Nuclear Waste Management Quarterly Progress Report April Through June 1979

**A. M. Platt
J. A. Powell**

September 1979

**Prepared for the U.S. Department of Energy
under Contract EY-76-C-06-1830**

**Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

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NUCLEAR WASTE MANAGEMENT
QUARTERLY PROGRESS REPORT
APRIL THROUGH JUNE 1979

Compiled by
A. M. Platt and J. A. Powell
Nuclear Waste Technology Program

September 1979

Prepared for
the U.S. Department of Energy
under Contract EY-76-C-06-1830

Pacific Northwest Laboratory
Richland, Washington 99352

FOREWORD

This document is one of a series of technical progress reports designed to report on commercial radioactive waste management programs at Pacific Northwest Laboratory. These programs are funded by the Department of Energy's Office of Nuclear Waste Management. The Commercial Radioactive Waste Immobilization Program is reported elsewhere. These reports are issued on a quarterly basis.

The prior report in this series is Nuclear Waste Management Quarterly Progress Report January Through March 1979, PNL-3000-1.

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1. DECONTAMINATION AND DENSIFICATION OF CHOP-LEACH CLADDING RESIDUES

T. M. Lambright - Project Manager

Fuel element cladding residues from the chop-leach head-end process constitute a low-density, high-surface-area metallic waste with a substantial actinide element contamination. The objective of this study is to develop methods for removal of long half-life transuranics from fuel cladding residues and to consolidate the decontaminated cladding into a dense, chemically unreactive form for efficient storage or burial. The study includes:

- 1. demonstration of a prototype system for combined descaling and densification of unirradiated scrap fuel cladding*
- 2. development of engineering data to provide the basis for scaleup to a production system*
- 3. evaluation of ground-water corrosion tests conducted on samples of alloyed ingots previously produced by the densification process.*

SUMMARY

A prototype system for decontaminating and densifying chop-leach cladding residues has been assembled in a building operated by the Pacific Northwest Laboratory. Pilot-scale chemical decontamination equipment and an Inductoslag ingot melting furnace are set up on a simulated hot cell floor plan. The system was designed to use an HF/Ar gas mixture to descale scrap cladding pieces (autoclaved, unirradiated scrap) in the decontamination prototype and then to melt the treated scrap in the induction furnace to produce ingots.

The ingot melting furnace has been inactive since successful tests showed that it could produce smooth-sided ingots from various alloys of Zircaloy,[®] stainless steel, and Inconel.[®] Combined operation of the furnace

and the prototype chemical decontamination equipment was planned after final testing and readiness of the decontamination equipment. Several equipment and process problems were identified in five descaling tests of the decontamination equipment. A key problem was the generation of high-temperature conditions in the HF/Ar gas reactor. Hydrogen gas, produced by the reaction of hydrogen fluoride gas with the Zircaloy cladding pieces, reacted with the Zircaloy to produce zirconium hydrides and a large amount of heat. Equipment and procedures are being modified to prevent this problem during one last test of the decontamination equipment before the end of the program.

The Inductoslag melting furnace was reactivated and a successful ingot was produced in an experiment to show that the melting process could easily be interrupted with several startup-shutdown cycles if necessary.

[®] Zircaloy is a registered trademark of Westinghouse Electric Specialty Metals Division, Blairsville, PA.

[®] Inconel is a registered trademark of Huntington Alloys, Huntington, WV.

DECONTAMINATION PROCESS

The Pacific Northwest Laboratory's pilot-scale decontamination equipment is designed to "decontaminate" (descale) about 2 kg of chop-leach cladding residues per hour. The prototype equipment includes an HF gas reactor, an HF reactor furnace, HF and Ar gas supply systems, an aqueous washer/rinser, associated process solution tanks and piping, and control instrumentation including safety circuits. The basic components of this system have been described and diagramed in previous reports.⁽¹⁻³⁾ A full report on the development of the chemical decontamination process has been prepared.

A programmable sequencing system for the prototype equipment was installed to automatically control various operations during the descaling tests. A hull detector was installed to indicate the presence of cladding pieces in the HF reactor inlet pipe. A color videocassette camera and monitor were added to complete the equipment's videotape recording system.

Cladding pieces to be descaled are treated with an HF/Ar mixture in the gas reactor and then gravity fed through an air lock valve system into the aqueous washer/rinser. Two vacuum gate valves originally installed between the HF reactor and the washer/rinser were damaged by cladding pieces in early operating tests. This damage allowed water vapor to leak into the HF reactor from the washer/rinser. A rotary air lock valve replaced the two gate valves, and a cladding flow restrictor was installed to prevent jamming of the rotary air lock from excessive loading of the rotating chambers. An argon purge below the rotary air lock was installed to purge the region of water vapor.

The first descaling test after this modification (Test No. 3) had to be terminated

within 10 min because of excessive temperature in the HF reactor. It was first believed that water vapor leakage was the sole source of the problem, but further testing identified hydrogen gas as another source of overheating. Two ball valves and an improved argon purge system were installed after Test Number 3 to prevent further water vapor leakage. However, four subsequent descaling tests showed continued high temperatures and rapid pressure rises in the HF reactor.

It was determined that the mixing of argon and hydrogen fluoride gases was insufficient, and essentially undiluted hydrogen fluoride was reacting with the Zircaloy-4 hulls. The reaction created hydrogen, which caused the reactor pressure to rise rapidly. The major cause of the overheating was that the hydrogen would react with the Zircaloy to produce zirconium hydrides in a highly exothermic reaction. The heat released during the last test (Test No. 7) was great enough to melt through a Teflon[®] bellows seal at the cladding inlet port.

The problem of mixing the hydrogen fluoride and argon gases was solved by mixing the gases more thoroughly at a point farther from the reactor. The solution to the overheating can possibly be solved by removing the gas from the mouth of the reactor instead of from the cladding feed chute. This will prevent passage of hydrogen gas over the bed of cladding hulls that feeds the reactor. In the one test planned for before the end of the program, the argon flow rate will be increased to purge the atmosphere of hydrogen.

Excessive zirconium fluoride powder was also produced in the reactor and acted as a binding medium, causing the hulls to cluster. As the hulls continued to feed into the reactor, the powder bound enough together to

[®] Teflon is a registered trademark of E.I. Du Pont de Nemours, Wilmington, DE.

block the opening to the main reactor chamber. This clustering of hulls also caused mechanical interference which crushed several hulls as the reactor rotated.

DENSIFICATION PROCESS

The Inductoslag ingot melting furnace is the densification portion of the decontamination-densification equipment set up to process chop-leach cladding residues. Various alloys of Zircaloy, stainless steel, and Inconel have been cast in 21 melting tests described in previous reports.^(1,2,4) Two operational melting tests of the Inductoslag furnace were made this reporting period using the video-

tape recording and monitoring system. Replaying the videotape of the first test enabled the operator to verify the cause of a water leak in the furnace's induction coil. The position of the molten Zircaloy pool in the furnace crucible and an excessive power level caused the metal to splash over the crucible, shorting the induction coil and thereby burning a hole through one turn of the coil. The coil was repaired and a successful test of the Inductoslag furnace produced a 20-kg ingot with the desired smooth surface. The ingot was formed with three separate startups and shutdowns, experimentally indicating that the process can be easily interrupted if necessary.

REFERENCES

1. A. M. Platt and J. A. Powell, comps., Nuclear Waste Management Quarterly Progress Report, January through March 1978. PNL-2378-1, Pacific Northwest Laboratory, Richland, WA, August 1978.
2. A. M. Platt and J. A. Powell, comps., Nuclear Waste Management Quarterly Progress Report, April through June 1978. PNL-2378-2, Pacific Northwest Laboratory, Richland, WA, November 1978.
3. A. M. Platt and J. A. Powell, comps., Nuclear Waste Management Quarterly Progress Report, July through September 1978. PNL-2378-3, Pacific Northwest Laboratory, Richland, WA, January 1979.
4. A. M. Platt and J. A. Powell, comps., Nuclear Waste Management Quarterly Progress Report, October through December 1978. PNL-2378-4, Pacific Northwest Laboratory, Richland, WA, March 1979.

2. MONITORING METHODS FOR PARTICULATE AND GASEOUS EFFLUENTS FROM WASTE SOLIDIFICATION PROCESSES

P. W. Goles - Project Manager

The objective of this program is to develop reliable and accurate techniques for process monitoring and stack emission monitoring for future waste solidification facilities.

SUMMARY

Program activity during this quarter has been totally devoted to sample analysis. Preliminary results have been obtained and reported for many of the sought-after gaseous effluent species. Results from particulate analysis are also presented.

GASEOUS SAMPLE ANALYSIS

The major thrust during the present quarter has been directed toward analysis of vitrification samples taken during the latter part of the previous quarter. The major effluent species sampled for are listed in Table 2.1. Quantitative analytical results have been obtained for several of these species, allowing estimates of their off-gas concentration to be made. These results appear in Table 2.2. Since all analytical work has not been completed, and in many cases several independent methods of quantifying effluent species were employed, the results appearing in Table 2.2 should not be considered as final values. Moreover, the significance of these data with regard to the vitrification process cannot be addressed until more pre- and post-vitrification sample results become available.

