Humic acids in the WIPP

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WIPP Generalities

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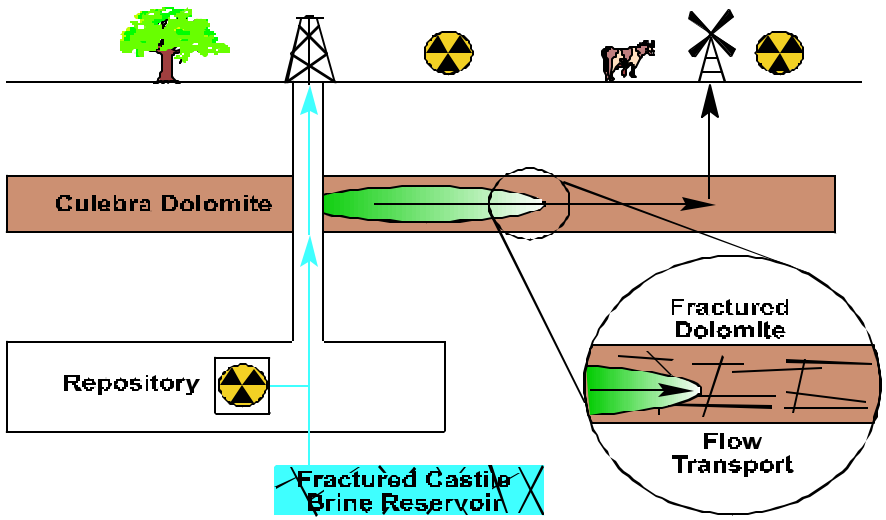
WIPP PA

•**Important radioelements for the WIPP:**
Pu, Am > **U, Th** >> **Np**

•**Predicted actinide oxidation states:**
Pu(III), Pu(IV), Am(III)
U(IV), U(VI), Th(IV),
Np(IV), Np(V)

•**Metal complexing Ligands present in wastes:**
Acetic acid: CH_3-CO_2H
Citric acid:$HO_2CCH_2C(CO_2H)(OH)CH_2CO_2H$
Oxalic acid: HO_2C-CO_2H
EDTA: $(CH_2CO_2H)_2N$-CH_2CH_2-$N(CH_2CO_2H)_2$
Lactic acid: $CH_3C(OH)HCO_2H$
HA



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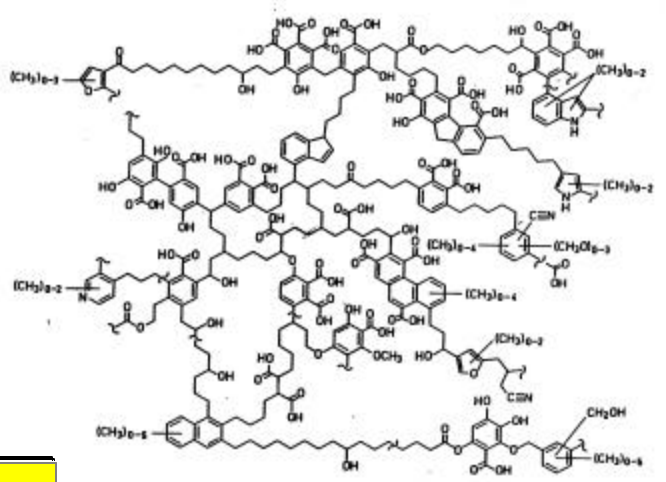
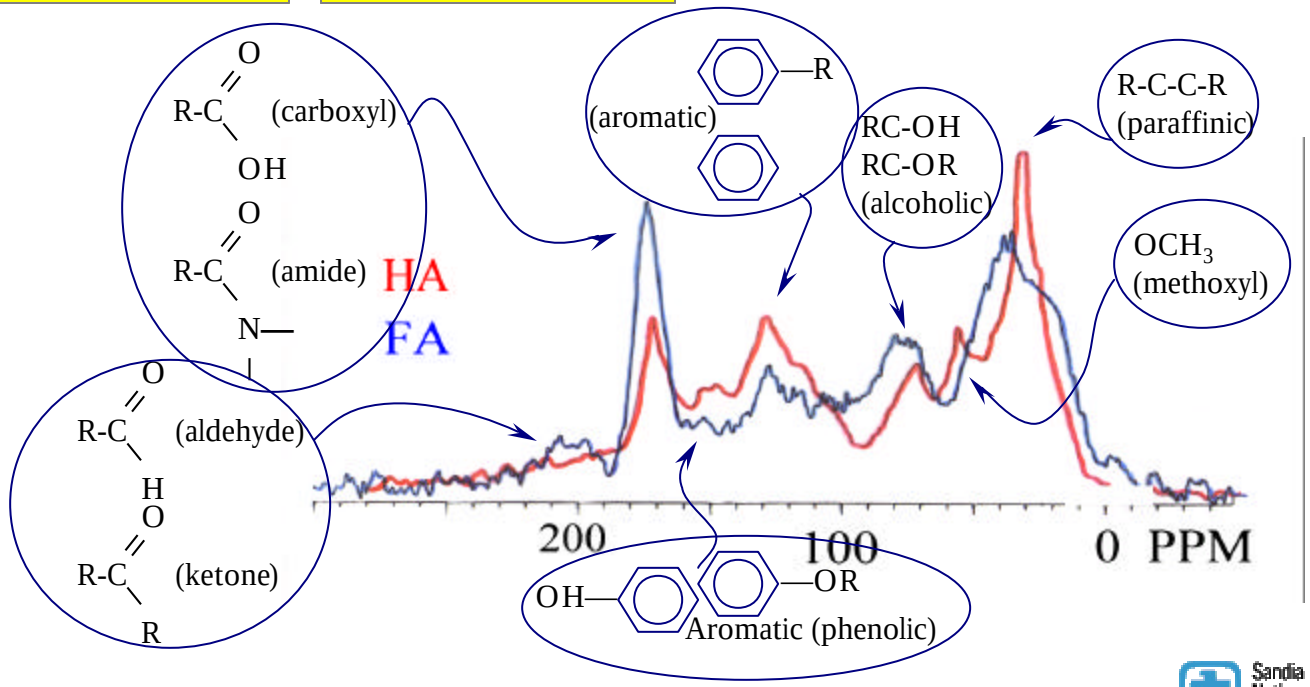
HA Generalities



From Schulten and Schnitzer, 1993

- Humic Substances (HS)
  - Fulvic Acids (FA) soluble at all pH
  - Humic Acids (HA) insoluble at low pH
  - Humin insoluble at all pH



