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ABSTRACT

The extraction of stable isotopes of Eu and Ce was investigated from simulated sodium-bearing waste (SBW) and dissolved zirconium calcine by TRUEX and CMP solvents at the Idaho Chemical Processing Plant (ICPP). Single batch contacts were carried out in order to evaluate the rare earth behavior in the extraction, scrub, strip and wash sections for the proposed flowsheets. It has been shown that these lanthanides are efficiently extracted from the sodium-bearing wastes into either solvent, are not scrubbed and are stripped from both of the extractants with dilute HEDPA. The extraction distribution coefficients for Ce and Eu are higher in the TRUEX solvent ($D_{Ce} = 11.7$, $D_{Eu} = 14.9$) compared with CMP ($D_{Ce} = 9.3$, $D_{Eu} = 7.23$) for SBW. The extraction distribution coefficients for Ce and Eu are considerably less in the TRUEX solvent (D_{Ce}=1.13, D_{Eu}=1.8) than in the CMP solvent (D_{Ce}=7.4, D_{Eu}=6.1) for dissolved zirconium calcine feeds. The lower distribution coefficients for the extraction of lanthanides in the TRUEX / dissolved zirconium calcine system can be explained by zirconium loading of the solvent. The data obtained also confirmed that Ce and Eu can be used as non-radioactive surrogates for Am in separation experiments with acidic solutions.

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INTRODUCTION

At present, the Idaho Chemical Processing Plant is carrying out a series of experiments in order to evaluate and compare the TRUEX and CMP processes for removing the actinides from two high-level waste streams. The first stream, sodium-bearing waste (SBW), was generated from decontamination and solvent wash activities associated with spent fuel reprocessing. The second is zirconium calcine from the solidification of fuel reprocessing raffinates, subsequently dissolved in HNO_3 . This calcine type represents the largest quantity of calcine inventory at the ICPP, approximately 80% of the total calcine volume. The behavior of actinides as well as some of the other coextracted elements such as Zr, Hg and Tc for both solvents and for both waste streams has been studied at the ICPP [1-5]. These radioactive streams also contain some rare earth elements such as Ce and Eu, whose chemistry in TRUEX and CMP extraction systems is of interest, particularly because it was assumed that the lanthanides behavior in these processes could be similar to that of the actinides. Thus, the purpose of this work was to determine the extraction, scrub, strip and wash distribution coefficients of the rare earth elements (specifically Ce and Eu) in the proposed TRUEX and CMP flowsheets for the treatment of sodium-bearing waste and dissolved zirconium calcine.

EXPERIMENTAL PROCEDURES

SBW and Dissolved Zirconium Calcine Feeds

TRUEX and CMP flowsheet tests were carried out using stable isotopes of Ce and Eu, spiked into non-radioactive simulated SBW and dissolved zirconium calcine solutions, respectively. SBW simulant was prepared in accordance with the average chemical composition of the major non-radioactive components in SBW. The composition of the SBW simulant is shown in Table 1.

A dissolved calcine simulant represents the composition of the non-radioactive components of the chosen dissolved zirconium calcine. This simulant is characterized in Table 2. Cr (VI) is present in a considerable amount (5.75E-3 M) in dissolved calcine solutions and is coextracted with the actinides, causing some physical problems. Prior to the test, hydrogen peroxide was added to this calcine simulant for reduction of Cr (VI) to the non-extractable Cr (III) form in order to suppress the extraction of Cr. This solution was allowed to stand for 24 hours to ensure equilibrium conditions were reached.

TRUEX and CMP Solvents

The TRUEX solvent used in these tests contained 0.2 M CMPO [octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide] and 1.4 M TBP in an Isopar-L® diluent. The solvent was prepared by the Quality Control Laboratory at the ICPP. The Am-241 extractions from the various concentrations of pure nitric acid solutions were performed to verify the CMPO purity and concentration [6]. The CMP [dihexyl-N,N-diethyl-carbamoylmethylphosphonate] solvent was prepared by QC Laboratory and contained 0.5 M CMP and 1.0 M TBP in Isopar-L®.

Prior to contacting the solvents with the feeds they were pre-equilibrated with 1.5 M HNO_3 three times for SBW flowsheets and with 3.5 M HNO_3 for dissolved zirconium calcine respectively.

Table 1. Composition of simulated sodium bearing waste (SBW).