PARTICULATE SAMPLE ANALYSIS

A particle size analysis of the vitrification of off-gas stream was completed during this reporting period. The isokinetic particle sample was examined utilizing a scanning electron microscope. Thirty-eight SEM-generated pictures ($2 \times 10^4 \times$) were evaluated with a Zeiss particle size analyzer. The resultant size-frequency distribution was analyzed empirically and by fitting the data to a log-normal distribution. Table 2.3 summarizes the results of this analysis.

TABLE 2.1. Important Process Effluents

Gaseous Effluents

^3H as HTO , TH and organics
 ^{14}C as CO , CO_2 and organics
 ^{129}I as I_2 , HOI and organics
 NO_x

Semivolatile Effluents

^{79}Se
 ^{99}Tc
 ^{106}Ru
 ^{125}Sb , ^{126}Sb
 $^{125\text{m}}\text{Te}$, ^{127}Te
 ^{134}Cs , ^{135}Cs , ^{137}Cs

Particulate Effluents

Fission products including $^{144}\text{CePr}$
 Activation products
 Heavy elements

TABLE 2.2. Gaseous Effluent

Isotope	Chemical Form	Concentration(a)	
		POG 88	Stack(b)
^{129}I	AI1	$8 \times 10^2 \text{ pCi/m}^3$	$8 \times 10^{-1} \text{ pCi/m}^3$
^3H	HTO	$1 \text{ } \mu\text{Ci/m}^3$	$1 \times 10^{-3} \text{ } \mu\text{Ci/m}^3$
^{99}Tc	Tc_2O_7	$7 \times 10^{-1} \text{ pCi/m}^3$	$7 \times 10^{-4} \text{ pCi/m}^3$
--	NO_x	0.5%	5 ppm
--	NO	0.3%	3 ppm

- a. Until all analytical results are completed, meaningful error assignments cannot be made. However, statistical counting uncertainties are all better (i.e., lower) than 5%.
- b. Process off-gas is diluted by a factor of 10^3 before being exhausted at the stack.

TABLE 2.3. Particulate Emissions

Parameter(a)	Empirical	Log Normal
Geometric mean diameter	0.13 μ	0.10 μ
Geometric standard deviation	1.51	2.01
Goodness of fit	--	0.975
Mass mean diameter	--	0.55 μ
Particle concentration	$168/\text{cm}^3$	--
Particle mass concentration(b)	84.7 pgm/cm^3	--

- a. All parameters related to undiluted process off-gas before final HEPA filtration.
- b. Assumed calcine density - 3 g/cm^3 .

3. TRU WASTE IMMOBILIZATION PROGRAM

C. R. Palmer - Project Manager

The objective of this program is to conduct a comparative assessment of alternative immobilization systems for selected transuranic wastes, and recommend the most promising technology for development and demonstration.

SUMMARY

Experiments were focused on refinement and characterization of a borosilicate glass composition for the bulk Rocky Flats Plant incinerator ash, and on completion of a feasibility study of sintered ceramic waste forms as host material for two transuranic wastes. For the ash a glass was selected that will be made in a pilot-scale in-can melting process test to be performed during the fourth quarter. The sintered ceramics study demonstrated that improved product quality can be obtained by appropriately selecting sintering additives and temperatures, and identified bentonite as a primary candidate for continued development.

LABORATORY GLASS DEVELOPMENT - G. B. Mellinger

Work was directed chiefly at developing and characterizing a glass for vitrification of incinerator ash from the Rocky Flats (RFP) rotary kiln incinerator. A series of melts were made based upon the 79-116 composition reported last quarter; in these melts the waste loading of the as-received ash was varied. The aim of the experiment was to examine the effect of various degrees of batch mixing on the product's homogeneity and leach resistance. Leach resistance of the glass was found to be very sensitive to waste loading, as shown in Figure 3.1. This sensitivity was

due mainly to the substantial alumina and silica concentrations in the ash, which increase glass chemical durability. However, to maintain a sufficiently low melting temperature, high concentrations of alkali and boron oxides were incorporated in the glass-forming additive. Thus when waste loading is reduced, a relatively high acid leach rate results. Subsequent experiments were designed to improve the product durability as well as its flexibility to nonideal mixing conditions. The resulting glass formulation, 79-160 shown in Table 3.1, was chosen as the composition which best met those objectives. Table 3.2 summarizes the characteristics of this laboratory glass.

Reagent chemicals will be used to supply the glass-forming cations to the melter feed batch because of the limited quantity of glass to be made during the test. Consequently, the alternative chemical forms of cation addition were considered. Tests were made to determine the sensitivity of product characteristics or process behavior to the choice of chemical forms. Although this showed no significant effects on product quality, the form of sodium did influence the batch melting rate. Glass batches for several compositions were prepared with the requisite sodium concentrations provided by borax and sodium metasilicate pentahydrate in one case, and alternatively by borax and sodium nitrate. The maximum melting rate at 1050°C in the first

FIGURE 3.1. Leaching Behavior of 79-116 Glass as a Function of Waste Loading

TABLE 3.1. Composition of RFP Bulk Ash Glass, 79-160 [TRU-RFP-1(2.33:1)79-161] and Frit 79-161

	Wt%	
	79-160	79-161
TRU-RFP-1 Ash	30.0	--
SiO ₂	26.0	37.2
B ₂ O ₃	12.0	17.2
Na ₂ O	11.0	15.7
Li ₂ O	2.0	2.9
K ₂ O	4.0	5.7
CaO	7.0	10.0
TiO ₂	4.0	5.7
ZnO	4.0	5.7

TABLE 3.2. Characteristics of Laboratory Glass 79-160
~~[TRU-RFP-1(2.33:1)79-161]~~

Viscosity, poise		
at 950°C		360
at 1050°C		110
at 1150°C		44
Bulk density, g/cm ³		2.68
Leaching rate, total wt		
Soxhlet	(24-hr)	1.2
Buffered pH 4	(19-hr)	16
Buffered pH 9	(19-hr)	0
Melting time, hr ^(a)		1
Corrosion rate, 304L SS, 1050°C		
Flux line, μm/day		8
Submerged, μm/day		0

a. Time to melt 300-g batch in a 304L SS cylinder, 4.5 cm dia x 10 cm, at 1050°C.

case was about 20% of the rate achieved with the nitrate. Sodium nitrate melts at 308°C, while the metasilicate melts at 1089°C. The nitrate batch also provides a convenient oxidant for the pyrolysis products and elemental carbon present in the ash. Table 3.3 summarizes data on the alternative batch compositions. Based on these data, glass 79-160B with sodium nitrate was chosen for the pilot scale test. Table 3.4 shows the batch composition that will be used.

CRYSTALLINE WASTE FORMS - J. M. Rusin

The scoping study of sintered ceramic pellets for consolidation of transuranic wastes was completed. Based upon the information developed during this study, it was concluded that the dispersibility of particulate waste residues such as ashes, resins, and filter media can be decreased significantly by choosing appropriate additives, cold pressing the mixture, and sintering at elevated temperatures.

Two nonradioactive wastes characteristic of Rocky Flats Plant operations were selected for the study. One composition represented the residue from fluidized-bed incineration of combustible trash, while the other represented blended wastes from several sources. Four series of samples were studied for each composition as follows: a) neat waste without additives (reference samples); b) waste with glass frit at 50 and 67 wt% levels; c) waste with silica at 50 and 67 wt% levels; d) waste with bentonite clay at 50 and 67 wt% levels. All samples were pressed at 140 MPa and subsequently sintered at temperatures between 700 and 1100°C. The selected additives may improve durability by providing a low-temperature vitreous phase to aid sintering, or by producing stable crystalline reaction phases. Selected samples from each series were characterized by bulk density, true density, distribution of particle sizes following impact, and leaching resistance. Sintering behavior (deformation, disintegration, etc.) was also qualitatively evaluated.

TABLE 3.3. Melting, Corrosion and Leaching Behavior of Alternative RFP Glass Batches

Batch ID:	79-158A ^(a)	79-158C ^(b)	79-159B ^(a)	79-159D ^(b)	79-160A ^(a)	79-160B ^(b)
Glass ID:	79-158	79-158	79-159	79-159	79-160	79-160
Waste loading, wt% TRU-RFP-1	30	30	40	40	30	30
Melting rate at 1050°C	slow	fast	very slow	fast	slow	very fast
Leach rate, total wt% lost						
Soxhlet (24 hr)	4.0	3.8	2.2	2.9	n/a	1.2
Buffered pH 4 (19 hr)	60	89	51	36	n/a	16
Buffered pH 9 (19 hr)	0.3	0.5	0.2	0.2	n/a	0
Corrosion rate (304L SS, 1050°C)						
Flux line, $\mu\text{m/day}$	100	115	42	42	20	8
Submerged, $\mu\text{m/day}$	8	4	1	1	3	0

a. Sodium added as $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$.b. Sodium added as NaNO_3 .

