Final

**PACIFIC NORTHWEST LABORATORY
DIVISION OF ISOTOPE DEVELOPMENT
PROGRAMS QUARTERLY REPORT:
OCTOBER - DECEMBER, 1967**

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Edited by R. L. Moore
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INTRODUCTION

This is the fifth report of a series initiated in 1966 to provide potential users with detailed and timely information on the results of the promethium isotopic fuels program and other radioisotope research being conducted at the Pacific Northwest Laboratory by Battelle for the Division of Isotope Development of the U.S. Atomic Energy Commission. The previous reports of the series are BNWL-385, BNWL-466, BNWL-570, and BNWL-681.*

SUMMARY

Promethium Purification and Conversion

Continued improvements have been made in the equipment and flowsheets used at PNL for producing purified ^{147}Pm and for converting this material to heat-source-grade sesquioxide. Changes in the hot-cell ion-exchange equipment, since it was originally installed about 2 years ago, are described (as are design improvements that have been incorporated in the in-cell recording optical spectrometer). Most of the ion-exchange columns are now of stainless steel construction rather than of glass, and column sizing has been changed to a sequence believed to be more nearly optimum.

Supporting laboratory work (not yet tested in the hot cell) indicates that NTA (nitrilotriacetic acid) should have

* Available from the AEC Division of Technical Information Extension, Oak Ridge, Tennessee.

significant advantages over the currently used eluting agent (DTPA). These advantages include higher processing rates, lower reagent cost, and a more favorable elution sequence. The solubility of promethium oxalate has been measured (as a function of acidity, temperature, and concentration of oxalate, NTA, DTPA, Na^+ , and NH_4^+), and conditions have been established for optimum recovery.

Properties of Promethium Oxide

The thermal diffusivity of Pm_2O_3 was measured (from 80 to 1600 °C) as a function of Sm_2O_3 content (12 to 20%). Sm_2O_3 appeared to have little effect on the thermal conductivity.

Observations are reported on the hydrolysis behavior of Nd_2O_3 , Pm_2O_3 , and Sm_2O_3 . All react with moisture (either atmospheric moisture or liquid water). This reaction causes either sintered or hot pressed pellets of these oxides to decompose in a short time, and it implies that encapsulation must be relied upon to prevent the spread of ^{147}Pm in an aqueous environment. Formation of mixed oxides (phosphates, vanadates, titanates, and tungstates) afforded no substantial protection.

The particle size of as-produced Pm_2O_3 was measured microscopically, and the size distribution is reported. All particles were smaller than 10 μ , and most were less than 5 μ .

PROMETHIUM PURIFICATION AND CONVERSION

A-CELL EQUIPMENT AND OPERATIONAL CHANGES

E. J. Wheelwright, F. P. Roberts, and E. A. Berreth

The restrained-band chromatographic ion exchange process and the equipment used to purify promethium were described in the first report of this series.⁽¹⁾ To date, 2 million curies of ^{147}Pm have been purified in the modest-sized equipment installed for this purpose in A-Cell of the PNL High Level Radiochemistry Facility. During two years of operation, it

has been necessary to decontaminate the cell only twice for equipment maintenance work. The first decontamination was required when the largest (14 in. diam, SS) column was found to be defective. More recently, one of the larger (4 in. ID) glass columns developed a crack in its water jacket (apparently due to cumulative radiation exposure). Advantage was taken of this opportunity to replace the larger glass columns with stainless steel columns and to change the column diameters to what is believed to be a more optimum sizing. The old and new sizes are shown in Table I. Success of these changes is confirmed by subsequent improvement in product purity and apparent decreases in waste losses. The first run (No. 17) since the modifications produced 362,000 Ci of purified product and a promethium material balance of 96.4%, versus an average material balance of about 90% in the previous runs.

TABLE I. A-Cell Promethium Purification Column Sizing

Column Number	Old		New	
	Size, in.	Material	Size, in.	Material
1	14 ID	SS	same	
1A	10 ID	SS	same	
2	8 ID	SS	same	
3	4 ID	Glass	6 ID	SS
4	4 ID	Glass	4 ID	SS
5	2 ID	Glass	3 ID	Glass
6	2 ID	Glass	2 ID	Glass
7	1 ID	Glass	1 ID	Glass
8	1 ID	Glass	1 ID	Glass

Note: All columns are 9 ft high and are operated with 8 ft resin beds.

