Electrolytic Treatment of ICPP Sodium-Bearing Waste Simulant (U)

by

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SUMMARY

Two proof-of-principle tests were conducted to determine if nitrate can be destroyed electrochemically in a simulated Idaho Chemical Processing Plant (ICPP) Sodium-Bearing waste. Both tests demonstrated the destruction of nitrate as well as the removal of other metals in the simulant. Metals removal is believed to be due to precipitation as a result of a change in the pH of the waste solution from strongly acidic to highly alkaline and reduction to a metal or metal oxide. Although gas evolution at the cathode was visible during each test, there were no visible signs of NO_x formation in either test.

EXPERIMENTAL

Electrochemical tests were carried out in a glass H-cell equipped with 2.5 cm² platinum flag electrodes. The ICPP Sodium-Bearing Waste simulant, identified as SIMULANTIV, was placed in the catholyte compartment and a 5.0 M sodium hydroxide solution was placed in the anolyte compartment. The electrodes were connected to a Hewlett Packard DC power supply (Model # 6281A). The power supply was switched on and the voltage gradually increased from 2.0 to 3.5 volts. Gas evolution was immediately visible at both electrodes. Electrolysis was continued at 3.5 volts for the duration of the test. No attempt was made to measure the amount of gas or analyze the off-gas for composition. However, no evidence of the generation of NO_x was observed during any test. Periodically, 5.0 mL samples of the catholyte were taken from the catholyte compartment and analyzed for nitrate concentration by ion chromatography and for elemental composition by inductively coupled plasma emission spectroscopy.

RESULT AND DISCUSSION

Two tests were conducted with the ICPP Sodium-Bearing Waste simulant. In the first test, the highly acidic simulant was electrolyzed directly as-received. In the second test, 50 wt % sodium hydroxide solution was added to the simulant resulting in a pH of 10.20 prior to electrolysis. In both tests, nitrate was observed to be destroyed as evidenced by the decrease in the nitrate concentration. The nitrate destruction rate was similar for both the highly acidic solution and the alkaline slurry (see Table I).

No NO_x was observed in either experiment. Previous tests with strongly alkaline SRS and Hanford waste simulants have indicated that N_2 , N_2O , or NH_3 are the only nitrogen-containing products of the electrochemical reduction. The absence of NO_2 in these tests is somewhat surprising since its presence has been reported in other tests with acidic nitrate solutions. Perhaps the generation rate is sufficiently slow that it is not observable, or the concentration of oxygen is so low in the catholyte that formation of the readily visible brown gas, NO_2 , does not occur.

Table I. Nitrate Concentration and Percentage Destroyed During Electrolysis**Test #1 - Acidic Waste Solution**

<u>Time (hr)</u>	<u>Nitrate (M)</u>	<u>% Destroyed</u>
0	4.34	0
5.4	3.61	17
17.9	1.40 ^a	68

Test #2 - Alkaline Waste Solution

<u>Time (hr)</u>	<u>Nitrate (M)</u>	<u>% Destroyed</u>
0	2.55	0
6.7	2.32	8.9
16.7	1.16 ^a	55

^a normalized based on before and after sodium concentrations determined by ICP/ES analysis.

Table II presents data on selected elements before and after each electrolysis test. Also included are the analytical results determined by INEL for the initial simulant solution. With the exception of Fe and P, there was very good agreement between the two sets of analytical results. Water was added at the conclusion of the acidic simulant test, but not at the conclusion of the alkaline slurry test. To compare the before and after electrolysis concentrations, the after-electrolysis concentrations were normalized based on the before and after sodium concentrations.

Elements are removed during electrolysis as a result of two mechanisms: (1) electrolytic reduction and (2) precipitation due to a decrease in the acid concentration. Alkaline earth species (Mg, Ca, Sr, and Ba) are removed only by precipitation. In aqueous systems, only those reactions that have potentials greater than that of water will occur. The reduction potentials for the alkaline earths are more negative than water, and therefore, will not occur in an aqueous system (see Table III). However, as the acidity decreases, the alkaline earths precipitate as hydroxides. The greater degree of removal of these species in the higher pH simulant is consistent with a higher final hydroxide concentration.

