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**Technical Progress Report
Private Sector Initiatives Between
the United States and Japan**

January 1991 - December 1991

DOE Research and Development Report

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Rockwell International

Rocketdyne Division

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ACRONYMS

CRIEPI	Central Research Institute for the Electric Power Industry
DAS	data acquisition system
DOE	Department of Energy
FY	fiscal year
HEPA	high-efficiency particulate air
JAPC	Japan Atomic Power Company
KHI	Kawasaki Heavy Industries
LMR	liquid metal reactor
MURR	Missouri University Research Reactor
P/T	partitioning/transmutation
SSFL	Santa Susana Field Laboratory
TRU	transuranic

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INTRODUCTION

The Private Sector Initiatives Program was started in mid-1987 under the cognizance of the Office of the Deputy Assistant Secretary for Reactor Systems, Development Technology (NE-50). The purpose of this program is to utilize industrial ties between U.S. firms and their Japanese counterparts, to enhance U.S. access to advanced Japanese reactor programs, and ultimately, to provide a basis for U.S. vendor participation in advanced Japanese liquid metal reactor (LMR) designs. The program includes participation from the three U.S. vendors: General Electric Company, Rockwell International, and Westinghouse.

Rockwell activities on the Private Sector Initiatives Program were implemented through an existing relationship with Kawasaki Heavy Industries (KHI). Rockwell and KHI reviewed their respective LMR research needs to identify and screen suitable areas for collaborative efforts. These areas were determined to be of mutual benefit and were approved by the Department of Energy (DOE) and Japan Atomic Power Company (JAPC). Rockwell and KHI performed their respective portions of tasks within these selected areas and exchanged results. Agreed-upon exchange areas for the Rockwell/KHI private sector initiatives collaborative efforts are

- Plant-type evaluations
- Shrouded inducer pump
- Inherent safe core
- Passive shutdown heat removal system
- Booster tube steam generator
- Advanced piping
- Transuranic (TRU) partitioning
- Dry sodium removal.

SUMMARY

This annual report for calendar year 1991 describes the efforts performed under the Private Sector Initiatives contract. The report also describes those efforts that have continued with private funding after being initiated under this contract.

Two privately funded, continuing activities are described in Tasks 1 and 2. The first task is the development of the shrouded inducer pump, which is funded by the Japan Atomic Power Company (JAPC), Kawasaki Heavy Industries (KHI), and Rockwell International. The second task is the development of a pyrochemical process, called TRUMP-S, for partitioning actinides from PUREX waste. This effort is funded by the Central Research Institute for the Electric Power Industry (CRIEPI), KHI, and Rockwell International.

TASK 1. SHROUDED INDUCER PUMP

1.1 OBJECTIVE

The objective of this task is to develop a shrouded inducer pump for the Demonstration Fast Breeder Reactor. The expectations are that the pump can be adapted to the requirements of other advanced liquid metal reactor (LMR) plants with little or no design modification. Successful completion of this scale-model pump development phase is expected to lead to a full-scale pump prototype design, fabrication, and test program.

1.2 ACCOMPLISHMENTS

Results of prior year activities are reported in the Private Sector Initiatives annual reports.¹⁻⁴ In 1991, the cylindrical kicker configuration for the 1/5-scale pump hardware was modified to include an annular diffuser configuration similar to the one originally tested with the bell kicker configuration. Previous tests had shown that this diffuser configuration was more efficient than the bladed diffuser configuration.

Test results for the modified configuration are shown in Figure 1. Pump head data as a function of pump discharge flow are shown for three rotor speeds. The normal operating range is shaded. The basic requirements for the pump are a discharge flow of 9.2 m³/min (2,430 gpm) with a pump head of 80 m (262 ft) maximum and 53.3 m (175 ft) minimum. The data show that the design exhibits a stable flow performance in the required region with margin on both the high and low flow sides.

The modified diffuser for the cylindrical kicker configuration had a head loss of 9.7 m at the design point compared to 12.7 m with the original bladed diffuser configuration. A comparison of the head-flow curves at the design rotor speed for the original and modified configurations is shown in Figure 2. The pump head increases 3 m to 93 m at the design point for the new configuration. The overall efficiency increases 2% to 77%.

