
Aqueous Geochemistry Relevant to U Ore Formation & Production

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Objectives

- Acid-base chemistry
- Precipitation chemistry
- Importance of complexation
- Redox chemistry
- A bit about U mineralogy
- Application of these concepts to understanding chemistry of U & co-constituents in solution and solid phases
 - U ore formation
 - U milling
 - In-situ recovery (ISR) of U

Units

- Liquid Phase Concentration
 - Mass/volume - mg/L, ug/L
 - Mass/Mass – mg/kg = ppm, ug/kg = ppb
 - Since $\rho_{\text{H}_2\text{O}} = 1 \text{ kg/L} \Rightarrow 1 \text{ mg/L} = 1 \text{ ppm}$
 - Moles/volume – M = Molar - moles/L. Use square brackets [i] to denote molar conc.
 - Moles/kg – m = Molal – moles/kg
 - Moles of Charge/Volume - N = normality – equivalents/L
 - Conc. as mg CaCO_3 /L for hardness & alkalinity
 - Conc. as mg NH_4 -N/L
- Solid phase concentration
 - Mass/Mass – mg/kg = ppm
 - % = 10,000 mg/kg = 1%

Important References

- Langmuir, D. (1997). Aqueous Environmental Geochemistry, Prentice Hall, Upper Saddle River, NJ, 600 p.
- Devoto, R. (1978). Uranium Geology & Exploration, Col. School of Mines, Golden, CO, 396 p
- Parkhurst, D.L., and Appelo, C.A.J., (2013). Description of input and examples for PHREEQC Version 3, A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p., (<http://pubs.usgs.gov/tm/06/a43>)
- Merritt, R.C. (1971). The Extractive Metallurgy of Uranium, Col. School of Mines Res. Inst., Golden, CO, 576 p.

Acid-Base Chemistry

- Importance
 - Affects solubility of all metals
 - Affects chemistry of most inorganic solutes
 -
- Principally concerned with Lewis acids:
 - Donate H^+

Dissociation Reactions

(Remember Freshman Chemistry?)

- Hypothetical acid:



$$K = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$

- In a solution, 4 unknowns: $[\text{HA}]$, $[\text{H}^+]$, $[\text{A}^-]$, $[\text{OH}^-]$
 - Always assume $[\text{H}_2\text{O}]$ is constant $\sim 55.6 \text{ mol/L}$

4 Types of Eqns. to Define Equilibrium

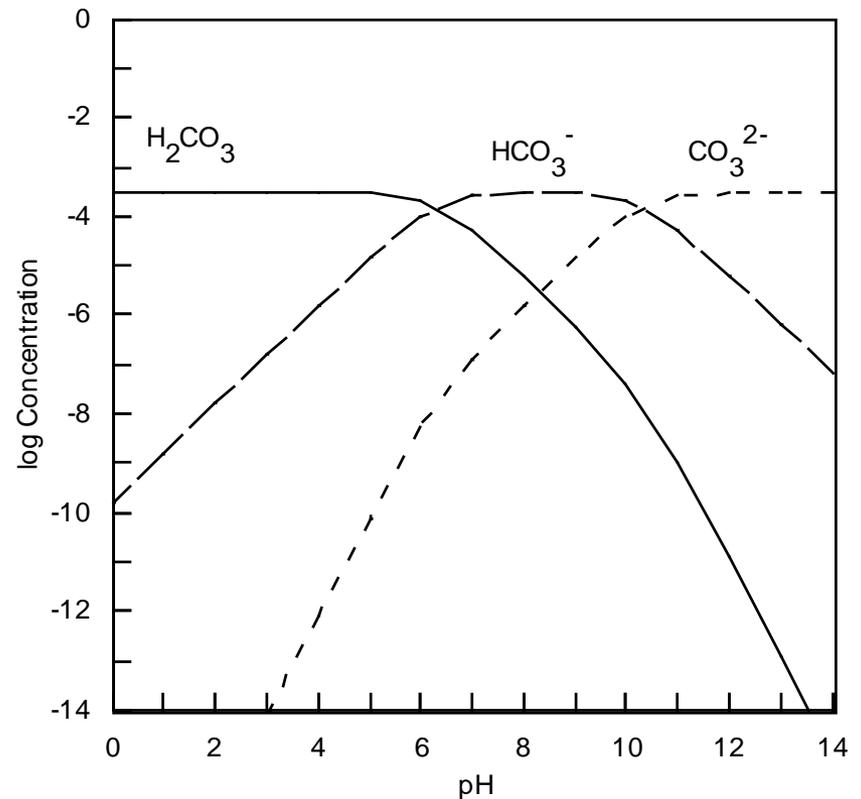
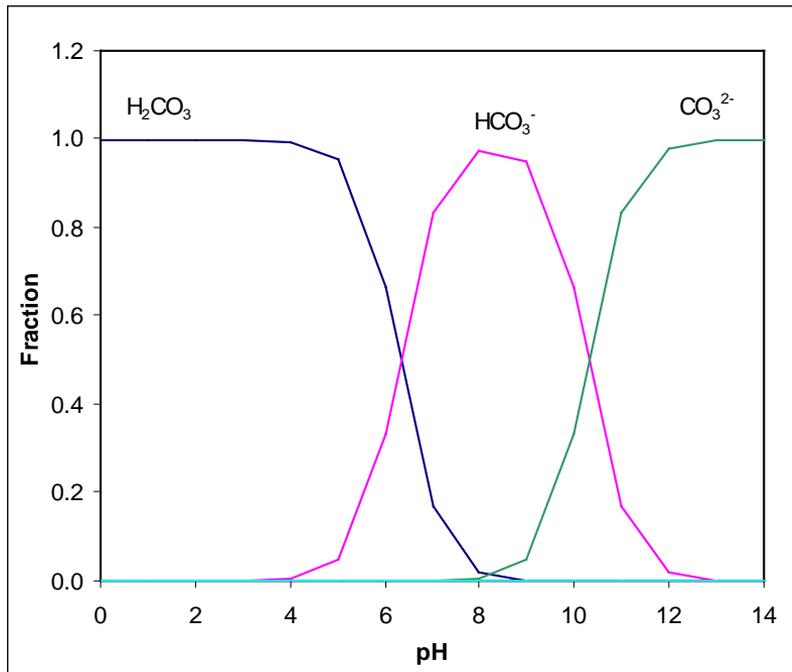
- Mass action:
$$K = \frac{[H^+][A^-]}{[HA]}$$
 - Dissociation of water:
$$K_w = [H^+][OH^-]$$
 - Mass balance:
$$C_{\text{total-A}} = [HA] + [A^-]$$
 - Electroneutrality:
$$[H^+] = [A^-] + [OH^-]$$
- Note: Theoretically work in terms of activity ($\{i\}$), but assume activity equals molar concentration in fresh water $\Rightarrow \{i\} = [i]$

Acid-Base Equilibrium

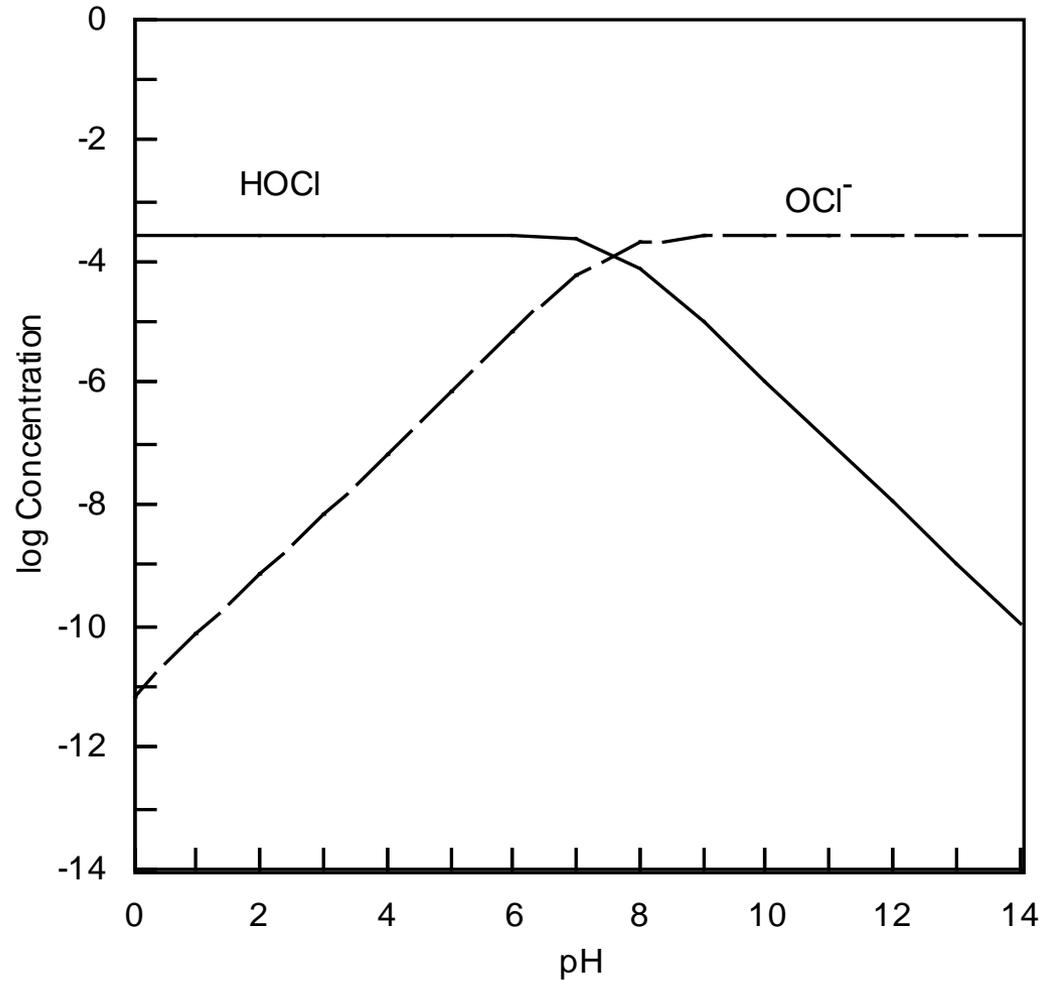
- Combine mass action & mass balance equations to get:
- $[HA] = F_1([H^+])$
- $[A^-] = F_2([H^+])$
- Can extend to poly-protic acids (H_nA)

Acid-Base Equilibria

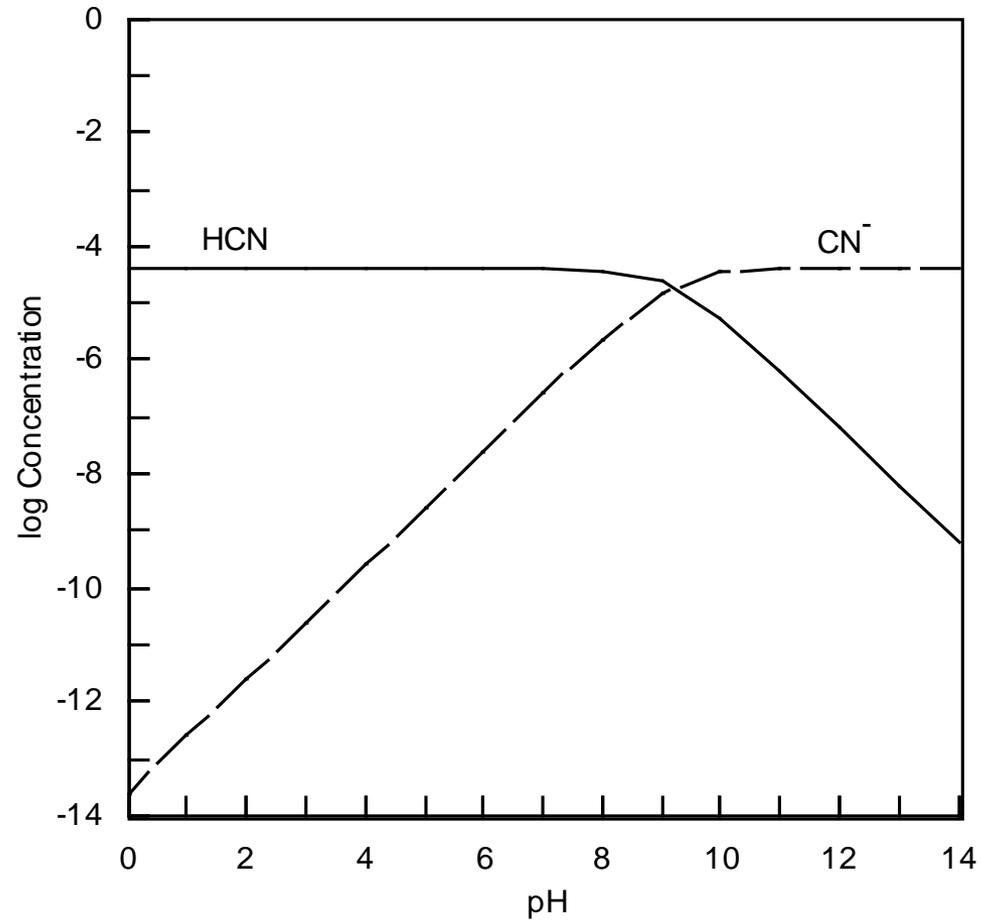
- Can use $F_1([H^+])$ & $F_2([H^+])$ to show Fraction vs pH or log Conc. vs pH



log Conc. vs. pH Diagrams



log Conc. vs. pH Diagrams

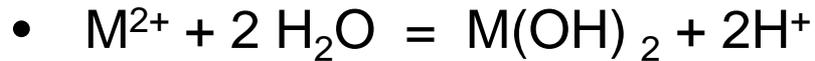


Solubility of Metals

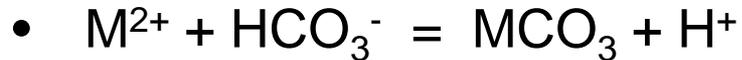
- Common types of metal precipitates:
 - Hydroxides - $M(OH)_x$
 - Carbonates - MCO_3
 - Sulfides - MS
 - Phosphates - MPO_4

Metal Hydroxides

- Equilibrium reactions:



$$K = \frac{[H^+]^2}{[M^{2+}]}$$



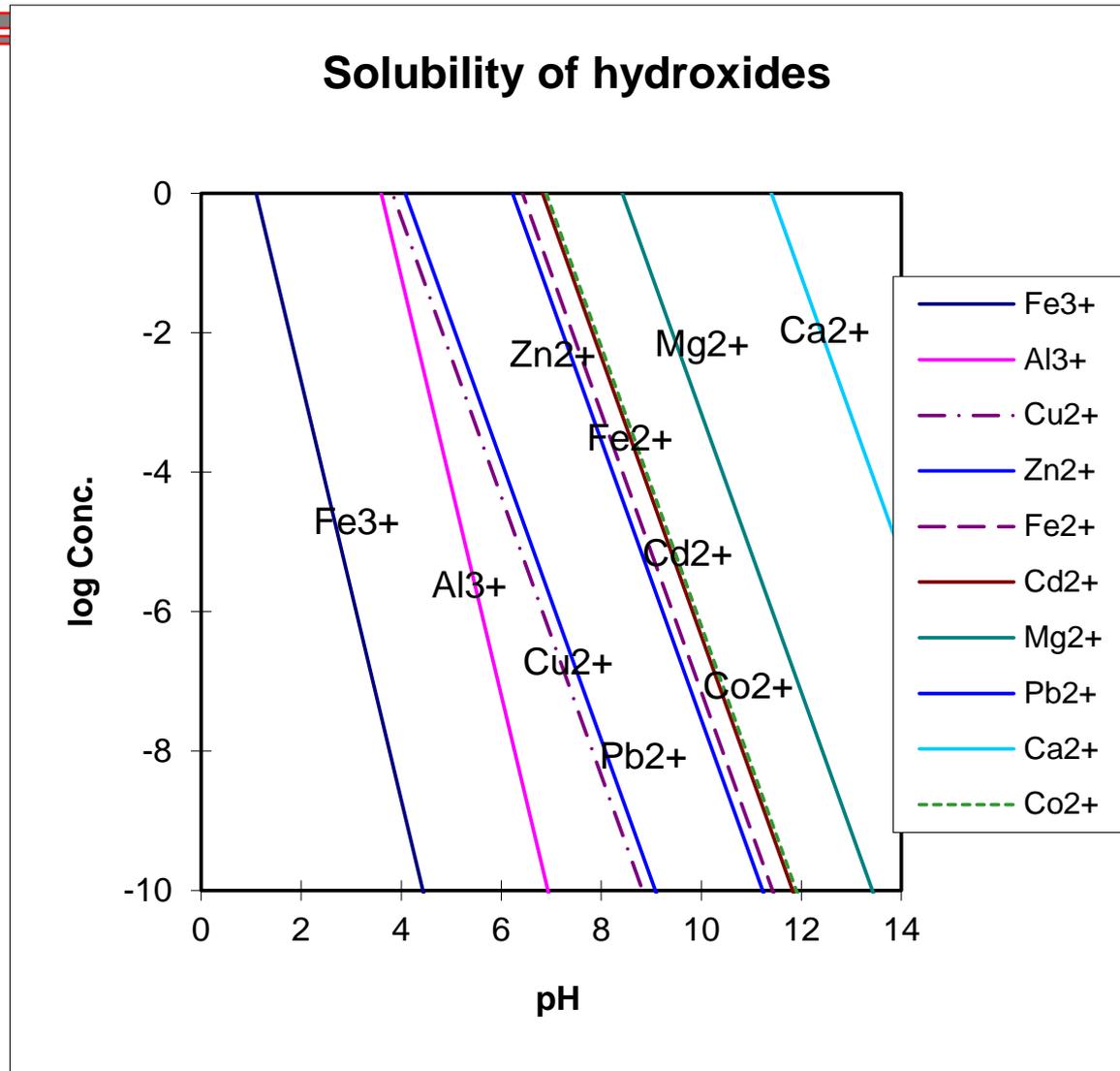
$$[K] = \frac{[H^+]}{[M^{2+}][HCO_3^-]}$$

