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Effect of Carbonate and Borate Complexation on Nd^{3+} and UO_2^{2+} Solubility in WIPP Brine

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Objectives

Research on the Waste Isolation Pilot Plant (WIPP) is still going on to support re-certification effort. Solubilities of two stable ions, UO_2^{2+} and Nd^{3+} (as analog for actinides (III)) were investigated under WIPP-relevant conditions.

The objectives of this work were

- to measure solubilities of uranium (VI) and neodymium (III) in long term experiments as a function of pC_{H+} and carbonate concentration in two WIPP simulated brines,
- to demonstrate the effect of complexation by carbonate and brine components on the solubilities of uranium (VI) and neodymium (III) under WIPP conditions.

WIPP conditions

- Temperature ~28 ± 3 ^{o}C,
- pC_{H+} ~ 8.5,
- Carbonate ~10^{-3} M,
- High ionic strength (Na^{+}, Mg^{2+}, Cl^{-}),
- Highly reducing environment,
- Microbial activity,
- α-radiation.

Composition and density of GWB and ERDA-6 simulated WIPP brines

Component	GWB brine [M]	ERDA-6 brine [M]
NaCl	2.874	4.254
$MgCl_2$	0.953	0.018
Na_2SO_4	0.166	0.159
NaBr	0.025	0.010
$Na_2B_4O_7$	0.037	0.015
KCl	0.437	0.092
$CaCl_2$	0.013	0.011
LiCl	0.004	-
Ionic strength	6.83	4.97
Density g/mL	1.216	1.183

Experimental limitations

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

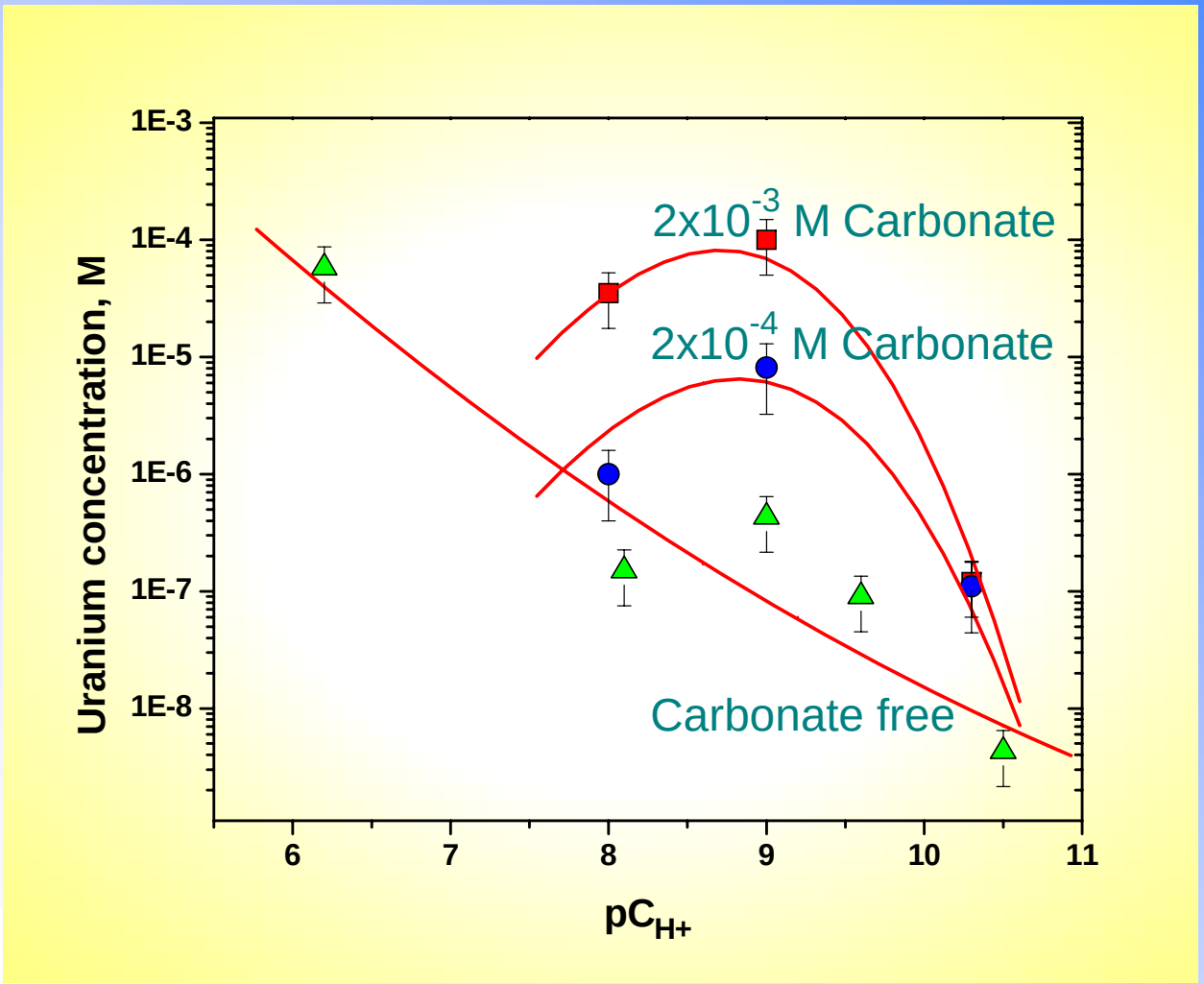
- The highest pC_{H+} , before the cloud point was observed, was:

  - for ERDA-6 was equal to 10.8,

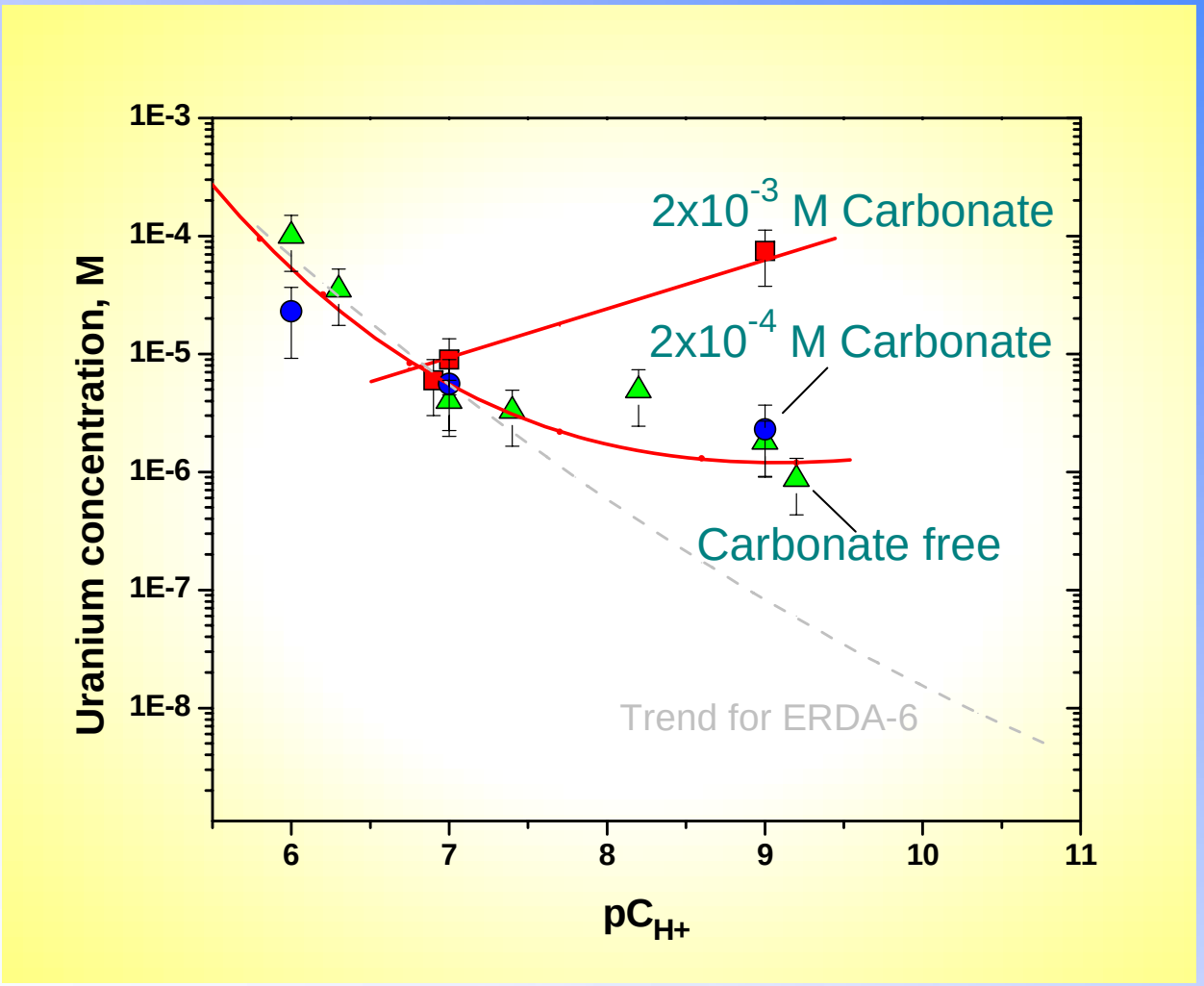
  - for GWB brine was equal to 8.7.

The data presented were generated in glove boxes with controlled atmosphere and equilibration times from 118 days up to 350 days.