Transition metals (Mn, Fe, Ni, Cr, and Mo) and main group metals (Cd, Pb, Zn, Al, and Sn) were also removed. Based on standard state reduction potentials, the transition metals and Cd, Pb, Zn, and Sn have reduction potentials more positive than water, and therefore could be electrochemically active. Aluminum has a lower reduction potential and therefore, is removed strictly by precipitation. Note that the removal of Zn, Al, Sb, and Sn is reduced when the slurry becomes more strongly alkaline during electrolysis, which is consistent with the amphoteric behavior of these elements. In some cases, the removal may be the combination of both mechanisms. For example, Cr^{6+} is soluble at high pH, whereas Cr^{3+} is not. Thus, removal of Cr^{6+} may occur by reduction of the Cr^{6+} to Cr^{3+} which can either precipitate as $\text{Cr}(\text{OH})_3$ or be further reduced to elemental Cr.

The increase in the Si concentration during electrolysis is believed to occur as the result of attack of the glass cell by the highly alkaline solution during the tests. Because of the variation in P concentrations between the LITCO and SRTC laboratories, the behavior of P during electrolysis is difficult to interpret. It is possible that the observed variation is due to analytical errors from interfering species, or as a result of electrolysis. Phosphate has a reduction potential less than that of water, and therefore, would not be expected to undergo direct electrochemical reactions. However, sparingly soluble phosphate solids could be produced during electrolysis resulting in the decrease in P concentration in the acidic solution test. The variation in the P concentration in the alkaline slurry test is not consistent with expected chemistry, and may be due to sample interferences and impurities in the NaOH used to neutralize the acidic solution.

CONCLUSIONS AND RECOMMENDATIONS

Proof-of-principle tests have demonstrated the destruction of nitrate and the removal of a large number of species in a simulated ICPP Sodium-Bearing waste solution. No evidence for the evolution of NO_x was observed in either test. During electrolysis the pH of the waste solution increases resulting in the precipitation of ionic species that are not soluble at higher pHs. It is recommended that additional tests be carried out to determine the limiting current for nitrate destruction, to perform a more accurate mass balance, to determine off-gas products, and to demonstrate nitrate destruction in a laboratory-scale flow cell reactor.

QUALITY ASSURANCE

The experimental work reported in this document was carried out as a scoping task activity. Experimental data are recorded in laboratory notebook, WSRC-NB-91-184. Analytical results that were determined by the SRTC Analytical Services Group were performed under routine QC/QA requirements according to established analytical method procedures.

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Table II. Elemental Composition of ICPP Sodium-Bearing Waste Simulant Before and After Electrolysis

	Concentration (mg/L)				
	Acidic Solution			Alkaline Solution	
	Before ^a	Before ^b	After ^{b,c}	Before ^b	After ^{b,c}
Ag	nd	<0.182	<0.182	<0.182	<0.18
As	nd	10.5	<1.82	<1.82	4.13
Se	nd	32.6	<9.1	<9.1	10.6
Ca	1560	1560	562	30.6	0.571
Cd	258	232	42.0	0.721	0.326
Ce	56.4	50.1	<1.82	<1.82	<1.82
Co	nd	<0.364	<0.364	<0.364	<0.364
Cu	nd	<0.091	<0.091	<0.091	<0.091
Mg	nd	120	35.9	0.405	<0.091
Mn	796	796	197	1.94	<0.091
Pb	224	238	<1.82	<1.82	9.87
Zn	nd	3.10	0.508	<0.091	0.540
Zr	nd	82.4	<0.455	0.701	<0.455
Al	17500	15600	1.97	104	5700
Ba	nd	0.519	<0.091	<0.091	<0.091
Fe	1520	368	<0.182	1.18	0.976
La	nd	2.03	<0.273	<0.273	<0.273
Li	nd	<0.091	<0.091	<0.091	<0.091
Mo	141	101	0.499	51.1	35.4
Na	29000	31700	31700	68700	68700
Ni	127	124	3.62	<0.455	<0.455
Sb	nd	31.2	<1.82	<1.82	9.71
Sn	nd	7.28	<0.637	<0.637	2.63
Sr	14.7	13.4	5.34	0.810	<0.091
Ti	nd	0.600	<0.091	<0.091	<0.091
V	nd	0.215	<0.091	<0.091	<0.091
B	182	191	35.0	87.3	71.0
Cr	350	318	<0.364	7.61	33.8
P	<2.84	97.4	<0.910	2.11	120
Si	nd	8.71	11.9	<0.546	16.9

nd = not determined

^a determined by INEL^b determined by SRTC^c detected elements are normalized to the Na concentration in solution before electrolysis