TABLE 3.4. Premelted Batch Composition for TRU-RFP-1 In-Can Melter Test

Component	wt%
TRU-RFP-1 Ash	30.0
KNO_3	7.1
TiO_2	3.3
ZnO	3.3
$\text{Na}_2\text{B}_4\text{O}_7$ (anhydrous)	14.3
CaSiO_3	12.0
Li_2SiO_3	5.1
NaNO_3	13.0
SiO_2	11.9
	100.0

Use of additives generally produced pellets with more desirable characteristics. Materials prepared with silica or bentonite additives produced the best samples, but required higher sintering temperatures ($>900^\circ\text{C}$). The glass frit samples were limited to 700 to

800°C sintering because of excessive melting and expansion at higher temperatures. All additives improved product densities (except for the blended waste at high sintering temperatures), but no additive was consistently superior with respect to density. Sample

behavior during an impact event did not vary significantly with additive or sintering temperature, although the distribution of fines from ash samples was to slightly smaller particles than fines from the blended waste. The fraction of fines smaller than 37 μm (the smallest screen used) ranged from 3 to 20%. Typical values for glass forms in the test are around 10%.

The relative leaching resistance of the four series of samples was evaluated using an accelerated static test with deionized water.

The procedure was to place 1 g of -200 mesh powder in 10 ml of water and hold at 90°C for 72 hr. The dissolved ions removed from the sample were analyzed using an inductively coupled plasma emission spectrometer. The results indicate that additives greatly increase the product resistance to leaching, and that resistance is significantly increased with higher sintering temperatures. For both waste types, pellets formed with 67 wt% bentonite at temperatures above 900°C produced the superior materials.

4. KRYPTON SOLIDIFICATION

G. L. Tingey - Project Manager

The objective of this program is to develop alternative techniques for storing radioactive krypton in a solid matrix. Two techniques are currently being investigated: 1) dissolution of krypton in low-density glass followed by densification at high temperatures and 2) entrapment of krypton in solids during ion sputtering.

SUMMARY

A deposit of stainless steel 3 mm thick containing 2 at.% krypton was generated in a 100-hr continuous sputtering run, demonstrating the reliability of the apparatus and providing samples for property measurements. Krypton has also been loaded into a porous SiO_2 sample at 34 MPa. Loadings of 6 to 7 cm^3 of $\text{Kr}(\text{STP})/\text{g}$ of SiO_2 have been achieved. Releases from these samples are extremely slow and would release <2% of the krypton in 10 yr at 420 C.

KRYPTON ENTRAPMENT DURING SPUTTERING -

G. L. Tingey, E. D. McClanahan and
M. A. Bayne

Krypton can be effectively trapped in sputter-deposited metal matrices by accelerating Kr^+ to the deposit as well as to the target during the sputtering process.⁽¹⁾ Previously, we have shown that krypton can be trapped in many metal systems from relatively pure, crystalline elemental metals to multi-component, crystalline and amorphous metal alloys. Recently we have demonstrated the ability to sputter-deposit thick metallic films containing krypton by sputtering a stainless steel sample 3 mm thick in 100 hr containing 2 at.% krypton. This experiment provided a demonstration of the reliability

of the equipment for extended runs and provided thick krypton-containing samples for measuring the sample properties. The deposit was very brittle and had a network of cracks throughout. It was readily handled, however, and retained the krypton gas very well up to temperatures of about 800 C. Property measurements are not complete, but a preliminary determination of the thermal conductivity yielded a value of about $0.3 \text{ W/cm}^3\text{-}^\circ\text{C}$. The density of the deposit was $7.0 \pm 0.1 \text{ g/cm}^3$ as compared to 7.9 g/cm^3 for the original target material. The density appeared to increase during gas release, which occurred from 800 to 1000°C , perhaps indicating that the lower density results from the krypton rather than being inherent to the sputter-deposited alloy.

DISSOLUTION OF KRYPTON IN LOW-DENSITY SILICA -

G. L. Tingey and W. J. Gray

We have previously reported⁽²⁾ that SiO_2 rods with about 30% porosity will trap and retain about 6 cm^3 of $\text{Kr}(\text{STP})/\text{g}$ of SiO_2 when loaded at a pressure of 34 MPa (5000 psi) followed by densification at 900 C. The form of the krypton in the matrix has not been determined. Two possibilities are considered: 1) dissolution in the glass matrix and 2) trapping of krypton in the very small pores of the SiO_2 . Differentiating between these

two cases is not an easy task, and perhaps the differences are not significant for storage of ^{85}Kr . We have, however, attempted to shed some light on the subject by measuring the krypton content after crushing a sample and classifying it into various particle sizes. The initial results indicate that no significant release of krypton occurs when a krypton-loaded SiO_2 sample is powdered down to about $72\text{ }\mu\text{m}$. However, when the particle size was reduced below $40\text{ }\mu\text{m}$, approximately 40% of the krypton was released. We have interpreted this to mean that most of the krypton was trapped in very fine pores and that about 40% of these are intercepted when the sample is divided into particles $40\text{ }\mu\text{m}$ in diameter.

Although the krypton content of the high-pressure-loaded SiO_2 samples is well below those of the sputter-deposited metals, this

process is attractive because of the very low release rates. We have attempted to quantify the release rate by holding a sample at 420°C for over 400 hr and periodically analyzing the gas evolved. We observed a very low release rate that decreased with time over this period. The fractional release rates measured were as follows:

- 8.3×10^{-7} for the first 140 hr
- 4.5×10^{-7} for the next 193 hr
- 2.3×10^{-7} for the next 72 hr

A plot of these data as a function of time shows that the rate decreases approximately as a function of $t^{1/2}$. Whether this rate decrease would continue for an extended time is yet to be determined. However, extrapolation of these data assuming no further decrease in rate would yield a total release of <2% of the krypton during the first 10 yr if the temperature was maintained at 420°C .

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5. CARBON-14 AND IODINE-129 FIXATION

L. L. Burger - Project Manager

The objective of this program is to develop and demonstrate the technology needed to safely and effectively immobilize iodine-129 and carbon-14 released from treatment of irradiated fuels.

SUMMARY

Preliminary results from Phase III of the cement leach study indicate CO₂ pretreatment and the addition of bentonite or sodium resinate to the cement to be the three most significant factors affecting the iodide leach rate.

A study was started to evaluate six factors suspected of influencing the leach rate of carbonate from carbonate-impregnated cement.

Characterization of solid adsorbents used for iodine recovery suggests the presence of chemical species other than pure I₂ and/or AgI. Iodine loading studies involving methyl iodide, NO₂, and H₂O have shown decomposition of the methyl iodide at 200 C before exposure to the solid adsorbent. Attempts to regenerate iodine-loaded silver faujasite with N₂O were unsuccessful.

Some preliminary comments have been made on criteria for disposal of ¹²⁹I.

IODINE LEACHABILITY - K. D. Wiemers

The first two phases of the study of the leaching of iodine from iodine-impregnated cement involved a parametric investigation of dynamic leaching methods and a screening study of factors affecting the iodine as iodate leach rate.⁽¹⁻³⁾ During this quarter, Phase III of the iodine leachability

study was completed, and the preliminary results from this study are reported here. In Phase III, seven factors suspected of influencing the leach rate of iodide from iodide-impregnated cement were screened using a Plackett-Burman design.⁽⁴⁾ These factors were: iodide solubility; concentration of iodide in the cement matrix; addition of silver ion, barium ion, bentonite, and sodium resinate to the cement; and carbon dioxide pretreatment. Reference 5 described these factors in detail.

Results from the first day of leaching for Phase III were statistically analyzed based on the incremental leach rate, R, cm/day. To determine the relative importance of the factors evaluated, the absolute value of each factor effect was ranked from largest to smallest. The top three factors, beginning with the most significant, were CO₂ pretreatment, addition of sodium resinate to the cement, and addition of bentonite to the cement. The CO₂ pretreatment and addition of bentonite to the cement decreased the iodide leach rate. Adding sodium resinate to the cement raised the iodide leach rate.

Use of HgI₂ as one of the fixation materials necessitated the application of an analytical method requiring longer than predicted analysis time. Therefore, results from the remainder of the leach study will not be available until the next quarterly report.

IODINE RECOVERY - K. D. Wiemers and
R. D. Scheele

Material Characterization

In previous zeolite loading and stripping studies, significant color changes have been observed in the molecular sieve materials. To document for future reference the actual chemical nature of the initial and final sieve materials, a more detailed determination of these color changes was made by heating a sample of iodine loaded (180 mg I/g Ag^om) hydrogen-pretreated, silver-exchanged mordenite to 500°C. Observations were made at 50° increments and are presented in Table 5.1. The results of this study suggest that 1) AgI was present in the loaded material; an increase in the yellow brilliance similar to that of pure AgI was observed between temperatures of 100 and 200°C; and 2) some of the iodine recovered from the gas stream during loading was in a form other than either pure physically adsorbed I₂ or pure AgI; iodine evolved between temperatures of 300 and 500°C.

Further attempts to characterize the initial and final sieve materials will include temperature studies with other related materials and investigation of the feasibility of various surface analytical techniques.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) have been used to aid in characterization.

DSC thermograms for silver-exchanged mordenite and faujasite have none of the characteristic energy excursions found for silver nitrate or silver oxide. The silver nitrate endotherms are very evident for silver nitrate-impregnated silica (AC 6120).