1.3 PROGRAM SUMMARY

The shrouded inducer pump is a small, compact pump, which can make a major contribution toward achieving a compact reactor assembly for an economic LMR design. Tests performed in 1991 have further demonstrated a design configuration that meets the requirements set forth for the scale-model pump development phase. The design configuration improvements that were tested resulted in an improvement in pump efficiency to 77%. This modified configuration with the cylindrical kicker and the annular diffuser was selected as the reference shrouded inducer pump design.

Figure 1. Head-Flow Performance Curves for Inducer Pump with Modified Diffuser

Figure 2. Head-Flow Performance Comparison of Inducer Pump with Original and Modified Cylindrical Kicker Configurations

TASK 2. TRU PARTITIONING

2.1 OBJECTIVE

The overall objective of the Rockwell International/Kawasaki Heavy Industries/Central Research Institute for the Electric Power Industry (Rockwell/KHI/CRIEPI) program is to develop a process to recover 99% of the remaining transuranic (TRU) materials (Np, Pu, Am, Cm) from PU-REX waste to simplify nuclear waste management. The purpose of the program is to separate the high-level nuclear waste into a TRU-rich stream and a TRU-depleted stream to reduce waste management costs. The actinide product can then be transmuted into stable products or stored. This can markedly reduce the amount of actinides in the waste requiring long-term isolation or repository emplacement and can supply significant quantities of fissile and fertile materials for power production during transmutation.

2.2 ACCOMPLISHMENTS

2.2.1 Methodology and Laboratory Development

Electrochemical test cells and methodology were developed at the Rockwell Santa Susana Field Laboratory (SSFL) using rare earths in the inert atmosphere glovebox. This technology was transferred to the Missouri University Research Reactor (MURR) Alpha Laboratory for use with actinides by interchange of laboratory personnel. Techniques to determine the rate limiting steps occurring at the anode and cathode were investigated. The rare earth tests suggested that precursor reactions at the cathode and anode (decomposition of the solvent chloride metal complexes) do not appear to be rate limiting and, therefore, should not interfere with deposition/dissolution reactions.

The computer program to operate the data acquisition system (DAS) was rewritten for an IBM computer. This new system was installed both at MURR and SSFL. The program operates the DAS during free energy studies. Changes and additions are made to the program as new electrochemical tasks are needed.

The MURR Alpha Laboratory was modified during FY 1991 to install fire sprinklers, open the floor drain, and add additional exhaust high-efficiency particulate air (HEPA) filters. These modifications were made as a compromise to settle the litigation on the safety of the Alpha Laboratory.

2.2.2 Actinide Study Test Results

A comparison of the measured actinide chloride free energy of formation with thermal data in the literature is given in Table 1 along with activity coefficients of actinide chlorides in LiCl/KCl eutectic electrolyte. Six papers were presented at national and international meetings on test results obtained on the TRUMP-S and partitioning/transmutation (P/T) studies.⁵⁻¹⁰

Table 1. Free Energies of Formation and Activity Coefficients for Actinide Chlorides in LiCl-KCl