Component	M	Component	M
Acid (H^+)	1.35	K	1.43E-1
Al	6.48E-1	Mn	1.42E-2
B	1.71E-2	Mo	1.49E-3
Cd	2.29E-3	Na	1.26
Ca	3.91E-2	NO_3	4.46
Ce	3.88E-4	Ni	2.20E-3
Cl	3.52E-2	Pb	1.08E-3
Cs	7.52E-5	PO_4	<9.18E-3
Cr	6.56E-3	Sr	1.70E-4
F	9.66E-2	SO_4	3.86E-2
Fe	3.10E-2	Zr	1.00E-3
Hg	2.88E-3		

Table 2. Composition of the dissolved calcine feed solution

Component	M	Component	M
Acid (H^+)	3.51	K	5.88E-04
Al	4.26E-01	Mo	1.78E-04
B	6.65E-02	Na	9.13E-03
Ca	6.51E-01	NO_3	6.04
Ce	3.88E-04	Ni	1.75E-03
Cl	<0.088	Pb	<1.93E-06
Cs	4.67E-03	Sr	8.39E-03
Cr	5.75E-03	SO_4	0.050
F	8.95E-01	Zr	2.13E-01
Fe	1.31E-02	Nd	4.07E-03

Experimental Procedure

Four different tests were performed using CMP and TRUEX solvents for SBW and dissolved calcine solutions. The experimental flowsheets are shown in Figures 1, 2, 3 and 4. Except for the 0.5 M CMP/SBW system, where the scrub section is absent, all of the flowsheets include sequentially 3 extraction contacts (E1, E2, E3), 3 scrubs (Sc1, Sc2, Sc3) and 3 strip contacts (St1, St2, St3), followed by 2 wash (W1, W2) contacts. All batch contacts were performed in test tubes by vortex mixing for 1 minute at an organic to aqueous phase ratio (O/A) of one. Phase separation was accomplished by centrifuging at 5000 rpm for one minute. The feeds spiked with Eu and Ce were first contacted with the pre-equilibrated solvents to determine the extraction distribution coefficients. The solvents were carried through the process for successive contacts either with fresh feed, scrub, strip or wash solutions. The loaded TRUEX solvents were scrubbed with 0.1 M NH_4F in 1.0 M HNO_3 to remove extracted zirconium from the solvent in both the TRUEX systems. The CMP/reduced dissolved calcine flowsheet utilized 0.05 M oxalic acid in 3 M HNO_3 as a scrub agent. The scrubbed solvents were stripped by 0.001 M HEDPA in 0.01 M HNO_3 and finally washed with 0.25 M Na_2CO_3 solution in all four systems.

