PA4-6

Migration 05 Conference,
Avignon, France
September 18-23, 2005

Interactions and Stability of Hypochlorite, Hydrogen Peroxide and Uranium (VI) in Brine

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LA-UR-05-7009

ABSTRACT

The stability of the two expected major radiolytic products, hypochlorite ion (OCl^-) and hydrogen peroxide (H_2O_2), in the Waste Isolation Pilot Plant (WIPP) brines was investigated. Additionally, the synergistic effect of each specie on the other, and their effect on uranium (VI) were established.

Each specie, OCl^- and H_2O_2, was unstable in brine, but the decomposition of OCl^- appeared slower than H_2O_2 decomposition at pH~9. After 2.5 days, there was a 33% decrease of OCl^- concentration and more than 50% decrease of H_2O_2 concentration observed in 5 M NaCl brine. These decompositions are probably caused by metallic impurities in brines. When bromide was present in solution, hypochlorite readily reacted with bromide to form hypobromite (OBr^-), which appears to be the more important radiolytic product than OCl^-.

The synergistic effects of OCl^- and H_2O_2 in 5 M NaCl brine were also studied. The data showed that OCl^- and H_2O_2 reacted together within the first 20 seconds of mixing. H_2O_2 totally decomposed OCl^- in a 1:2 ratio. The destabilization of OCl^- and H_2O_2 and their reaction with each other in brines indicate that significant buildup of these radiolytic products is unlikely to occur under repository conditions. Preliminary data on the effects of OCl^- and/or H_2O_2 on uranium (VI) in brine, showed clear evidence of a U(VI) - OCl^- complex formation and a peroxide precipitation fraction. This is in accordance with the few literature data, and will be studied more extensively to determine any possible impact on uranium solubility in brine.

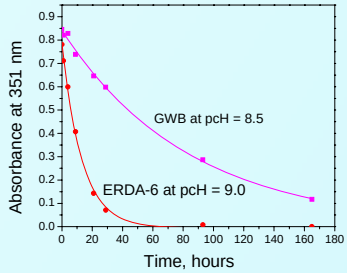
WIPP Brine Compositions

	ERDA-6		GWB	
Component	g/L	M	g/L	M
NaCl	248.6	4.254	167.8	2.874
$MgCl_2.6H_2O$	3.667	0.018	193.4	0.953
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 (M)	4.965		6.839	
Density (g/mL)	1.183		1.216	

ERDA-6 - Energy Research and Development Administration Well 6 represents the fluids in Castile brine reservoirs
GWB - Generic Weep Brine represents brine from the Salado Formation

HYDROGEN PEROXIDE STABILITY IN BRINES

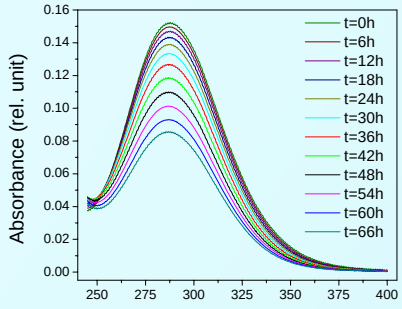
Hydrogen peroxide is unstable in brines. The decomposition constants are equal to 0.012 $hour^{-1}$ for GWB (high magnesium brine) and 0.075 $hour^{-1}$ for ERDA-6 (low magnesium brine). In 2.5 days, only half of the H_2O_2 concentration remained in 5 M NaCl brine. Reaction with metallic impurities are probably the main cause for decomposition.



Decomposition of hydrogen peroxide as a function of brine composition.

HYPOCHLORITE STABILITY IN SIMPLIFIED BRINES

Hypochlorite ion is unstable in brines. In 2.5 days, a 33% decrease of OCl^- concentration was observed in 5 M NaCl brine. Even though high purity chemicals were used, trace metal impurities in these synthetic brines may be the main cause for decomposition. In the WIPP greater instability is expected due to the much higher metal concentration expected.



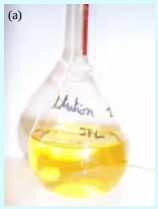
Absorption spectra showing the decomposition of hypochlorite ion in 5M NaCl simplified brine ([OCl^-] initial = 2 mM at pH = 10.7).

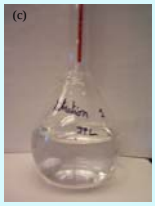
To confirm spectrometry data, iodometric titration of OCl^- was developed, based on the following reactions:

$$OCl^- + 2\,I^- + 2\,H^+ \longrightarrow Cl^- + I_2 + H_2O$$

$$2\,S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2\,I^-$$

Pictures show color changes of hypochlorite solutions during iodometric titration (a) after addition of excess iodide, (b) after addition of starch, and (c) at the end point of the titration.