The iodine-loaded silver solid sorbent system showed widely variant results. The hydrogen-reduced silver mordenite began losing elemental iodine at ~300°C. Neither "as received" silver mordenite or faujasite lost weight, except as water, prior to 400°C. At this point a slow weight loss began. Silver iodide was the expected iodine chemical form on all three materials. Based on TGA experiments, it begins volatilizing unchanged at 600°C. The loss of iodine from the iodine-loaded "as received" silver

TABLE 5.1. Ag^om, I Color Characterization as a Function of Temperature

Temperature, °C	Observations
25	Color: 80% maroon, 19% light yellow, 1% gray
100	Color: 95% yellow-tan, 5% bright yellow
150	Color: 80% tan, 20% bright yellow
200	Color: 75% bright yellow, 25% tan
250	Color: 90% bright yellow, 10% tan
300	Color: 95% pink-tan, 5% maroon, I ₂ evolved
350	Color: 50% maroon, 25% pink, 24% cream, 1% orange, I ₂ evolved
400	Color: 99% violet-cream, 1% orange, slight amount I ₂ evolved
450	Color: 50% light yellow, 50% light gray, slight amount I ₂ evolved
500	Color: 50% light yellow, 50% light gray, no I ₂ evolution observed

zeolites, prior to the observed vaporization temperature of silver iodide, may be explained partly by a rate effect due to increased dispersion of silver iodide on the zeolite surface.

The results generally support the previous conclusion that iodine in forms other than AgI can be rather tightly bound to zeolites.

Methyl Iodide Removal

Preliminary studies involving the CH_3I removal efficiency of various adsorbent materials in the presence of water vapor and NO_2 suggested that at temperatures of 200°C , CH_3I decomposed before contact with the recovery bed. Gas chromatographic analysis of the influent indicated the presence of nitromethane, methyl nitrate, methanol, and ethane. Iodine was also detected by using starch paper. Presently the kinetics of the $\text{CH}_3\text{I}/\text{NO}_2/\text{H}_2\text{O}$ reaction are being studied in detail to better characterize the chemical composition of the influent gas used in these iodine recovery studies.

Silver Zeolite Recycle

The free energy for the reaction between N_2O and silver iodide-forming silver oxide and elemental iodine becomes favorable for the reaction to occur at $\sim 400^\circ\text{C}$. A test was carried out to examine this reaction. Iodine-loaded silver faujasite (Ag°f) was exposed to flowing N_2O at temperatures from 25° to about 400°C . No iodine was detected. Thermogravimetric experiments using pure AgI showed no reaction up to 600°C . It is quite likely that there is no kinetic mechanism available, i.e., no intermediate complex that permits the reaction to occur.

CRITERIA - L. L. Burger

A major obstacle to selecting a storage or disposal system for ^{129}I is that criteria have not been established. Thus no standard exists against which the suitability of a process or concept can be judged. Establishment of criteria requires analysis of biological-medical data, individual and population doses, and the environmental (local and worldwide) capacity for the nuclide, including pathways. A risk analysis also is needed which includes the technological and economic penalties associated with control of the nuclide. Specific examples of factors that need to be considered include:

1. In pathway analyses, both continuous releases and burst releases, the chemical form of the iodine released and kinetic and thermodynamic factors should be considered.
2. A waste form should not contain chemical species, or elements capable of forming these species, that are equally or more hazardous than the ^{129}I being sequestered.
3. A waste form must be designed to withstand environmental conditions encountered between manufacture and final disposal, i.e., temperature, physical shock, and water contact. A clear distinction should be made between storage and disposal.
4. Risk analysis should include the benefits of the energy production which created the wastes. A corollary of this criterion is that providing safe disposal should not excessively burden other energy or material resources.
5. The process must be adaptable to ^{129}I from all collection methods.

6. The process should be maintained safely and easily in a radioactive environment.
7. Side streams from the fixation process should be easily recycled to recover any ^{129}I , and waste streams from the process itself should be minor.
8. Economic penalties for the overall ^{129}I control must be reasonable.

Tables 5.2 and 5.3 present data pertinent to the question. It is noted that most of the iodine resides in the ocean and that if all the ^{129}I produced in the nuclear industry by the year 2000 were transferred to the ocean, its concentration would be $8 \times 10^{-15} \text{ Ci/m}^3$. This is seven orders of magnitude below the MPC for uncontrolled area.⁽¹²⁾ However, since it is dose rather than concentration that is important, these figures alone are not definitive. It appears that the total burden of ^{129}I may not be the critical issue.

Further considerations of ^{129}I disposal criteria based on dispersion and upon the suggested 5 mCi/GWe-yr release limit⁽¹³⁾ have been assembled and are undergoing internal review.

CARBON-14 LEACH STUDY - R. D. Scheele

Carbon-14 will most likely be removed from the fuel cycle process as a metal carbonate,⁽¹⁴⁾ and a logical storage or disposal process is immobilization in cement. To evaluate the stability of this proposed waste form, factors suspected of affecting the leach rate of carbonate from carbonate-impregnated cement were screened using a Plackett-Burman statistical design. The six factors studied were: 1) high initial carbon dioxide leachate concentration, 2) solubility of the carbonate compound, 3) carbonate concentration in the cement, and

TABLE 5.2. Natural Iodine Distribution(a)

	<u>Concentration</u>	<u>Total Amount, kg</u>
Sea water	0.052 g/t	7.0×10^{13}
1 km earth's ^(b) crust	0.3 g/t	8.4×10^{11}
Atmosphere	10^{-7} g/m^3	3.8×10^8

- a. Data from Chemical Rubber Handbook, from Mellor,⁽⁶⁾ Bruner,⁽⁷⁾ and Tadmor.⁽⁸⁾
- b. Exclusive of Chile nitrate deposits, which contain about 0.2 I⁽⁶⁾ and as much as 3.3×10^{13} kg of I₂.⁽⁷⁾

TABLE 5.3. Production of ^{129}I by Fission

	<u>Ci</u>	<u>kg</u>
GWe-yr/yr	1.25	7.2
1500 t/yr, reprocessing plant per yr	55	320
Total to yr 2000	10^4	6×10^4
Present inventory ^(a)	35	200
Natural inventory ^(b)	2	1

- a. Estimates of Russell and Hahn.⁽⁹⁾
- b. Assumes $^{127}\text{I}/^{129}\text{I} = 10^{13}$.⁽¹⁰⁻¹¹⁾

addition of the following to the cement,
4) cation which will form a very insoluble carbonate, 5) cation which will form an insoluble sulfate, and 6) air entraining agent

to reduce cement permeability. The statistical levels for these factors are given in Table 5.4. Analytical data are now being collected for the statistical analysis.

TABLE 5.4. Factors for ^{14}C Leach Study

Factors	Minimum and Maximum Statistical Levels	
	Ambient	Saturated
Initial leachate carbon dioxide concentration		
Carbonate solubility, M CO_3^{2-} , SrCO_3 , and K_2CO_3	10^{-5}	8.1
Carbonate concentration, g SrCO_3 or K_2CO_3 /g dry cement	0.03	0.15
Excess Sr^{+2} additive, g $\text{Sr}(\text{NO}_3)_2$ /g dry cement	0	0.15
Sodium resinate additive, g Na resinate/g dry cement	0	0.01
$\text{Ba}(\text{NO}_3)_2$ additive, g $\text{Ba}(\text{NO}_3)_2$ /g dry cement	0	0.03

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6. WASTE MANAGEMENT SYSTEM STUDIES

J. V. Robinson - Project Manager

The objectives of this program are to evaluate alternative systems for treatment and disposal of radioactive wastes and to develop information required to ensure effective communication with the public.

SUMMARY

No progress report was submitted for this period. The next quarterly report will cover results of the six-month period.

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7. WASTE MANAGEMENT SAFETY STUDIES

W. K. Winegardner - Project Manager

The objectives of this program are to aid in assuring that waste management and its inherent safety function are given proper emphasis as various alternative fuel cycles become viable; develop assessment methods; identify portions of waste management systems that could benefit by safety design emphasis.

SUMMARY

The first draft was completed of a report that describes and demonstrates an analytical approach for evaluating predisposal waste management systems of alternative nuclear fuel cycles. Assessment of ^{85}Kr management with and without recovery, to provide insights into tradeoffs between waste management by accumulation and by dispersion, continued. Initial projections of the type, frequency, and radiological consequences of accidents during krypton recovery/storage operations were completed.

FUEL CYCLE ASSESSMENT - P. J. Pelto

A first draft was completed of the report Comparative Techniques for Alternative Fuel Cycle Waste Management Systems. Selected summary material is abstracted below.

...The present nonproliferation policy in the United States has resulted in a re-evaluation of nuclear fuel cycle concepts. The choice of a nuclear fuel cycle involves considerations of many important economic, safety, and environmental considerations. Some examples presently being examined in DOE research and development programs include nonproliferation characteristics and uranium resources

utilization. Radioactive waste management is another consideration of importance.

...This report describes an analytical approach for evaluating predisposal waste management systems for alternative nuclear fuel cycles. The initial application of this approach to the once-through fuel cycle and the coprocessed $\text{UO}_2\text{-PuO}_2$ fuel cycle is reported. The purpose of this initial application is to demonstrate the analysis approach, provide relative comparisons between the once-through and the coprocessed fuel cycle waste management operations, and to identify information needs required for a more comprehensive analysis.