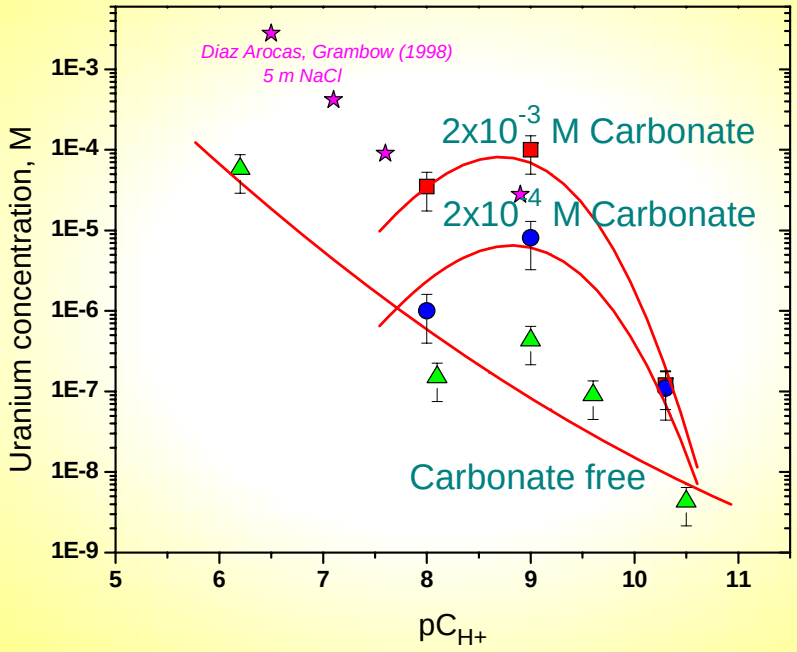
Effect of carbonate on UO_2^{2+} solubility in ERDA-6 brine



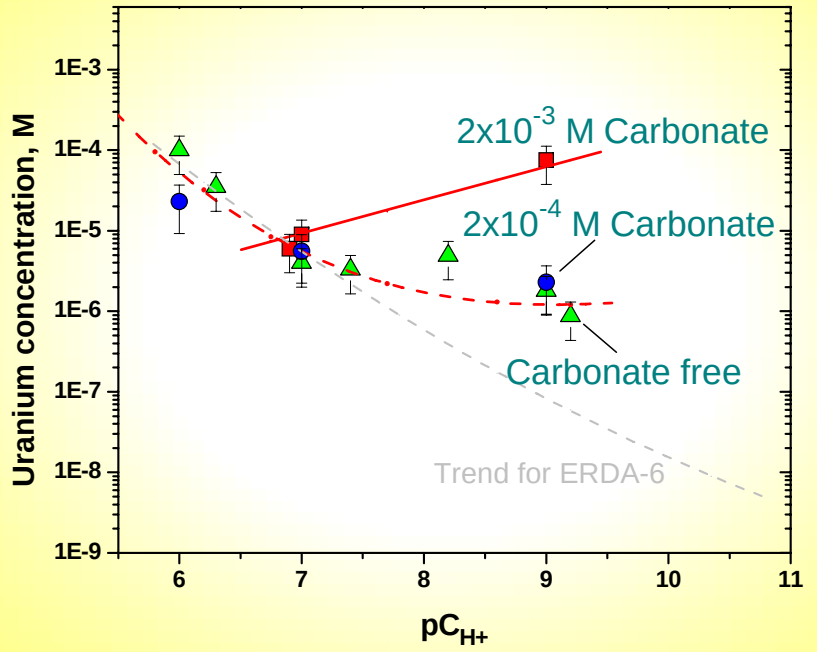
Effect of carbonate on UO_2^{2+} solubility in GWB brine



