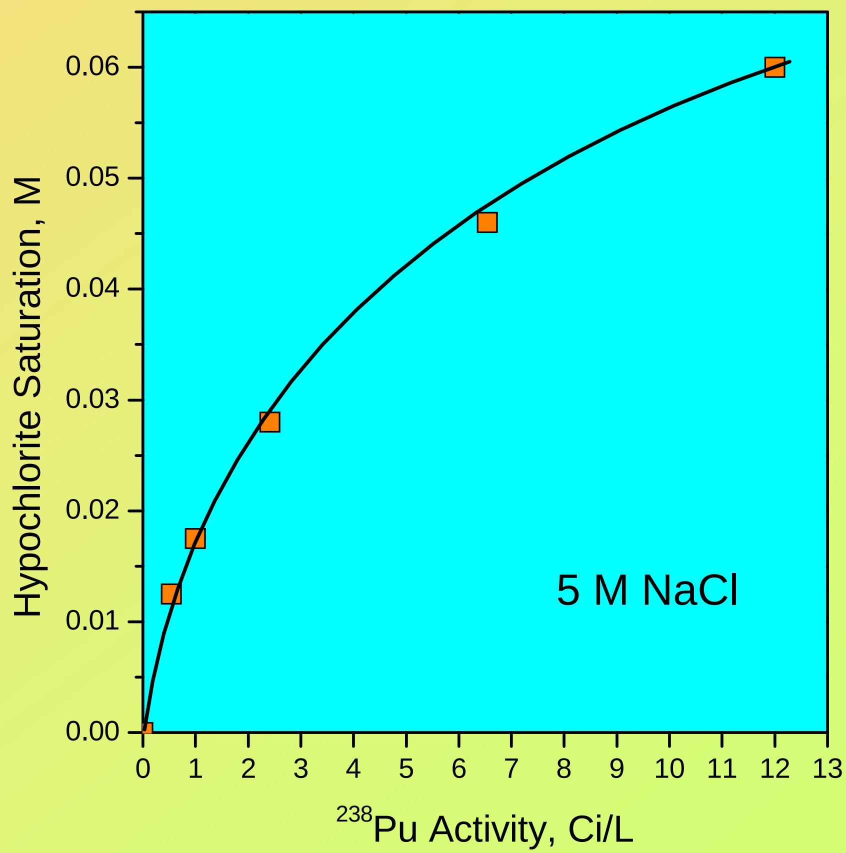
$$OCl^- + Br^- \leftrightarrows Cl^- + OBr^- + \ldots$$

Dependence of hypochlorite generation as a function of absorbed dose of α radiation and NaCl concentration



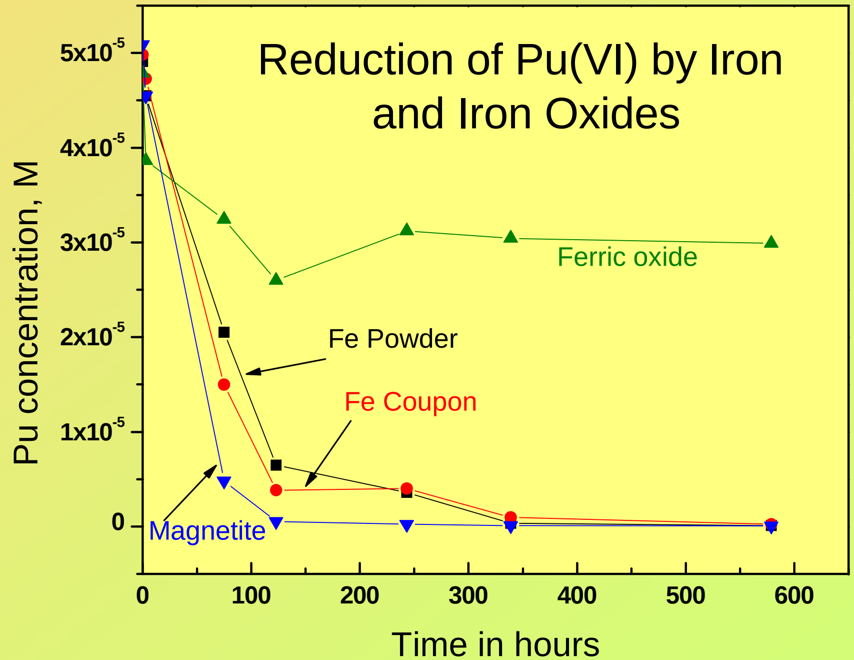
Primary G-values calculated for different chloride concentrations

Cl^- concentration, [M]	G_{H2O2}	$G_{ClOH\cdot}$
5	0.23	0.55
4	0.27	0.50
3	0.32	0.44
2	0.40	0.38

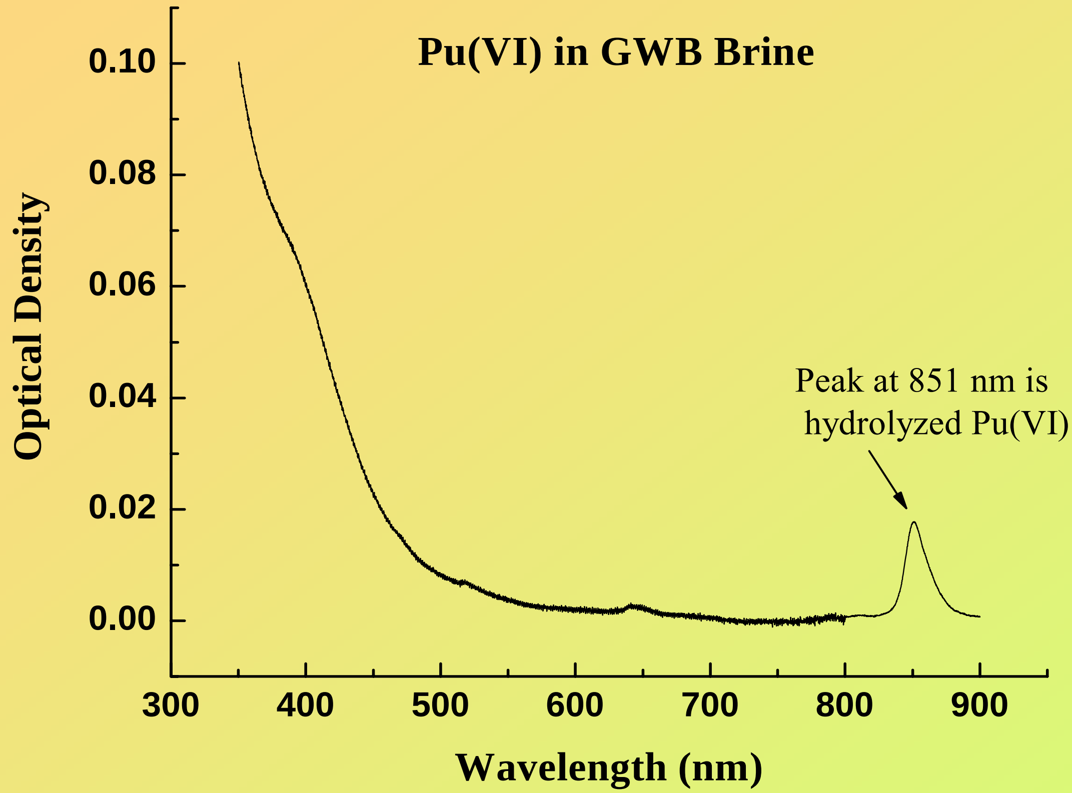


*Kelm M., I. Pashalidis, I.J. Kim Applied Radiation and Isotopes, **51,** (1999) 637-642.*

Effect of various forms of iron on plutonium (VI) reduction in ERDA-6 brine at pC_{H+}=9.2 and anoxic conditions



The presence of Fe^{0} and Fe^{2+} resulted in the rapid loss of plutonium from solution. In the case of ferric oxide some loss of Pu was noted, but residual concentrations remained high and it was (postulated) due to sorption not reduction/precipitation. The most complete and rapid loss of Pu occurred for magnetite which was the only iron phase that contained Fe^{2+}. These results show that Fe^{0} and Fe^{2+} effectively remove dissolved plutonium from brine.