Element	Temperature (°C)	$-\Delta G^{\circ}_{\text{exp}}$ (kcal/ mole)	E° Cl_2/Cl^- (V)	n^1	$-\Delta G^{\circ}_{\text{cryst}}^2$ (kcal/ mole)	$-\Delta G^{\circ}_{\text{fus}}^3$ (kcal/ mole)	$-\Delta G^{\circ}_{\text{liq}}$ (kcal/ mole)	Activity Coefficient (γ_{MCl_3})	
								Crystal ⁴	Liquid ⁴
U	400	174.82	2.527	3.36	170.58	4.32	166.26	4.2×10^{-2}	1.7×10^{-3}
	425	173.87	2.513	3.06	169.32	4.08	165.24	3.8×10^{-2}	2.0×10^{-3}
	450	172.92	2.499	3.25	168.09	3.87	164.22	3.5×10^{-2}	2.3×10^{-3}
	500	171.02	2.472		165.60	3.33	162.27	2.9×10^{-2}	3.3×10^{-3}
Np	400	188.47	2.724	2.93	179.34	4.86	174.48	1.1×10^{-3}	2.9×10^{-5}
	425	187.35	2.708	3.31	178.08	4.56	173.52	1.3×10^{-3}	4.7×10^{-5}
	450	186.23	2.692	3.24	176.76	4.23	172.53	1.4×10^{-3}	7.2×10^{-5}
	500	184.00	2.660	3.14	174.18	3.63	170.55	1.7×10^{-3}	1.6×10^{-4}
Pu	400	196.08	2.834		192.63	5.28	187.35	7.6×10^{-2}	1.5×10^{-3}
	425	194.90	2.817	2.91	191.25	4.92	186.33	7.2×10^{-2}	2.1×10^{-3}
	450	193.73	2.800	2.88	189.90	4.56	185.34	7.0×10^{-2}	2.9×10^{-3}
	500	191.37	2.766	3.01	187.17	3.84	183.33	6.5×10^{-2}	5.3×10^{-3}
¹ Illustrative only, data exhibits scatter ² Bureau of Mines data (L. B. Pankratz, Bulletin 674 [PB84-233329], U.S. Bureau of Mines, Albany, OR [1984]) ³ Calculated from heat and temperature of fusion ⁴ Standard state basis									

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2.2.2.1 UCl₃ Replicate Runs

Four free energy of formation replicate runs on UCl₃ were made at 450°C. These data gave $E^\circ_{\text{UCl}_3}$ values that agreed within 1 mV of $E^\circ_{\text{UCl}_3} = 1.293$ V versus the Ag/AgCl reference electrode. This demonstrates the excellent replication of data which can be generated by the electrochemical cells and DAS. In one run, the electrodeposition was continued until the uranium concentration in the salt was decreased to the ppm range. The potential versus logarithm of concentration for the run showed linear behavior over four orders of magnitude of concentration as required by the Nernst equation. This shows that the actinides can be separated pyrochemically from molten salt solutions by electrodeposition of the actinide down to the levels below that required to meet the program goals.

2.2.2.2 PuCl₃ Replicate Run

A free energy replicate run of PuCl₃ in LiCl-KCl electrolyte was made at 450°C to demonstrate the reproducibility of the data. These data showed the Pu/PuCl₃ potential versus concentration data was reproducible to within 3 mV.

2.2.2.3 U/Cd Activity

Two uranium (U) in cadmium (Cd) activity runs were made to verify the literature data. The first U/Cd test was only moderately successful, but the second test verified the literature data (Table 2). At saturation, the U in Cd potential was depressed up to about 50 mV compared to the U/UCl₃ potential at similar UCl₃ concentrations and temperature. Thus, the activity coefficient for U in Cd was about 15 for a saturated solution. This agrees well with the data generated by Johnson et al.¹¹

Table 2. Activity Coefficients for Saturated Solutions of Actinides Dissolved in Cadmium

Element	Temperature	This Work Activity Coefficient (γ)	Johnson et al.	
			Activity Coefficient (γ_{liq})	Cd Solubility (mole fraction, X)
U	400	15	52	2.5×10^{-3}
	425		63	4.4×10^{-3}
	450		82	7.6×10^{-3}
	500		94	1.4×10^{-2}
Np	400		1.8×10^{-3}	3.7×10^{-3}
	425		3.4×10^{-3}	6.3×10^{-3}
	450		6.1×10^{-3}	1.0×10^{-2}
	500		1.9×10^{-2}	2.2×10^{-2}
Pu	400	3.1×10^{-5}	1.4×10^{-5}	7.2×10^{-3}
	425		3.0×10^{-5}	9.1×10^{-3}
	450		6.2×10^{-5}	1.2×10^{-3}
	500		2.1×10^{-4}	1.8×10^{-2}

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2.2.2.4 Pu/Cd Activity

Two plutonium (Pu) in Cd activity runs were made. The second test was more successful than the first test. At saturation, the Pu in Cd is depressed about 0.3 V compared to Pu metal exposed to the same concentration of PuCl_3 in LiCl/KCl electrolyte. Thus, the Pu activity coefficient in Cd is 3×10^{-5} ; this is in good agreement with the Johnson¹² activity coefficient data of 6×10^{-5} for Pu in Cd at 450°C.