Comparison the uranyl ion solubilities in two brines

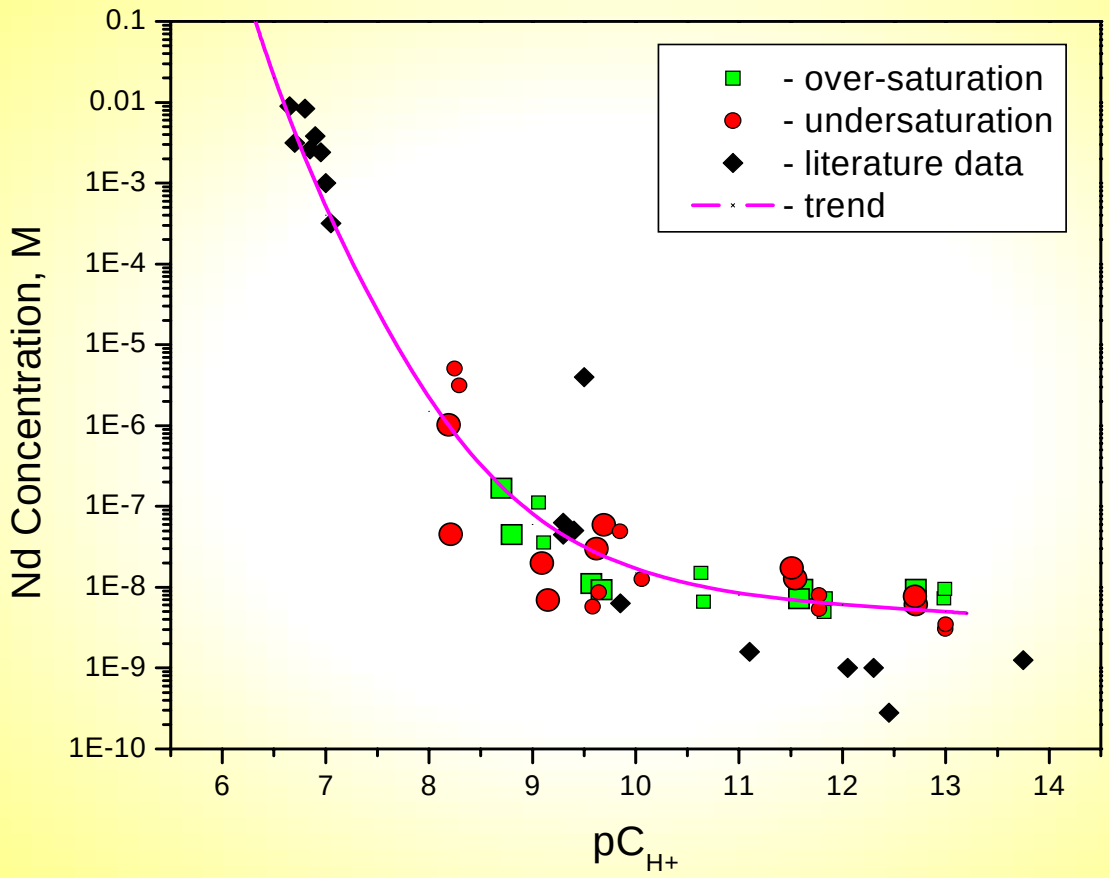


ERDA-6

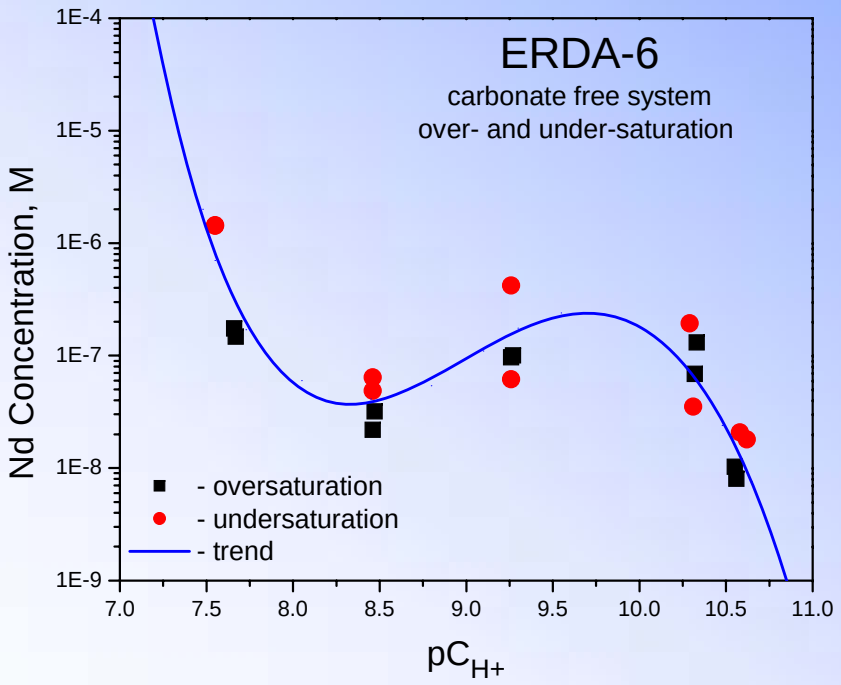


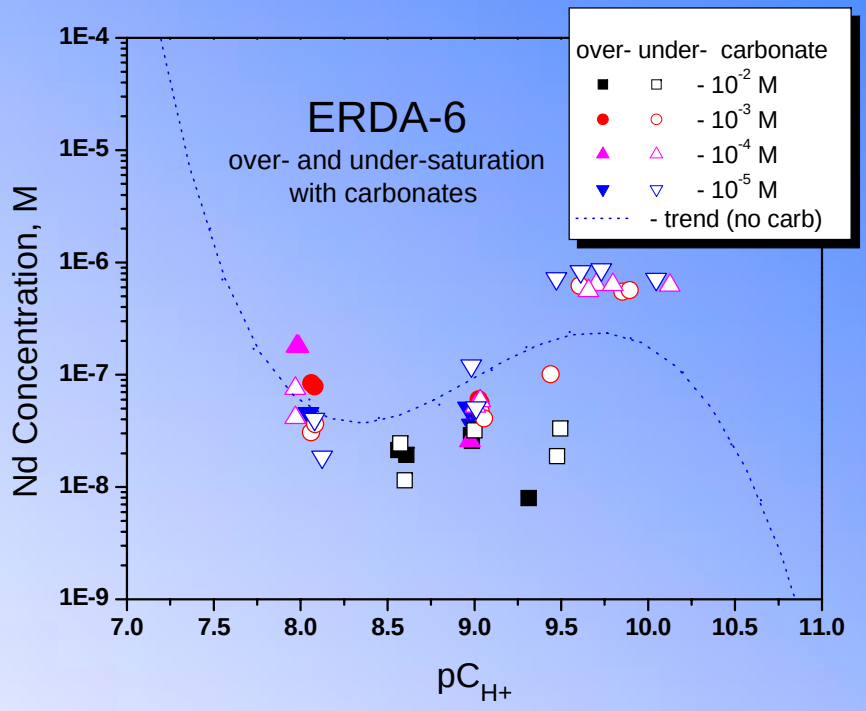
GWB

Neodymium (III) solubility in carbonate-free 5 M NaCl as a function of pC_{H+}