- Oxides vs. Hydroxides:

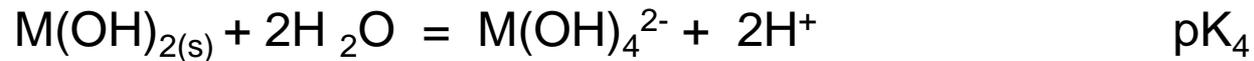
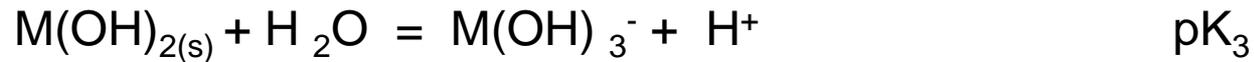
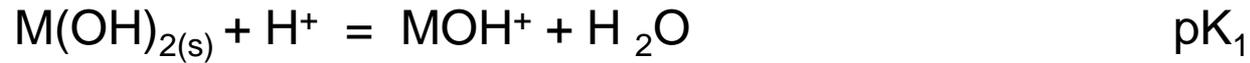


Solubility of hydroxides

pH	pK	Slope
Fe ³⁺	3.3	-3
Al ³⁺	10.8	-3
Cu ²⁺	7.65	-2
Zn ²⁺	12.45	-2
Fe ²⁺	12.85	-2
Cd ²⁺	13.65	-2
Mg ²⁺	16.84	-2
Pb ²⁺	8.16	-2
Ca ²⁺	22.8	-2
Co ²⁺	13.8	-2

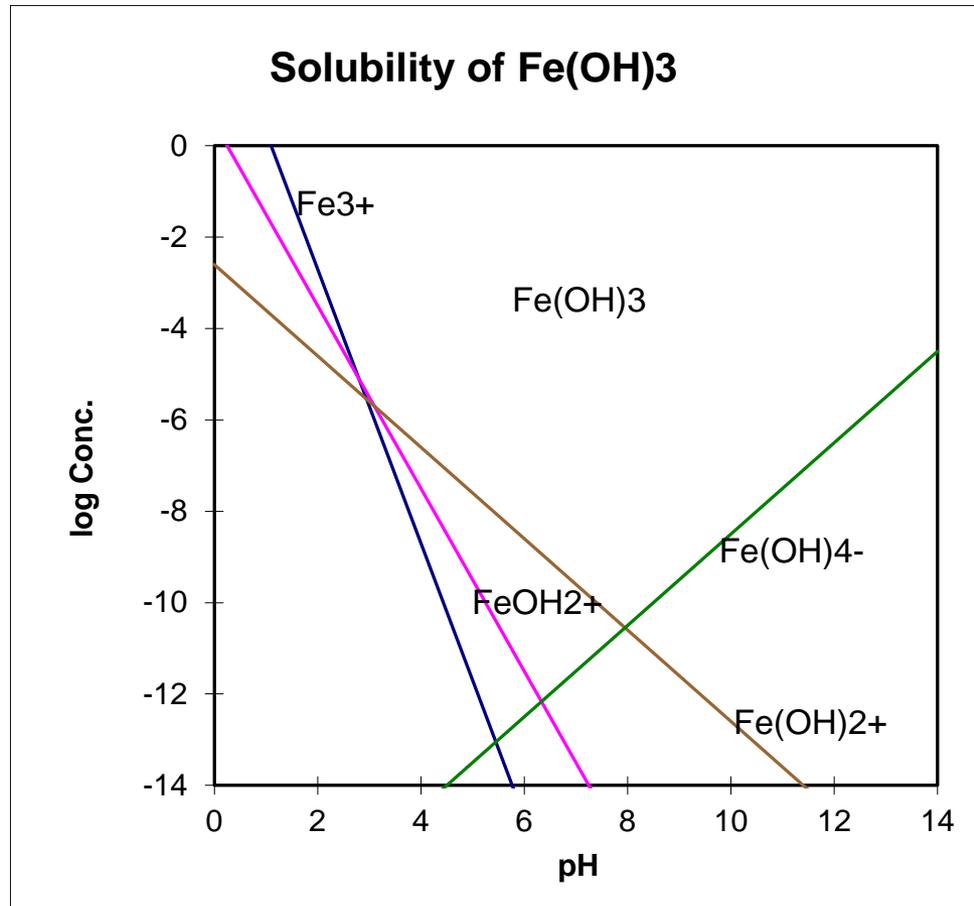


Hydroxyl complexes

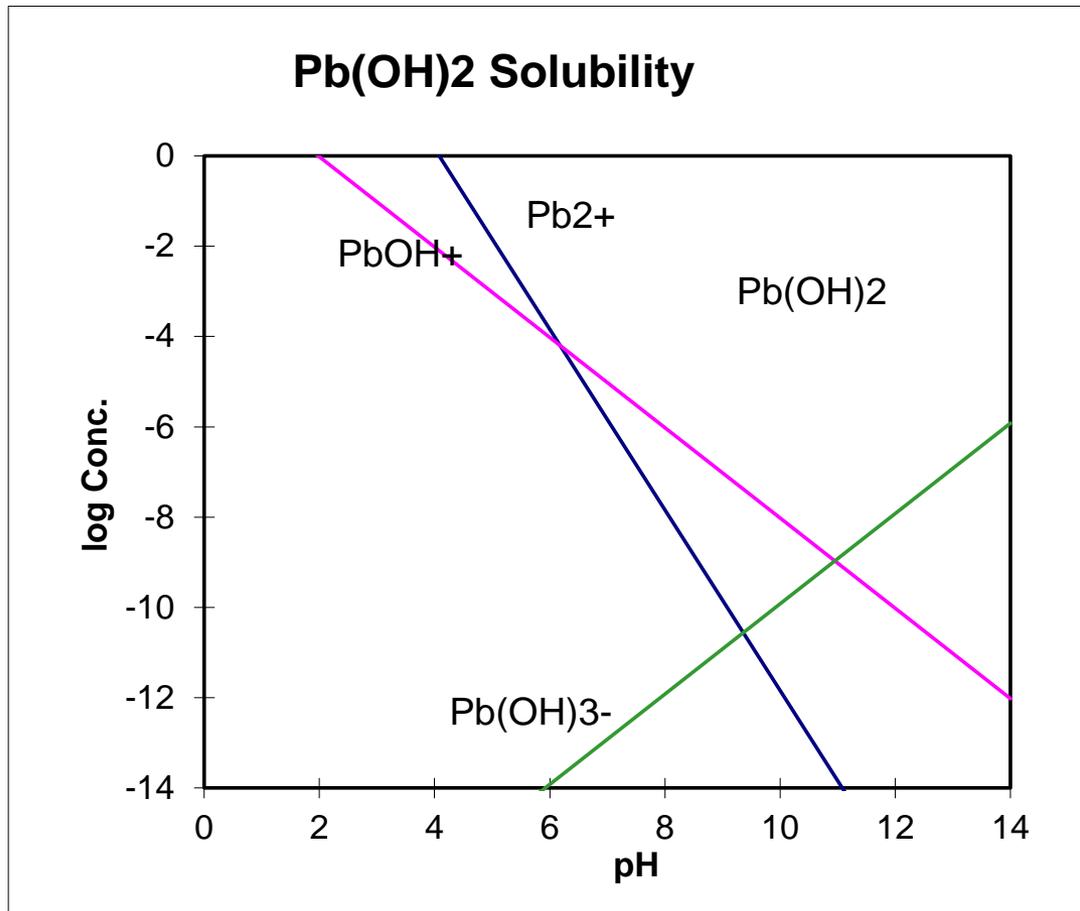


- Complexation affects solubility

Solubility of $\text{Fe}(\text{OH})_3$

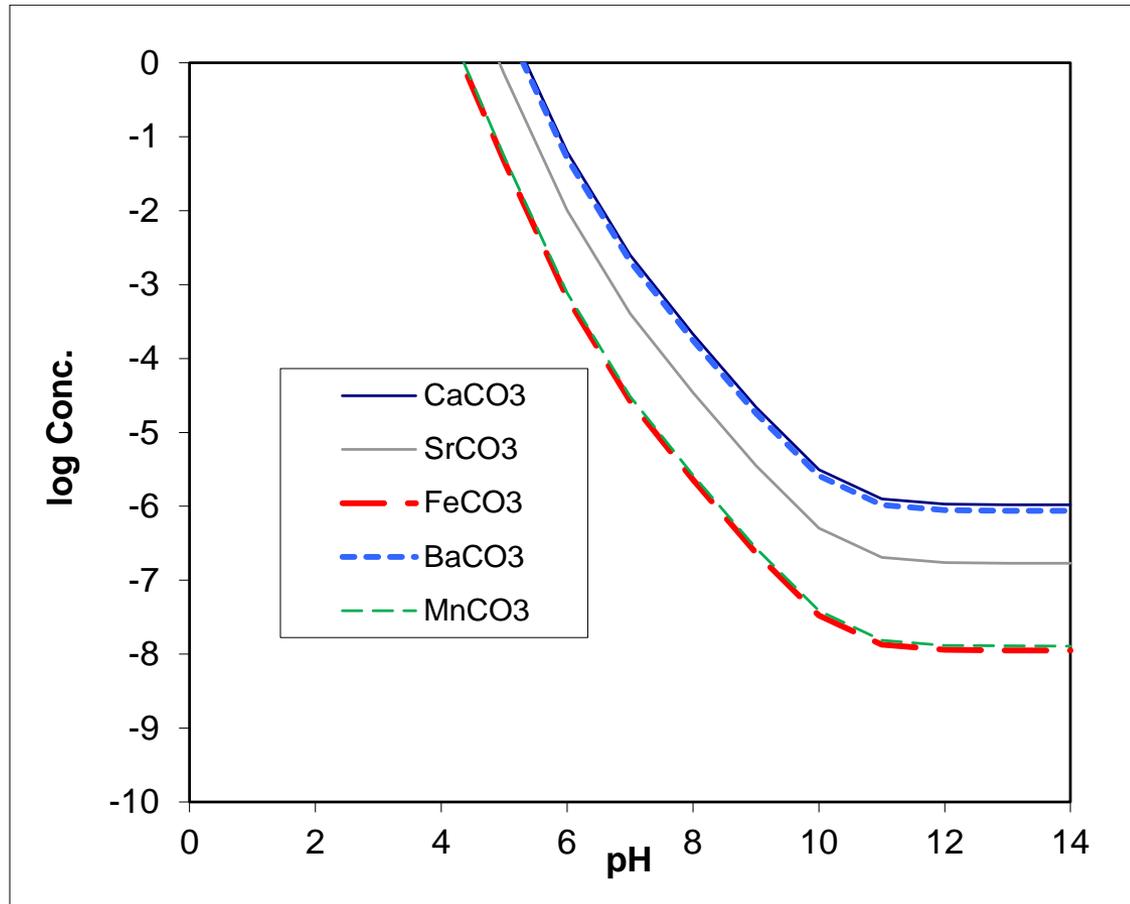


Solubility of $\text{Pb}(\text{OH})_2$



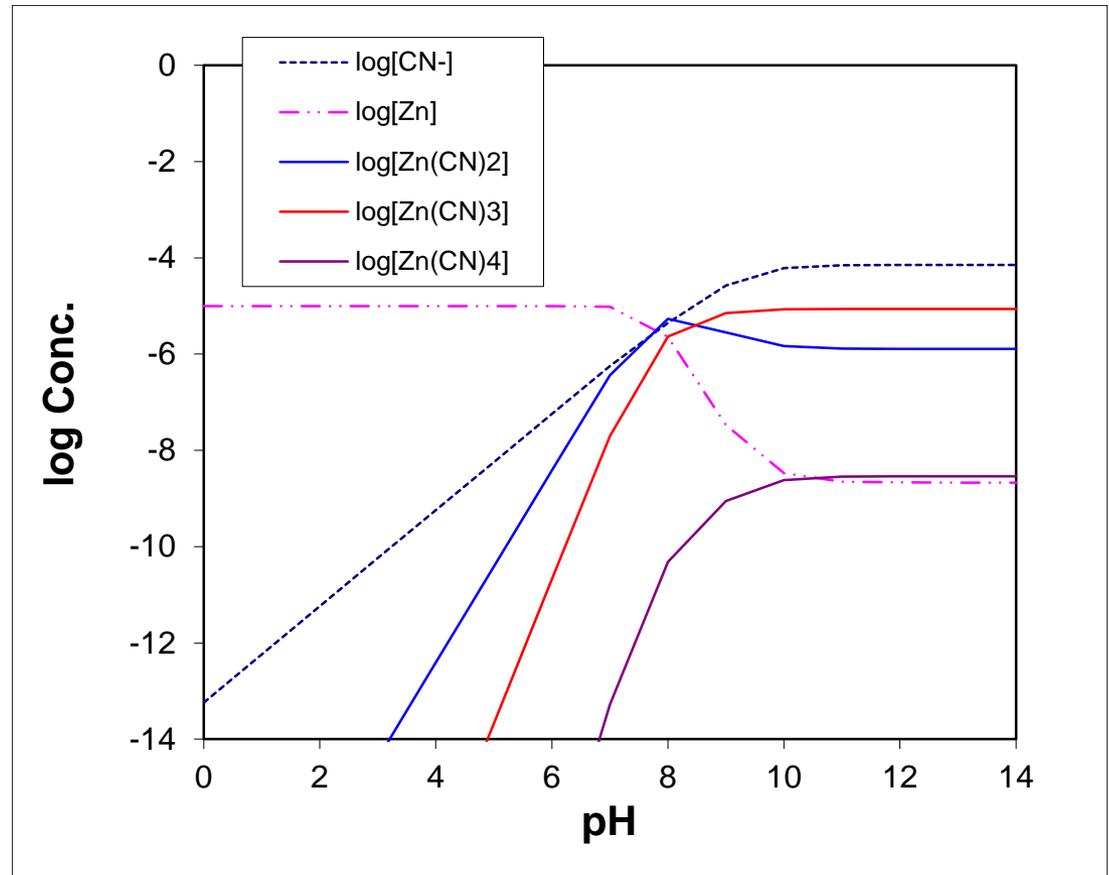
Carbonate solubility

$(MCO_{3(s)} = M^{2+} + CO_3^{2-})$



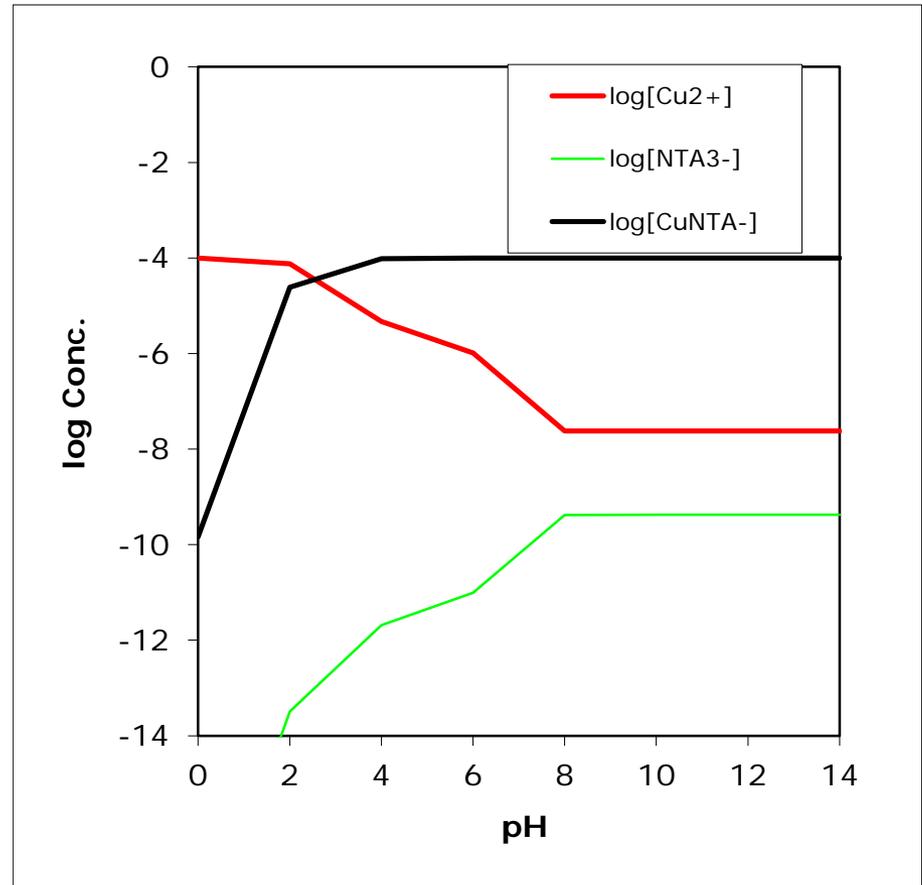
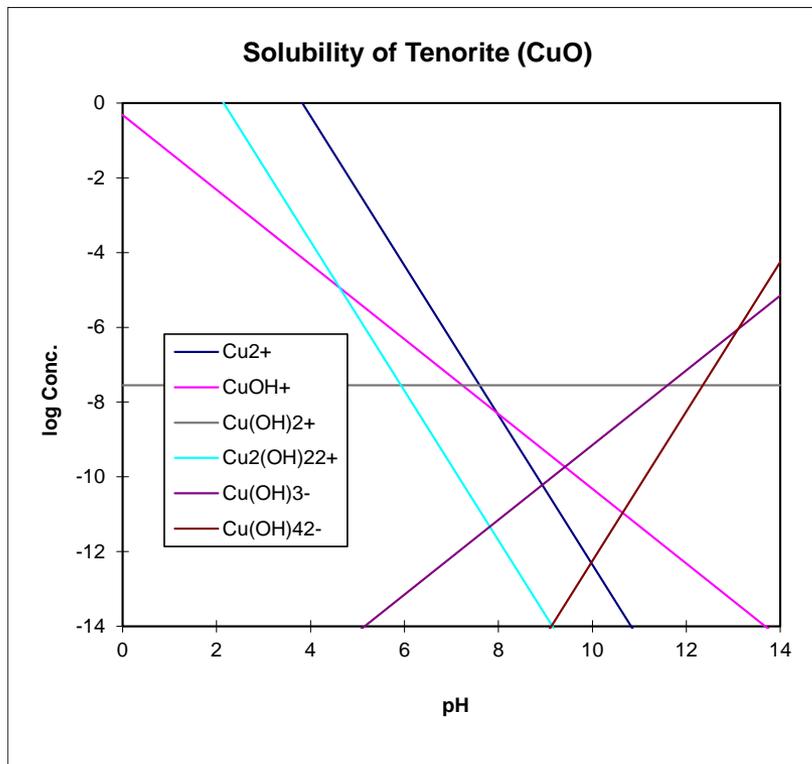
Zinc Complexation by Cyanide