Table III. Electrochemical Series for Species in the ICPP Sodium-Bearing Waste Simulant

Reaction					E° (V)	
	K ⁺	+	e ⁻	=	K	-2.931
	Cs ⁺	+	e ⁻	=	Cs	-2.92
	Ba ²⁺	+	e ⁻	=	Ba	-2.912
	Sr ²⁺	+	2e ⁻	=	Sr	-2.89
	Ca ²⁺	+	2e ⁻	=	Ca	-2.868
	Na ⁺	+	e ⁻	=	Na	-2.71
	Ce ³⁺	+	3e ⁻	=	Ce	-2.483
	Mg ²⁺	+	2e ⁻	=	Mg	-2.372
	SiO ₃ ²⁻	+	e ⁻	=	Si + 6OH ⁻	-1.697
	Al ³⁺	+	e ⁻	=	Al	-1.662
ZnO ₂ ⁻	+	2H ₂ O	+	2e ⁻	= Zn + 4OH ⁻	-1.215
PO ₄ ³⁻	+	2H ₂ O	+	2e ⁻	= HPO ₃ ²⁻ + 3OH ⁻	-1.05
SO ₄ ²⁻	+	H ₂ O	+	2e ⁻	= SO ₃ ²⁻ + 2OH ⁻	-0.93
H ₃ BO ₃	+	3H ⁺	+	e ⁻	= B + 3H ₂ O	-0.8698
		2H ₂ O	+	2e ⁻	= H ₂ + 2OH ⁻	-0.828
		Zn ²⁺	+	2e ⁻	= Zn	-0.7618
		Cr ³⁺	+	3e ⁻	= Cr	-0.744
AsO ₄ ³⁻	+	2H ₂ O	+	2e ⁻	= AsO ₂ ⁻ + 4OH ⁻	-0.71
AsO ₂ ⁻	+	2H ₂ O	+	3e ⁻	= As + 4OH ⁻	-0.68
SbO ₃ ⁻	+	H ₂ O	+	2e ⁻	= SbO ₂ ⁻ + 2OH ⁻	-0.59
NO ₂ ⁻	+	H ₂ O	+	e ⁻	= NO + 2OH ⁻	-0.46
		Cd ²⁺	+	2e ⁻	= Cd	-0.4030
		Co ²⁺	+	2e ⁻	= Co	-0.28
		Ni ²⁺	+	2e ⁻	= Ni	-0.257
CrO ₄ ²⁻	+	4H ₂ O	+	3e ⁻	= Cr(OH) ₃ + 5OH ⁻	-0.13
		Pb ²⁺	+	2e ⁻	= Pb	-0.1262
		Fe ³⁺	+	3e ⁻	= Fe	-0.037
		2H ⁺	+	2e ⁻	= H ₂	0.0000
NO ₃ ⁻	+	H ₂ O	+	2e ⁻	= NO ₂ ⁻ + 2OH ⁻	0.01
2NO ₂ ⁻	+	3H ₂ O	+	4e ⁻	= N ₂ O + 6OH ⁻	0.15
		Sn ⁴⁺	+	2e ⁻	= Sn ²⁺	0.151
MnO ₄ ²⁻	+	2H ₂ O	+	2e ⁻	= MnO ₂ + 4OH ⁻	0.60
2NO	+	H ₂ O	+	2e ⁻	= N ₂ O + 2OH ⁻	0.76
		Fe ³⁺	+	e ⁻	= Fe ²⁺	0.771
2NO ₃ ⁻	+	4H ⁺	+	2e ⁻	= N ₂ O ₄ + 2H ₂ O	0.803
		N ₂ O ₄	+	2e ⁻	= 2NO ₂ ⁻	0.867
NO ₃ ⁻	+	3H ⁺	+	2e ⁻	= HNO ₂ + H ₂ O	0.934
NO ₃ ⁻	+	4H ⁺	+	3e ⁻	= NO + 2H ₂ O	0.954
HNO ₂	+	H ⁺	+	e ⁻	= NO + H ₂ O	0.983
2HNO ₂	+	4H ⁺	+	4e ⁻	= N ₂ O + 3H ₂ O	1.297
2NO	+	2H ⁺	+	2e ⁻	= N ₂ O + H ₂ O	1.591
		Ce ⁴⁺	+	e ⁻	= Ce ³⁺	1.61
N ₂ O	+	2H ⁺	+	2e ⁻	= N ₂ + H ₂ O	1.766

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