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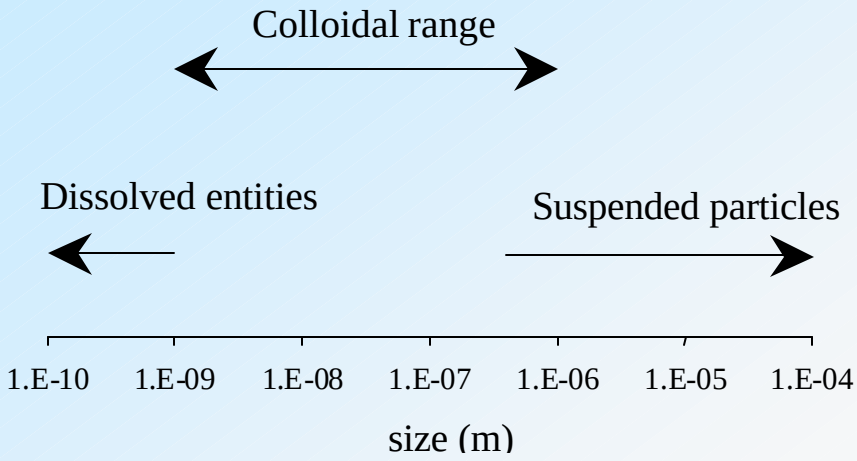
HA Generalities (cont.)

- **Sizes**

FA: 5 Å (≈150 MW) to 12 Å (≈3,500 MW)
HA: 10 Å (≈3,000 MW) to 300 Å (≈300,000 MW)

- **Concentrations reported**

soil: 0 - 10 % of HS
fresh water: 0.1-50 ppm DOC
ocean water (surface): 0.5-1.2 ppm DOC
groundwater: 0.1-10 ppm DOC



Size ranges of aqueous particles.
(Adapted from Gaffney et al., 1996)

HA: strong metal complexant

Metal – Ligand complexation:

$$M^{n+} + mL^{p-} ? ML_m^{n-mp}$$

Equilibrium constant = Stability constant:

$$\beta_m = \frac{\left[ML_m^{n-mp}\right]}{\left[M^{n+}\right]\left[L^{p-}\right]^m}$$

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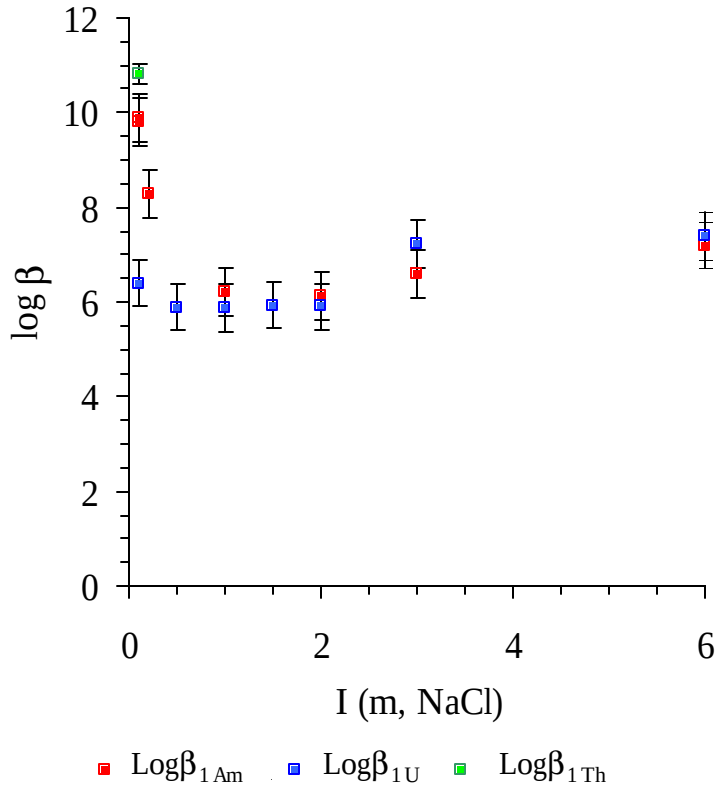
HA complexes stability constants



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- Choppin and Labonne-Wall.*Journal of Radioanalytical and Nuclear Chemistry, 221 (1-2), 67-71 (1997*).
- Labonne-Wall et *al. Actinides speciation in high ionic strength media, Ed. Reed et al., 199-211 (1999).*
- Wall et *al. Radiochimica Acta, 90, 563-568 (2001).*

Experimental work performed at FSU, supported at Sandia National Laboratories by US DOE, and at FSU under a Sandia-approved quality assurance program.

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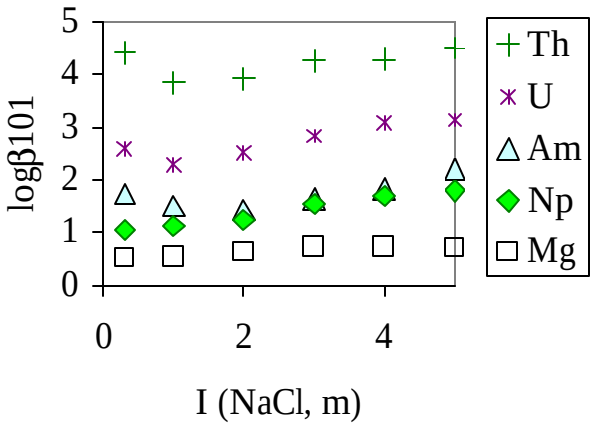
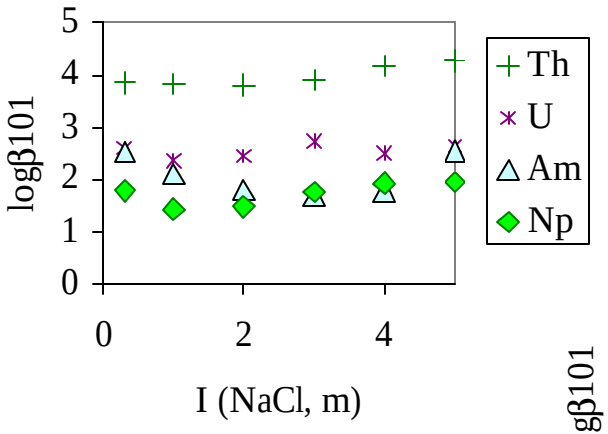
Stability constants of organic complexes determined for WIPP