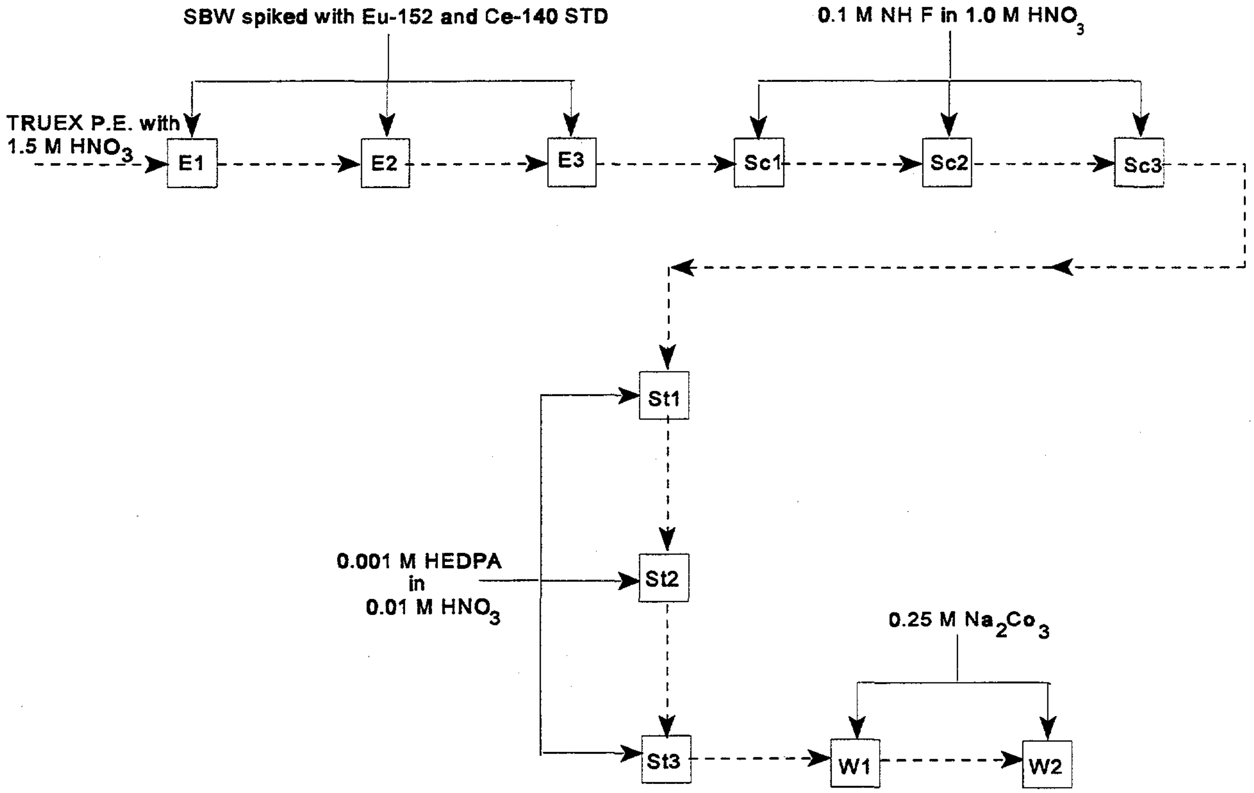

Figure 1. Schematic of the TRUEX/ SBW flowsheet.

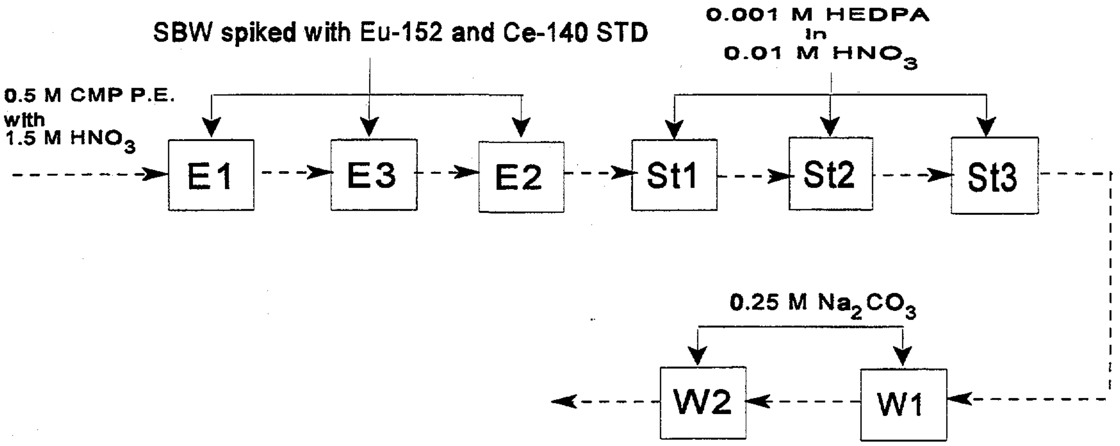

Figure 2. Schematic of 0.5 M CMP/ SBW flowsheet.