The absorption spectrum of the plutonium in GWB brine. Since the pH is ~ 9, the plutonium is hydrolyzed (complexed with hydroxide) resulting in a 20 nm shift in the absorption maximum to 851 nm. The absorption spectrum of this solution was stable over the three-month period that it was monitored.

Solubility of Nd(III) and U(VI)

The goal of this research is to provide the experimental data for the solubility of trivalent and hexavalent actinides.

In this study neodymium (III) was used as a redox-invariant analog for Am (III) and Pu (III).

The experiments in each approach are conducted in GWB and ERDA-6 as a function of pC_{H+} and carbonate concentration.

Simplified brine, 5 M NaCl, was used for comparison.

Experimental limitations:

- The highest concentration of carbonate ion in GWB and ERDA-6 brine, before the cloud point was observed, was determined to be 2- 4 x 10^{-2} M.

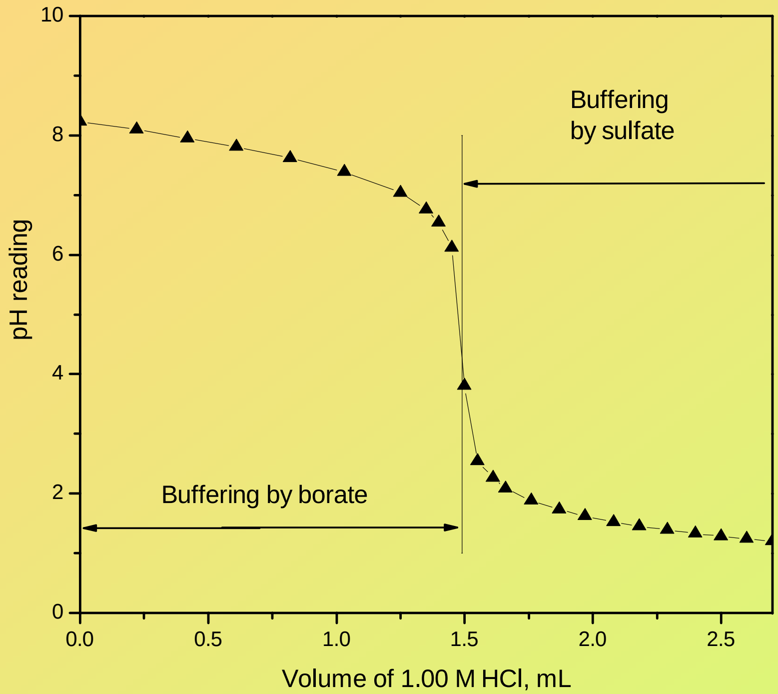
- The highest pC_{H+} , before the cloud point was observed, was:

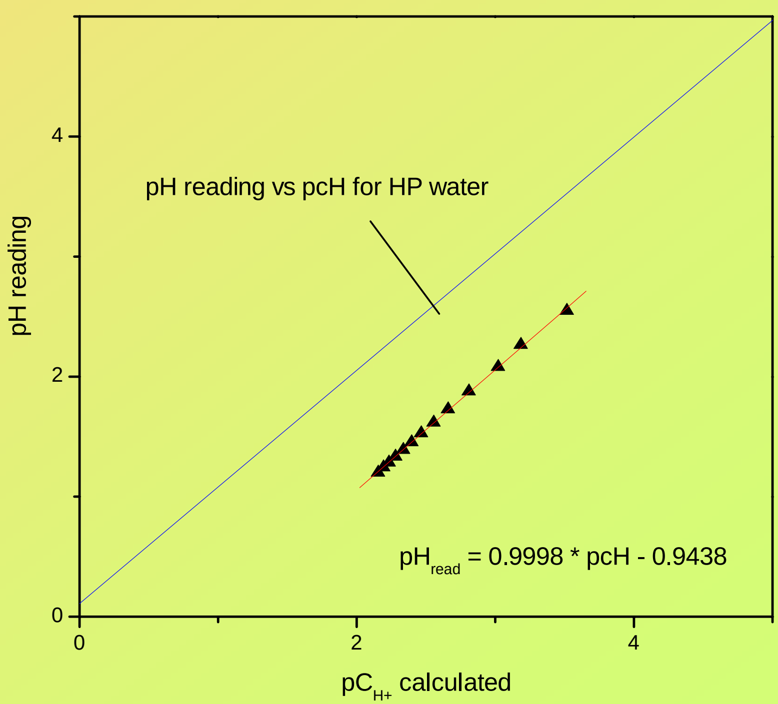
  - for Erda-6 was equal to 10.8,

  - for GWB brine was equal to 8.7.