H_2O_2/OCl^- INTERACTIONS IN SIMPLIFIED BRINE

Experimental observations made about H_2O_2 and OCl^- mixtures in 5M NaCl brine are:

- OCl^- and H_2O_2 react together and, in this context, affect each other's stability in brine,
- The reaction is fast, less than 20 seconds after mixing,
- H_2O_2 totally decomposes OCl^- when the $[OCl^-]/[H_2O_2]$ ratio is less than 2.

Considering these results, we can expect OCl^- and H_2O_2 to be highly unstable in synthetic WIPP brines. A more comprehensive analysis that weighs the production of these radiolytic products with their apparent instability needs to be done to fully understand the impact of these products on actinide speciation in the WIPP.

URANIUM INTERACTIONS WITH OCl^- : LITERATURE DATA

Introduction of hypochlorite ion in precipitates was determined by XRD in solubilities studies of schoepite ($UO_3.xH_2O$) with hypochlorite ion in 0.1M NaCl at 25°C, in a CO_2-free atmosphere.

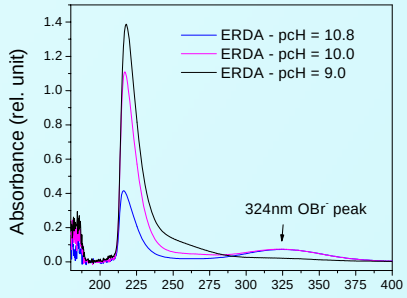
Kim W.H., Choi K.C., Park K.K., Eom T.Y. (1994). "Effects of Hypochlorite Ion on the Solubility of Amorphous Schoepite at 25°C in Neutral to Alkaline Aqueous Solutions." Radiochimica Acta **66/67**: 45.

FORMATION OF HYPOBROMITE IN BRINES

Absorption spectra of hypochlorite ion solutions in ERDA-6 brine ([OCl^-] initial = 2 mM at pcH = 9) show that bromide (Br^-), a brine component, reacts with the hypochlorite ion to form hypobromite ion (OBr^-) according to the following reaction:

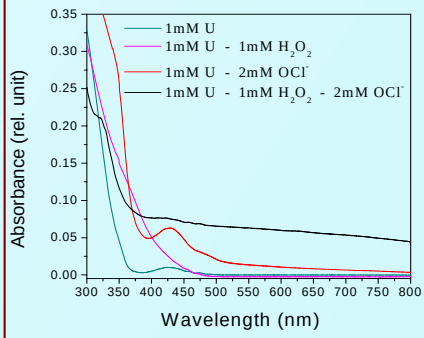
$$OCl^- + Br^- \rightarrow OBr^- + Cl^-$$

OBr^-, like OCl^-, is also an oxidizing specie (E^o=0.76V), that may facilitate the oxidation of actinides in the WIPP – this reactivity has however not been established and is the subject of future studies.



Absorption spectra showing the hypobromite peak at 324 nm in ERDA-6 at pcH 9,10 and 10.8.

U(VI)/H_2O_2/OCl^- INTERACTIONS IN SIMPLIFIED BRINE



Absorption spectra of four U-H_2O_2-OCl^- mixtures in 5M NaCl brine show evidence for a uranyl complexes with H_2O_2 and/or OCl^- .

Interactions of H_2O_2 and OCl^- with U(VI) exist in brine. We observed a yellow precipitate in U-OCl^- solution, and a white precipitate in U-H_2O_2 solution. Liquid Scintillation Counting showed that both precipitates contain uranium. The complexes generated are being studies to establish their potential impact on uranium solubility in brines.

CONCLUSIONS

Hydrogen peroxide and hypochlorite ion are expected to be highly unstable in WIPP brines, because :

1. Each specie, hydrogen peroxide and hypochlorite ion, is unstable in WIPP brines, because of metallic impurities.
2. In the presence of bromide in WIPP synthetic brines, hypochlorite is decomposed into hypobromite.
3. Hydrogen peroxide and hypochlorite rapidly react with each other in 5M NaCl brine.

However, hydrogen peroxide and hypochlorite can generate uranyl peroxide and yellow uranyl precipitates, respectively, in 5M NaCl brine, leading to a possible change in uranium solubility.

ACKNOWLEDGEMENTS

The authors would like to express their thanks to Dr. Andrzej Rafalski (INCT, Warsaw) and Sally Ballard (CEMRC) for technical assistance.

This research was sponsored by the US Department of Energy, Carlsbad Field Office.