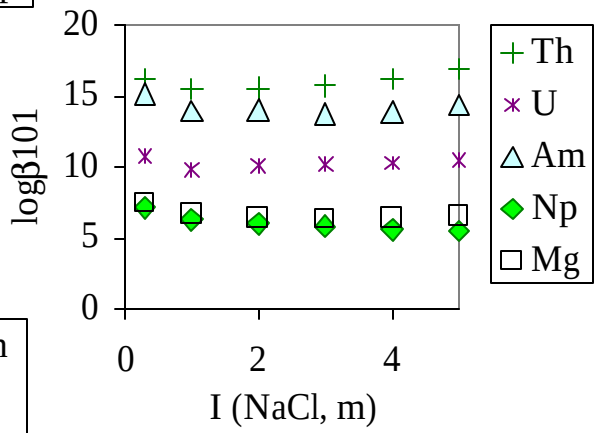
Acetic acid



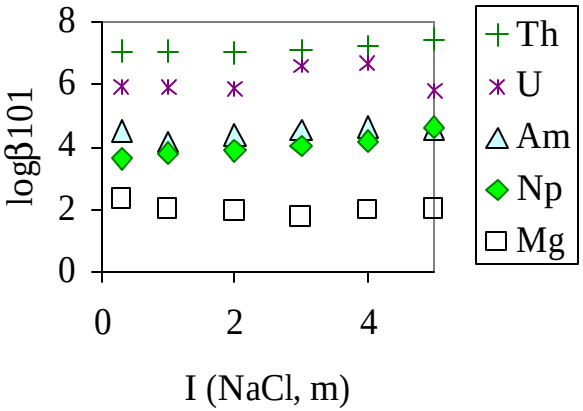
Lactic acid



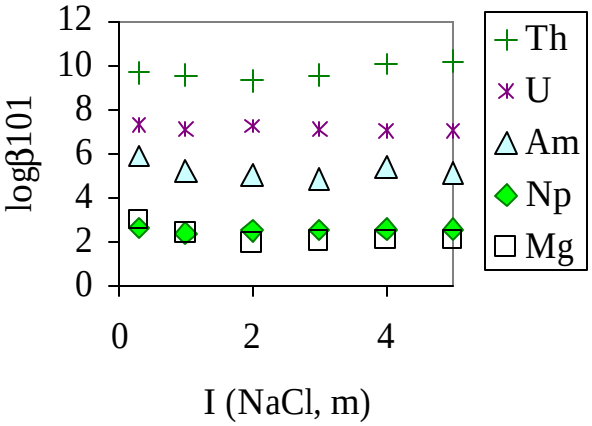
EDTA



Oxalic acid



Citric acid



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Effect of HS on metals concentration:

Solubility of Nd, Th, and U

Medium = ERDA-6

	[HA] = 0 ppm	[HA] = 8 ppm
[Nd] (M)	$3.88\ 10^{-8}$	$7.44\ 10^{-8}$
[Th] (M)	$3.83\ 10^{-8}$	$8.29\ 10^{-5}$
[U] (M)	$1.11\ 10^{-6}$	$9.11\ 10^{-5}$

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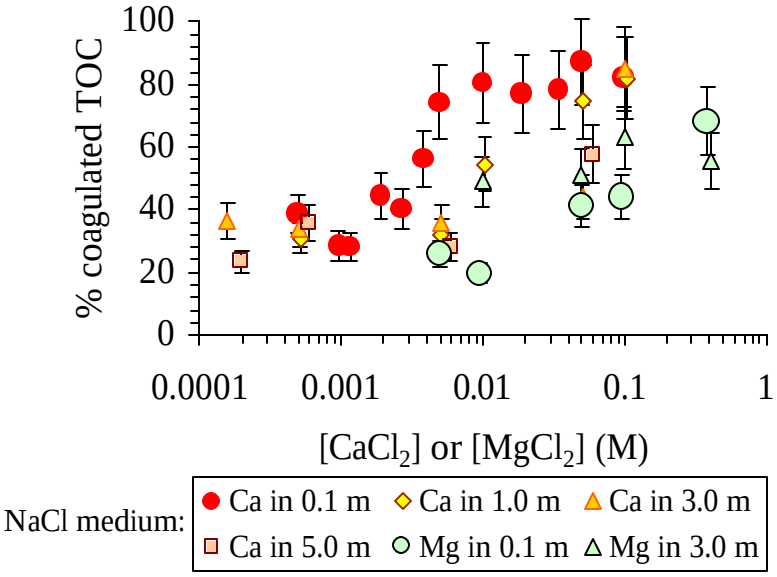
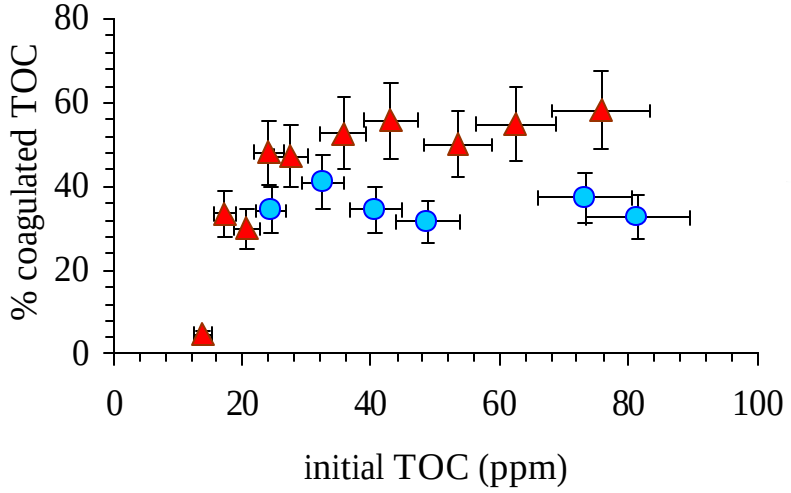
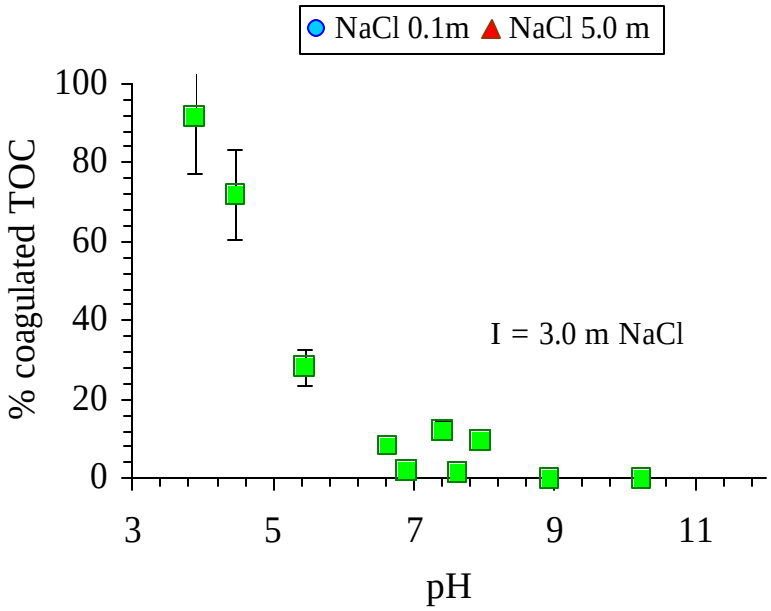
HA solubility in WIPP