DISPERSION/ACCUMULATION TRADE-OFF ASSESSMENT - P. J. Mellinger

Assessment of ^{85}Kr management techniques, with and without recovery, is being used to provide insights into trade-offs between management by accumulation/containment and by dispersion/dilution. During the recovery and storage operations, unforeseen accidents can occur. Projections of the type, frequency, and radiological consequences of such accidents were completed. Accidents were postulated for a cryogenic

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krypton recovery process and krypton cylinder filling, interim storage, long-term storage, and decommissioning. Work continued on occupational dose calculations for the cryogenic

recovery and storage processes. Work was begun on the report that will describe this trade-off study.

8. WASTE ISOLATION SAFETY ASSESSMENT PROGRAM

A. Brandstetter - Project Manager

M. A. Harwell - Assistant Project Manager

The objectives of the Waste Isolation Safety Assessment Program (WISAP) are to:

- 1. develop the capabilities needed to assess the post-closure safety of geologic repositories*
- 2. obtain scientifically defensible generic and site-specific data necessary for safety assessments*
- 3. provide, as needed, studies to further support these data and analyses*
- 4. demonstrate the assessment capabilities by performing analyses of reference sites*
- 5. apply the assessment methodology to assist the National Waste Terminal Storage Program in site selection*
- 6. perform repository site analyses responsive to the time schedule and to the level of sophistication required to meet the licensing needs of the National Waste Terminal Storage Program.*

TASK 1 - RELEASE SCENARIO ANALYSIS -

G. L. Benson

Work was conducted on the salt dome reference site analysis for use in the Preliminary Information Report (PIR). In addition to supplementing the discussion of disruptive phenomena and expanding our analysis of the natural dissolution and human-induced solution mining scenarios, work was carried out on the possible hydrologic flow rates for the base case solution mining scenario. Using the three-dimensional finite element code, DAVIS FE,⁽¹⁻³⁾ a simplified model of the near-dome hydrology was created for calculating the possible flow rates through the repository. The model indicated that within 300 to 500 years after initiation of the breach it would be possible to dissolve a volume of salt representing the entire repository. Since it is impossible to describe adequately how the solutioning might occur around the repository, it was pessimistically assumed that poten-

tially the entire repository inventory could be vulnerable to leaching after 300 years. It is important to note that this model was developed based upon regional geohydrologic data because of the lack of near-dome information. For this reason, there is much uncertainty in the results; however, because of the conservative assumptions made during the model development, the results are also assumed to be conservative.

Work is under way in an attempt to provide geochemical bounds for the ground waters entering and leaving the repository. The importance of bounding the geochemical parameters of the transport solutions has become increasingly obvious as work on the PIR continues. This point is readily exemplified by the fact that both the K_d values and solubility coefficients of the various radionuclides can vary by orders of magnitude, with only small changes in pH and other geochemical parameters.

TASK 2 - WASTE FORM RELEASE RATE ANALYSIS -

D. J. Bradley

A subcontractor workshop was held at the Battelle Seattle Research Center. Presentations on related activities at Los Alamos, Sandia, the U.S. Geological Survey, and Atomic Energy of Canada, Ltd., were given. A workshop document is being prepared.

Spent fuel study activities included starting oxidation effect scouting tests on UO_2 , obtaining the distribution of the radionuclides in spent fuel leach samples using shielded electron microprobe, and completing spent fuel particle size analysis for input into the PIR analyses.

High-level waste glass leaching studies activities included receiving data on the release of technetium from simulated waste glass. In other activities, autoclave studies of the hydrothermal reactions of doped and undoped glass beads in synthetic ground waters were partially completed. The rest of the tests will be completed by the end of the summer quarter. Analyses of the results of the current autoclave tests show that temperature, time, and solution composition all influence the behavior of waste glass in hydrothermal experiments. In a cooperative experimental study by PNL and Lawrence Livermore Laboratories, leach rates of simulated high-level reactor wastes are being compared using two different leach methods. PNL uses a modification of the standard IAEA leaching method, and LLL is using a new single-pass leaching system in which fresh leachant solution is continuously flowed over the sample. Initial analyses of the leachant solutions for silicon, cesium, and strontium were made with the inductively coupled plasma emission spectrometer. Results were mixed. The apparatus is an effective, efficient means of analyzing the solutions

for a number of elements; however, acidification of samples affects the accuracy and precision of the analyses.

TRU waste studies at Brookhaven National Laboratory (BNL) this quarter analyzed an incinerator ash sample from a Rocky Flats rotary kiln. The results of the BNL analysis are based upon a DC arc emission spectroscopy measurement of a 5-g sample. They show that the characteristics of the ash are significantly different from the simulated ash composition used previously. Formulation work using "cold" ash with cement solidification indicated that the ash behaves much differently from the simulated ash compound used earlier. This difference is largely attributable to the physical structure of the ash. The cement waste form developed for the experimental program consists of 30 wt% ash, 30 wt% cement, and 40 wt% water. The ash content of this formulation is lower than that developed for the simulated ash because of the significantly higher water content requirements of the actual ash.

Leaching mechanism studies were conducted at Argonne National Laboratory (ANL). Experiments have recently been started at ANL to study the feasibility of using extended x-ray adsorption fine-structure (EXAFS) to study the bonding of actinides in silicate glasses. EXAFS could prove to be an invaluable tool in understanding glass structure because of the technique's ability to yield specific structural data even in complex multicomponent systems. Structural information contained in EXAFS data may also be valuable in determining the form in which the actinides exist in leach solutions. Also, static leaching measurements of PNL glass beads were started at ANL in an oxygen-free environment. The preliminary results show a varied response to temperature and some evidence that the leached material is not bound in siliceous fragments.

TASK 3 - RELEASE CONSEQUENCE ANALYSIS -

J. R. Raymond

The WIPP Site Comparison Release Consequence Analysis was completed. The analysis serves as a mutual check of the WISAP hydrologic models with Sandia models by providing an independent check of the calculations. PNL performed the hydrologic modeling by using essentially the same input parameters and geohydrologic interpretation as Intera used.

The WISAP hydrologic modeling methodology includes various levels of modeling capability, from simple one- and two-dimensional analytical methods, to complex three-dimensional models with heat and solute transport. The conceptual model of the WIPP site hydrogeology required the use of the intermediate level VTT model, which is a two-dimensional, multilayer, finite difference model solving the Boussinesq equations for ground-water flow and allowing the various layers to be connected via an interaquifer transfer coefficient.

The results of the WISAP modeling of the WIPP hydrologic system indicate that for the same conceptual model (i.e., hydrologic interpretation) essentially the same results are achieved as those obtained with the Intera Model. This should be expected, since the various hydrologic codes use essentially the same flow equations.

Work was completed on the PIR (Salt Dome) hydrologic model for the bounding test case. The near-dome hydrologic model was completed, and model runs were made to generate cavern flow rates and velocities for source terms (leach rate and nuclide concentrations) and to determine salt dissolution rates. The leach rate model was modified to handle the multiple distribution of particle sizes for the spent fuel and to consider the progres-

sive exposure of the repository fuel inventory with time (as salt is dissolved from the cavern).

TASK 4 - SORPTION/DESORPTION ANALYSIS -

R. J. Serne

The first draft of the second Task 4 workshop document was completed. A manuscript on plutonium speciation in slightly oxidized ground waters was submitted to the journal Science. An overview speech on the interface of Task 4 with Task 2 was presented at the WISAP Task 2 Workshop in Seattle on May 24-25. Recommendations for Waste-Rock Interactions program plans were prepared for use by the Earth Sciences Working Group, which has been charged to develop a master Earth Sciences Technical Plan that DOE will submit to Congress in support of budget requests. An invited overview paper, "Methods Used to Estimate Geochemical Aspects of Radionuclide Migration from Waste Repositories," was presented at the annual American Nuclear Society meeting in Atlanta.

Geologic sample needs and sampling protocol for representative samples of Gulf Coast salt dome sediments were discussed with the Office of Nuclear Waste Isolation. Discussions were held with geologic site managers with the objective of expediting the receipt of representative samples from which an adequate K_d data base can be developed for use in site qualification and licensing.

Work continued in evaluating sorption-desorption methodologies. Argonne National Laboratories (ANL) investigated the dependence of $K_d(\text{Cs})$ on tracer cesium concentration using oolitic limestone and a synthetic ground water. The ANL results show that the $K_d(\text{Cs})$ values increase as the cesium concentration decreases. These results disagree

with classical ion-exchange theory, which predicts that K_d values should become independent of tracer concentration at low concentrations. The results might help to explain the high variability of $K_d(\text{Cs})$ values obtained for limestone in the controlled sample program. In additional experiments, ANL personnel monitored breakthrough from intact limestone columns using rock equilibrated water.