Low pC_{H+} limit and pC_{H+} vs. pH reading in ERDA-6 brine

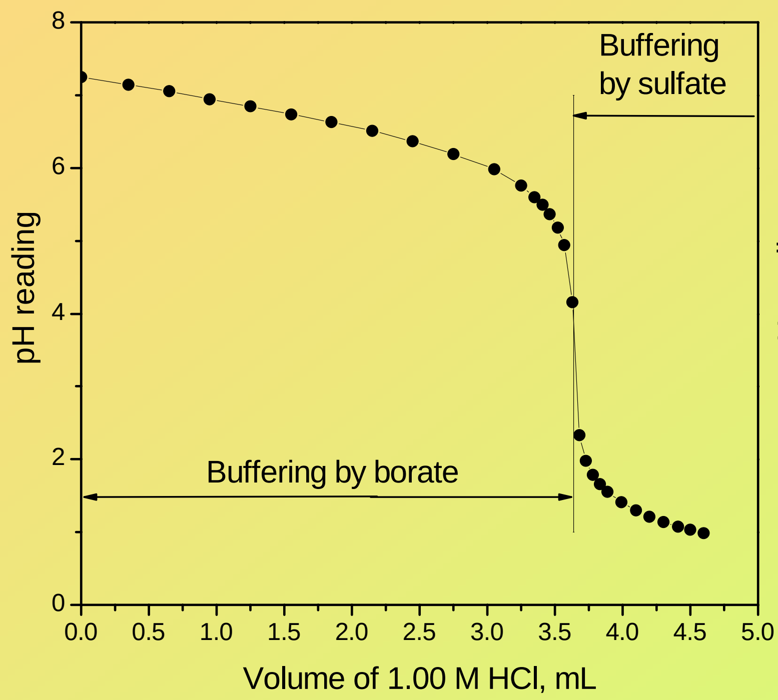
Base/Acid Titration in ERDA-6 Brine

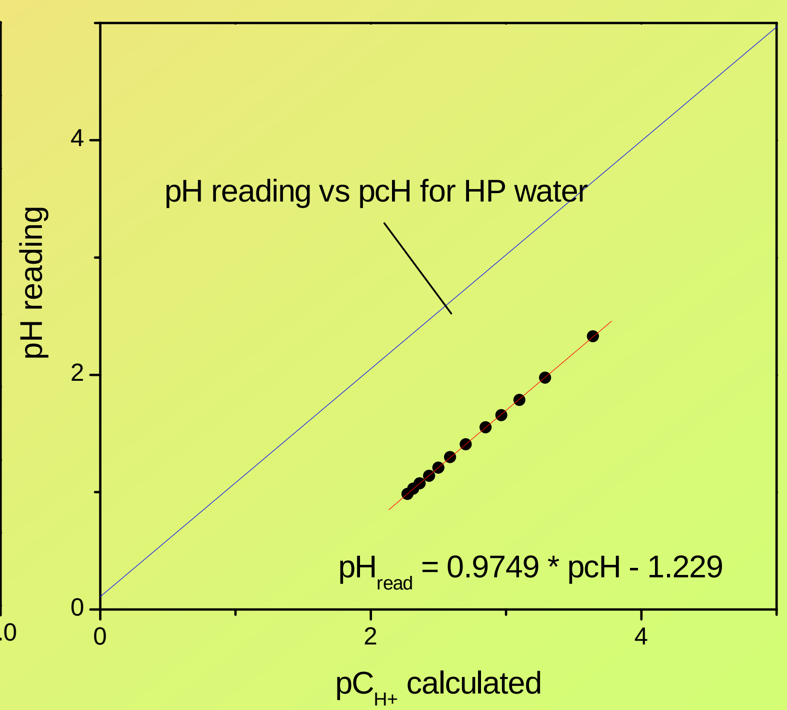




Low pC_{H+} limit and pC_{H+} vs. pH reading in GWB brine

Base/Acid Titration in GWB Brine





ERDA-6

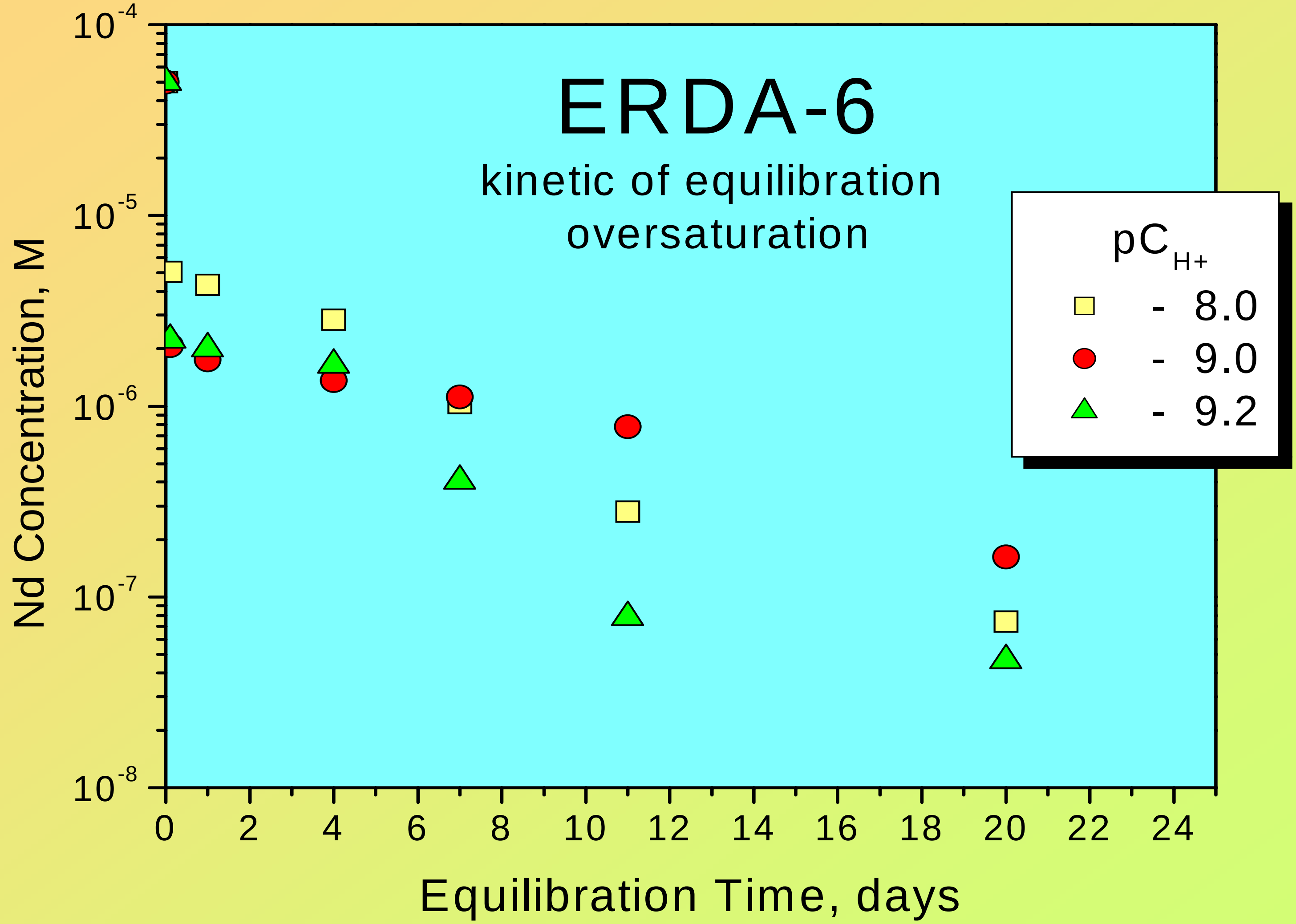
- pC_{H+} range 7.5 – 12
- Initial carbonate concentrations:

  0 (carbonate free), 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} M
- $NdCl_3$ solution was used as a spike in the over-saturation approach
- Initial Nd(III) concentration was $5x10^{-5}$ M and U(VI) was $1.7x10^{-5}$ M

ERDA-6 cont.