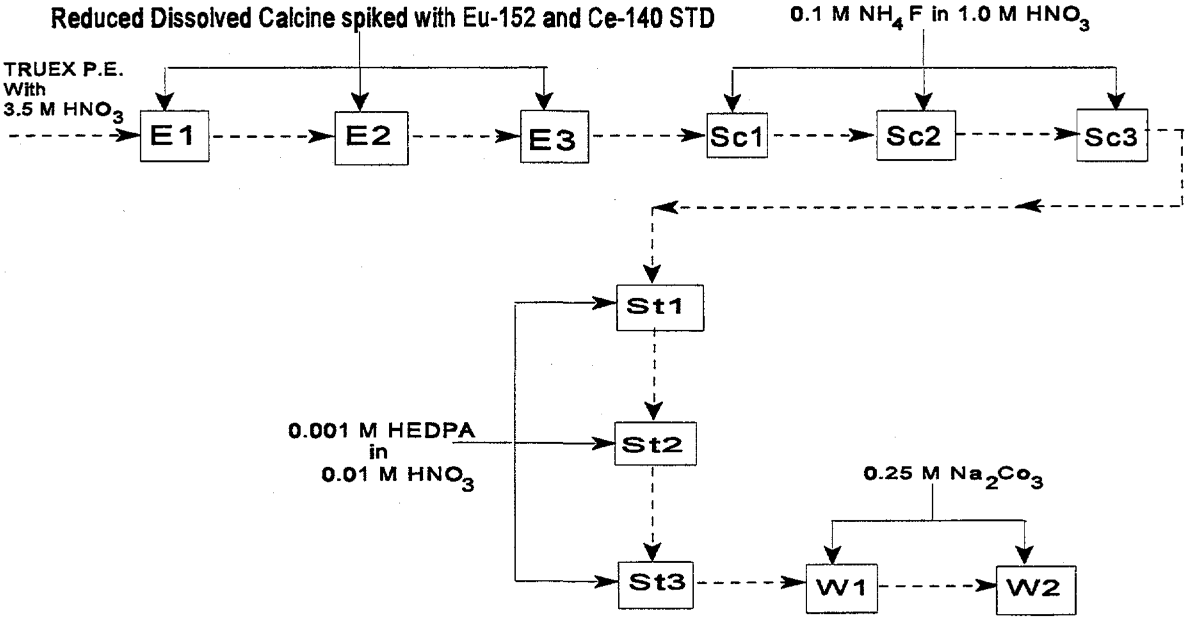

Figure 3. Schematic of the TRUEX/ dissolved zirconium calcine flowsheet.

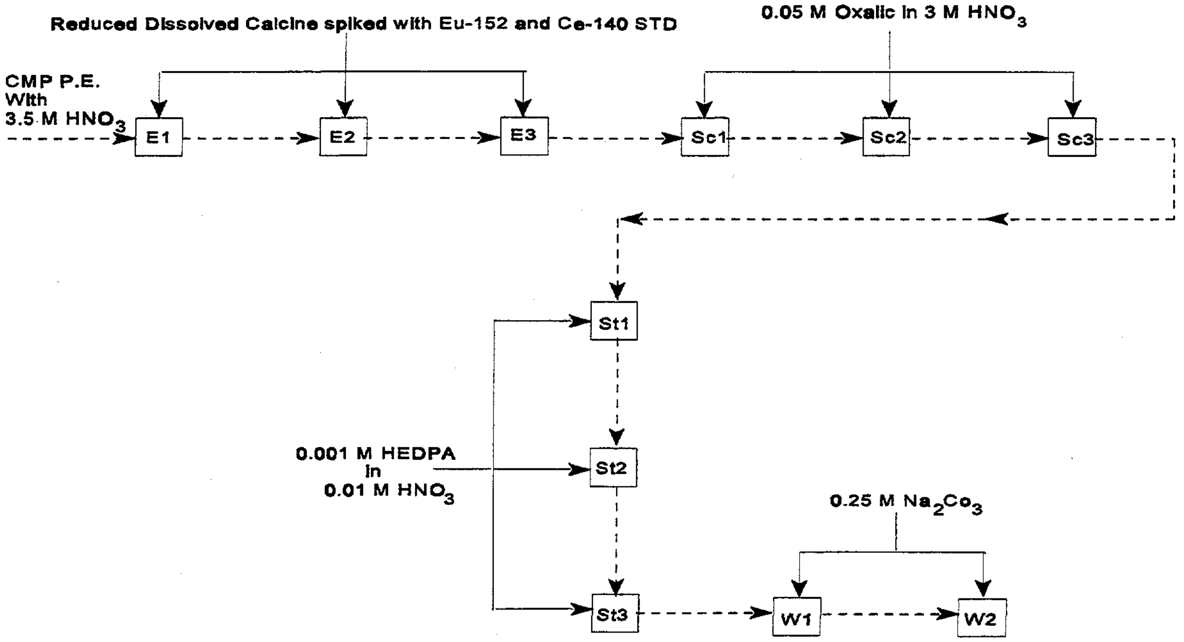

Figure 4. Schematic of the 0.5 M CMP/ dissolved zirconium calcine flowsheet.

Analytical Procedure

Samples of aqueous feed and raffinates from each contact (extraction, scrub, strip or solvent wash) were taken for spectrochemical analysis. The sample concentration was determined by an ICP atomic emission spectrophotometer and the distribution coefficients of the elements being studied were calculated. Because there is no method for directly analyzing the TRUEX and CMP solvents, all the organic samples were stripped with 0.25 M HEDPA in 0.05 M HNO_3 at an O/A=0.2. The material balances determined from the concentrations of Eu and Ce in the HEDPA strips of the organic samples and aqueous samples were typically 100% ± 10%, indicating that the elements were quantitatively stripped from the organic phases. Analyses of the aqueous phases provided a method for the indirect analysis of the organic phase and subsequent determination of distribution coefficients.