At Los Alamos Scientific Laboratories (LASL) experiments continued to evaluate K_d dependencies on methodology. Results show that the continued use of blanks tends to bias K_d calculations to lower values. If no rocks are present, then nuclides such as rare earths and actinides exhibit substantial wall adsorption. However, if crushed rocks are present, very little wall adsorption occurs. Further experiments on the effects of phase separation were performed on samples of ground water. Influent samples (prior to contact with rock) and effluent samples were filtered before and after centrifugation. Unexpectedly, both solutions contained similar amounts of filterable material. Additional experimentation was performed and the results raise a question as to what size fraction species should be considered transportable in ground water. Other experiments at LASL investigated the sensitivity of K_d measurements to variations in particle size of crushed rock, temperature, and contact time for the nuclides plutonium, americium, and uranium. The K_d values for plutonium and americium were not significantly affected by particle size but were by contact time. Temperature effects were complicated by the experimental method of K_d calculation. Variations among replicates were considerable, with differences averaging more than an order of magnitude. Using the same experimental

procedures and materials, two independent investigators found general agreement (20% variability) for the nuclides cesium, barium, strontium, cerium, and europium. Column experiments were started at LASL on crushed tuff, crushed granite, and intact or fractured core material to compare with batch K_d results.

Oak Ridge National Laboratory (ORNL) researchers studied the effects of clay purification, pH, and temperature on sorption of cesium, strontium, europium, and americium. Purification of clays and clay drying techniques did not affect the sorption of strontium onto several montmorillonite clays. Other experiments showed that the pH of salt brines can significantly affect K_d values. The sorption of cesium, strontium, and europium onto Al_2O_3 from salt brines was also studied. The differences in K_d values for strontium and cesium between room temperature and 80 C were determined for salt brine waters. The results suggest that at the higher temperatures surrounding waste canisters, multivalent cation adsorption may be preferred over monovalent cations. The adsorption of americium as a function of pH from a granitic ground water and salt brine was studied for several minerals.

At Lawrence Livermore Laboratories (LLL) dynamic sorption experiments on intact cores of tuff continued. The breakthrough of Sr^{2+} and TcO_4 was observed and compared to results from batch K_d experiments. Batch K_d work with plutonium was performed, with complications caused by container adsorption and filtration.

Studies at the Georgia Institute of Technology show that the adsorption of cesium onto basalt is not significantly affected by the presence of oxygen. The results support thermodynamic predictions.

At Pacific Northwest Laboratory (PNL) work continued on batch adsorption-desorption experiments using 12 minerals, 4 rocks, and 4 generic ground waters. Work also continued on installing all of the WISAP-generated K_d data into the computerized information retrieval system. At LLL work continued on storage of thermodynamic data required for nuclides in the Levine code. At LBL the computer code MINEQL Stanford+1 was received for use on the Lawrence Berkeley Laboratory computer. Final feasibility studies for in situ testing were made at the Climax Stock, NTS, and a proposal for a tracer study has been written.

Long-term studies of rock-water interaction were continued. Long-term studies (6-month duration) were performed with 20 g of crushed rock in contact with 300 ml of the appropriate ground water. Accelerated weathering of the rocks under both oxidizing and oxygen-free conditions is being performed. No surface textural differences appear to exist between rocks weathered by oxidizing or by reducing conditions.

The transport of kaolin particles through crushed basalt is under investigation. At a velocity of 0.8 cm/min, the majority of the Kaolin particles (70 to 85%) are retained within the basalt column. Studies were also performed this quarter to determine the ability of basalt to adsorb technetium under low oxygen conditions. These studies show that the adsorption of technetium by basalt is dependent upon the mass of technetium present.

Researchers at PNL have determined the solubilities of $^{239}\text{PuO}_2(\text{s})$ and $^{239}\text{Pu}(\text{OH})_4(\text{s})$ under natural environmental conditions. They used these data to predict the nature of solid phases present in contaminated soils and the total concentration of plutonium that can be expected in soil solutions when these plutonium solids are present. The sorption of plutonyl by kaolinite, montmorillonite, vermiculite, and biotite was also studied.

Finally, a major effort was performed during this quarter to generate data for the Hainesville salt dome.

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9. WELL-LOGGING INSTRUMENTATION DEVELOPMENT FOR SHALLOW LAND BURIAL

R. L. Brodzinski - Project Manager

The objectives of this research program are to develop appropriate well-logging equipment capable of determining ^{90}Sr , ^3H , and the transuranics at sensitivity levels which will provide useful information for the proper operation of a shallow land burial site.

SUMMARY

Experiments on the neutron activation analysis of ^{90}Sr have been initiated. Data reduction of the Phoswich detector ^{90}Sr experiments has been continued, and an open literature publication describing this technology is being prepared.

A tritium logging system has been designed which can measure elemental tritium or tritiated water either as liquid or vapor.

Three descriptions of technology developed in this program were presented at the Symposium on Recent Advances in Nuclear Analytical Methods, April 1-6, 1979, in Honolulu, Hawaii.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING ^{90}Sr - R. L. Brodzinski, T. M. Tanner, and H. L. Nielson

Experiments on the neutron activation analysis of ^{90}Sr have been initiated. Several thermal neutron irradiations have been completed in a subcritical ^{252}Cf /enriched ^{235}U neutron multiplier facility. The gamma-ray spectra from the irradiated samples are currently being interpreted to determine the quantities of ^{91}Sr generated.

Data reduction from the Phoswich detector experiments for the determination of ^{90}Sr

has been continued, and an open literature publication is being prepared describing the utility and sensitivity of this technique.

A paper entitled "A Well-Logging Technique for the In Situ Determination of ^{90}Sr ," by R. L. Brodzinski and H. L. Nielson, was presented at the Symposium on Recent Advances in Nuclear Analytical Methods, April 1-6, 1979, in Honolulu, Hawaii.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING TRITIUM - C. Menninga and R. L. Brodzinski

A tritium logging system has been designed which can measure elemental tritium or tritiated water either as liquid or vapor. When sampling air for both elemental tritium and tritiated water vapor, the various stages of the analytical system are: 1) a filter to remove particulate matter, 2) a catalyst (probably palladium) to convert elemental tritium (and tritium-free hydrogen carrier gas) to water, 3) a thermoelectric cold trap to collect the water vapor generated, 4) a reducing chamber (probably an interchangeable canister of heated magnesium), and 5) an anticoincidence shielded gas proportional chamber supplied with propane to provide a suitable counting gas mixture.

When sampling water the same process stages are utilized as for sampling air with the following pretreatment stages incorporated: 1) a filter to remove particulate matter from the water, 2) a metering device to select an appropriate sample volume and to mix it with an aliquot of tritium-free air, and 3) a reducing chamber (again probably an interchangeable canister of heated magnesium) to provide an input mixture of hydrogen and air to the sampling system described above.

The gas proportional counter system consists of an annular tritium counting chamber with porous walls and both internal and external anticoincidence chambers. Pulse height discrimination is used to further

reduce extraneous events in the tritium counting chamber, and, if required, pulse shape discrimination can also be employed.

DEVELOPMENT OF LOGGING SYSTEMS CAPABLE OF MEASURING ACTINIDES - R. L. Brodzinski

Papers by R. L. Brodzinski entitled "A Technique for the In Situ Determination of Transuranic Elements in Relatively Inaccessible Locations" and "A Technique for In Situ Moisture Level Determinations in Relatively Inaccessible Matrices" were presented at the Symposium on Recent Advances in Nuclear Analytical Methods, April 1-6, 1979, in Honolulu, Hawaii.

10. MONITORING AND PHYSICAL CHARACTERIZATION OF UNSATURATED ZONE TRANSPORT

S. J. Phillips - Project Manager

The objective of this project is to develop monitoring instrumentation systems and burial media-waste characterization methods to evaluate the migration of contaminants from disposal sites for low-level solid wastes.

SUMMARY

Laboratory testing of radionuclide transport in unsaturated soil columns was completed under the FY-1979 project objectives. Cobalt, tritium, strontium, and iodine were evaluated for mobility in Hanford sediments under several conditions, including 1) variable flux density, 2) homogeneous/heterogeneous configurations, 3) isotope concentration, and 4) contaminant solution volume/sediment volume ratios.

Instrumentation of a field test site was completed. This site is located adjacent to a retired radwaste burial site and is used to monitor atmospheric and soil conditions capable of inducing the transport of radionuclides from burial sites. Data from instruments installed within this site is being collected and analyzed.

LABORATORY - G. W. Gee and A. C. Campbell

The flow of water and radionuclides and sorption of radionuclides within partially saturated geohydrologic media is an important consideration to radioactive waste burial. To quantify water flow and radionuclide migration from shallow land waste burial sites, tests determining water flux, retardation, and distribution coefficients

(K_d s) are being conducted. K_d analysis of cobalt, tritium, iodine, technetium, and strontium in two different salt solutions have been analyzed.

Layered columns of Hanford soil sediments were tested under partially saturated conditions. Flow rates of 1.9 cm/day were used with tritium, ^{125}I and ^{60}Co -EDTA pulse tracers in a low salt solution [0.15 M NaNO_3 , 0.01 M KNO_3 , and $0.002 \text{ M Ca(NO}_3)_2$] to more closely approximate field conditions.

A curve-fitting routine (Wierenga, personal communication 1979,) determined from effluent data the retardation factors used in calculating column distribution coefficients (K_d) of the isotopes. K_d values were calculated using the equation

$$K_d = (R-1) \frac{\theta}{\rho}$$

where

R = the retardation factor

θ = the volumetric water content
(cm^3/cm^3)

ρ = the soil bulk density (g/cm^3).