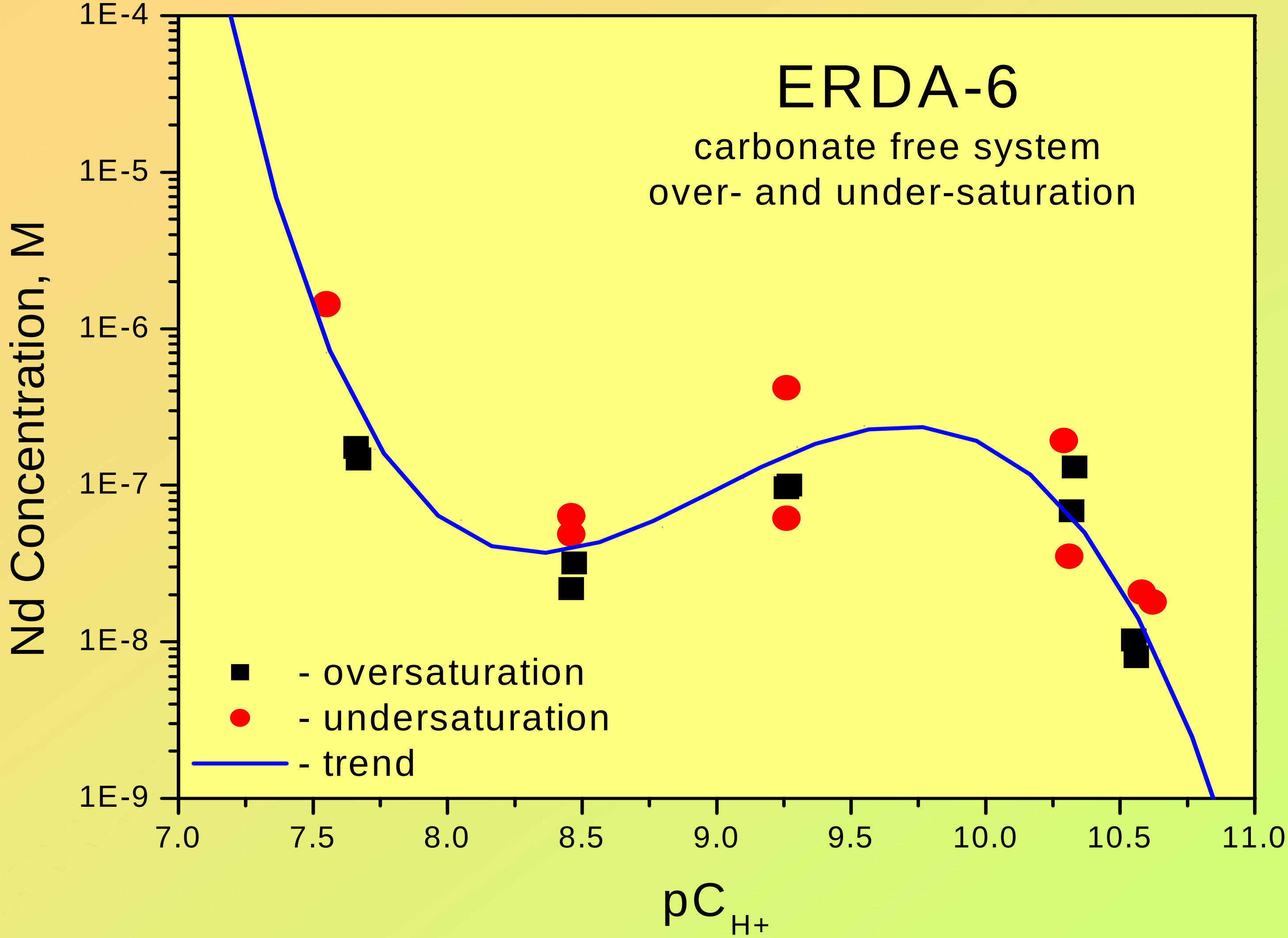
- $NdOH(CO_3)$ solid, prepared in our lab, was used in the under-saturation approach with carbonate
- $Nd(OH)_3$ solid, commercial from Alfa Aesar, was used in the under-saturation approach without carbonate
- All carbonate free experiments were conducted in the nitrogen glove box and carbonate ion was removed from the brine prior to the experiment

Nd (III)



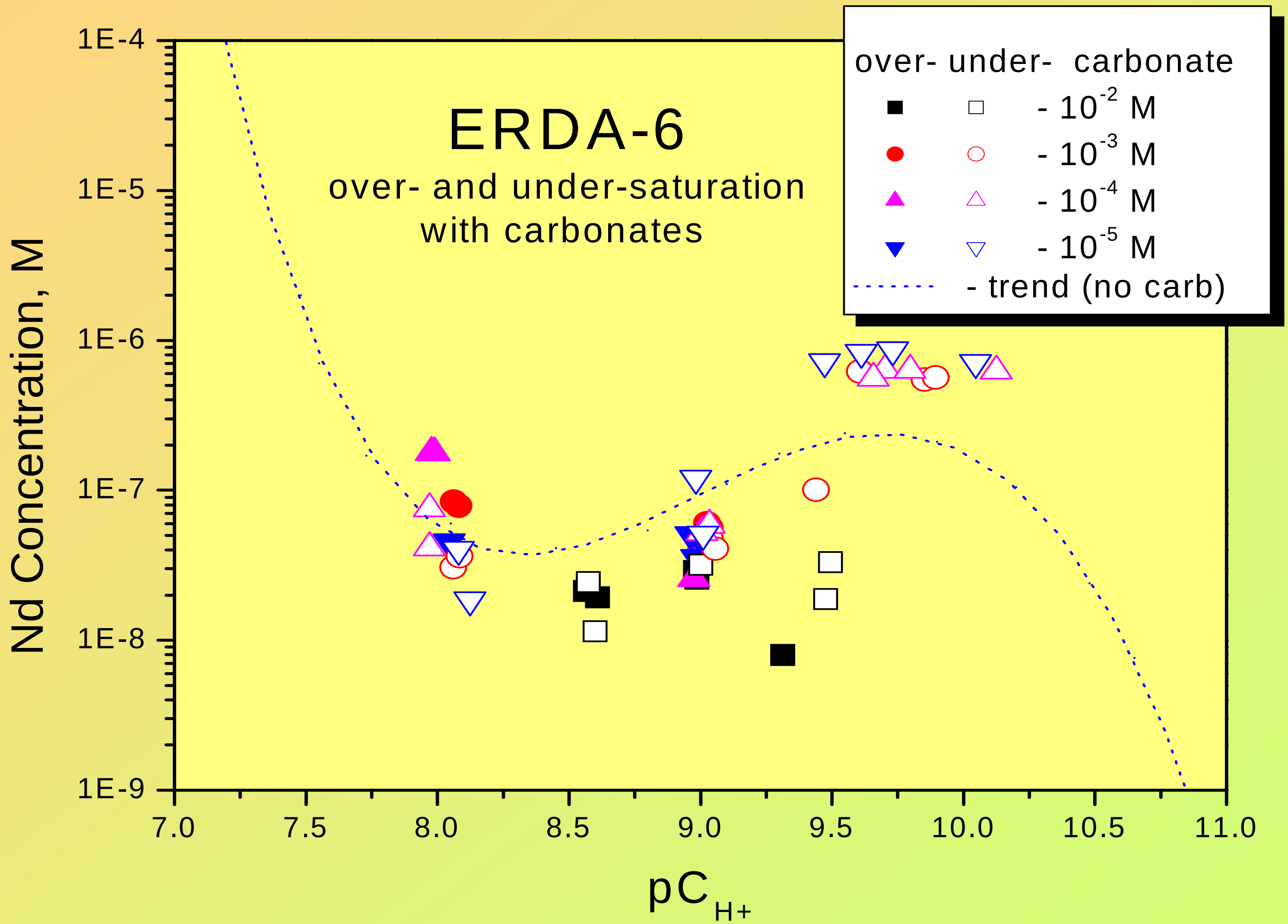
ERDA-6
kinetic of equilibration
oversaturation
pC H+
- 8.0
- 9.0
- 9.2
Nd Concentration, M
10-4
10-5
10-6
10-7
10-8
0
2
4
6
8
10
12
14
16
18
20
22
24
Equilibration Time, days

Nd (III)