- CN^- forms strong complexes with many transition metals
- Widely used in milling & ore processing (e.g. heap leach of Au)



Cu Complexation by NTA

- Nitrilotriacetic acid ($\text{N}(\text{CH}_2\text{CO}_2^-)_3$)



Saturation Index (SI)

- Arbitrary rx: $AB_{(s)} = A + B$

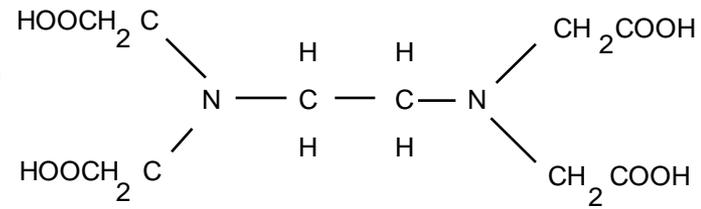
$$K_{so} = \{A\}_{equil} \{B\}_{equil}$$

$$SI = \log \left[\frac{\{A\}_{actual} \{B\}_{actual}}{\{A\}_{equil} \{B\}_{equil}} \right] = \log \left[\frac{\{A\}_{actual} \{B\}_{actual}}{K_{so}} \right]$$

- $SI > 0$ - Soln. is supersaturated
- $SI < 0$ - Soln. is undersaturated
- $SI = 0$ - Soln. is in equilibrium

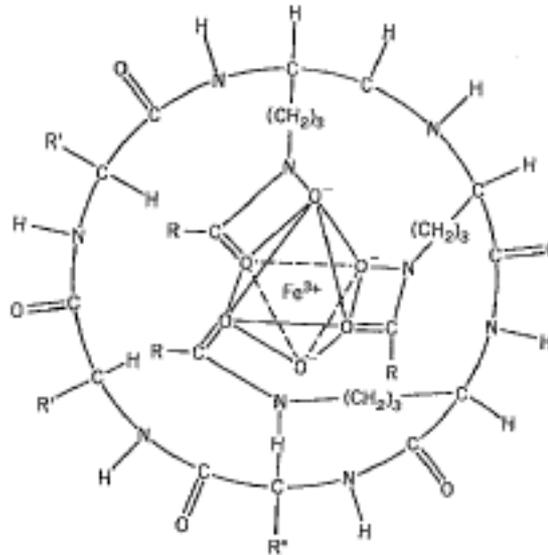
Complexation by Organics

- Organic molecules can form multiple bonds with central metal atom (chelate or complex)
- Ethylenediaminetetracetic Acid (EDTA)



Structure of EDTA

- Ferrichrome complex



Geochemical Modeling

- 5 types of equations
 - Mass action expressions - Chemical equilibria equations
 - Mass balances – Account for total mass of each constituent
 - Electroneutrality conditions - $\Sigma(+ \text{ ions}) = \Sigma(- \text{ ions})$
 - Individual ion activity coefficients – Convert $[i]$ to $\{i\}$
 - Calculation of ionic strength – Adjust for high TDS

Geochemical Models

- PHREEQC*
 - WATEQF*
 - SOLMINEQ.88
 - EQ3/6
 - MINTEQ
-
- * <http://h2o.usgs.gov/software/>

PHREEQC Example – U Complexation

Reading input data for simulation 1.

DATABASE C:\Program Files (x86)\USGS\Phreeqc Interactive 3.1.7-
9213\database\minteq.v4.dat

SOLUTION 1-1 Uranium Solubility

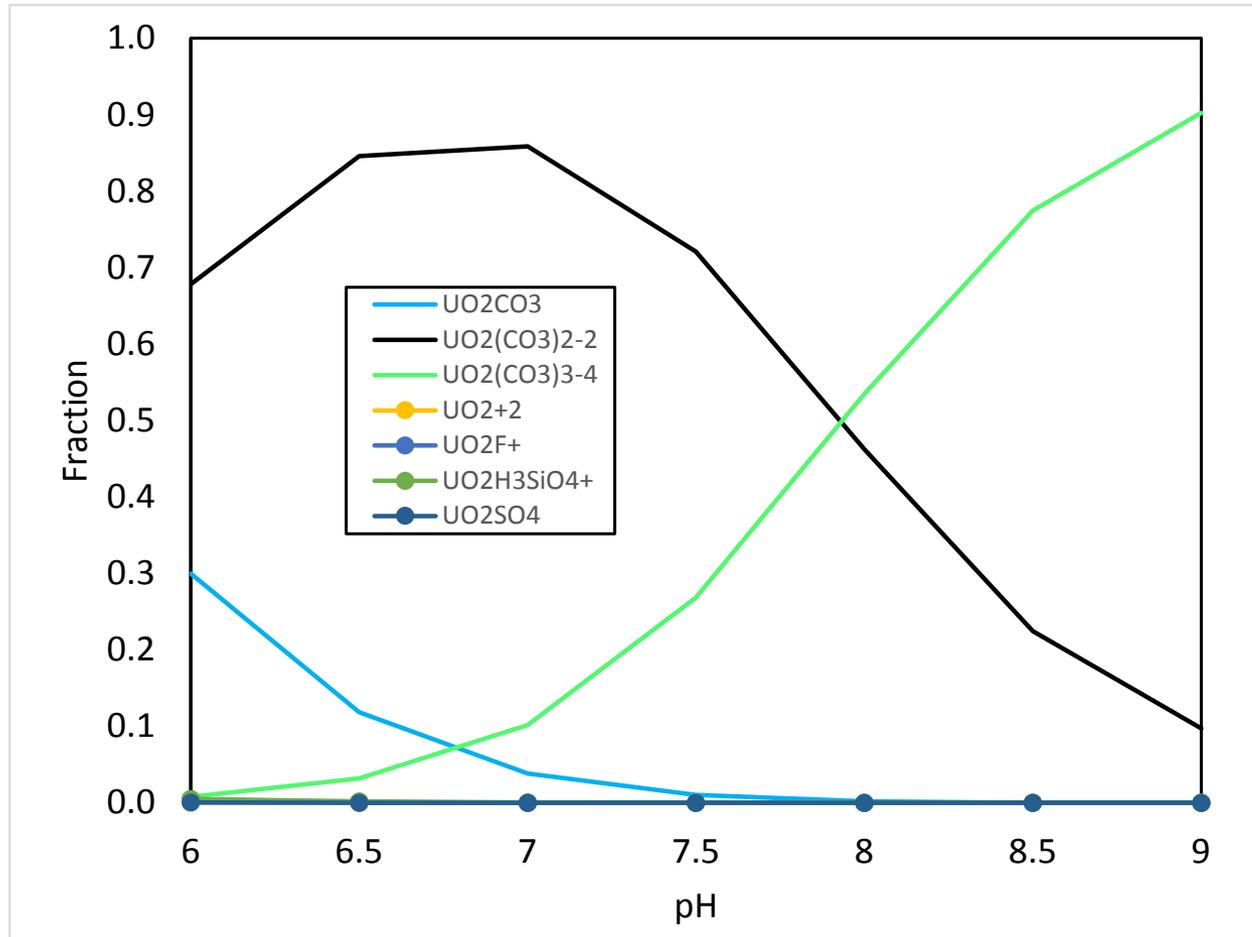
temp 25
pH 7.6
pe 10
redox pe
units mg/l
density 1
Alkalinity 112
Al .1
Ba .1
Ca 44.1
Cu .13
K 4.6
Mg 7.4
Na 31.0
Si 23.4
F .85
Cl 33.8
N(5) 5.5
S(6) 80.3
U(6) .06
water 1 # kg

END

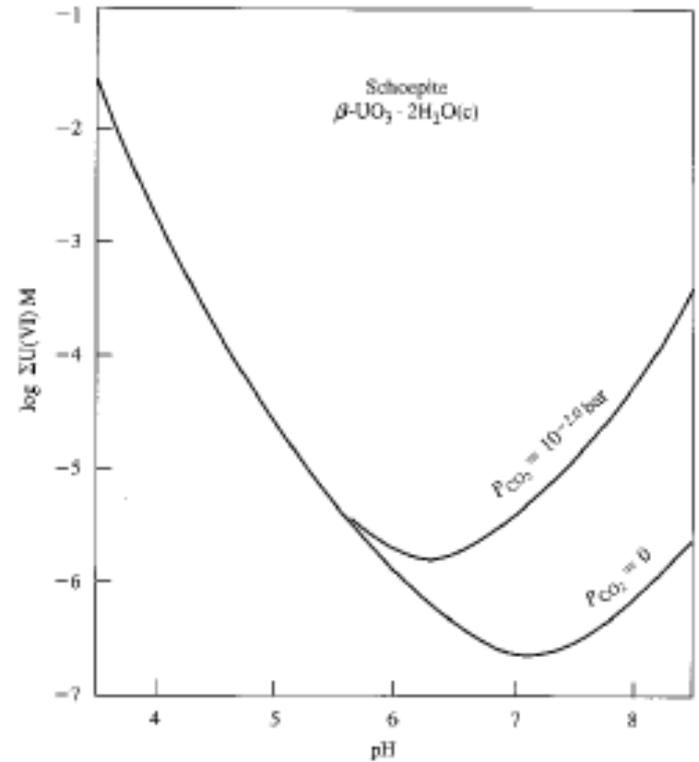
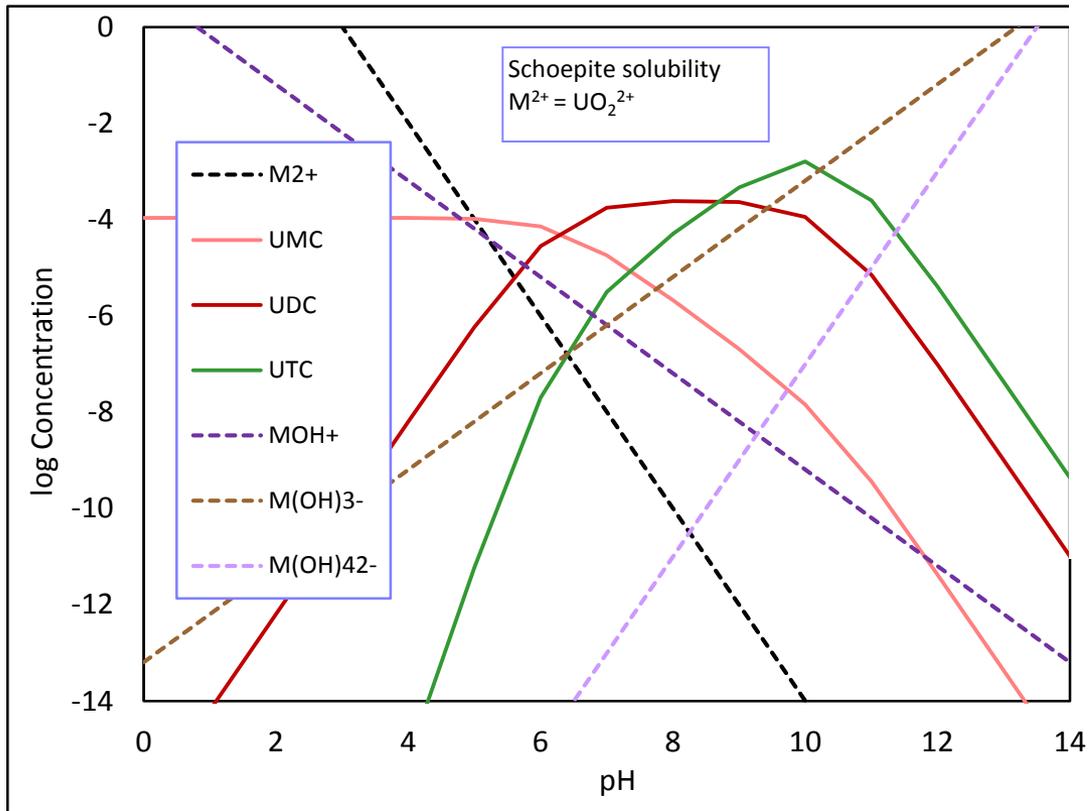
PHREEQC Output – U Species at pH 7.6

Total U Conc. (M)	2.522e-07				
	Molality	Activity	Log Mol.	Log Act.	Log γ
UO ₂ (CO ₃) ₂₋₂	1.704e-07	1.172e-07	-6.769	-6.931	-0.162
UO ₂ (CO ₃) ₃₋₄	7.978e-08	1.788e-08	-7.098	-7.748	-0.650
UO ₂ CO ₃	1.931e-09	1.931e-09	-8.714	-8.714	0.000
UO ₂ H ₃ SiO ₄ ⁺	3.317e-11	3.021e-11	-10.479	-10.520	-0.041
UO ₂ OH ⁺	8.836e-12	8.047e-12	-11.054	-11.094	-0.041
UO ₂ F ⁺	9.645e-13	8.784e-13	-12.016	-12.056	-0.041
UO ₂ + ₂	2.235e-13	1.595e-13	-12.651	-12.797	-0.147
UO ₂ SO ₄	1.256e-13	1.256e-13	-12.901	-12.901	0.000
UO ₂ F ₂	1.011e-13	1.011e-13	-12.995	-12.995	0.000
UO ₂ (SO ₄) ₂₋₂	1.251e-15	8.610e-16	-14.903	-15.065	-0.162
UO ₂ F ₃ ⁻	1.112e-15	1.013e-15	-14.954	-14.994	-0.041
UO ₂ Cl ⁺	2.489e-16	2.267e-16	-15.604	-15.645	-0.041
(UO ₂) ₂ (OH) ₂₊₂	1.562e-16	1.075e-16	-15.806	-15.969	-0.162
UO ₂ NO ₃ ⁺	1.259e-16	1.146e-16	-15.900	-15.941	-0.041
(UO ₂) ₃ (OH) ₅₊	1.157e-16	1.054e-16	-15.937	-15.977	-0.041
UO ₂ F ₄₋₂	4.667e-19	3.211e-19	-18.331	-18.493	-0.162