HA might coagulate due to:

- high ionic strength solutions
- presence of multivalent cations in brines
- dissolution of the engineering barrier?







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Wall and Choppin. *Appl. Geochem. (2003).*

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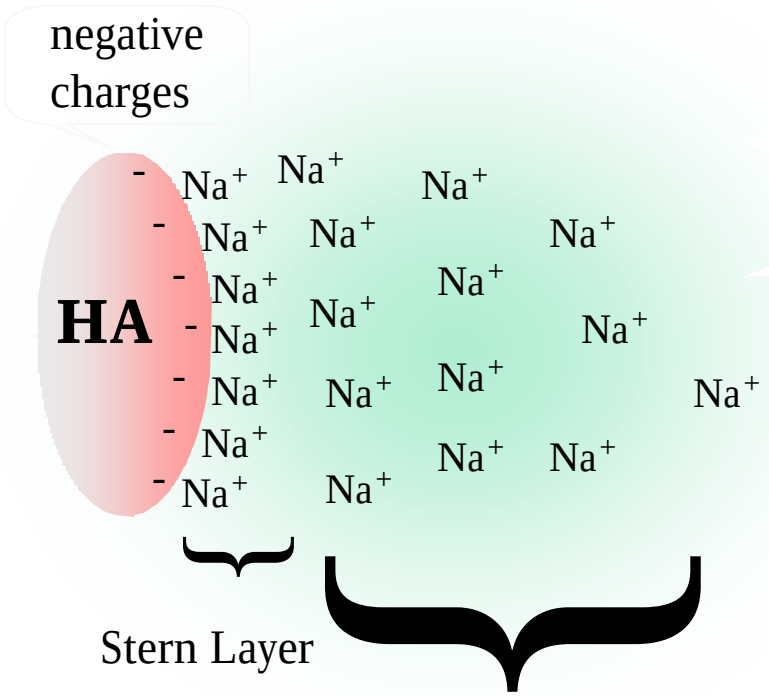
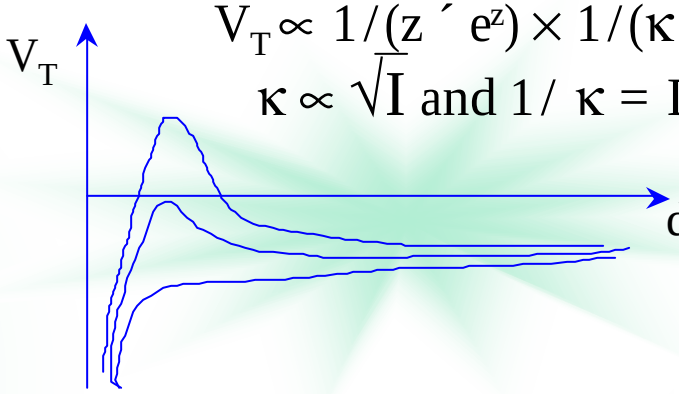
HA solubility - DLVO Theory





$$V_T \propto 1/(z \cdot e^z) \times 1/(\kappa \times e^{\kappa})$$

$$\kappa \propto \sqrt{I} \text{ and } 1/\kappa = \text{DL thickness}$$

coagulation ↗ if:

- ✓ z ↗
- ✓ I ↗
- ✓ cation radius ↘
- ✓ [HA] ↗
- ✓ pcH ↘

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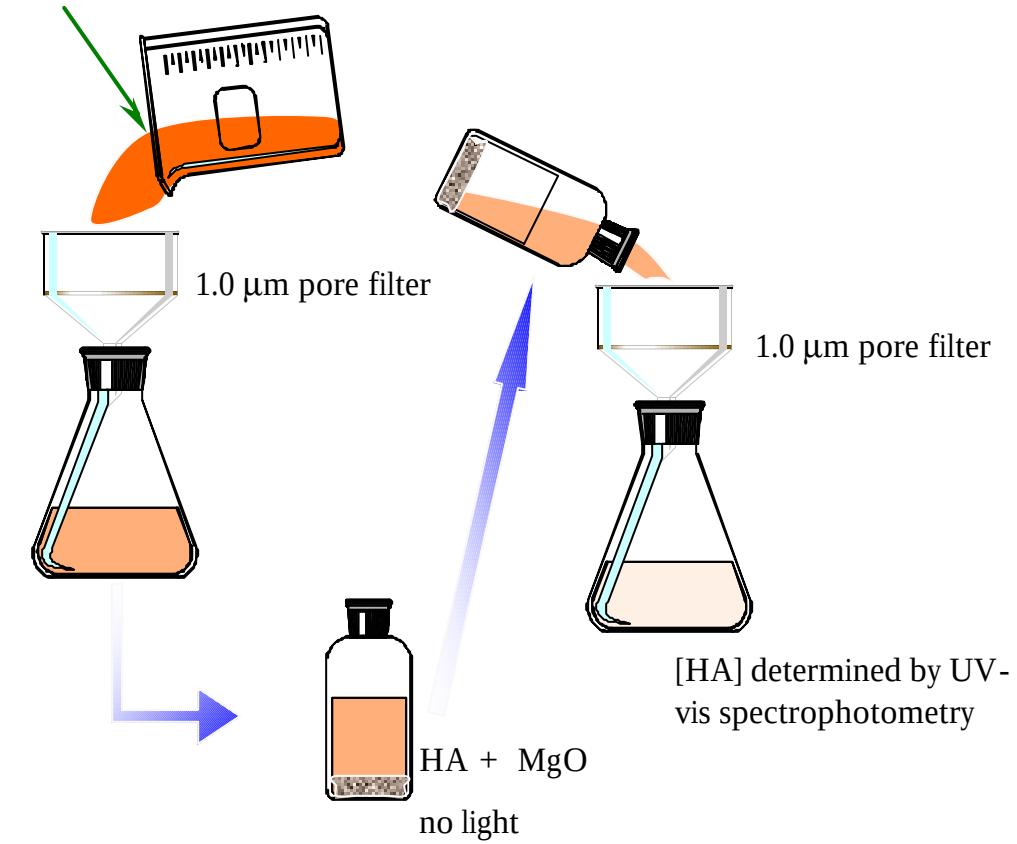
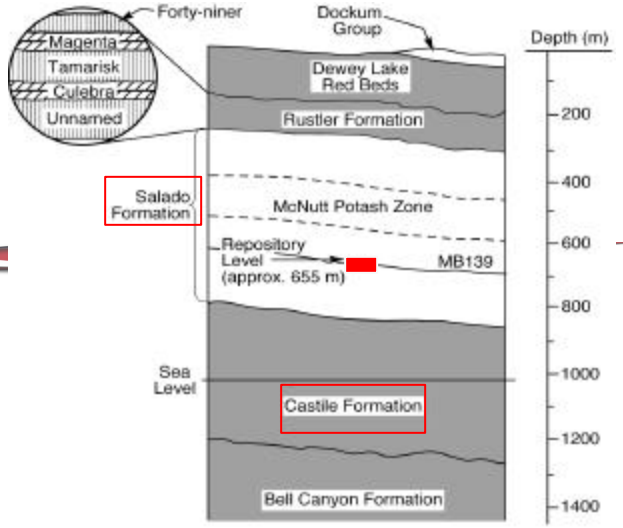
HA solubility in WIPP