2.2.2.5 Np/Cd Activity

Since the activity data obtained for the actinides (Table 2) in cadmium agreed well with the literature, it was decided to accept Johnsons¹³ activity of Np in Cd data without verification to maintain the program schedule.

2.2.2.6 Am/Cd Activity

The americium (Am) in Cd activity was measured during 1991. The activity coefficient of Am in Cd was found to be about 3.5×10^{-4} at 450°C, or an order of magnitude greater than that of plutonium.

2.2.3 Americium Free Energy Tests

2.2.3.1 Results of Literature Survey

Two authors have attempted to derive equations for the free energy of formation of AmCl_2 and AmCl_3 . Using standard thermodynamic techniques and measured and estimated quantities, Alire et al.¹⁴ derived an equation which projected that molten AmCl_2 would have a standard potential of -2.84 V at 450°C. Using Pu/ PuCl_3 free energies along with Pu/Am equilibrium constants and some questionable assumption on activity coefficients, Leary et al.^{15,16} derived an equation that projected molten AmCl_2 would have a standard potential of -2.95 V at 450°C. An evaluation of the techniques used to calculate the AmCl_2 liquid standard potentials indicated that Alire's value is probably superior to that obtained by Leary.

The predicted free energies/equivalent for AmCl_2 and AmCl_3 are sufficiently close so that either valence or both values may be found under certain TRUMP-S processing conditions. For example, AmCl_3 is probably present in the chlorination product, but AmCl_2 is probably present in the chemical reduction product, and both are probably present in the transition from the chlorination product to the reduction product. Leary did demonstrate that in molten salt extraction of Am from Pu, AmCl_2 is the dominant species in equilibrium with PuCl_3 and Pu/Am metal.

2.2.3.2 Free Energy Tests

About 15 free energy tests have been run. These tests have illustrated that the Am/ AmCl_x chemistry is complex, and reproducing the free energy data has been extremely difficult. Several

observations can be reported even though the phenomenon responsible for some of the observations are not fully understood.

Literature data indicated that for AmCl_x mole fractions of 10^{-2} to 10^{-5} , the Am/AmCl_2 potential should be between -1.80 to -1.95 V versus the Ag/AgCl reference electrode (mole fraction $\text{AgCl} = 0.00481$), while the Am/AmCl_3 potential should be about -1.60 to 1.75 V. Am/AmCl_x potentials have been obtained from about -1.60 to about -1.98 V over this concentration range in different tests. Therefore, it appears that both AmCl_2 and AmCl_3 are present in the salt solution.

At low deposition currents (0.1 mA or less), it appears that electrodepositions can continue indefinitely with little change in potential. This could be attributed to alpha decay, which leaves a charge imbalance in the vicinity of the Am and can result in reoxidation of some Am metal present. Depending on the decay energy or charge transfer utilization assumed, alpha decay reoxidation of Am metal could account for microamp to milliamp current inefficiencies under the test conditions used.

With the other actinides, electrodepositions were made and the cathode potentials were allowed to reach steady state before the cathode potential reading was made. Steady state was assumed when the potential did not change more than 0.5 mV in 15 min. At this point, about 20 to 30 min after deposition was discontinued, the cathode potential with time was essentially flat. With Am, flat steady-state potentials were not attainable probably because of alpha decay reoxidation of Am metal and alpha recoil steadily stripping the electrode of the Am metal deposit.

The free energy tests demonstrate that both AmCl_2 and AmCl_3 can be present in the salt. Since the Am/AmCl_2 potentials are projected to be much closer to the rare earth chloride potentials than are the Am/AmCl_3 potentials, the Am/AmCl_2 measurements are the ones required for separation efficiency projections. Therefore, the measurement of the Am/AmCl_2 potential was emphasized.

The projected Am/AmCl_x standard potentials for AmCl_3 and AmCl_2 at 450°C are calculated from Alire's equations to be $E_{\text{AmCl}_3} = -2.79$ V and $E_{\text{AmCl}_2} = -2.84$ V. The Am/AmCl_2 projected and observed values are given in Figure 3. The dark line is the projected AmCl_2 potentials from the literature and the points are potential measurements obtained for the various tests. These data show good agreement between the projected potential and the measured values. The measured potentials and slope are in much better agreement with those projected for AmCl_2 than for AmCl_3 .