U Complexation



U Solubility – Carbonate Complexation



Langmuir, 1997

PHREEQC Output – Saturation Indices at pH 7.6

Phase	SI	log IAP	log K ₂₉₈	Formula
Al(OH)3(a)	-1.19	9.61	10.8	Al(OH)3
Al2O3	-0.43	19.22	19.65	Al2O3
Al4(OH)10	-2.74	19.96	22.7	Al4(OH)10SO4
AlOHSO4	-5.64	-8.87	-3.23	AlOHSO4
Alunite	-3.1	-4.5	-1.4	KAl3(SO4)2(OH)6
Anhydrite	-2.08	-6.44	-4.36	CaSO4
Antlerite	-2.72	6.07	8.79	Cu3(OH)4SO4
Aragonite	-0.37	-8.67	-8.3	CaCO3
Artinite	-7.31	2.29	9.6	MgCO3:Mg(OH)2:3H2O
Atacamite	-1.68	5.71	7.39	Cu2(OH)3Cl
Azurite	0.02	-16.88	-16.91	Cu3(OH)2(CO3)2
Ba(OH)2·8H2O	-15.48	8.91	24.39	Ba(OH)2:8H2O
BaF2	-9.27	-15.09	-5.82	BaF2
Barite	0.41	-9.57	-9.98	BaSO4
Boehmite	1.03	9.61	8.58	AlOOH
Brochantite	-0.97	14.25	15.22	Cu4(OH)6SO4
Brucite	-5.34	11.5	16.84	Mg(OH)2
Calcite	-0.19	-8.67	-8.48	CaCO3
CH4(g)	-120.47	-161.52	-41.05	CH4
Chalcanthite	-7.66	-10.3	-2.64	CuSO4:5H2O
Chalcedony	0.14	-3.41	-3.55	SiO2
Chrysotile	-4.52	27.68	32.2	Mg3Si2O5(OH)4
CO2(g)	-2.57	-20.72	-18.15	CO2
Cristobalite	-0.06	-3.41	-3.35	SiO2
Cryolite	-14.47	-48.31	-33.84	Na3AlF6
Cu(OH)2	-0.49	8.18	8.67	Cu(OH)2
Cu2(OH)3NO3	-3.93	5.32	9.25	Cu2(OH)3NO3
Cu2SO4	-29.99	-31.94	-1.95	Cu2SO4
CuCO3	-1.03	-12.53	-11.5	CuCO3
CuF	-13.82	-18.73	-4.91	CuF
CuF2	-16.93	-15.81	1.12	CuF2
CuF2·2H2O	-11.26	-15.81	-4.55	CuF2:2H2O
Cumetal	-15.57	-24.33	-8.76	Cu
CuOCuSO4	-12.42	-2.12	10.3	CuOCuSO4
Cuprite	-12.05	-13.45	-1.41	Cu2O
CuSO4	-13.24	-10.3	2.94	CuSO4
Diaspore	2.74	9.61	6.87	AlOOH
Dolomite	-1.34	-17.88	-16.54	CaMg(CO3)2
Dolomite	-0.79	-17.88	-17.09	CaMg(CO3)2

Phase	SI	log IAP	log K ₂₉₈	Formula
Epsomite	-4.86	-6.98	-2.13	MgSO4:7H2O
Fluorite	-1.45	-11.95	-10.5	CaF2
Gibbsite	1.32	9.61	8.29	Al(OH)3
Gummite	-5.27	2.4	7.67	UO3
Gypsum	-1.83	-6.44	-4.61	CaSO4:2H2O
Halite	-7.57	-5.97	1.6	NaCl
Halloysite	2.83	12.4	9.57	Al2Si2O5(OH)4
Huntite	-6.35	-36.31	-29.97	CaMg3(CO3)4
Hydromag	-16.59	-25.36	-8.77	Mg5(CO3)4(OH)2:4H2O
K-Alum	-18.55	-23.72	-5.17	KAl(SO4)2:12H2O
Kaolinite	4.97	12.4	7.43	Al2Si2O5(OH)4
Langite	-3.24	14.25	17.49	Cu4(OH)6SO4:H2O
Lime	-20.65	12.05	32.7	CaO
Magnesite	-1.76	-9.22	-7.46	MgCO3
Malachite	0.96	-4.35	-5.31	Cu2(OH)2CO3
Melanothite	-19.39	-13.13	6.26	CuCl2
Mg(OH)2	-7.29	11.5	18.79	Mg(OH)2
MgF2	-4.37	-12.5	-8.13	MgF2
Mirabilite	-7.99	-9.1	-1.11	Na2SO4:10H2O
Nantokite	-10.65	-17.38	-6.73	CuCl
Natron	-10.02	-11.33	-1.31	Na2CO3:10H2O
Nesquehondite	-4.55	-9.22	-4.67	MgCO3:3H2O
O2(g)	-12.69	70.4	83.09	O2
Periclase	-10.08	11.5	21.58	MgO
Portlandite	-10.76	12.05	22.8	Ca(OH)2
Quartz	0.59	-3.41	-4	SiO2
Rutherfordite	-3.81	-18.31	-14.5	UO2CO3
Schoepite	-3.59	2.4	5.99	UO2(OH)2:H2O
Sepiolite	-2.99	12.77	15.76	Mg2Si3O7.5OH:3H2O
Sepiolite	-6.01	12.77	18.78	Mg2Si3O7.5OH:3H2O
SiO2(am-g)	-0.7	-3.41	-2.71	SiO2
SiO2(am-f)	-0.67	-3.41	-2.74	SiO2
Spinel	-6.12	30.73	36.85	MgAl2O4
Tenorite	0.54	8.18	7.64	CuO
Thenardite	-9.42	-9.1	0.32	Na2SO4
Thermonatrite	-11.97	-11.33	0.64	Na2CO3:H2O
UO2(NO3)2	-31.83	-19.68	12.15	UO2(NO3)2
UO2(NO3)2	-24.54	-19.68	4.85	UO2(NO3)2:2H2O
UO2(NO3)2	-23.07	-19.68	3.39	UO2(NO3)2:3H2O
UO2(NO3)2	-21.73	-19.68	2.05	UO2(NO3)2:6H2O
UO2(OH)2	-3.21	2.4	5.61	UO2(OH)2
UO3	-5.3	2.4	7.7	UO3
Witherite	-3.24	-11.81	-8.57	BaCO3

PHREEQC Saturation Indices for Select Species

pH = 7.6				
Phase	SI	log IAP	log K ₂₉₈	Formula
Al(OH)3(am)	-1.19	9.61	10.8	Al(OH)3
Anhydrite	-2.08	-6.44	-4.36	CaSO4
Aragonite	-0.37	-8.67	-8.3	CaCO3
Calcite	-0.19	-8.67	-8.48	CaCO3
Cu(OH)2	-0.49	8.18	8.67	Cu(OH)2
CuCO3	-1.03	-12.53	-11.5	CuCO3
Dolomite(disc)	-1.34	-17.88	-16.54	CaMg(CO3)2
Gibbsite	1.32	9.61	8.29	Al(OH)3
Gummite	-5.27	2.4	7.67	UO3
Gypsum	-1.83	-6.44	-4.61	CaSO4:2H2O
Magnesite	-1.76	-9.22	-7.46	MgCO3
Quartz	0.59	-3.41	-4	SiO2
Rutherfordine	-3.81	-18.31	-14.5	UO2CO3
Schoepite	-3.59	2.4	5.99	UO2(OH)2:H2O
SiO2(am-ppt)	-0.67	-3.41	-2.74	SiO2
UO2(NO3)2	-31.83	-19.68	12.15	UO2(NO3)2
UO2(NO3)2:2H	-24.54	-19.68	4.85	UO2(NO3)2:2H2O
UO2(NO3)2:3H	-23.07	-19.68	3.39	UO2(NO3)2:3H2O
UO2(NO3)2:6H	-21.73	-19.68	2.05	UO2(NO3)2:6H2O
UO2(OH)2(bet)	-3.21	2.4	5.61	UO2(OH)2
UO3	-5.3	2.4	7.7	UO3

Redox Chemistry

- Responsible for energy in biological rxs. (chemosynthetic organisms)
- Organic compounds can be destroyed by oxidation (mineralization)
- Toxicity of many metals depends on oxidation state (Cr, As, Se...)
- Solubility of metals depends on oxidation state

Definitions

- Oxidation = loss of e^-
- Reduction = gain of e^-
- Oxidant = compound which accepts e^-

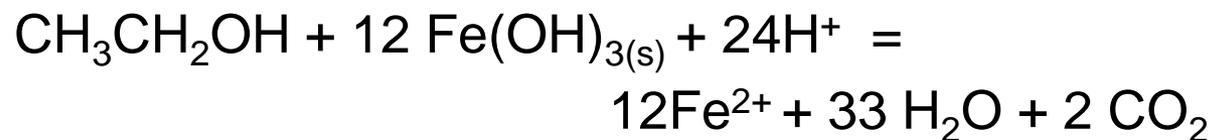
- Use Roman Numerals to indicate oxidation state of metal as Fe(II), Fe(III), S(-II), S(VI), U(IV), U(VI)

Nomenclature

Species	Suffix	
	Oxidized Form	Reduced Form
Metals	-ic (ferric, manganic, mercuric)	-ous (ferrous, manganous, mercurous)
Oxyanions	-ate (nitrate, sulfate, arsenate, selenate)	-ite (nitrite, sulfite, arsenite, selenite)
Most reduced form	-ide (sulfide, arsenide, selenide)	

Redox Equilibrium

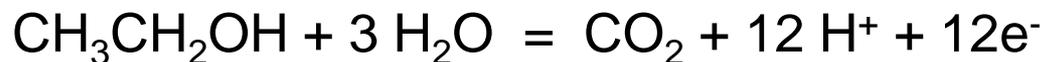
- Equilibrium constant for overall rx.:



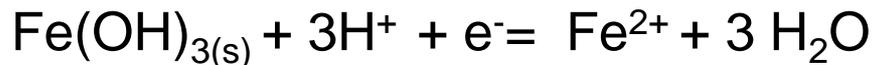
$$K = \frac{[\text{Fe}^{2+}]^{12} P_{\text{CO}_2}^2}{[\text{CH}_3\text{CH}_2\text{OH}][\text{H}^+]^{24}}$$

Redox Equilibrium: Write as Half Reactions

- Equilibrium constant for half rxs.:



$$K_{\text{ox}} = \frac{P_{\text{CO}_2} [\text{H}^+]^{12} [\text{e}^-]^{12}}{[\text{CH}_3\text{CH}_2\text{OH}]}$$



$$K_{\text{red}} = \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^3 [\text{e}^-]}$$

pe

- $pe = -\log\{e^-\}$
- Analogous to $pH = -\log\{H^+\}$
- Take logs of equilibrium expression:
$$\log K = -3 \log[H^+] - \log\{e^-\} + \log[Fe^{2+}]$$
- Rearrange:
$$pe = \log K - 3 pH + \log[Fe^{2+}]$$

Thermodynamics

- Nernst equation:

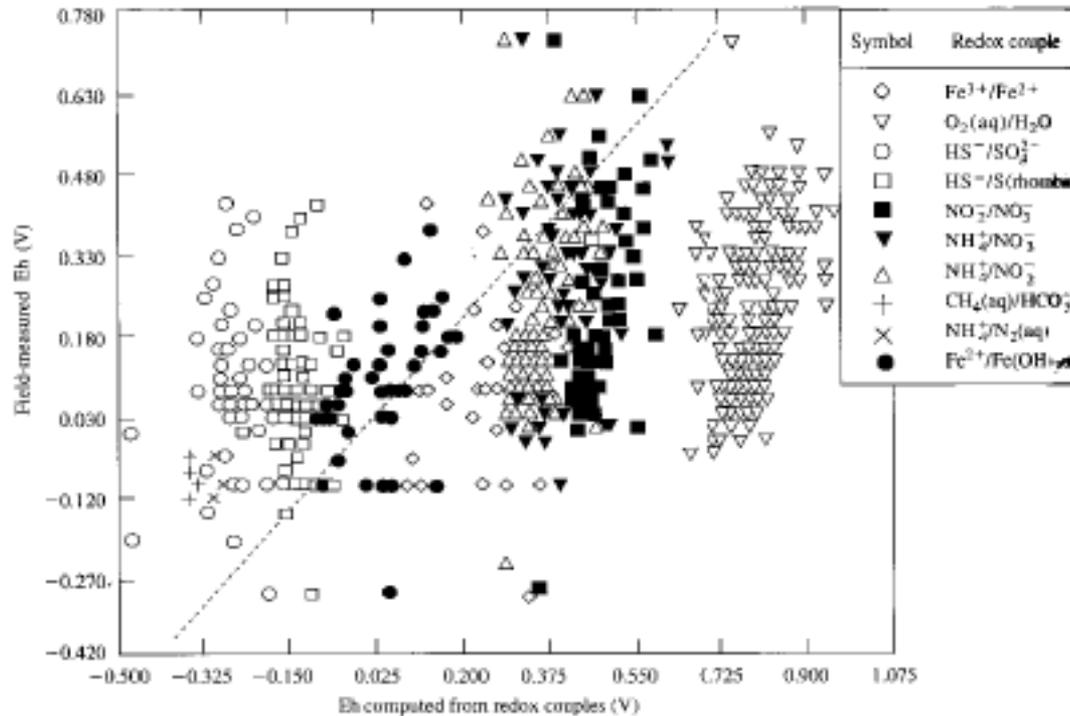
$$E_h = E_h^{\circ} + \frac{2.3 RT}{nF} \log \left[\frac{\prod \{\text{ox}_i\}}{\prod \{\text{red}_i\}} \right]$$

- Relationship between E_h & pe :

$$E_h = \frac{2.3 RT}{F} pe$$

In Principle Can Measure Eh But Not Really

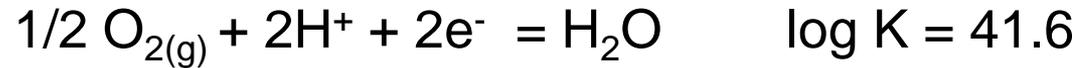
(Lindberg & Runnels, *Science*, 225 (4665) pp. 925-927.1984)



- Compare measured Eh to Eh calculated from redox couples
 - One of my favorite papers

pe-pH diagrams

- Upper boundary:



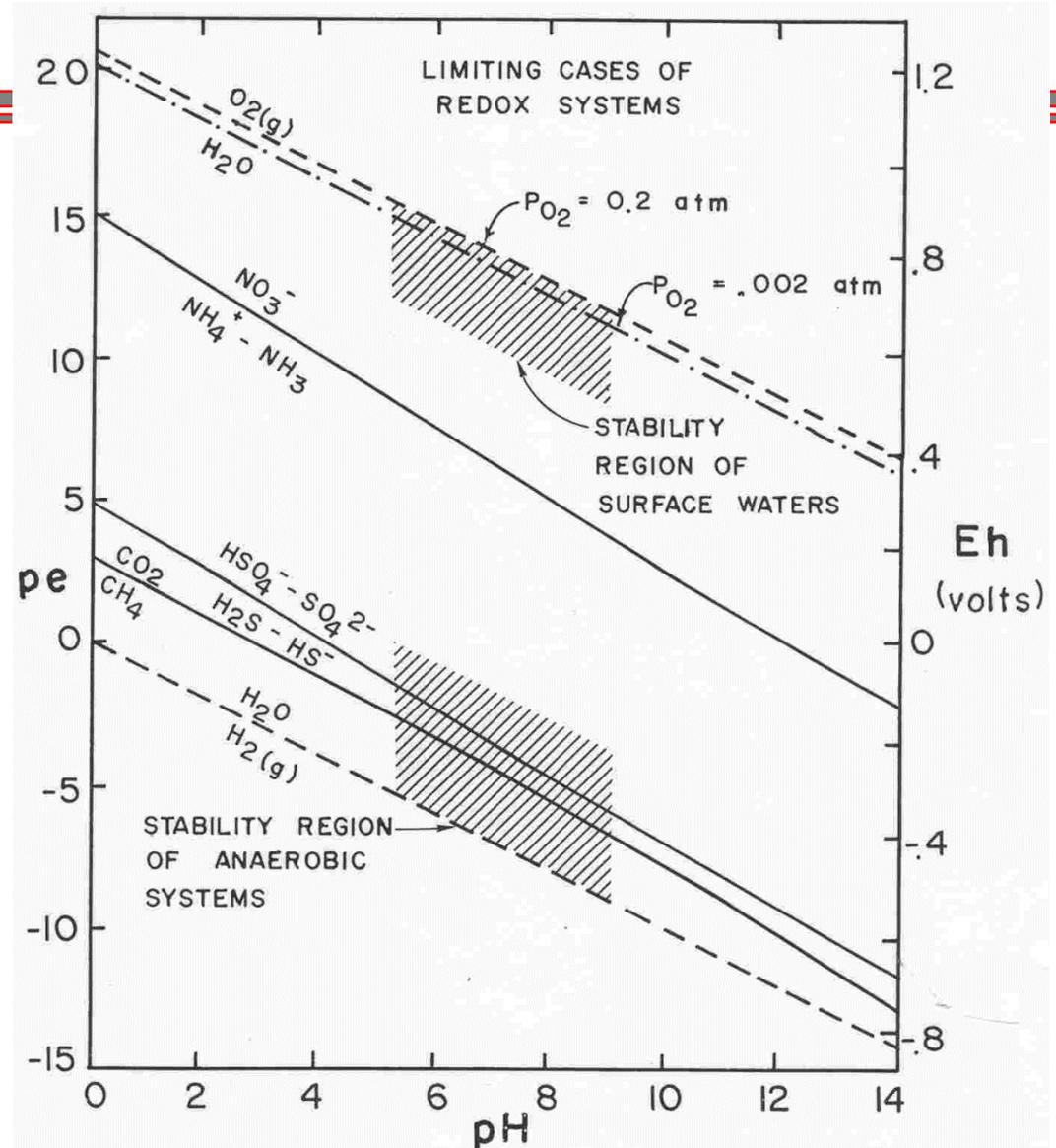
$$\text{pe} = 20.8 + \frac{1}{4} \log P_{\text{O}_2} - \text{pH}$$