	GWB[1]	ERDA-6[2]
$B(OH)_x^{3-x}$	158 mM	63 mM
Na^+	3.53 M	4.87 M
Mg^{2+}	1.02 M	19 mM
K^+	467 mM	97 mM
Ca^{2+}	14 mM	12 mM
SO_4^{2-}	177 mM	170 mM
Cl^-	5.86 M	4.8 M
Br^-	27 mM	11 mM
TIC	-	16 mM
pH	-	6.17

[1] Snider (2003). [2] Popielak (1983).

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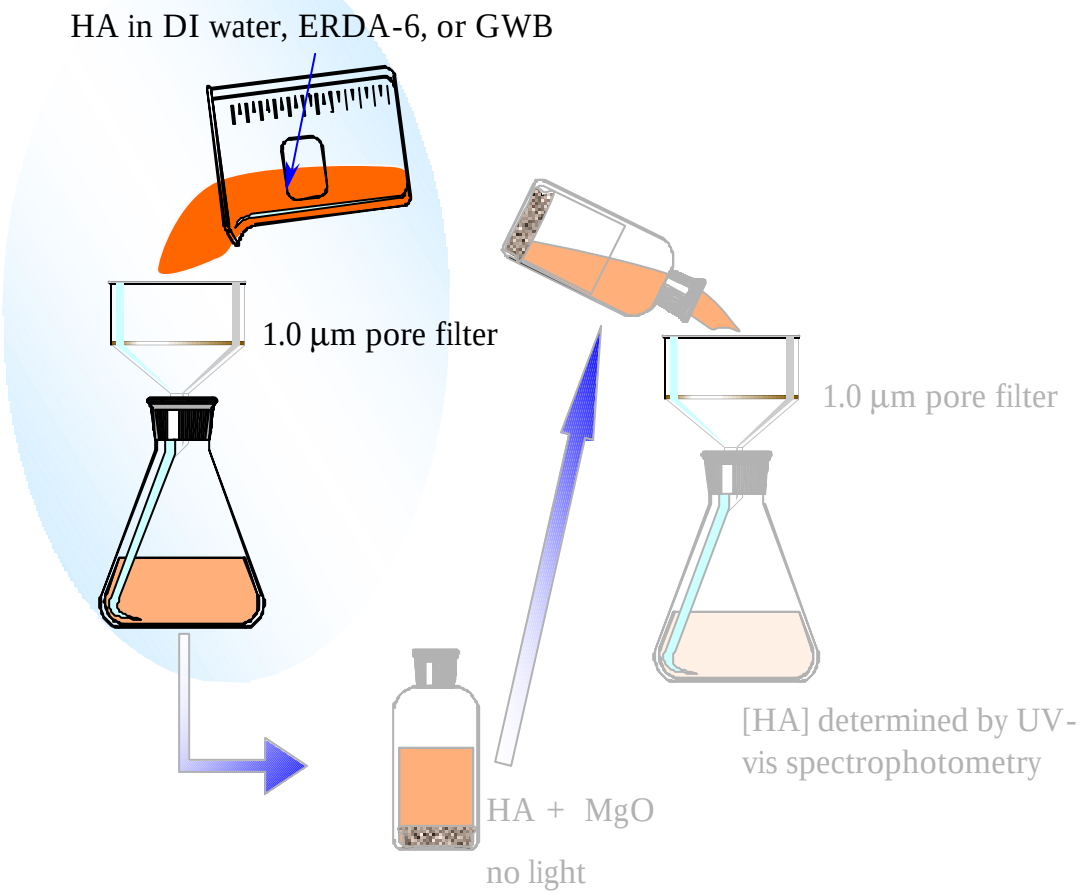
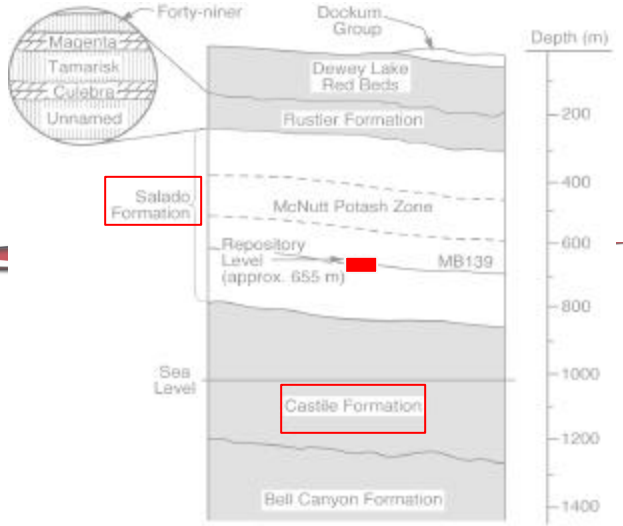
HA solubility in WIPP