Solubility of neodymium (III) as a function of pC_{H+} in ERDA-6 brine

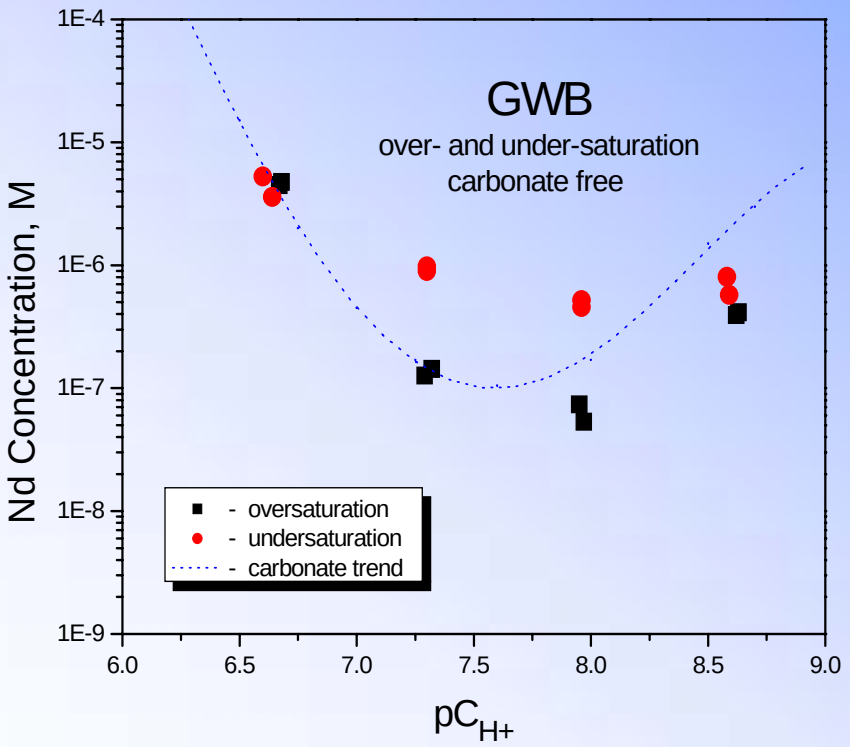


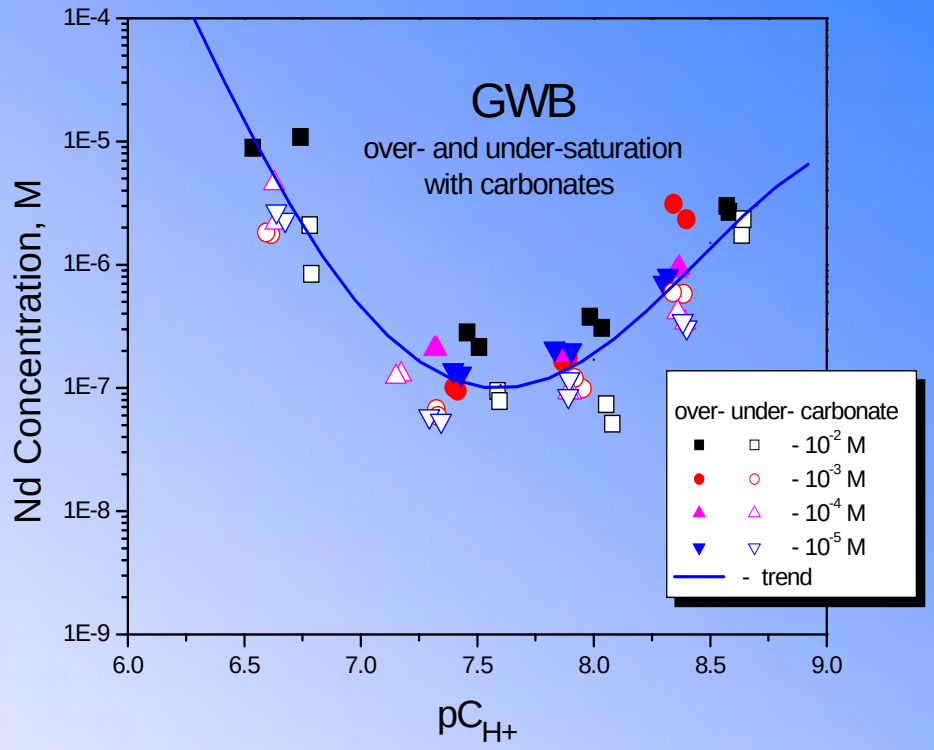


carbonate-free

with carbonate

Solubility of neodymium (III) as a function of pC_{H+} in GWB brine





carbonate-free **with carbonate**

Thermodynamic data

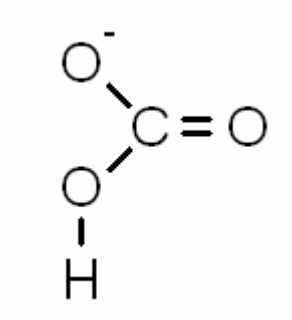
$UO_2(OH)_2$	log K_s	-22
$UO_2^{2+} + CO_3^{2-}$	log β_1	8.6
	log β_2	16.2
	log β_3	22.6
$Nd(OH)_3$	log K_s	-23
$Nd^{3+} + CO_3^{2-}$	log β_1	5.5
$Nd^{3+} + B_4O_7^{2-}$	log β_1	?