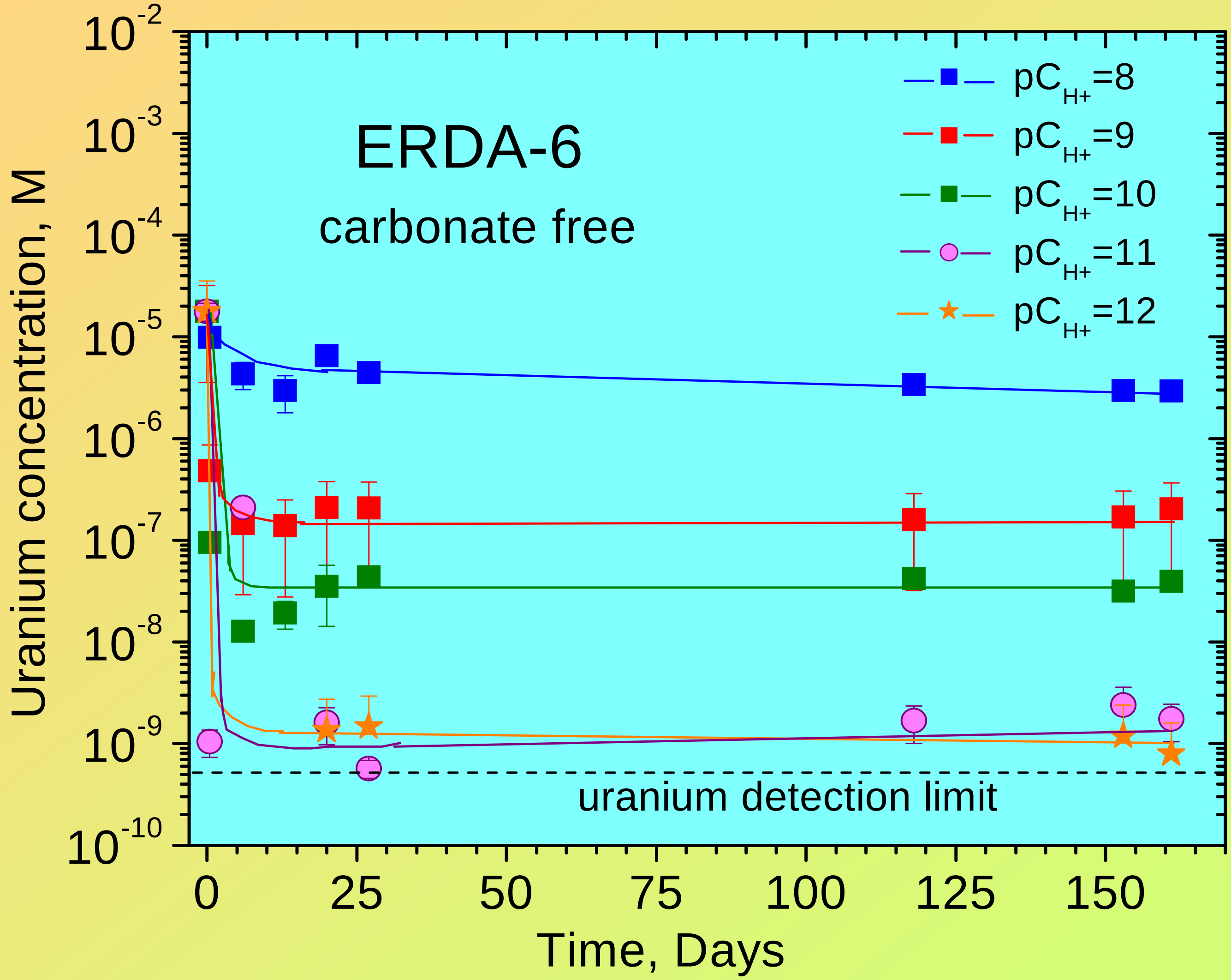


ERDA-6
carbonate free system
over- and under-saturation
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
Nd Concentration, M
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
pC H+
- oversaturation
- undersaturation
- trend

Nd (III)

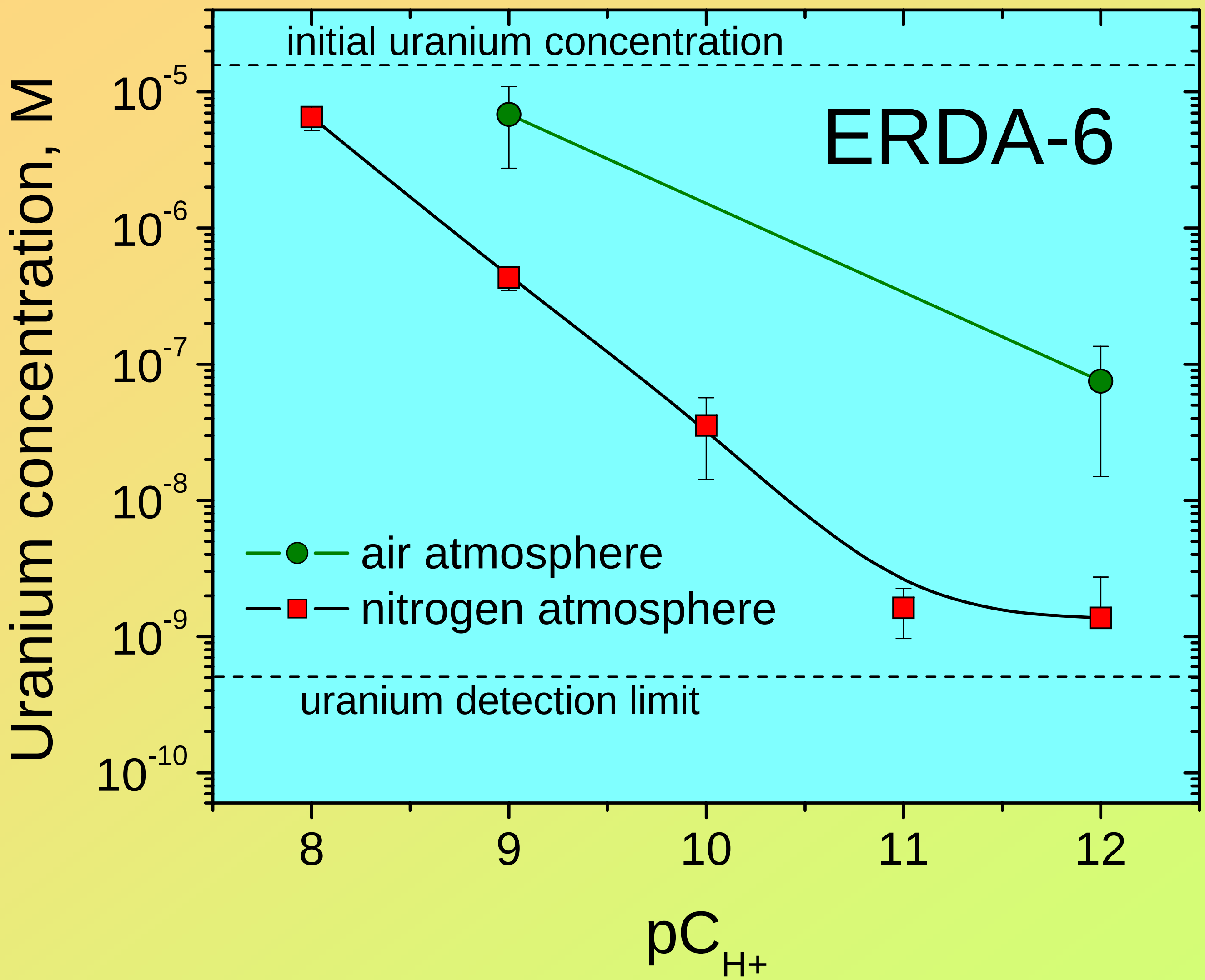

ERDA-6
over- and under-saturation
with carbonates
over- under- carbonate
- 10^-2 M
- 10^-3 M
- 10^-4 M
- 10^-5 M
- trend (no carb)
Nd Concentration, M
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
pC H+

U (VI)



ERDA-6
carbonate free
pCH+=8
pCH+=9
pCH+=10
pCH+=11
pCH+=12
uranium detection limit
Uranium concentration, M
Time, Days
10-2
10-3
10-4
10-5
10-6
10-7
10-8
10-9
10-10
0
25
50
75
100
125
150

U (VI)



initial uranium concentration
ERDA-6
air atmosphere
nitrogen atmosphere
uranium detection limit
Uranium concentration, M
10-5
10-6
10-7
10-8
10-9
10-10
8
9
10
11
12
pCH+