Probably the most successful of the electrodeposition tests was Test 563. A plot of the cathode potential versus the log of AmCl_2 mole fraction is given in Figure 4. A line with $n = 2$ slope is drawn through the measured cathode potentials. High cathode potentials (~ 2.0 V) were observed initially, but then potentials near expected literature values were obtained. This initially high potential may have reduced any AmCl_3 to AmCl_2 . The data have too much scatter to unequivocally specify that only AmCl_2 was present during the electrodeposition.

The measured potentials for all tests are similar to the projections of potentials for AmCl_2 , but are above projections of potentials for AmCl_3 . If the average of the measured potentials and the

Figure 3. Projected and Observed AmCl_x Potentials

Figure 4. Test 563 - Free Energy of Am/AmCl_x at 450°C

average of the logarithms of the mole fractions are taken as the observed potential for the above tests, the standard potentials and free energies can be calculated for AmCl_2 and AmCl_3 . The results show an E_0 of -2.94 V for AmCl_3 and -2.85 V for AmCl_2 . These average data are in better agreement with projected potentials for AmCl_2 than for AmCl_3 . The corresponding free energy, $\Delta G^\circ/\text{equivalent}$, for AmCl_2 is 65.7 kcal/mole.

2.2.4 Americium Voltammetry Tests

Cyclic voltammetry is a common technique employed in understanding aqueous and molten salt systems. The potential is swept in a cathodic direction (more negative potentials) followed by an anodic sweep. The resulting current monitored during the potential sweeps gives information on the types of electrochemical reactions that take place and the potentials at which they occur. The advantage of this technique is that it takes a short time to perform; from a few seconds to a couple of minutes. A disadvantage of cyclic voltammetry is that potentials of electrochemical reactions are not as accurate as those obtained in an equilibrium technique.

A series of cyclic voltammetry sweeps were run on a 0.0014 mole fraction solution at 500 , 200 , 100 , 50 , 20 , and 10 mV/s as shown in Figure 5. While scanning in the cathodic direction (upper curves), two major peaks are observed, one at about -90 mV versus Li_2Sb and another at -400 mV. The cathodic peak at about -400 mV is clearly visible at the lower scan rates, but becomes indistinct and lost in the high background at higher scan rates. On the anodic sweep, the stripping peak (a dip)

Figure 5. Cyclic Voltammetry at 450°C

at -250 mV corresponds to the reoxidation of americium. A broad series of dips from 0 to +500 mV represent oxidation of Am^{2+} to Am^{3+} . Another pair of small oxidation and stripping peaks was observed around +900 mV, which is the potential one would expect for Cd.

The cathodic and anodic peaks at -400 mV and -250 mV, respectively are consistent with deposition of an insoluble species such as Am metal. The equilibrium potential, -0.38 ± 0.02 V, was chosen as being about midway between the potential where deposition begins on the cathodic sweep and the potential where dissolution begins on the anodic sweep. This potential corresponds to -1.94 ± 0.02 V versus Ag/AgCl ($X = 0.00487$), -3.15 ± 0.02 V versus Cl_2/Cl^- , and an E_o of -2.94 V and ΔG° of -67.8 kcal/equivalent for AmCl_2 . In rare earth studies, it was found that cyclic voltammetry potentials had to be corrected by as much as 50 to 100 mV to obtain the equilibrium standard potentials. Thus, the $E^\circ_{\text{AmCl}_2}$ obtained is probably much closer to the Alire value of 2.84 V than indicated by the uncorrected value of -2.94 V.