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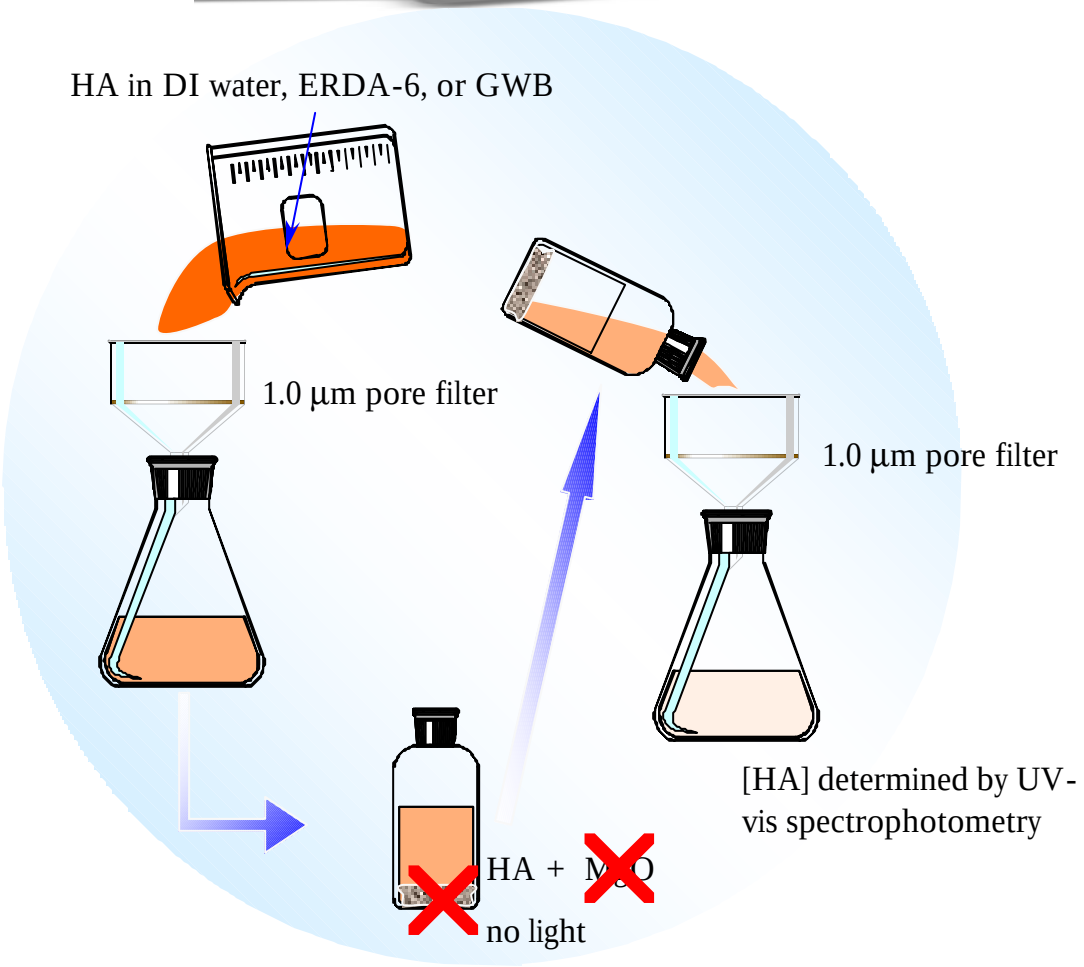

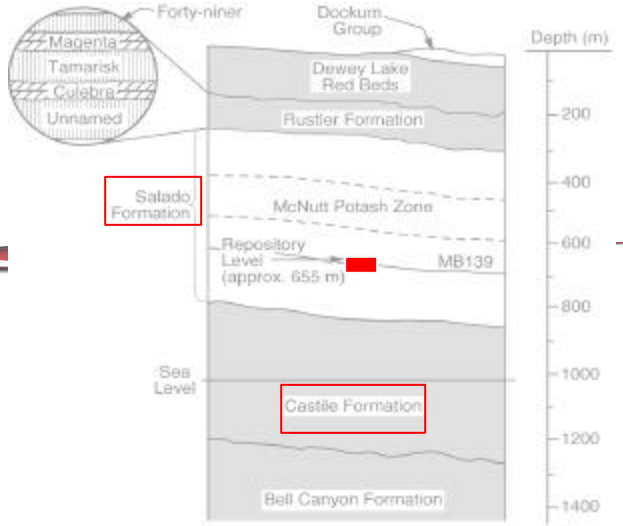

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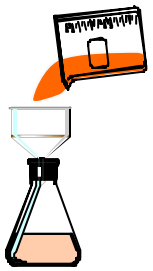
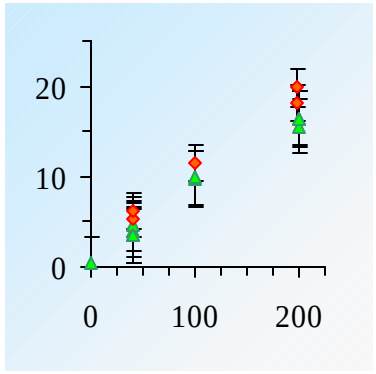
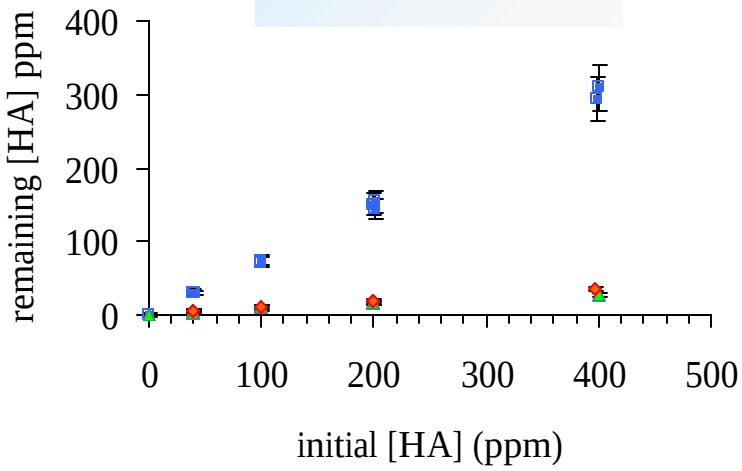
HA coagulation in absence of MgO