Calculated K_d values were then compared with their corresponding tracer breakthrough points, which are the pore volumes of effluent representing 50% of the influent concentration. Figure 10.1 shows the lower calculated K_d values corresponding to the lower

FIGURE 10.1. Comparison of Calculated K_d Values and Column Tracer Breakthrough Values for Soil B

tracer breakthrough values. Strontium breakthrough values for two additional columns of soil B were 5.05 and 7.14 pore volumes. Their calculated K_d values were 0.638 and 0.753, respectively. The linear regression line of Figure 10.1 predicted values of 0.620 and 0.932, respectively. Recognition of the K_d breakthrough value relationship permits preliminary comparisons between the experimental parameters.

Tracer breakthrough values did not differ significantly from those of the individual soils for each tracer. Ranges of tracer breakthrough values for the soils are listed in Table 10.1. Tritium exhibited behavior typical of either soil. The higher ^{125}I breakthrough values of the layered system are attributed to soil A. Soil A also influenced movement of the cobalt complex. These tests indicate that tracer movement is impeded by the soil with the greater retentive properties, but further experiments are advised.

Columns of soil A had previously retained 70% of a $^{60}\text{Co-EDTA}$ pulse. In the layered

columns, where soil B was added on top, only 14 to 20% of the cobalt was retained. The maximum $^{60}\text{Co-EDTA}$ ever retained by soil B in prior tests was 12%, and the average 6%. Cobalt that is not complexed with EDTA is highly adsorbed by the Hanford soils. Replacement in the EDTA complex by another cation made the cobalt readily available for adsorption. This cobalt exchange mechanism within the A columns was limited because subsequent tests on the same columns showed very little retention. Monitoring of the column effluents for EDTA on layered columns using a "new" A layer would have verified this explanation.

Variations in water flux of the tracer pulses did not influence breakthrough values for ^3H , $^{60}\text{Co-EDTA}$ and ^{95}mTc . It was expected that lower flow rates would result in greater sorption, and therefore greater breakthrough values. The lines in Figure 10.2 connect consecutive column runs. Technetium breakthrough exhibited no change during the 25-fold increase in water flux. Both cobalt and tritium showed slightly

TABLE 10.1. Tracer Breakthrough Values, Pore Volumes

	^3H	^{125}I (20 ppm I)	^{60}Co -EDTA
Soil B	0.96-1.20	1.04-1.05	1.24-1.37
Soil A	1.16-1.17	-	2.15
Layered B Soils A	1.13-1.20	1.12-1.24	2.12-2.20

FIGURE 10.2. Column Tracer Breakthrough Values as Influenced by Solution Flux Rates for Soil B

(from 0 to 12%) greater tracer breakthrough values at the higher water flux. However, a range of breakthrough values existed at each flux level for each isotope. Different values were obtained from different columns. Two tritium and cobalt columns are shown to illustrate differences between columns and tracers in their response to increased fluxes. In addition, Co-EDTA measurements made at an intermediate flow rate with other columns of soil B yielded breakthrough values greater than those at the high flux levels. Movement of radionuclides under high versus low flux conditions would be more serious because of the increased volume of liquid and nuclide moving. Testing of layered columns at varying flow rates is suggested for comparison with the observed trend of soil B.

Laboratory studies completed to date suggest that 1) distribution coefficients of those radionuclides studied are not a function of saturation; 2) column distribution coefficient determinations are superior to batch-type determinations; and 3) distribution coefficients vary with radionuclide concentration at low levels.

PHYSICAL MODELING - G. W. Gee and K. O. Schwarzmiller

The objectives of this task for FY-1979 were completed during last quarter.

FIELD MONITORING - S. J. Phillips, K. O. Schwarzmiller, and M. D. Campbell

Characterizing and monitoring shallow land radioactive waste burial sites require in

situ installation and operation of sensors capable of measuring radionuclide migration and environmental parameters. Construction of a field test site has been completed and instruments installed capable of monitoring mass and energy balance parameters. These parameters control the rate and magnitude of water and radionuclide transport at radwaste burial sites. A field test facility was constructed to use for evaluation of controlled monitoring systems. Additional instruments and transducer systems have been recently installed at this facility to measure the energy budget within the geologic media.

To permit evaluation of the effects of increased precipitation on radionuclide transport, the test facility is equipped with an irrigation system (Figure 10.3) that applies artificial rainfall over one-half of the facility. This artificial rainfall is applied at about the same frequency as ambient storm events in such a way as to double the amount that has actually fallen.

It is hypothesized that additional rainfall may increase the movement of radionu-

FIGURE 10.3. Irrigation System at Test Facility

clides through the geohydrologic system. To test this theory, downwell monitoring of radionuclides is being done routinely. To permit this monitoring, cobalt and tritium contaminated sediments have been emplaced within discrete layers within the test facility. Cobalt-60 is actively monitored with a sodium-iodide detector system and tritium is passively monitored by destructive testing using liquid scintillation.

11. DETECTION AND CHARACTERIZATION OF MOBILE ORGANIC COMPLEXES OF FISSION PROJECTS

J. A. Franz - Project Manager

The objective of this project is to determine the important mobile or volatile organic complexes of fission and activation products found in the storage of low-level wastes in shallow land burial facilities.

SUMMARY

During this quarter Tc(III, IV and V) citrate complexes have been prepared. Methods have been formulated for overcoming mixed oxidation state products, with positive results being observed in the Tc(III-IV) citrate solution mixture. The Tc(III) component of this mixture can be oxidized to Tc(IV) with iodine. Because ESR studies have been hampered by difficulties with equipment, arrangements have been made with another facility to conduct the studies.

STUDY OF MOBILITY CHARACTERISTICS OF ORGANIC COMPLEXES - L. Y. Martin and J. A. Franz

Considerable progress has been made this quarter in the preparation of Tc(III, IV and V) citrate complexes that will be used in ESR studies. The preparation of these complexes has been described by Münze.⁽¹⁻³⁾ Table 11.1 provides pertinent data on their characterization and preparation. Much time was spent in our preparation of Tc(V) citrate because of ambiguities in published accounts of the preparation of these complexes. Tc(V) citrate is a pale turquoise-colored product with a characteristic absorption band in the visible region at ~700 nm (25).^{*} Reduction

of TcO_4^- using SnCl_2 (0.05M in 0.1M HCl, concentration determined by iodometric titration) where the Sn/Tc molar ratio was 1:1 and the citrate/Tc molar ratio was 9:1 (as specified in the literature) was producing Tc(IV) citrate, a rose or violet colored solution with an absorption band at 560 nm. Tc(V) citrate was eventually produced by precomplexing the SnCl_2 with citrate (1:1) and using this as the reducing agent. This Sn(II) citrate complex is functioning as a milder reducing agent than SnCl_2 .

Even under these conditions a trace amount of Tc(IV) citrate complex still appears to form, as can be seen in the spectrum in Figure 11.1. The 560 nm band of Tc(IV) has shifted slightly to higher energy 520 nm. A mixture of oxidation state products (III and IV) was also observed during the preparation of Tc(III) citrate, as seen in Figure 11.2. The ease with which the IV oxidation state product forms confirms the stability of IV oxidation state in the chemistry of technetium. We are taking two approaches to overcoming the difficulties of mixed oxidation state products: 1) chromatographic separations of the mixed products and 2) modified synthetic techniques. Encouraging results have been observed concerning approach 2. Treating a Tc(III)-(IV) citrate mixture with I_2 results in the oxidation of the III component to IV. The blue-green

^{*}Molar absorptivity.

TABLE 11.1. Characteristics of Technetium Citrate Complexes

Oxidation State	Color	Sn(II)/Tc(a)	Citrate/Tc(a)	pH	UV - Visible Absorbances, nm	Comments
III	Green	4	~30	-	800(150), ^(b) 640(~200)	Extremely air-sensitive
IV	Violet	2	~10	-	520(425, sh 290(3600) sh 245(8000)	Reasonably air-stable
V	Pale turquoise	1	9	7	700(27), sh 290(3600)	Easily reduced to IV

a. Molar ratios.

b. Molar absorptivity.

FIGURE 11.1. Mixture of Tc(IV) and (V) Citrate
Concentration $3.80 \times 10^{-3}M$

solution slowly changes to a magenta-colored solution as the I_2/Tc molar ratio slowly increases. This change in the UV spectrum is represented in Figure 11.2. Only a trace of the 640 nm Tc(III) band is visible at $I_2/Tc = 3.48$. We plan to use chlorine water on Tc(IV) and (V) citrate mixture and hope to oxidize the IV component to the V. The prepa-

ration of Tc(III) citrate will be repeated using a freshly prepared Sn(II)-citrate solution and rigorously excluding all oxygen.

ESR examination of these complexes has been delayed by unforeseen equipment difficulties with onsite facilities. We have since made arrangements with an offsite facility to conduct these studies.

FIGURE 11.2. Oxidation of Tc(III) Citrate by I_2

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12. ELECTROPOLISHING FOR SURFACE DECONTAMINATION OF METALS

R. P. Allen and H. W. Arrowsmith - Project Managers

The objective of this program is to develop electropolishing and related metal cleaning and finishing techniques into an integrated large-scale decontamination system capable of decontaminating large volumes of TRU and other surface-contaminated solid waste.