To better understand the cathodic peak at -90 mV versus Li_2Sb and the associated anodic peaks between 0 and +500 mV, a series of cyclic voltammetry sweeps was performed over the potential range +1250 to -350 mV. This potential region is not cathodic enough to cause the deposition of Am metal, which begins to happen at about -380 mV versus Li_2Sb . These scans were carried out at sweep rates of 500, 200, 100, 50, 20, and 10 mV/s as shown in Figure 6. The anodic dip at -250 mV is absent in these scans confirming that this is actually the stripping peak associated with Am metal deposition at more cathodic potentials. The simplicity of the anodic peak from 0 to +500 mV in Figure 6 compared to that in Figure 5 may be due to the reaction $\text{Am} + 2\text{Am}^{3+} \rightleftharpoons \text{Am}^{2+}$. In Figure 5, a significant amount of Am metal is still being stripped off the working electrode as the anodic sweep approaches the region where oxidation of Am^{2+} to Am^{3+} occurs.

Additional cyclic voltammetry tests were carried out at 450 and 416°C at 0.00074 Am mole fraction. The results of these tests are summarized in Table 3. Comparison of these potentials to those of rare earths indicates that electroseparation of Am from lanthanides is possible.

Table 3. Summary of Americium Potentials Estimated from Voltammetry

Temperature (°C)	450	450	416
Initial mole fraction Am	0.00141	0.00074	0.00074
$E_{\text{Am}^{+3}/\text{Am}^{+2}} \text{ vs Ag/AgCl (V)}$	-1.45 ± 0.02		
$E_{\text{Am}^{+3}/\text{Am}^{+2}} \text{ vs Cl}_2/\text{Cl}^- \text{ (V)}$	-2.66 ± 0.02		
$E_{\text{AmCl}_2} \text{ vs Ag/AgCl (V)}$	-1.94 ± 0.02	-1.96 ± 0.02	-1.98 ± 0.02
$E_{\text{AmCl}_2} \text{ vs Cl}_2/\text{Cl}^- \text{ (V)}$	-3.15 ± 0.02	-3.17 ± 0.02	-3.19 ± 0.02
$E^\circ_{\text{AmCl}_2} \text{ vs Cl}_2/\text{Cl}^- \text{ (V)}$	-2.95 ± 0.02	-2.95 ± 0.02	-2.98 ± 0.02
$\Delta G^\circ_{\text{AmCl}_2} \text{ (kJ/mole)}$	569 ± 4	569 ± 4	574 ± 4

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Figure 6. Cyclic Voltammetry at Reduced Scan Range

2.2.5 Effect of Am Activities on Separation

Americium will be the most difficult actinide to separate from rare earths. Since the electrochemical properties were unavailable, they were estimated in the initial separation efficiency projections.⁹ The original projection indicated that 99.9% of the Am could be separated from typical PUREX waste composition and an actinide deposit containing the Am would contain only about 7 wt.% rare earths.

This year's TRUMP-S program has measured several properties of Am. The potential of Am in AmCl_2 solution measurements are in good agreement with Alire's prediction and suggest that the standard potential of liquid AmCl_2 is -2.85 V at 450°C .

The cyclic voltammetry tests indicate that Am metal will be in equilibrium with AmCl_2 in the process, not AmCl_3 . The slope for the Am/AmCl_2 potential versus concentration is greater than the slope for Am/AmCl_3 . Thus, the Am/AmCl_2 potential will reach the rare earth Nd/NdCl_3 potential at a higher concentration and make it more difficult to effect electrolytic separations. Also, the potential of Am in Cd is more positive than originally projected, making it more difficult to remove the Am from the Cd solvent and decrease the Am/rare earth separation efficiency.

The net effect of the Am/AmCl_x potential, the Am/AmCl_2 slope, and the Am in Cd potential is that the Am/rare earth separation efficiency is decreased somewhat. Whereas we had originally

predicted 99.9% Am removal with actinides composing about 93% of the cathode deposit, we now predict 99.9% Am removal with actinides composing about 91% of the deposit.

2.3 PROGRAM SUMMARY

The data obtained to date show that the TRUMP-S process is feasible and cost-effective. The electrochemical data for U, Np, and Pu is summarized in this report along with the recently measured data for Am. The experimental chloride free energies of formation have been determined along with the activity coefficients in LiCl-KCl electrolyte and in Cd solvents. Using this data to predict separation efficiency for actinides from the rare earths indicates that a 99.9% removal of Am, the most difficult actinide to separate, is possible with actinides composing about 91% of the separated stream.

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