- Lower boundary:



$$\text{pe} = \frac{1}{2} \log P_{\text{H}_2} - \text{pH}$$

General pe-pH Diagram



pe-pH diagrams

General diagram with common
redox couples

N

S

Hg

Se

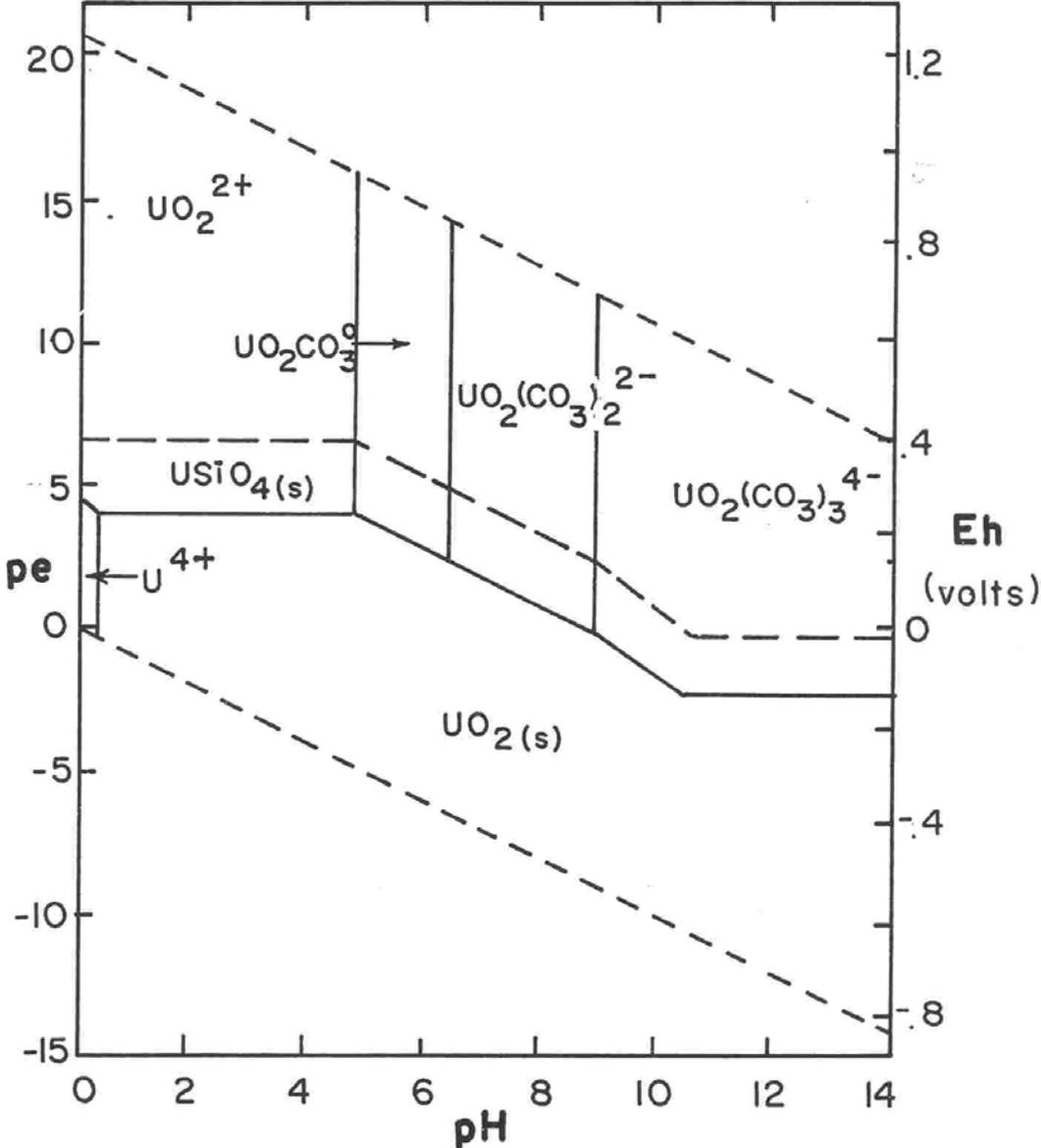
U

Cd

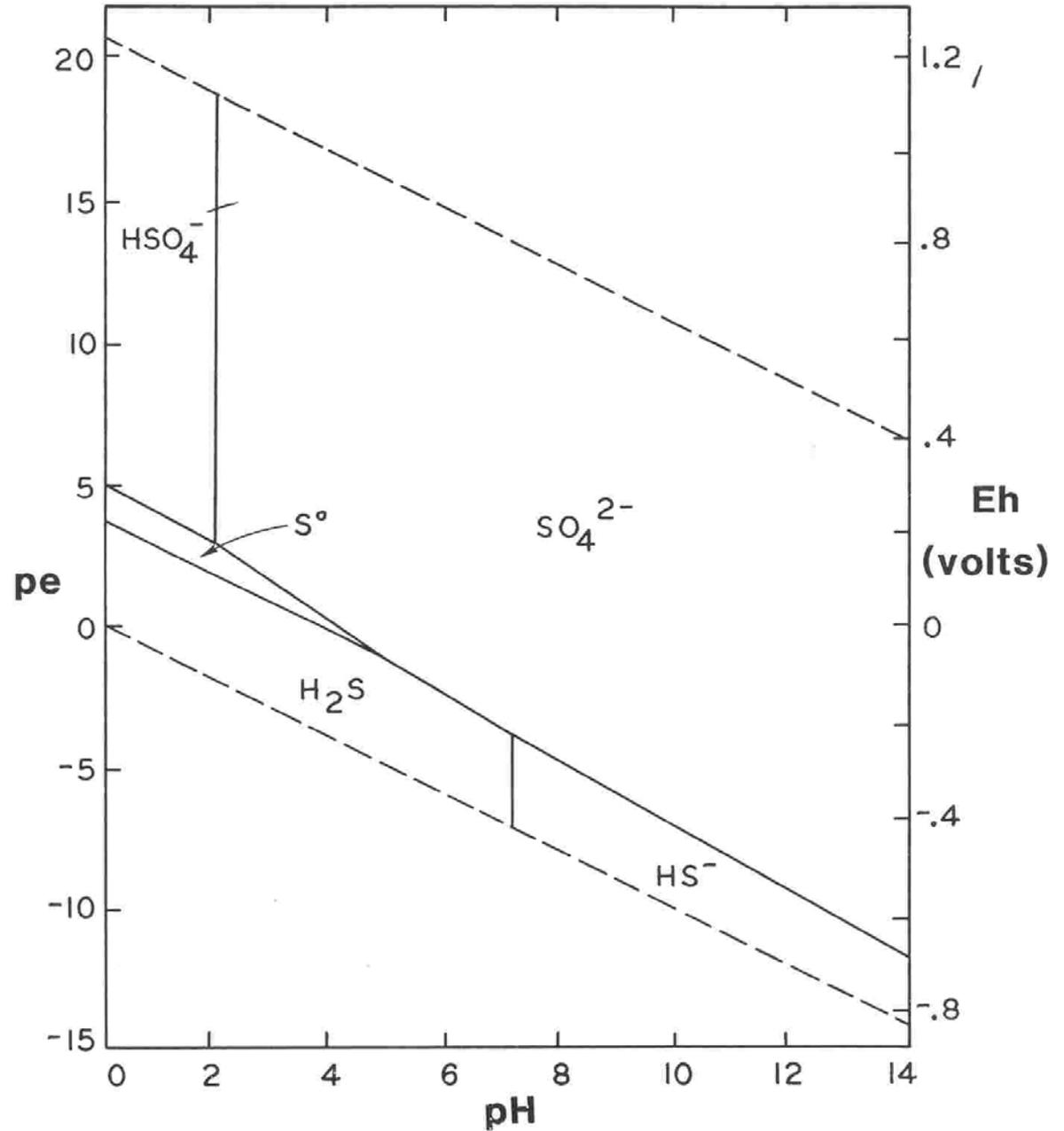
Cr

Fe

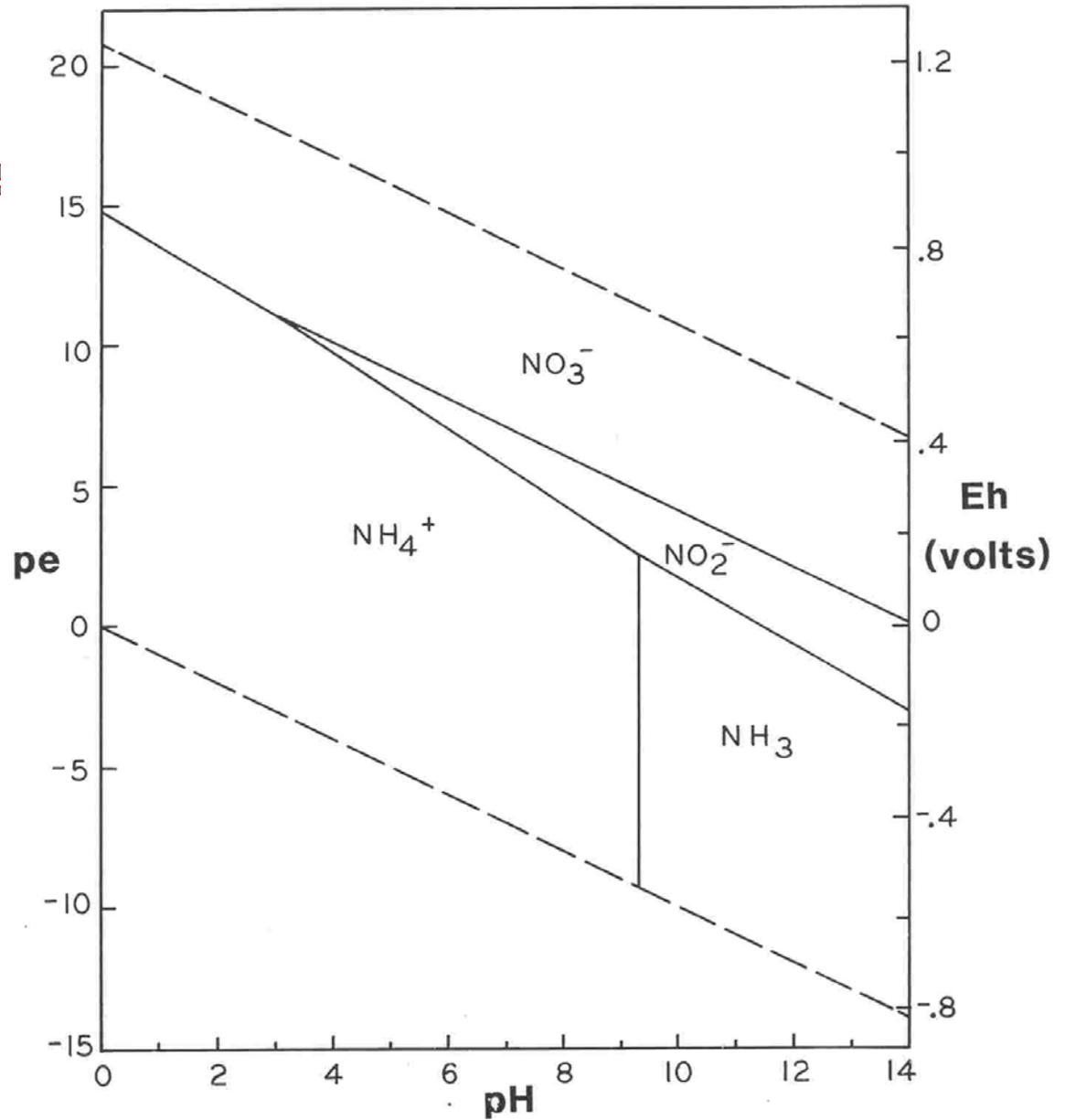
pe-pH Diagram for Uranium



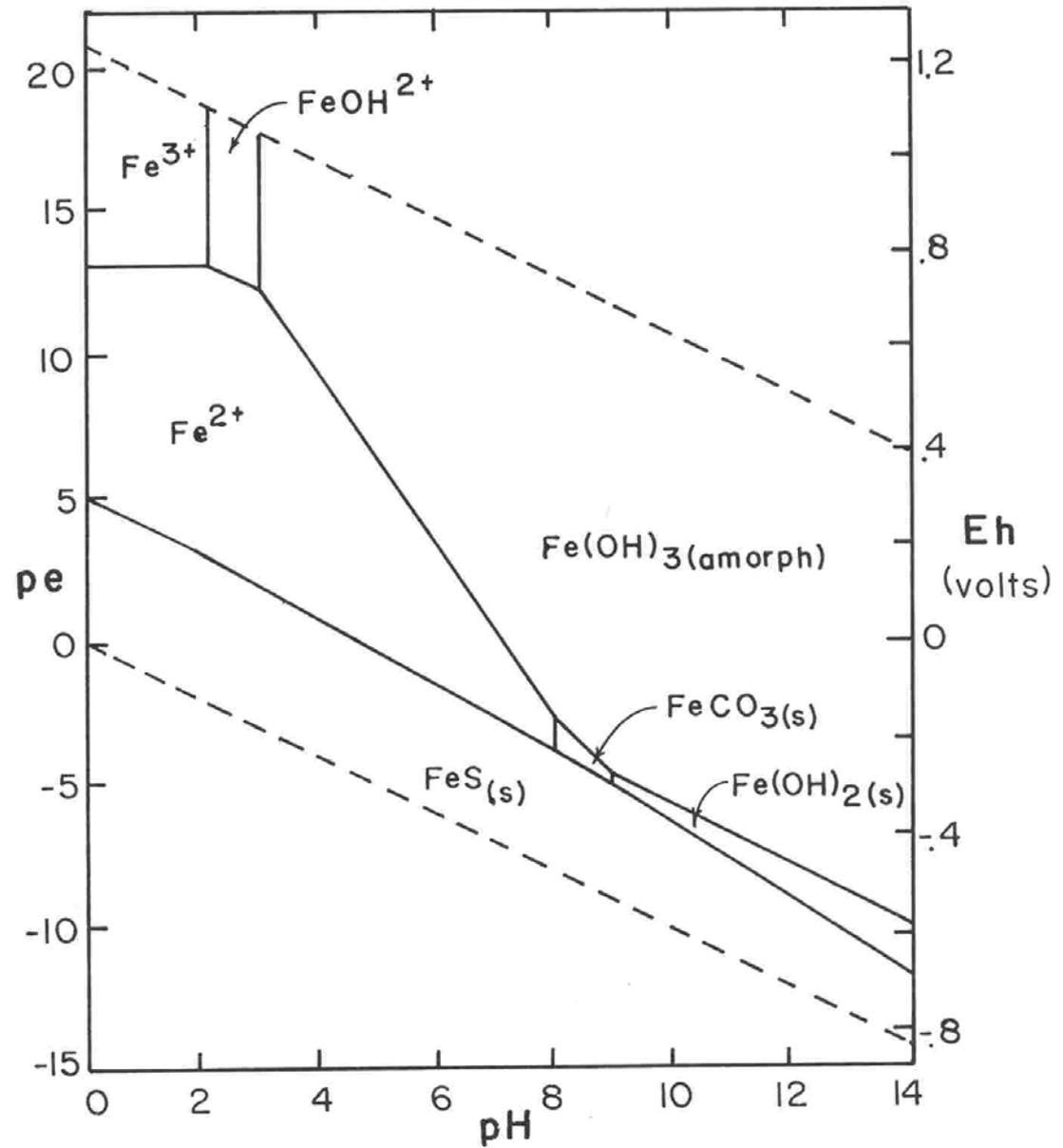
Sulfur



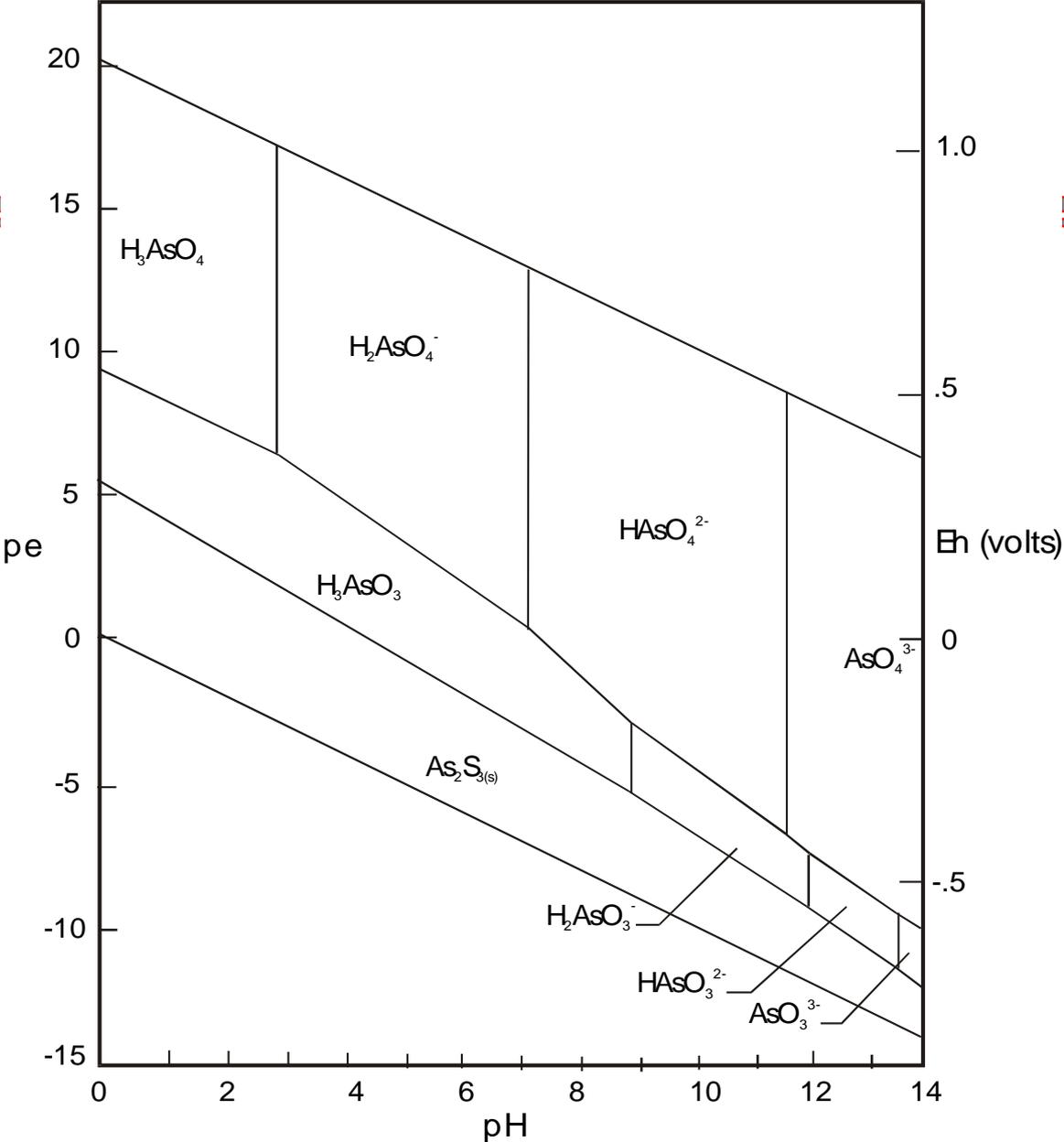
Nitrogen



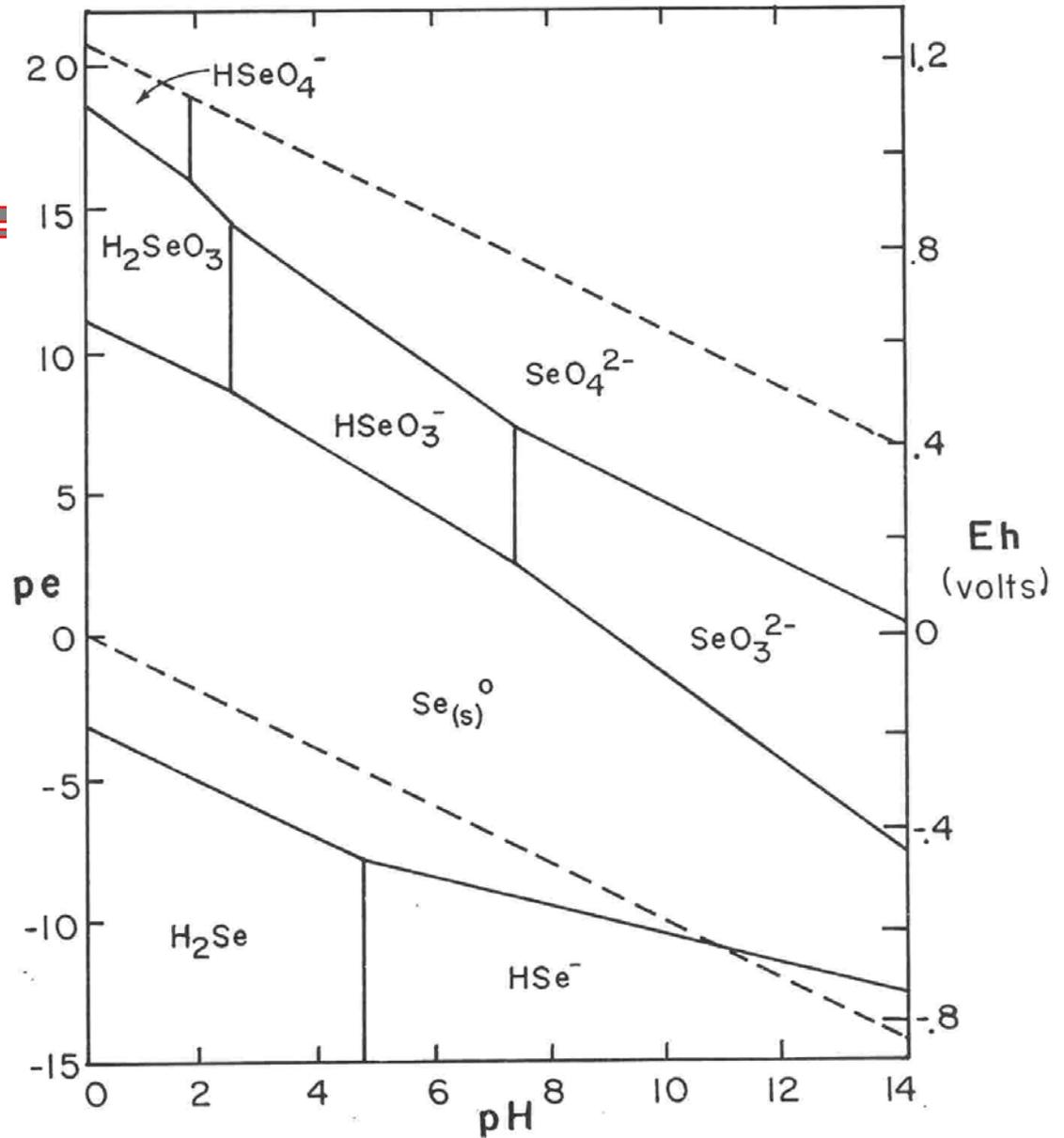
Iron



Arsenic



Selenium



Some U Minerals Important to Southwest

Mineral	Formula	Mineral	Formula
<u>Oxides</u>		<u>Vanadates</u>	
Becquerelite	$7\text{UO}_3 \cdot 11\text{H}_2\text{O}$	Carnotite	$\text{K}_2(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 1-3\text{H}_2\text{O}$
Schoepite	$2\text{UO}_3 \cdot 5\text{H}_2\text{O}$	Tyuyamunite	$\text{Ca}(\text{UO}_2)_2(\text{VO}_4)_2 \cdot 8-10\text{H}_2\text{O}$
Uraninite	UO_2		
		<u>Silicates</u>	
<u>Carbonates</u>		Coffinite	$\text{U}(\text{SiO}_4)_{1-x}(\text{OH})_{4x}$
Andersonite	$\text{Na}_2\text{Ca}(\text{UO}_2)(\text{CO}_3)_3 \cdot 6\text{H}_2\text{O}$	Uranophane	$\text{Ca}(\text{UO}_2)_2(\text{SiO}_3)(\text{OH})_2 \cdot 5\text{H}_2\text{O}$