GWB

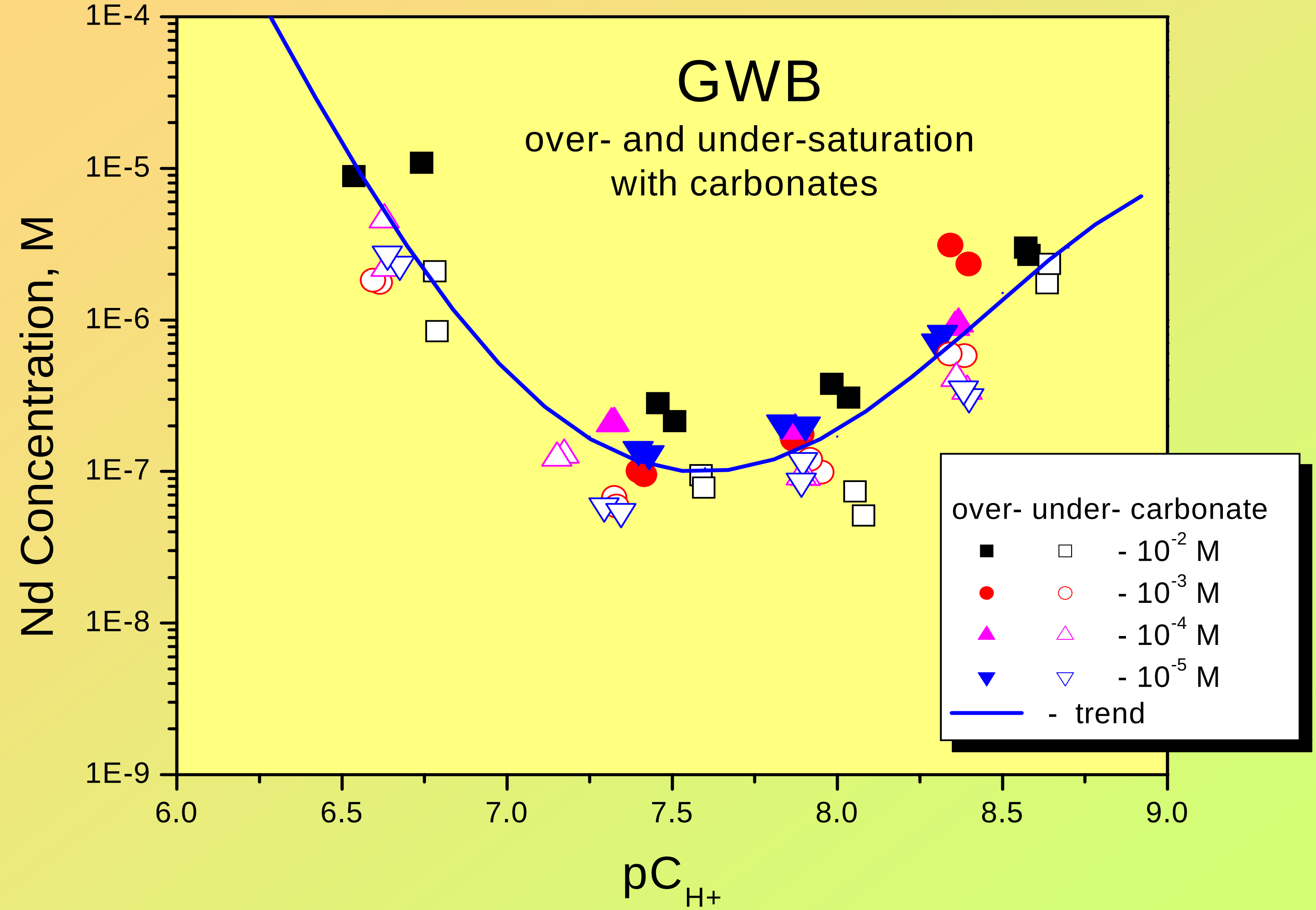
- pC_{H+} range 6.5 – 8.5
- Initial carbonate concentrations:

  0 (carbonate free), 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} M
- $NdCl_3$ solution was used as a spike in the over-saturation approach
- Initial Nd(III) concentration was $5x10^{-5}$ M

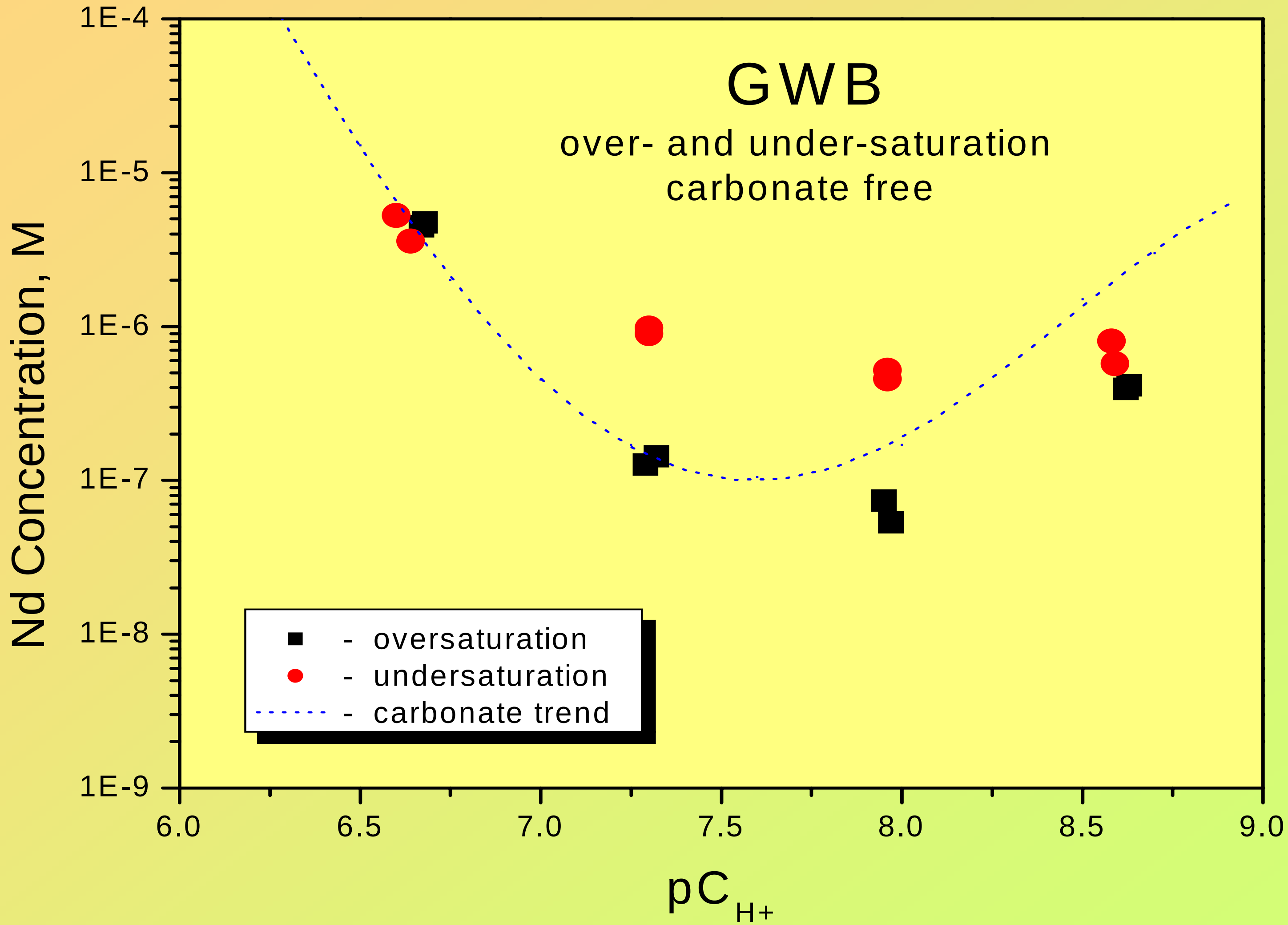
GWB CONT.