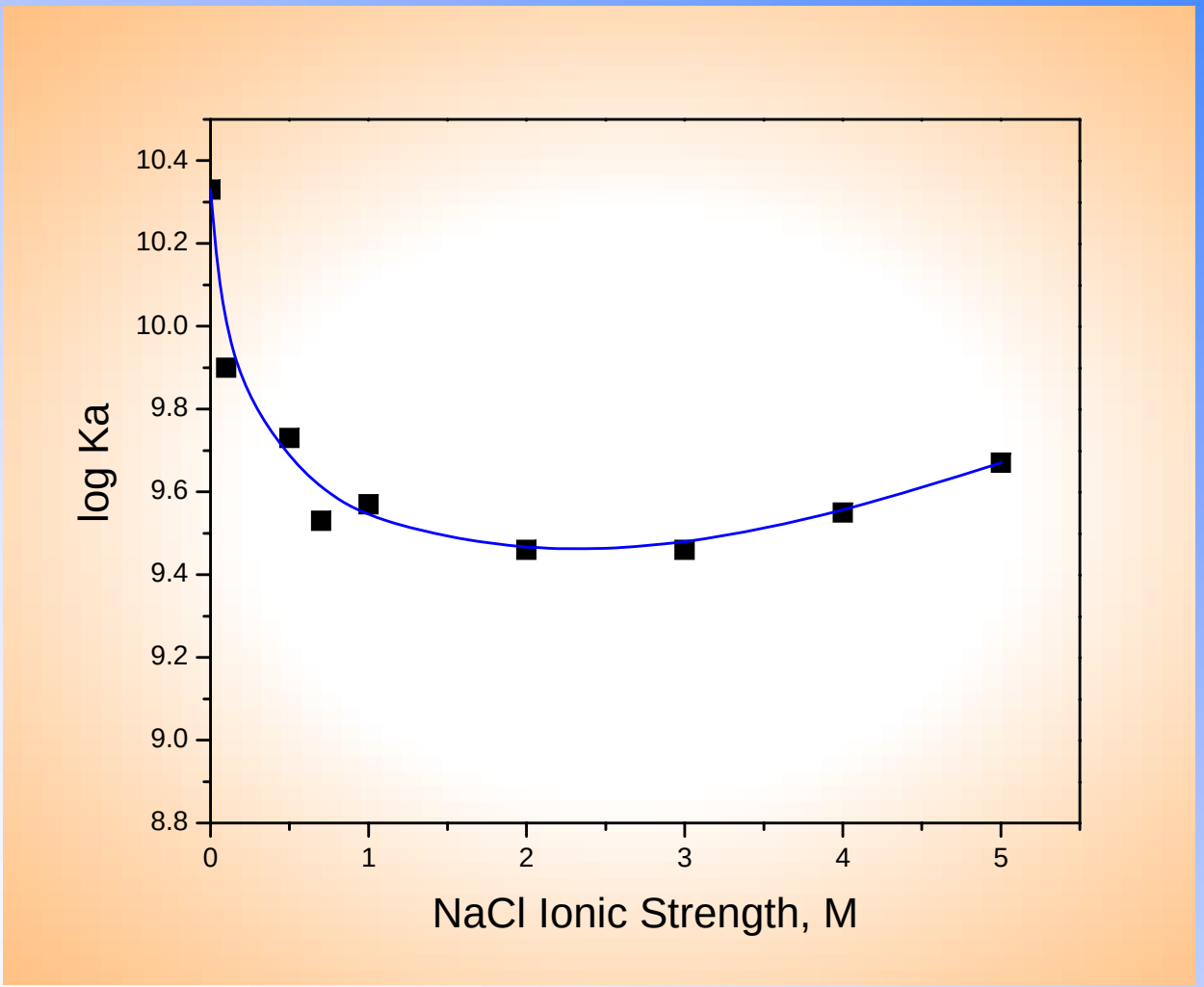
$$\beta_n = \frac{[ML_n]}{[M][L]^n}$$

$$K_{s,ML_n} = [M][L]^n$$

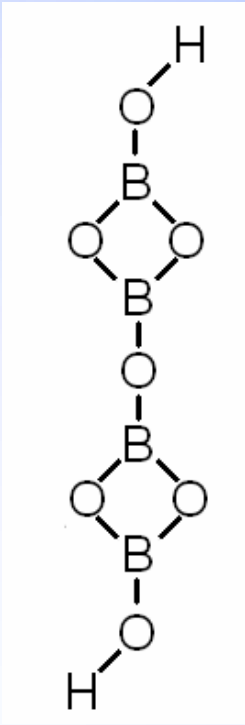
Reference: Critical Stability Constant NIST Database, 2004.

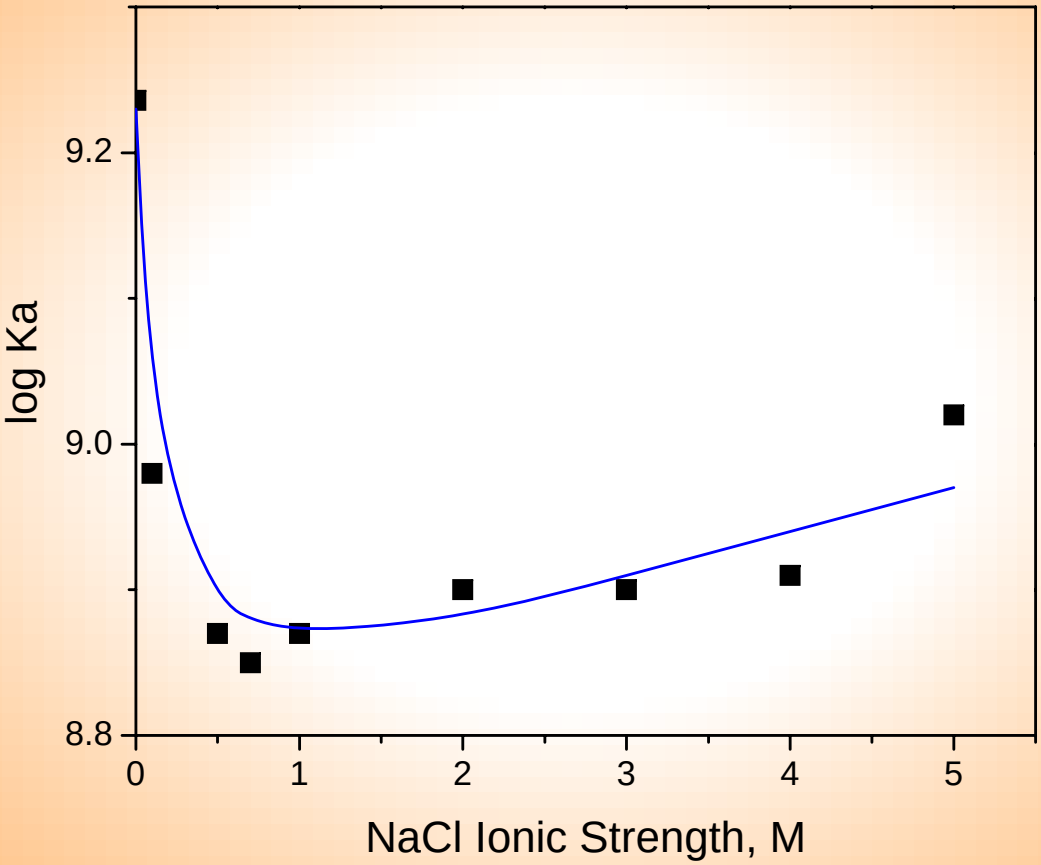
Dissociation constant of carbonic acid as a function of ionic strength at 25 °C