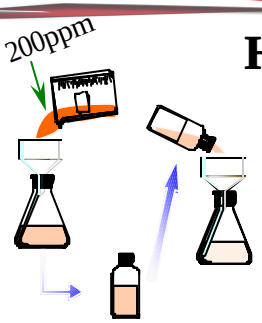


HA coagulation, t=0, no MgO

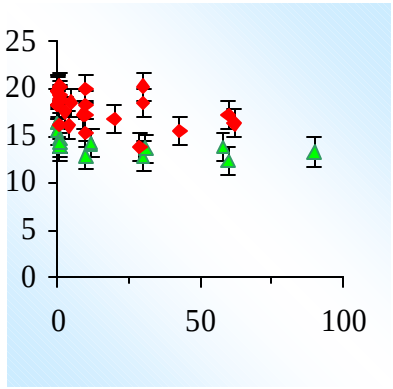


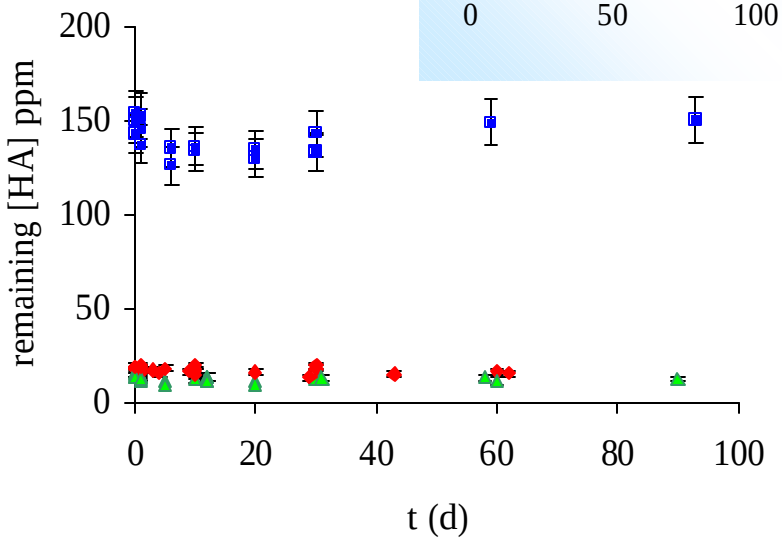


DI water ▲ 95% ERDA-6 ◆ 95% GWB



HA coagulation, no MgO





▲ 95% ERDA-6 ◆ 95% GWB

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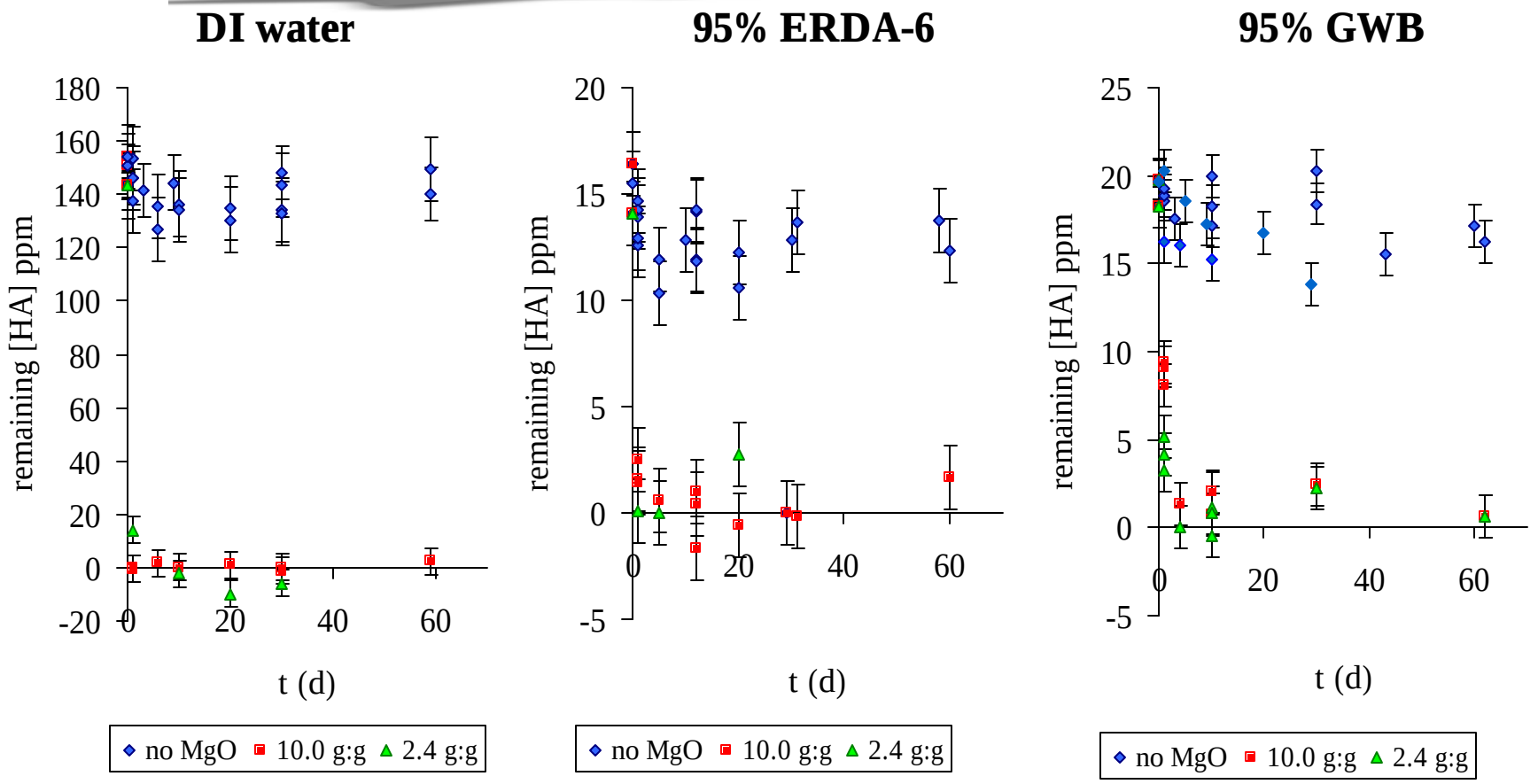
HA coagulation in presence of Fisher MgO