- $NdOH(CO_3)$ solid, prepared in our lab, was used in the under-saturation approach with carbonate
- $Nd(OH)_3$ solid, commercial from Alfa Aesar, was used in under-saturation approach without carbonate
- All carbonate free experiments were conducted in the nitrogen glove box and carbonate ion was removed from the brine prior to the experiment

Nd (III)

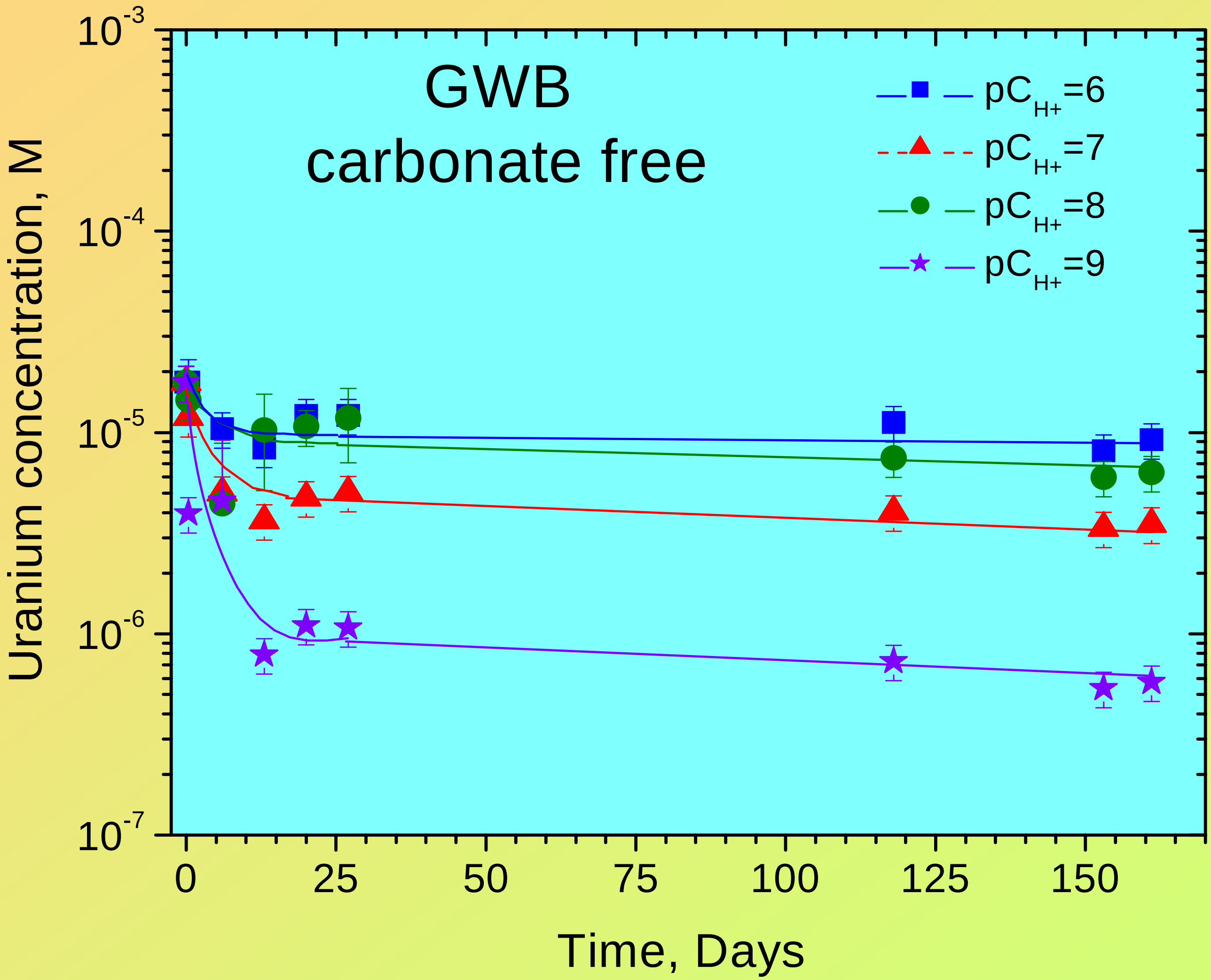

GWB
over- and under-saturation
with carbonates
Nd Concentration, M
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
6.0
6.5
7.0
7.5
8.0
8.5
9.0
pC_{H+}
over- under- carbonate
- 10^{-2} M
- 10^{-3} M
- 10^{-4} M
- 10^{-5} M
- trend

Nd (III)



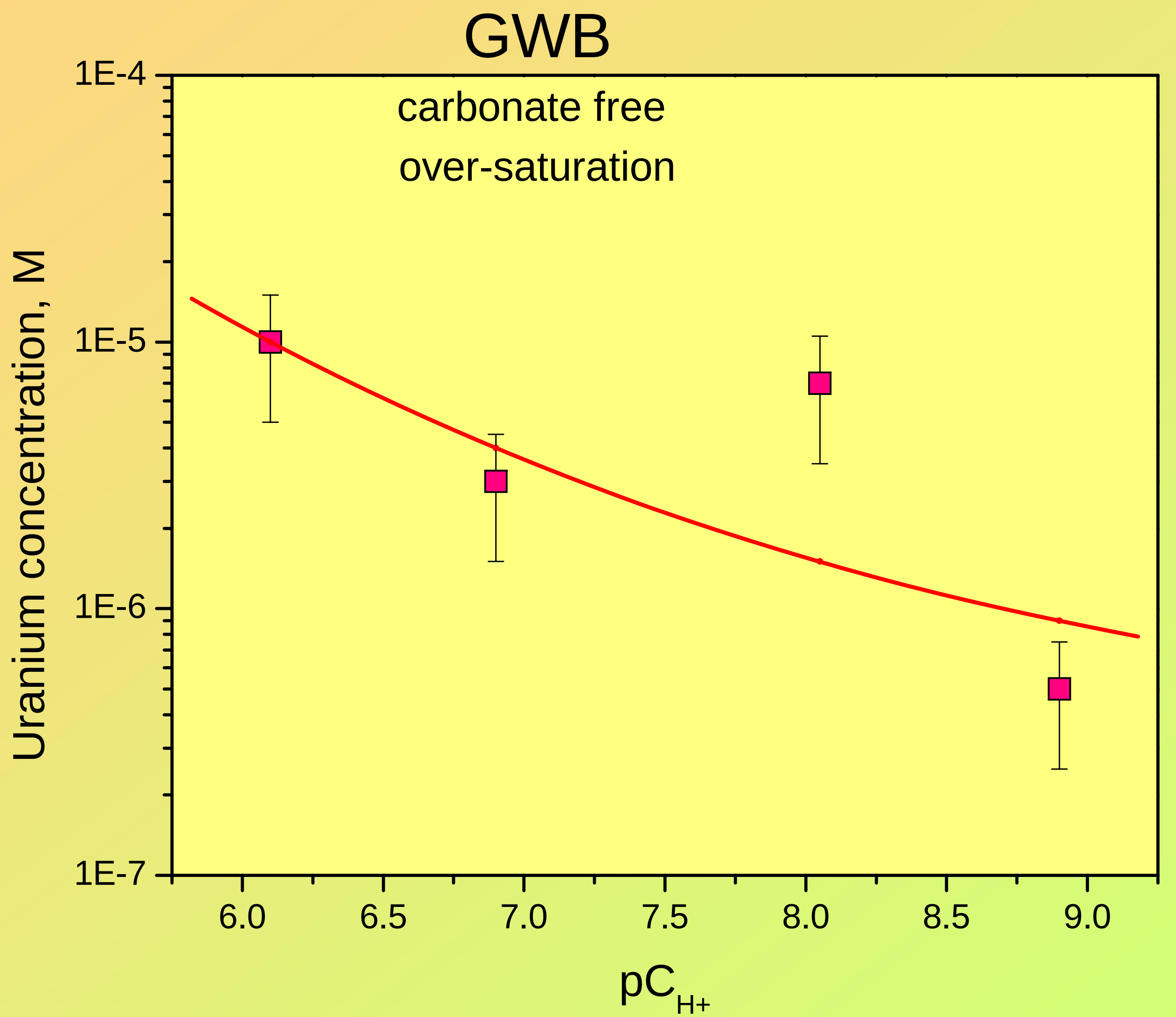
GWB
over- and under-saturation
carbonate free
Nd Concentration, M
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
6.0
6.5
7.0
7.5
8.0
8.5
9.0
pC H+
- oversaturation
- undersaturation
- carbonate trend