Schroëckingerite	$\text{NaCa}_3(\text{UO}_2)(\text{CO}_3)_3(\text{SO}_4)\text{F} \cdot 10\text{H}_2\text{O}$		
		<u>Multiple Oxides</u>	
<u>Molybdates</u>		Brannerite	$(\text{U,Ca})(\text{Nb,Ta,Ti})_3\text{O}_9 \cdot \text{H}_2\text{O}$
Umohoite	$(\text{UO}_2)(\text{MoO}_4) \cdot 4\text{H}_2\text{O}$		
Others: Arsenates Fluorides Phosphates Sulfates			

Types of U Ore Deposits (Devoto, 1978)

- Magmatic & igneous rocks
 - Crustal abundance ~2 ppm
 - Associated with granites & similar rocks
 - Some vein formation - felsic igneous & metamorphic rocks (Schwartzwalder Mine)
- Sedimentary environments
 - Depositional (syngenetic) - placer & marine deposits
 - Diagenetic (epigenetic) - ground water transport & deposition
 - Weathering & transport as U-carbonate
 - Deposition in reducing zone - Roll front deposits
 - With Organic C, Mo, V, Se, As, S, CaCO₃, feldspars, Fe-Mg Silicates

Role of Redox in Diagenetic (Epigenetic) Formation of Sandstone U Deposits

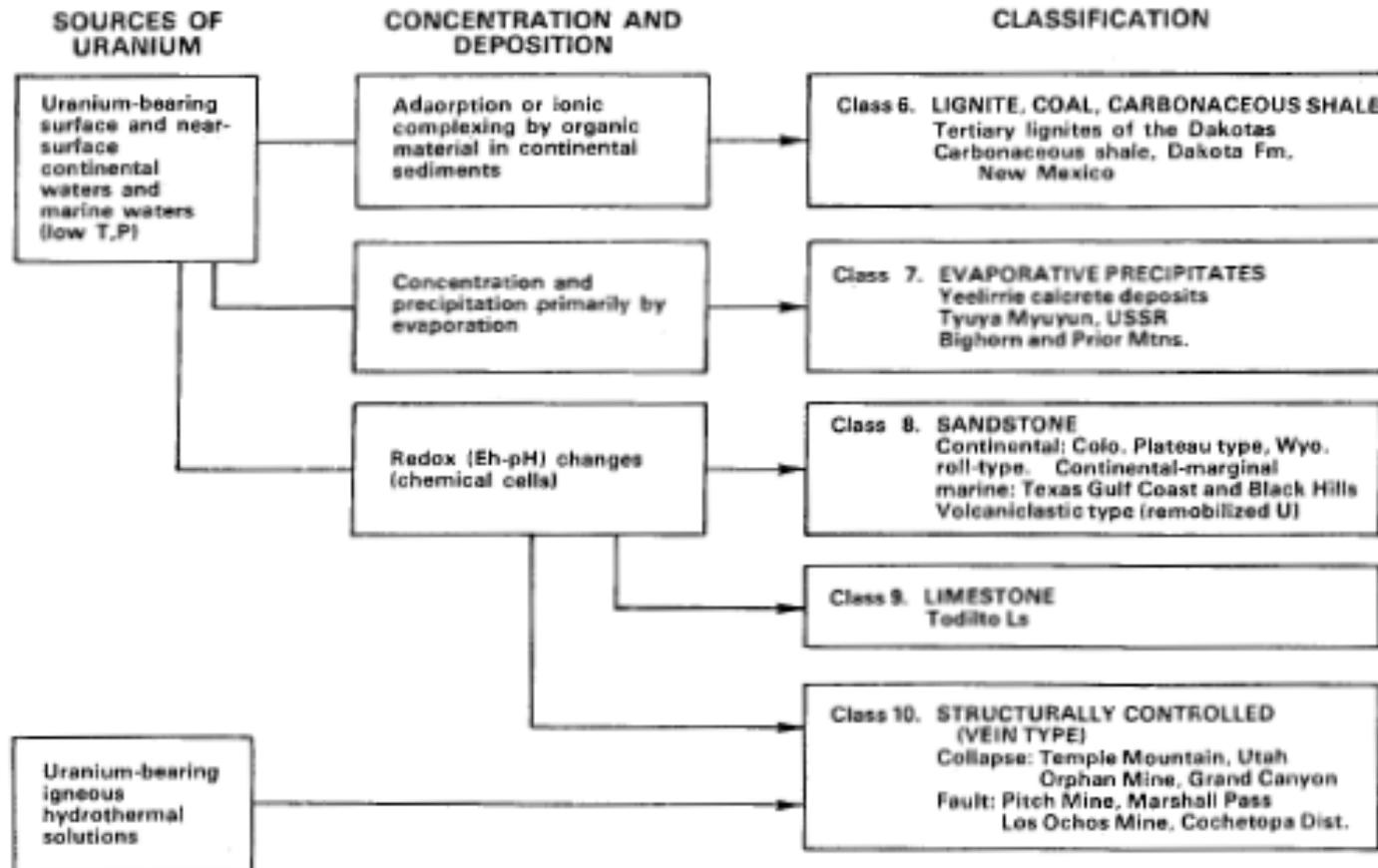


Table 7a. **EPIGENETIC URANIUM DEPOSITS** (Jonas, 1977).

pe-pH Diagram for Uranium

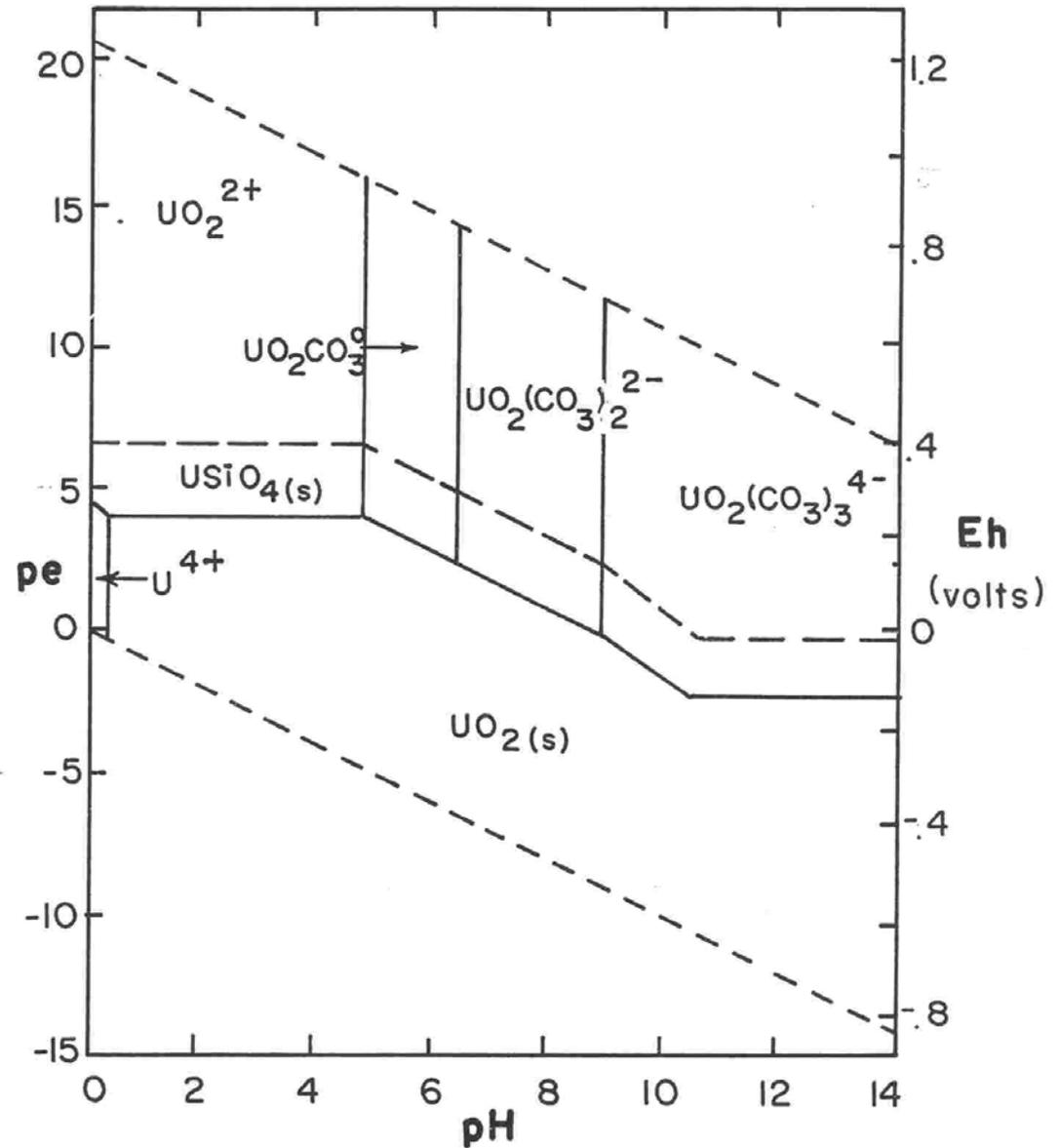
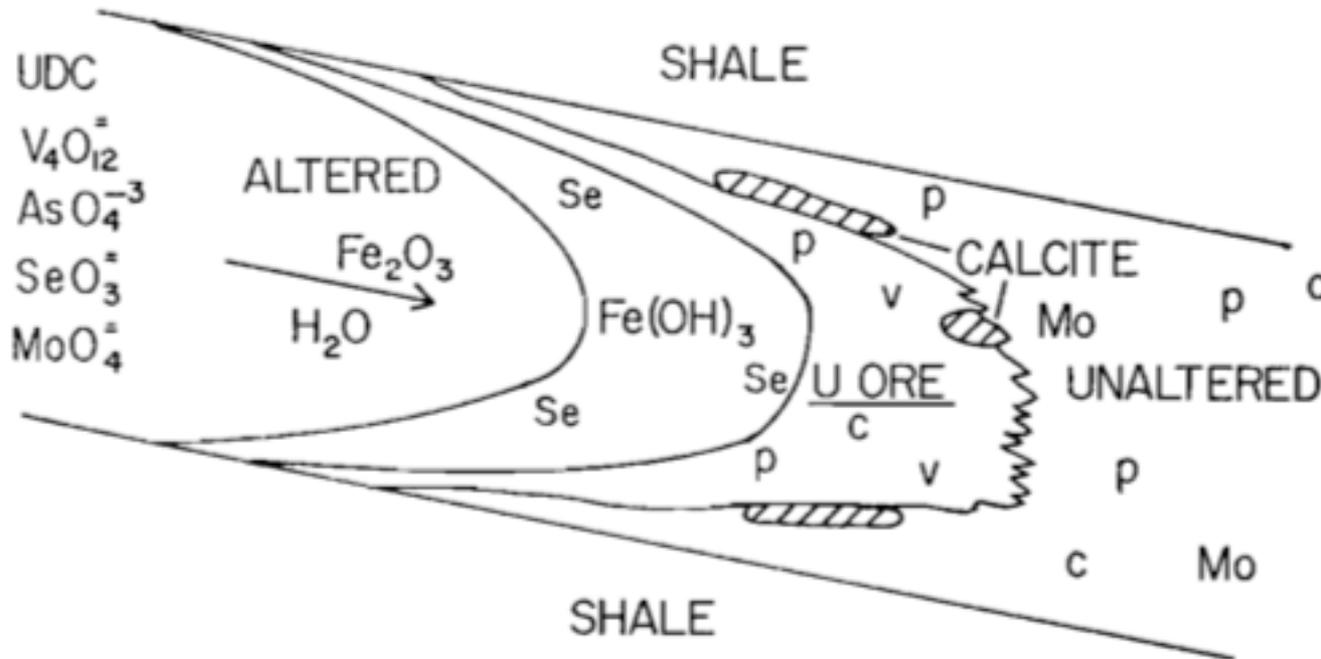
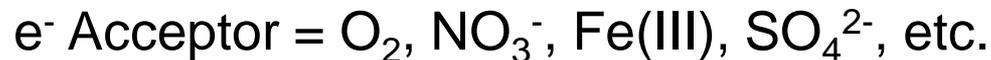