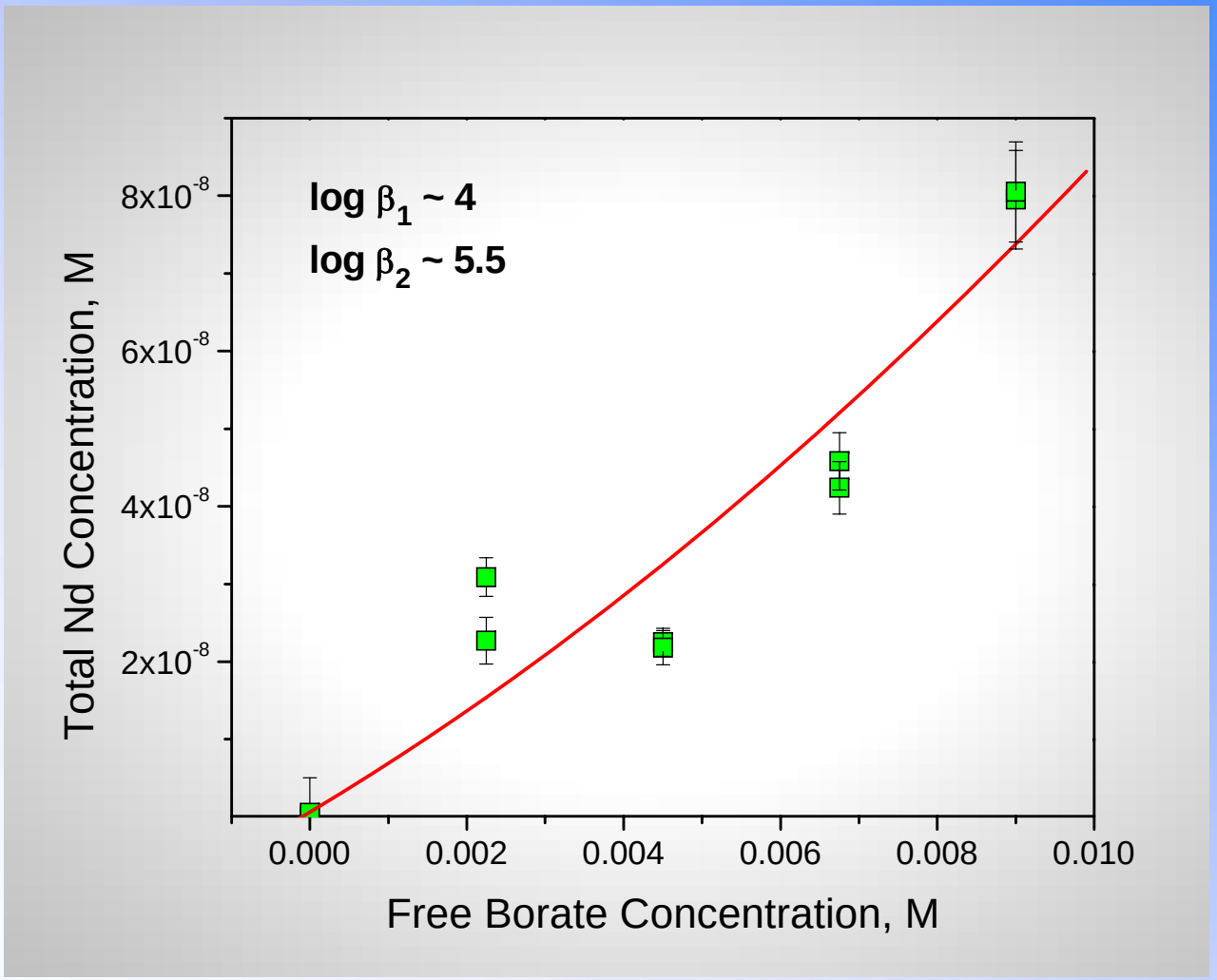


Dissociation constant of boric acid as a function of ionic strength at 25 °C





Determination of stability constant for Nd^{3+} with borate complexation in water at pH = 8.0



Conclusions

- ✓ In carbonate-free systems, the uranium solubility at pC_{H+} = 8.5 was ~ 2 x 10^{-7} M in ERDA-6 and ~2 x 10^{-6} M in GWB.
- ✓ In the carbonate presence an expected significant increase (1.5-2.5 orders of magnitude) in uranium solubility was found at pC_{H+} = 8.5.
- ✓ Nd^{3+} solubility at pC_{H+} = 8.5 was ~1 x 10^{-7} M in ERDA-6 and ~1 x 10^{-6} M in GWB brines.
- ✓ In the presence of carbonate, there was essentially no visible effect on the neodymium solubility.

Conclusions

- ✓ Complexation with borate was found to significantly impact the neodymium solubility.
- ✓ Log β_1 ~ 4 is an introductory value for this complexation reaction. *Accurate determination is in progress*.
- ✓ Rough calculation of neodymium (III) concentration in brine using this constant gave a good agreement with the experimental data.
- ✓ We expect good modeling fit when neodymium (III) with borate stability constant and Pitzer parameters will be determined and introduced to the database.

Acknowledgments

This work was conducted under the Actinide Chemistry Repository Science Program and sponsored by Department of Energy Carlsbad Field Office.

The view of waste and magnesium oxide placed in a WIPP Disposal Room. On March 7, 2007 the amount of 87,518 containers are disposed in the underground.