U (VI)



GWB
carbonate free
pC$_{H+}$=6
pC$_{H+}$=7
pC$_{H+}$=8
pC$_{H+}$=9
Uranium concentration, M
Time, Days
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
0
25
50
75
100
125
150

U (VI)



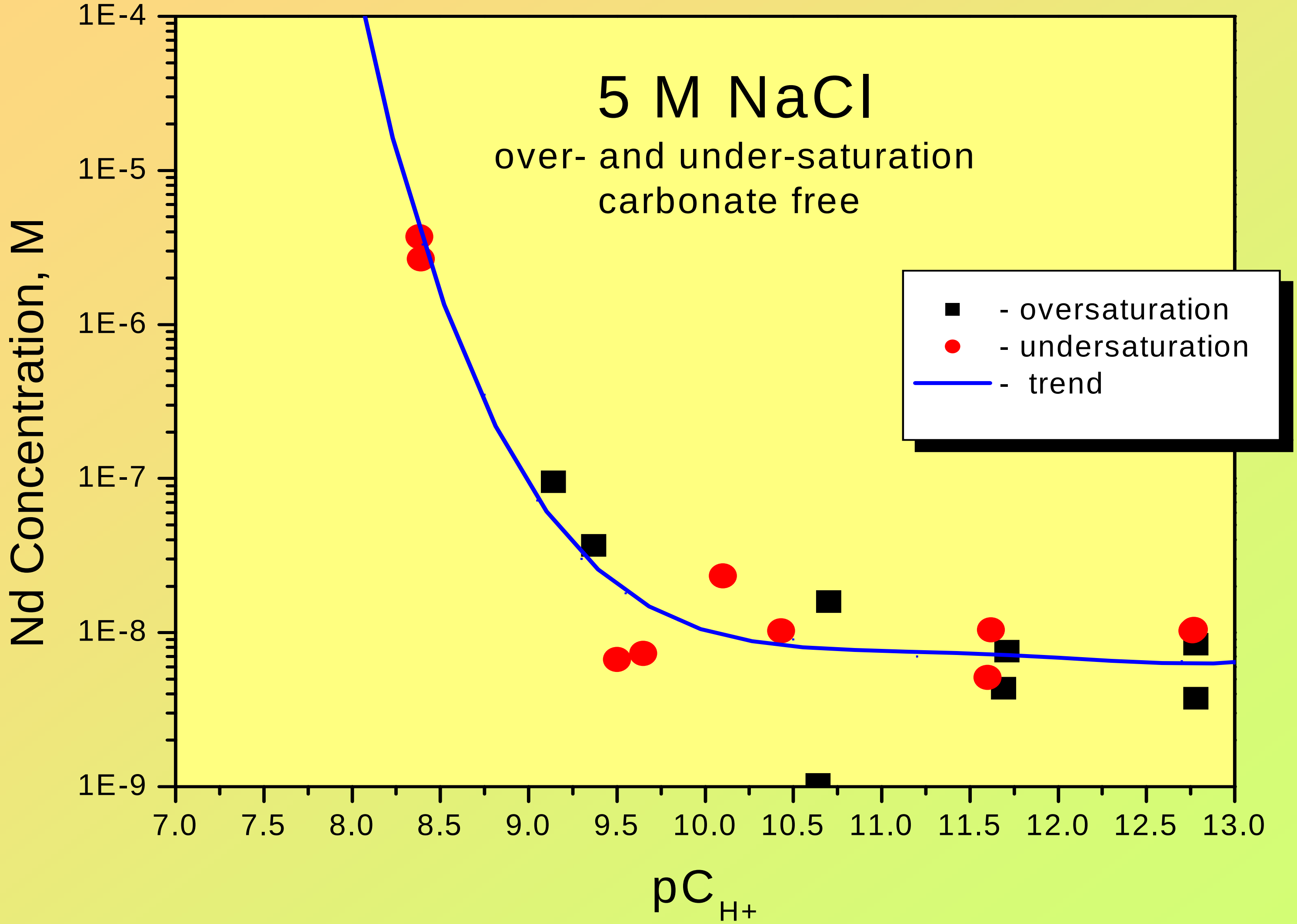
GWB
carbonate free
over-saturation
1E-4
1E-5
1E-6
1E-7
Uranium concentration, M
6.0
6.5
7.0
7.5
8.0
8.5
9.0
pC_{H+}

5 M NaCl

- pC_{H+} range 8.0 – 13.0
- Initial carbonate concentrations:

  0 (carbonate free), 10^{-5}, 10^{-4}, 10^{-3} and 10^{-2} M
- $NdCl_3$ solution was used as a spike in the over-saturation approach
- Initial Nd(III) concentration was $5x10^{-5}$ M

Nd (III)



5 M NaCl
over- and under-saturation
carbonate free
- oversaturation
- undersaturation
- trend
Nd Concentration, M
1E-4
1E-5
1E-6
1E-7
1E-8
1E-9
7.0
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
11.5
12.0
12.5
13.0
pC_{H+}

Conclusions:

The solubility experiments are still going on but preliminary conclusions can be made.

- The trend in Nd(III) solubility measured as a function of pC_{H+} in 5 M NaCl is in good agreement with literature data, however measured solubility is slightly higher than those reported in lower concentrations of NaCl.
- Nd(III) and U(VI) solubilities are greater in GWB brine than in ERDA-6 brine.
- The neodymium data obtained from over-saturation experiments is very close to data obtained from under-saturation experiments. It means that in many cases a steady state was achieved.
- Almost no effect of carbonate on Nd(III) solubility was observed.

Conclusions:

The following Nd(III) solubilities at pC_{H+} = 8.5 were measured:

	With carbonate	No carbonate
ERDA-6	2×10^{-8} M	4×10^{-8} M
GWB	3×10^{-7} M	3×10^{-7} M

Calculated* :

	Estimated with Microbial Presence	Estimated with Microbial Absence
Castile Brine	1.69×10^{-7} M	1.77×10^{-7} M
Salado Formation Brine	3.07×10^{-7} M	3.07×10^{-7} M

**Brush L.H., and Xiong Y. Actinide Solubility for the WIPP PAB Calculations, unpublished analysis (2005)*