Diagram of Roll Front Deposit



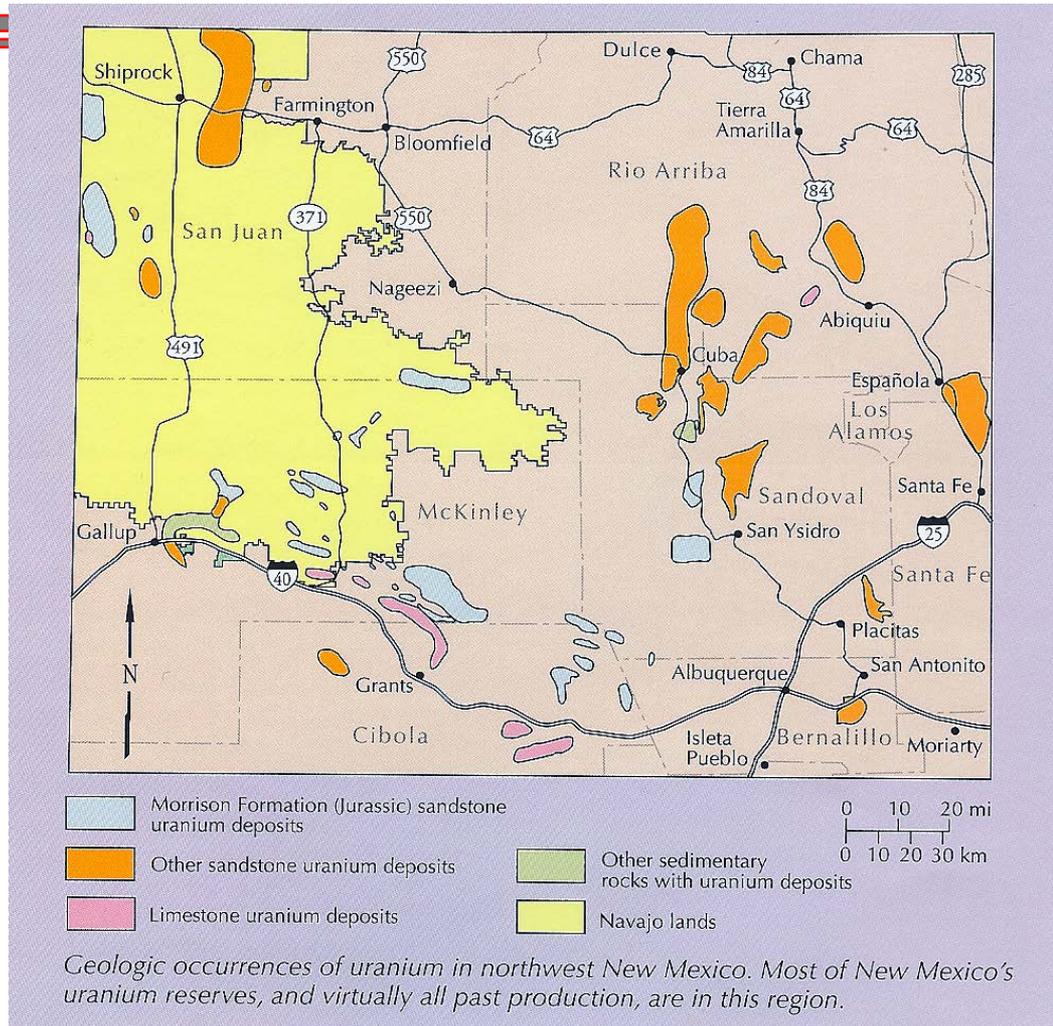
- Roll front represents redox sequence from oxidizing to reducing conditions most likely as result of microbial reactions



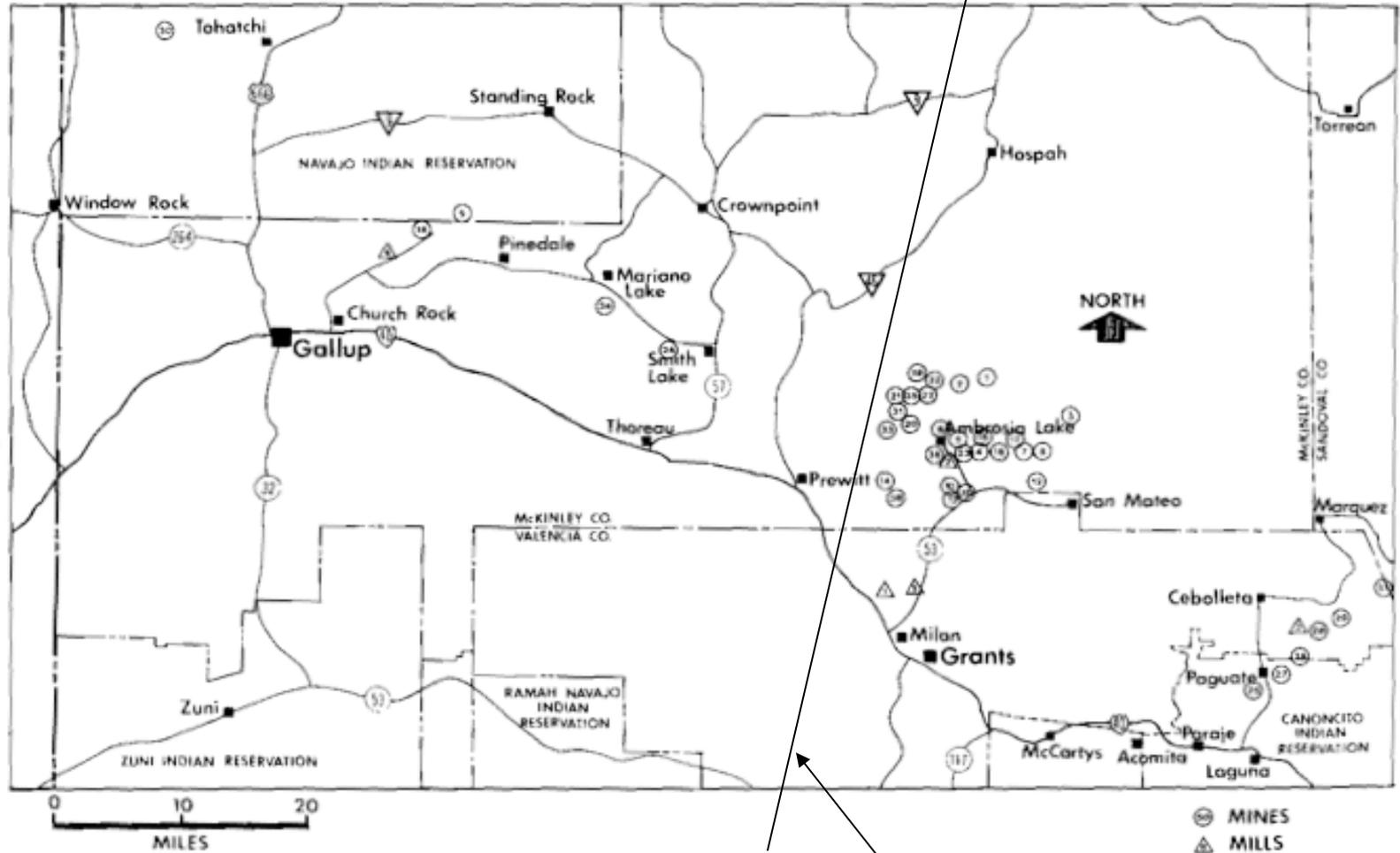
- Formation of minerals requires mobilization to reducing zone then subsequent reduction & precipitation

U Resources in Grants Mineral Belt

- (NMBGMR Report)



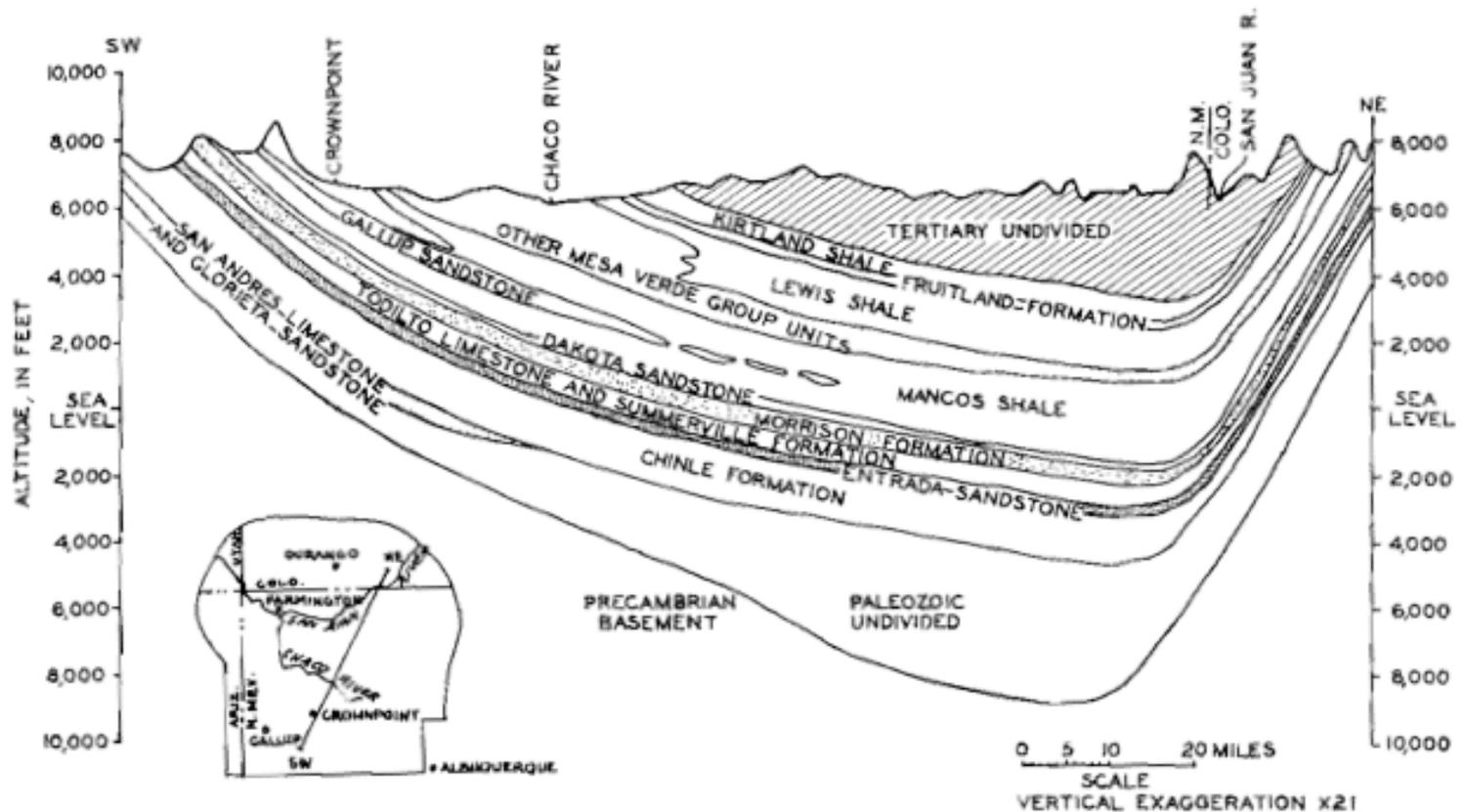
Mines & Mills in 1980 (SJBRUS, 1981)



**EXISTING
MILLS & MINES**

Cross section on next slide

General Cross Section of San Juan Basin

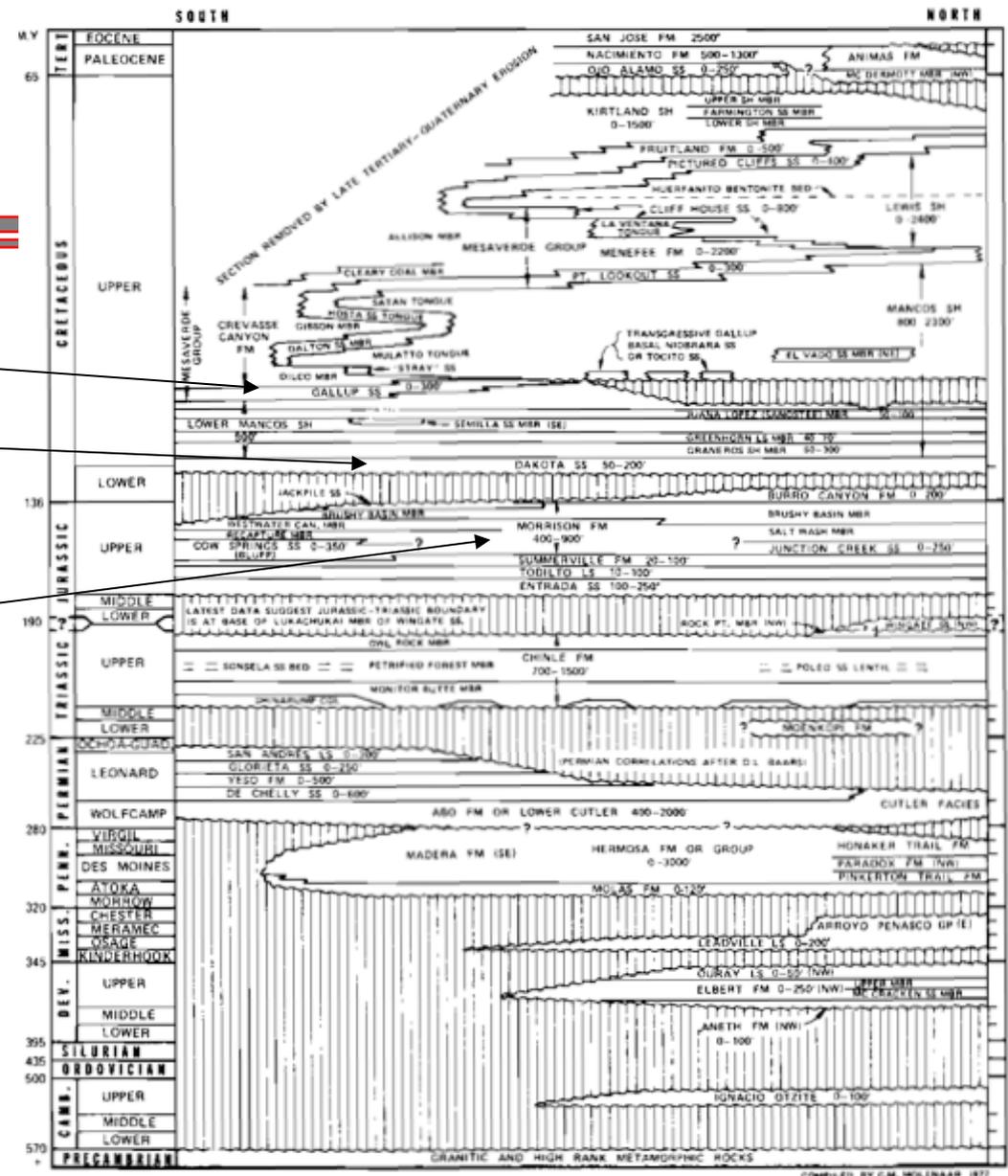


GENERALIZED GEOLOGIC SECTION SHOWING MAJOR AQUIFERS

Geologic Cross Section

(SJBRUS, 1981)

SAN JUAN BASIN TIME-STRATIGRAPHIC NOMENCLATURE CHART



Gallup Sandstone

Dakota Sandstone

Morrison Formation

Source: USGS

Figure III-3

Formation Absent

U Mining

- Conventional mining
 - Open pit mine - Laguna Jackpile Paguate Mine
 - Underground mining
- Requires mine dewatering - up to 3,000 gal/min
- Large power requirements for ventilation (Palo Verde nuclear generating station)