RESULTS AND DISCUSSION

The behavior of lanthanides was evaluated in the sodium-bearing waste and dissolved zirconium calcine for both the TRUEX and CMP solvents. The distribution coefficients for Eu and Ce are shown in Tables 3 and 4. In general, the data obtained demonstrate that the rare earths are efficiently extracted from the sodium-bearing waste into either solvent, are not scrubbed and are stripped from both of the extractants with dilute HEDPA. The extraction distribution coefficients for Eu and Ce are higher into the TRUEX solvent in comparison with CMP for SBW. This is expected because CMPO is a much stronger complexant than CMP. The fact that the distribution coefficients for the extraction of lanthanides from the dissolved calcine feed into the TRUEX solvent are lower, can be explained by the higher concentration of zirconium in this feed than in SBW. Zirconium can load the TRUEX solvent and suppress the extraction of both elements. The effect of the solvent loading can be avoided in the CMP / dissolved zirconium calcine flowsheet (Figure 4), because the CMP does not appreciably extract zirconium.

The dissolved zirconium calcine feed was spiked with Ce and Eu in the form of $Ce(NO_3)_3 \bullet 6H_2O$ and Eu_2O_3 respectively. In order to prevent the extraction of chromate, the calcine feed was reduced with hydrogen peroxide prior to contact with both of the solvents. During previous testing it was noticed that small amounts of chromate in the solvent caused third-phase formation and interfacial crud, therefore, eliminating the extraction of chromate by reducing Cr (VI) to Cr (III) has simplified the calcine flowsheets. Based on the difference of the electric potentials [7], hydrogen peroxide will not reduce Eu (III) to Eu (II). Cerium, added as Ce(III), is expected to remain in the trivalent state and not oxidize to Ce (IV). Thus it was assumed that both of the lanthanides were in a trivalent form in the feed solutions.

Table 3. Europium distribution coefficients

Contact	D_{Eu} TRUEX/SBW	D_{Eu} TRUEX/Calcine	D_{Eu} CMP/SBW	D_{Eu} CMP/Calcine
E1	16.9	2.7	8.3	6.8
E2	14.7	1.5	6.7	5.7
E3	13.1	1.2	6.7	5.9
SC1	7.9	4.2	---	2.3
SC2	47.0	10.9	---	2.6
SC3	45.6	18.9	---	2.5
ST1	1.7	4.7	0.35	0.4
ST2	0.2	0.5	0.04	0.06
ST3	0.02	0.04	<0.01	<0.3
W1	<0.07	<<0.4	<5	<5
W2	<5	<<5	<5	<5

The Eu and Ce distribution coefficients obtained in these four tests are in a good agreement (see Table 5) with data for Am (III) which were obtained as part of another study [8]. Thus it is concluded, that both of the rare earth elements can be used as non-radioactive surrogates for Am in TRUEX or CMP extraction studies with acidic solutions. It is also apparent that the rare earth elements will follow the actinides through the separation process and report to the high-activity waste fraction. This is expected to have no effect on the volume of high-level waste glass produced, or adversely affect the performance of the separations processes. The use of trivalent rare-earth elements as Am surrogates in non-radioactive separations tests, primarily in the 5.5-cm Centrifugal Contactor Mockup, is recommended.

Table 4. Cerium distribution coefficients

Contact	D_{Ce} TRUEX/SBW	D_{Ce} TRUEX/Calcine	D_{Ce} CMP/SBW	D_{Ce} CMP/Calcine
E1	13.2	1.8	10.8	8.1
E2	10.6	0.9	8.9	7.1
E3	9.7	0.7	8.3	6.9
SC1	9.0	4.6	---	4.0
SC2	130.2	13.0	---	4.3
SC3	75.7	25.3	---	4.2
ST1	2.4	7.5	0.7	0.9
ST2	0.4	0.9	0.08	0.1
ST3	0.02	0.08	<0.3	<0.7
W1	<2.5	<1.1	<5	<5
W2	<5	<5	<5	<5

Table 5. Extraction distribution coefficients for Eu, Ce and Am.