g:g = g liquid:g solid

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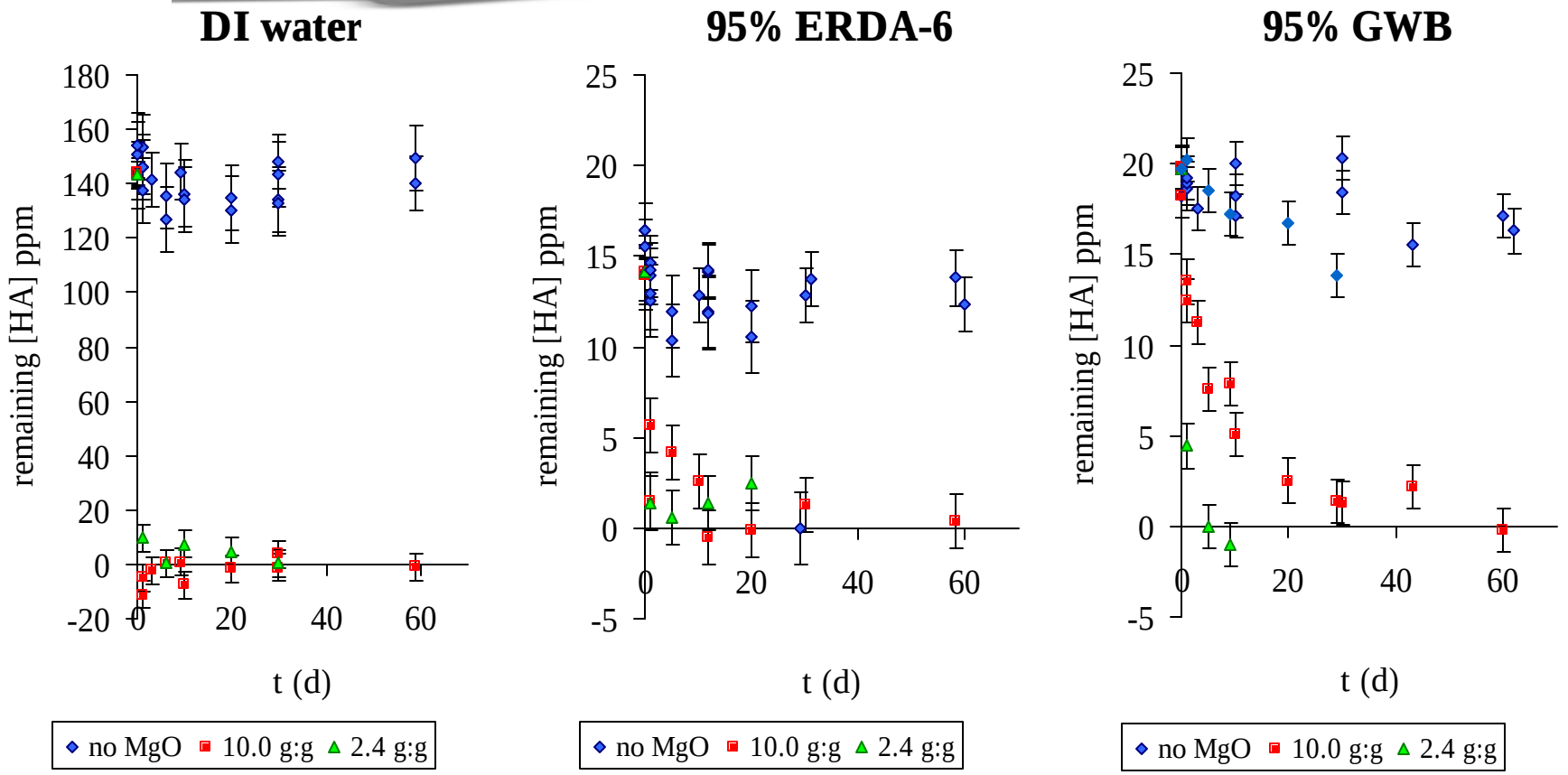
HA coagulation in presence of Premier MgO



g:g = g liquid:g solid

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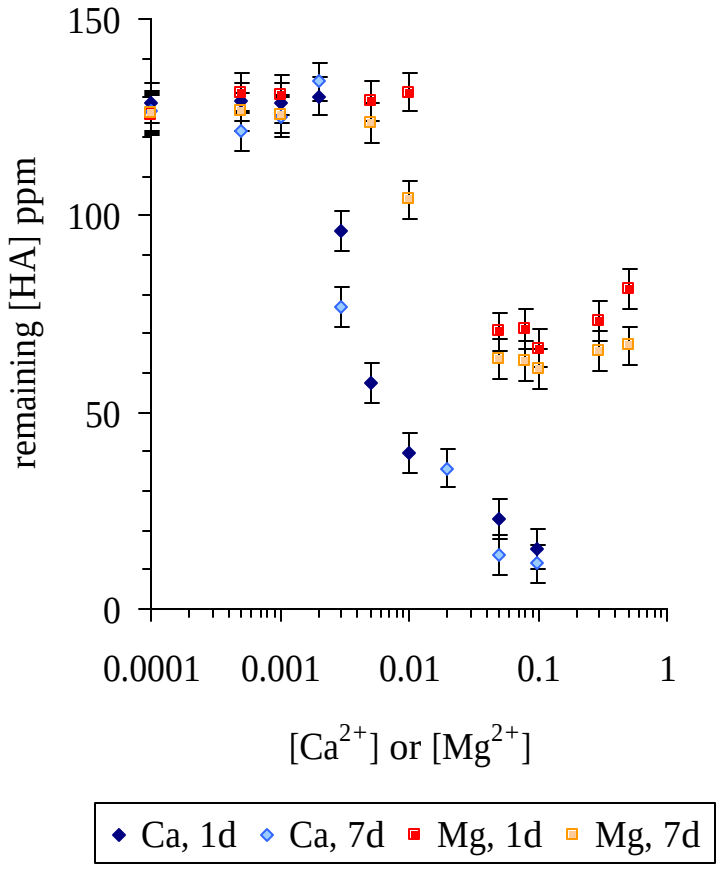
HA coagulation in presence of Ca, Mg

DI water, t: 1d, 7d



Example of Ca and Mg concentration from MgO dissolution:

		g:g	t	[Mg] (M)	[Ca] (M)
DI water	F MgO	10.0	60 d	0	0
DI water	P MgO	10.0	9 d	$5\ 10^{-4}$	0.021
DI water	P MgO	2.0	9 d	$2\ 10^{-4}$	0.024
ERDA6	P MgO	10.0	60 d	0	0.013
ERDA6	P MgO	2.0	60 d	0	0.013

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