- In situ leach (ISL) mining
 - Mainly in So. TX, & WY
 - Little impact on ground water resources
 - Little surface disturbance
 - Difficult to restore aquifer quality

Average Weighted Concentration of Mine Water Discharges

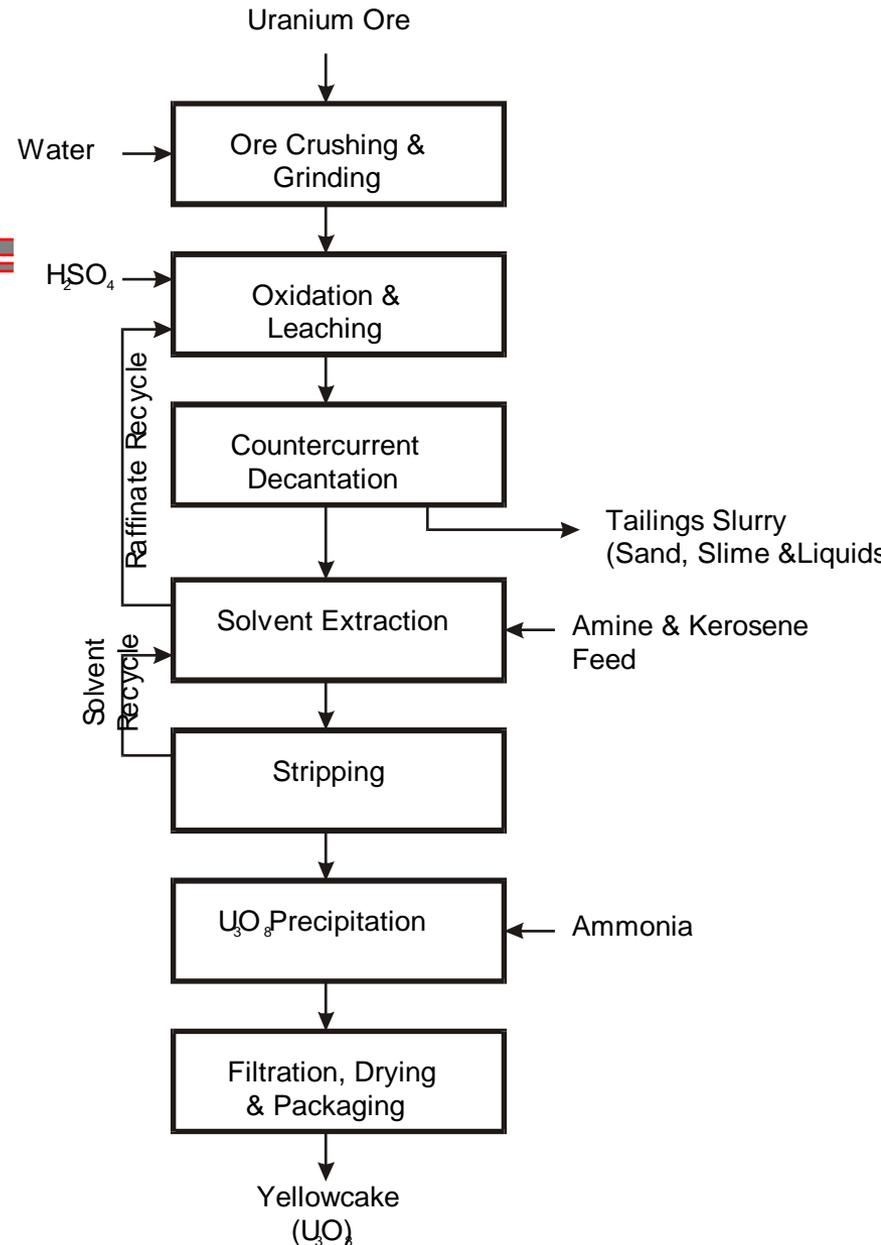
Constituent	1975	1978
Flow	9.27 Mgal/d	13.5 Mgal/d
TDS	-	911
Se	0.059	.088
U	9.83	0.694
V	0.73	0.033
Ra-226	92.8 pCi/L	

Major Aquifers in San Juan Basin

Aquifer	Thickness (ft)	TDS (mg/L)
Alluvium	0-100	200-9,200
Kirtland Shale	0-1,500	700 – 4,000
Gallup Sandstone	0-500	300 – 4,000
Dakota Sandstone	0-250	300-59,000
Morrison Formation	50-800	170-5,600

U Milling

- Acid (or alkaline) leach process
 - Oxidize U(IV) to U(VI)
 - Dissolve in acid (or base)
 - Recover by solvent extraction or IX
 - Precipitate as U_3O_8
- Acid leach - low Ca in ore (leach at $pH < 2$)
- Alkaline leach - high Ca in ore (leach at $pH > 10$)



Kerr McGee U Mill Tailings (1980)



Kerr McGee/Quivira

(2012)



Mill Tailings Decant Water Quality

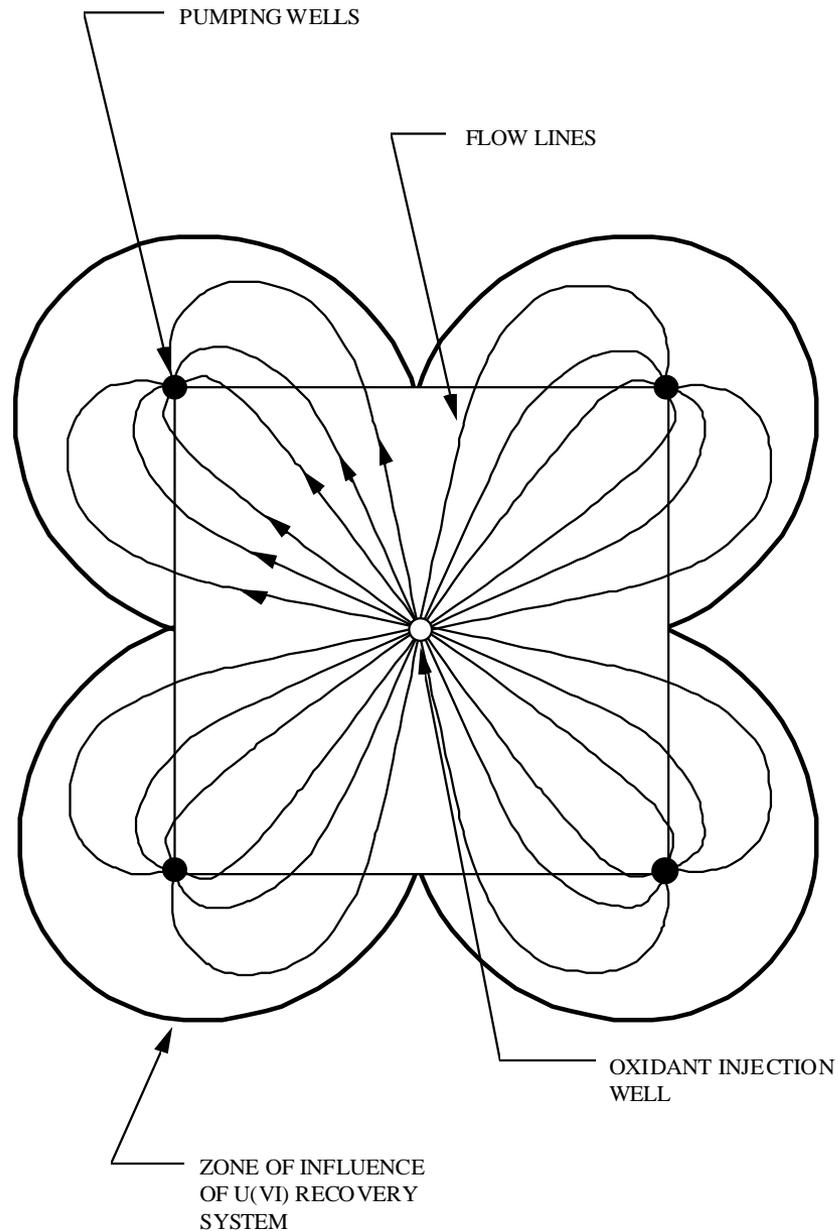
Constituent	SDWA MCL (mg/L)	4 Acid Mills in NM	1 Alkaline Mill in NM
As	.010	1.3	5.0
Mo		0.9	98.0
NH ₃ (as N)		400.0	16.0
Se	.050	29,700.	8,400.
U	.030	74.0	14.0
TDS	500.	39,800.	25,400.
pH		1.05	10.1
Ra-226 (pCi/L)	5.	70.0	58.0
Gross-α (pCi/L)	15.0	38,000.	6,700.

IX Recovery of Uranium

- $2(\text{R-Cl}) + \text{UDC}^{2-} = \text{R}_2\text{-UDC} + 2\text{Cl}^-$
 - $\text{UDC}^{2-} = \text{UO}_2(\text{CO}_3)_2^{2-}$
 - R = IX resin sites
- Given: Q = 1 gpm, U = 5 mg/L, pH = 7.3, resin capacity = 1.1 meq/g
- Find:
 - UDC^{2-} conc. (meq/L)
 - Mass of resin to treat water for 1 yr

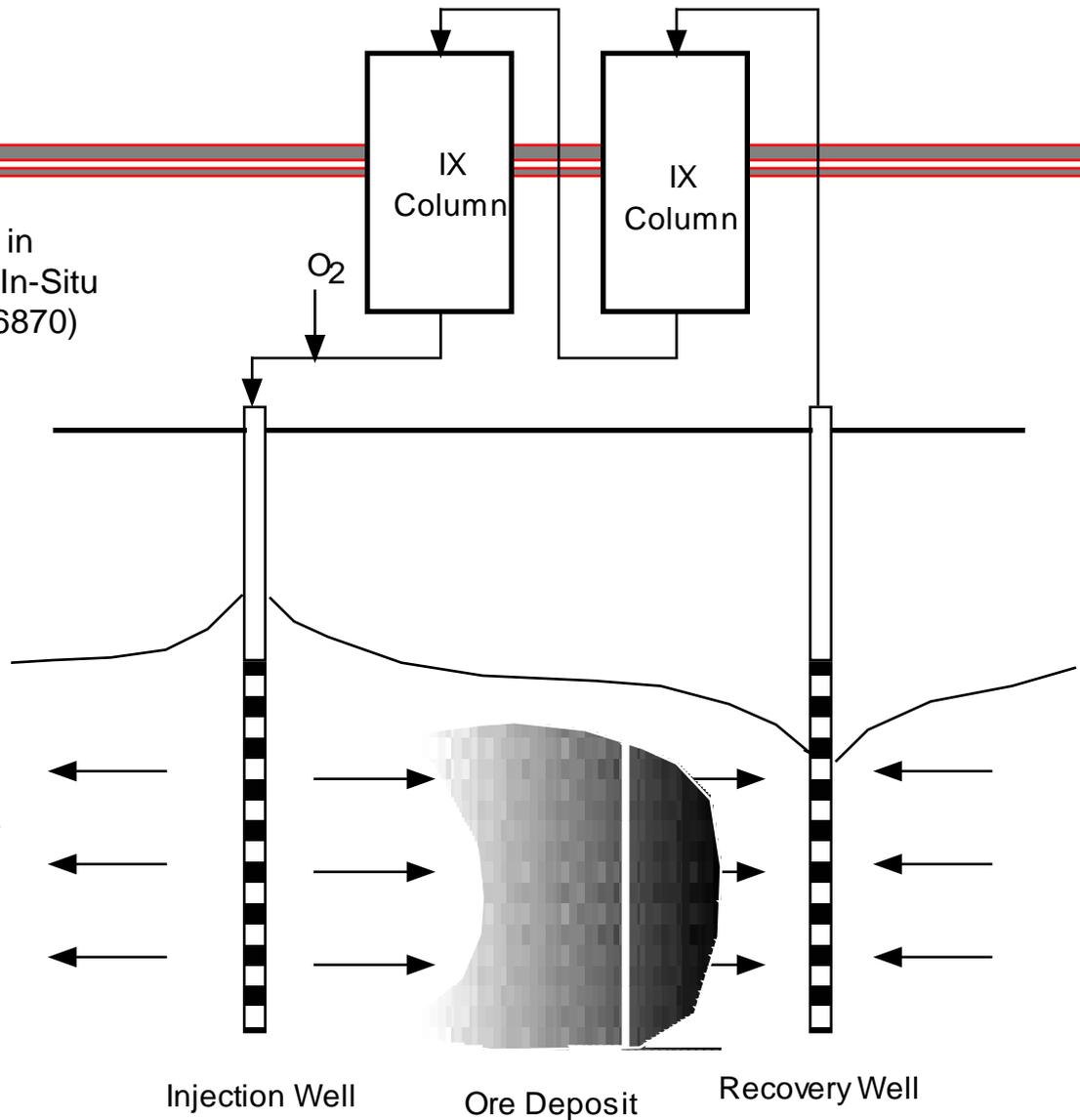
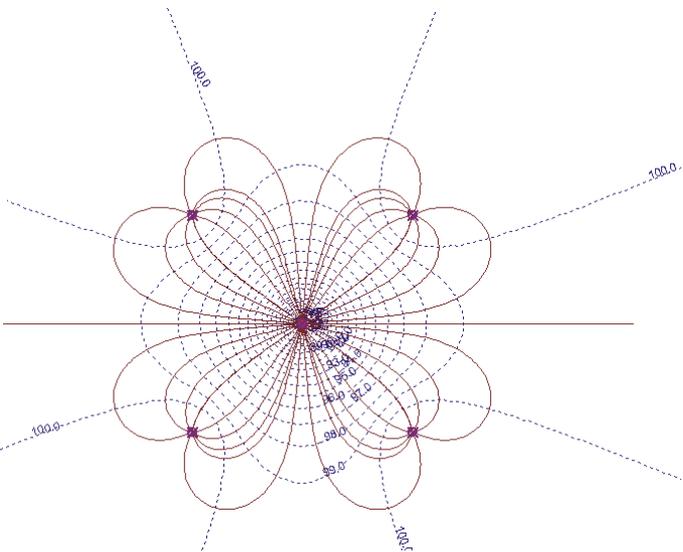
In Situ Recovery (ISR)

- Objective is to solubilize & mobilize U by reversing diagenetic processes
 - Introduce oxidizing conditions
 - Form mobile U complexes



In situ leaching

Consideration of Geochemical Issues in
Groundwater Restoration at Uranium In-Situ
Leach Mining Facilities (NUREG/CR-6870)

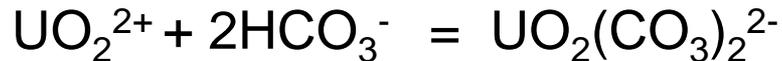


Ion Exchange

- 2 important criteria
 - Capacity – measured in no. charged sites/gram (~1 meq/g)
 - Selectivity
- 3 selectivity rules
 - Preference for polyvalent ions
 $\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{Cl}^-$
 $\text{UTC}^{4-} > \text{UDC}^{2-} > \text{HCO}_3^-, \text{Cl}^-$
 - Preference for high Z elements ($Z_U = 92$)
 $\text{UDC}^{2-} > \text{SO}_4^{2-} > \text{CO}_3^{2-}$
 - Rules reverse at very high ionic strength (i.e. saturated NaCl)
 - Note: $\text{UTC}^{4-} = \text{uranyl tri-carbonate} = \text{UO}_2(\text{CO}_3)_3^{4-}$

Chemistry of ISR

- Oxidation by O₂ from U(IV) to U(VI):



- Lixiviant = leaching solution
- Raffinate = leaching solution containing dissolved U
- U(VI) recovered by ion exchange (R = resin sites)
$$2\text{R-Cl} + \text{UO}_2(\text{CO}_3)_2^{2-} = \text{R}_2\text{-UO}_2(\text{CO}_3)_2 + 2\text{Cl}^-$$

IX Recovery of Uranium - 2

- UDC^{2-} conc. = $5\text{e-}3 \text{ g/L} \cdot 1/238 \text{ g/mol} \cdot 2 \text{ eq/mol}$
- UDC^{2-} conc. = $4.2\text{e-}5 \text{ eq/L}$

- Vol. of water in 1 yr = $5.26\text{e}5 \text{ gal} = 1.99\text{e}6 \text{ L}$
- Total UDC^{2-} equivs. = $1.99\text{e}6 \text{ L} \cdot 4.2\text{e-}5 \text{ eq/L}$
- $= 83.6 \text{ eq}$
- Resin reqts. = $83.6 \text{ eq} \cdot 1/1.1\text{e-}3 \text{ eq/g} = 76.0 \text{ kg}$

Ground Water Restoration

- Generally goal is to meet pre-mining water quality criteria. In some states water does not meet SDWA, hence relaxed pressure to achieve SDWA criteria
- Restoration involves circulating clean water through formation. May use RO treated water.
- In NM many U bearing formations have high quality water. State may require restoration to background. Not clear that it can be achieved.

Restoration Strategies

- Sweep (i.e. flush)
 - May require use of RO water
 - Water quality may be incompatible with formation mineralogy
- Addition of chemical reducing agent
 - Sulfide (HS^-) has been considered for tailings piles
- Stimulate microbial reduction
 - Has been tried at Rifle, CO U mill site
 - Requires addition of organic substrate (MeOH, acetate, lactate, sugars, vegetable oil)
- Chemical precipitating agent – PO_4^{3-}