	Distribution Coefficients (E3 Contact)		
System	Am	Ce	Eu
TRUEX/SBW	32.1	9.7	13.1
CMP/SBW	10.8	8.3	6.7
TRUEX/CALCINE	1.99	0.7	1.2
CMP/CALCINE	7.06	6.9	5.9

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APPENDIX:

EXPERIMENTAL DATA

Table 6. Eu data from TRUEX flowsheet tests

	TRUEX/SBW		TRUEX/Dissolved Calcine	
Sample	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100
Feed	468.9	---	455	---
E1-O	450.6	101.8	324.5	98
E1-A	26.6		121	
E2-O	912	105.9	461.5	99
E2-A	61.8		311	
E3-O	1265	98.6	520	104
E3-A	96.6		434	
SC1-O	1172	104.4	441	105
SC1-A	148.5		104	
SC2-O	1011.5	88.1	396	100
SC2-A	21.5		36.2	
SC3-O	893.5	90.3	339.5	90
SC3-A	19.6		18	
ST1-O	585	103.4	297.5	106
ST1-A	338.6		63.5	
ST2-O	104.7	95.1	95	100
ST2-A	451.6		202	
ST3-O	1.5	94.3	2.6	72
ST3-A	97.2		65.9	
W1-O	<0.3	ND	0.6	ND
W1-A	4.1		1.6	
W2-O	<0.3	ND	0.5	100
W2-A	<0.06		0.1	

ND - Not Determined

Table 7. Ce data from TRUEX flowsheet tests

	TRUEX/SBW		TRUEX/Dissolved Calcine	
Sample	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100
Feed	636.7	---	571	---
E1-O	644.5	108.9	343	93.5
E1-A	49		191	
E2-O	1140	97.4	422.5	99.8
E2-A	107.7		490	
E3-O	1539.5	95.6	415.5	101.2
E3-A	158.2		590	
SC1-O	1415.5	102.1	349.5	102.4
SC1-A	156.5		75.8	
SC2-O	1247.5	88.8	319.5	99.8
SC2-A	9.6		24.6	
SC3-O	1137	92.3	306.5	99.7
SC3-A	15		12.1	
ST1-O	808.5	100.6	269.5	99.6
ST1-A	335.5		35.9	
ST2-O	215.4	99	127	98.3
ST2-A	585		138	
ST3-O	4.4	92.2	8.4	90
ST3-A	194.3		106	
W1-O	<3	ND	<5	ND
W1-A	1.2		4.72	
W2-O	<3	ND	<5	ND
W2-A	<0.6		<1	

ND - Not Determined

Table 8. Eu data from CMP flowsheet tests

	CMP/SBW		CMP/Dissolved Calcine	
Sample	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100
Feed	468.9	---	455	---
E1-O	439	105	420.5	106
E1-A	53.2		62.2	
E2-O	820	104	710	95.4
E2-A	123.2		125	
E3-O	1166.5	104	1045	104.8
E3-A	175.4		176	
SC1-O	---	---	705	96.6
SC1-A	---		304	
SC2-O	---	---	530	104.4
SC2-A	---		206	
SC3-O	---	---	343	90.8
SC3-A	---		138	
ST1-O	287.6	94.5	101	105.2
ST1-A	814.4		260	
ST2-O	10.7	101.3	4.4	77.6
ST2-A	280.6		74	
ST3-O	<0.3	ND	<0.5	ND
ST3-A	45.1		1.7	
W1-O	<0.3	ND	<0.5	ND
W1-A	<0.06		<0.1	
W2-O	<0.3	ND	<0.5	ND
W2-A	<0.06		<0.1	

ND - Not Determined

Table 9. Ce data from CMP flowsheet tests

	CMP/SBW		CMP/Dissolved Calcine	
Sample	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100	ICP Results (mg/l)	Mass Balance (%) (out/in) x 100
Feed	548.2	---	571	---
E1-O	536.5	106.9	530	104.3
E1-A	49.6		65.3	
E2-O	1016	104.3	970	100.5
E2-A	114.8		137	
E3-O	1440.5	103.2	1350	100.3
E3-A	173.2		196	
SC1-O	---	---	1050	97.3
SC1-A	---		264	
SC2-O	---	---	860	100.9
SC2-A	---		199	
SC3-O	---	---	675	97
SC3-A	---		159	
ST1-O	563.5	95	323.5	103
ST1-A	805		372	
ST2-O	40.7	99.2	31.7	78.7
ST2-A	518.3		223	
ST3-O	<3	ND	<5	ND
ST3-A	11.4		7	
W1-O	<3	ND	<5	ND
W1-A	<0.6		<1	
W2-O	<0.3	ND	<5	ND
W2-A	<0.06		<1	

ND - Not Determined