SUMMARY

Testing was completed on an alternative alkaline electrolyte for Rocky Flats. The major advantage of this electrolyte is the formation of a filterable precipitate that contains essentially all the plutonium or beta/gamma contamination. Disadvantages include poor throwing power and the need for substantially higher current densities and operating temperatures.

An effective anti-splatter compound has been identified that should facilitate the sectioning of contaminated components using plasma arc torch cutting techniques. This spray-on film prevents adherence of dross at cutting distances as close as 6 in.

Some promising fixatives have been identified for containing the contamination on glove boxes and other components during disassembly and sectioning operations. Tests show that these fixatives are readily removed in the vibratory finisher.

Modifications to the vibratory finishing system to improve its operation with steel media and its rinsing capabilities include

- a new vibrating tub that doubles the drain capacity
- a containment lid to reduce splashing
- design of a new sludge tank
- installation of a spray washer system.

Detailed criticality analysis on the present vibratory finisher indicates that the sludge tank will be the limiting unit for criticality safety in the vibratory finishing system.

The ability to decontaminate small items without racking has been demonstrated by using a barrel electropolishing system to remove uranium contamination from molybdenum.

DECONTAMINATION STUDIES

To evaluate an alternative alkaline electrolyte developed at Rocky Flats, 50.6 ft² of transuranic-contaminated stainless steel from Hanford and Rocky Flats glove boxes was processed. The removed transuranic materials precipitated out of solution and became part of the approximately 32 g of sludge per liter of electrolyte that was formed during electropolishing. Filtration removed most of this sludge and radioactivity from the electrolyte. The ability of this electrolyte to precipitate contaminants indicates that its use would be an effective approach for reducing exposure in decontamination operations involving high contamination levels.

Disadvantages of the alkaline electrolyte included poor throwing power (about one-sixth that of phosphoric acid) and the need for higher current densities and operating

temperatures. Poor throwing power would make this electrolyte unsuitable for barrel electropolishing and in situ systems. The high current densities would necessitate heavy, bulky racks and leads, which are cumbersome and increase the handling time required for processing material. The high temperatures (70 to 90°C) required for optimum decontamination would cause vaporization of the electrolyte and contamination of nearby surfaces.

PRETREATMENT STUDIES

Modifications to the vibratory finishing system have been completed. A new vibrating tub was designed and installed that doubled the drain capacity of the previous tub. This should increase compound flow through the machine and, thus, more effectively remove contamination from the vibratory finisher. The compound addition system was changed to provide for adding liquid compound more uniformly into the vibrating tub. A containment lid was also installed to reduce the splashing of the liquid and to minimize the spread of contamination from parts introduced into the machine.

Supporting equipment for the vibratory finisher has also been improved. A commercial dishwasher (Figure 12.1) designed for minimal water use was installed in the sectioning and pretreatment facility as a final rinse for material processed in the vibratory finisher. Initial testing indicates that this will enhance decontamination and reduce process time.

A new sludge tank for the vibratory finisher has also been designed. Its main features include a reduced volume to minimize secondary liquid waste and a slab geometry to provide a greater degree of criticality safety. A criticality analysis of the new sludge tank indicates that the new slab geom-

etry sludge tank, with full water reflection, will remain subcritical to a plutonium concentration of 40 g Pu/l and, with nominal water reflection, will have $K_{eff} \leq 0.95$ to a plutonium concentration of 80 g Pu/l. The volume of this tank will be 80 l.

A detailed criticality analysis was also conducted on the present vibratory finisher. The calculated K_{eff} at a plutonium density of 1000 g Pu/l in the interstitial solution was, with 1-in. water reflection, $K_{eff} = 0.77$ and, with 5-in. water reflection, $K_{eff} = 0.87$. Thus the vibratory finisher can tolerate a higher plutonium solution concentration than can the sludge tank. Previous experience has shown that higher radionuclide concentrations are to be expected in the sludge tank than in the vibratory finisher. Therefore the sludge tank will be the limiting unit for criticality safety in the vibratory finishing system.

To facilitate disassembly and sectioning operations, studies were initiated to evaluate the effectiveness of various substances to fix smearable surface contamination. Initially, five substances were tested for ease of application, drying time, durability, method of removal, and compatibility with selected decontaminants. Other characteristics evaluated included flammability, odor, and safety hazards.

Two substances were identified as being most useful: a polyvinyl alcohol and a polybutyl dispersion. Both of these are commercially available. The polyvinyl alcohol forms a tough, clear, very durable film. A light film, <1 mil, is sufficient to fix contamination. The film can be removed with a caustic solution and is readily removed by the vibratory finisher. The polybutyl dispersion forms a resilient, durable, translucent film. A light film, <1 mil, will fix contamination. Films of 1 mil or more can be stripped intact.

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FIGURE 12.1. Commercial Dishwasher Used to Rinse Material Processed in the Vibratory Finisher

A pressure sprayer was developed capable of quickly applying either fixative over large areas with minimal disturbance to the contamination. The sprayer consists of a pressurized reservoir, a connecting hose, and a wand equipped with a specially fabricated spray nozzle. Only the wand and hose enter the contaminated area.

The usefulness of these fixatives was demonstrated during operations in a transuranic-contaminated facility. The facility had contamination levels of 4×10^6 dis/min·100 cm² on horizontal surfaces. Entries made before the use of the fixatives resulted in a contamination level of 40,000 dis/min·100 cm² on personnel's protective suits. Similar entries made after applying the polyvinyl alcohol to the work area resulted in no detectable contamination on personnel protective suits. During a subsequent entry into

this same facility, the entire floor area was sprayed with the polybutyl dispersion. Entries made after this application resulted in contamination levels of only 600 dis/min·100 cm² to personnel's shoe covers.

SECTIONING STUDIES

Significant achievements in sectioning studies included installation and testing of the plasma arc torch in the stainless steel sectioning and pretreatment facility. In addition, an effective anti-splatter compound has been identified that should substantially facilitate the sectioning of contaminated components using plasma arc torch cutting techniques. This spray-on film, which was selected after analysis of five anti-splatter compounds, prevents adherence of dross at cutting distances as close as 6 in. It has

also been determined that the resulting film can be readily removed from the metal surfaces by processing in the vibratory finisher.

CRITICALITY SAFETY/CONTAMINATION MEASUREMENT STUDIES

The plutonium solution assay system developed by Los Alamos Scientific Laboratory for monitoring process solutions and effluents has been delivered and is now operational. The detection limit with this system at the 3σ level is 0.7 MPC for plutonium and 0.01 MPC for americium for a 10,000 sec count. This detection limit can be further improved by concentrating the samples.

ELECTROPOLISHING TECHNOLOGY

Studies are under way to investigate the effectiveness of barrel electropolishing techniques (Figure 12.2.) in reducing contamination levels and eliminating the need

for racking. A rotating barrel (9 in. dia by 8 in. long) shown in Figure 12.3 was modified by replacing the standard button contacts with bolts that extend 4 in. into the barrel to prevent stacking of the 4-in.² test plates. About 324 in.² of surface area could be electropolished at any one time using this barrel.

Tests were also conducted to determine the effect that the amount of material has on the effective current density operating on the objects to be electropolished. With the power supply set at 15 V(dc), the load was varied from 0 to 384 in.². The gross current varied from 210 to 330 A. Results of these tests are shown in Table 12.1.

To reduce the amount of current (210 A) drawn by the barrel with no load, the stainless steel contacts were replaced by copper contacts 3 in. long and the electrolyte was changed to a sulfuric/phosphoric acid solution. A high-resistance film prevented erosion of the copper contact, and the current requirements of the barrel dropped to 50 A.

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FIGURE 12.2. Schematic of Barrel Electropolishing System

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FIGURE 12.3. Rotating Barrel Used to Decontaminate Small Items Without Racking

TABLE 12.1. Variation of Apparent Current Density with the Surface Area Being Electropolished

Area of Load, in. ²	Current, A	Current Density, A/in. ²
0	210	--
32	231	0.66
64	249	0.61
96	261	0.53
128	270	0.47
160	282	0.45
192	300	0.47
288	323	0.39
384	330	0.31

To evaluate the effect of barrel rotation speed on the effective current density attainable with a given load, the barrel was loaded with 128 in.² of stainless steel plates. A voltage of 15 V(dc) was applied between the barrel and the cathode, resulting in an ef-

fective current density on the plates of 0.52 A/in.² at 1.5 rpm. At 4 rpm the effective current density was 0.33 A/in.². Based on these results, the barrel speed should be reduced to the lowest possible speed consistent with good agitation of the parts.

To test the decontamination capabilities of barrel electropolishing, 6.3 lb of uranium-contaminated molybdenum, consisting of forty 3.5-in.² pieces, were loaded into the barrel. An applied voltage of 15 V(dc) resulted in a current of about 350 A, of which 150 A was drawn by the barrel. The initial contamination level of the molybdenum

was 200,000 counts/min (β, γ) and 20,000 dis/min·cm² (α). After 30 min of processing, the contamination level was reduced to 151 $\pm$ 221 counts/min and 228 $\pm$ 369 dis/min·100 cm². An additional run of 53 min resulted in a radiation reading of <100 counts/min and <200 dis/min·100 cm².

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