Each run results in the production of several thousand gallons of radioactive waste which must be transported in shielded casks to the 200 Areas (about 30 miles distant) for disposal. This represents a sizable expense since cask shipment costs 3 to \$6/gal (depending on cask size); it also poses a continuing scheduling problem. Accordingly, stringent efforts have been made to reduce the volume and activity of the waste, and a substantial measure of success has been achieved. The volume of highest level waste (that containing ^{144}Ce) has been reduced dramatically by allowing the cerium to band, moving it to the second column, and eluting it from this column with a minimum volume of nitric acid. The volume of this waste (the "\$6/gal" variety) has been reduced progressively from 1000 gal/run to only 125 gal in recent runs. (Some increased resin damage results from this mode of operation, but the trade-off is advantageous for our operation.) The other large volume waste is that produced during the subsequent elution cycles. By careful segregation, the volume of this "\$3" waste has been reduced by about 70%. It was segregated by activity level into that which can be transported by tank truck (at a cost of only a few cents per gallon) and that requiring cask handling.

Other process improvement work, described in the following sections, was aimed at:

- Further improvement of the in-cell spectrometer
- Search for a superior eluting agent
- Improvement of the oxalate precipitation step
- Better characterization of the Pm_2O_3 product.

Reference

1. Pacific Northwest Laboratory Radioisotope Technology Programs Quarterly Report, October - December, 1966, BNWL-385, p. 15. Pacific Northwest Laboratory, Richland, Washington.

MARK-II IN-CELL RECORDING OPTICAL SPECTROMETER

U. L. Upson

The in-cell recording optical spectrometer, which has proved invaluable in operating the A-Cell ion exchange equipment, has undergone extensive modification and improvement since first reported.^(1,2)

The optical system, which previously employed a Beckman DU monochromator extending into the operating gallery normal to the front-face wall, has been modified to incorporate a single-pass grating monochromator, in an assembly firmly attached to the cell wall (Figure 1). This modification not only eliminates accidental misalignment, and interference with cell operations, but also yields approximately 100-fold increase in optical efficiency. The resultant negligible relative dark current permits elimination of automatic dark-current suppression, significantly simplifying the programming circuitry.

Other changes include electronic sensing and control of the measured wavelength, with eleven switch-selectable scan limits (preset to encompass the absorption peaks of interest), and timed programming of the sample sequence and scan frequency. Each of two in-cell flow optical cells can be separately programmed for automatic scanning over any selected region. These modifications yield greater versatility, simplified operation, and minimum operator attention. A formal report on the final design is being written.

References

1. Pacific Northwest Laboratory Radioisotope Technology Programs Quarterly Report, October - December, 1966, BNWL-385, p. 15. Pacific Northwest Laboratory, Richland, Washington.
2. U. L. Upson and E. J. Wheelwright. An In-Cell Recording Optical Spectrometer, BNWL-337. Pacific Northwest Laboratory, Richland, Washington, December 1966.

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FIGURE 1. Photo of Spectrophotometer

INVESTIGATION OF NTA AS A REPLACEMENT FOR DTPA IN THE ION-
EXCHANGE PURIFICATION OF PROMETHIUM

E. J. Wheelwright and T. R. Myers

Ion-exchange separation processes utilizing ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) for the final purification of promethium have been described previously.^(1,2) The process currently in use at Battelle-Northwest utilizes an improved DTPA ion-exchange elution flowsheet,⁽³⁾ but suffers from two deficiencies. In the normal DTPA elution sequence, yttrium (a fission product present in most promethium feed solutions) elutes in a position between samarium and promethium. The elution sequence is, therefore, Zn^{+2} , Am^{+3} , Eu^{+3} , Sm^{+3} , Y^{+3} , Pm^{+3} , Nd^{+3} , Pr^{+3} , Ce^{+3} , La^{+3} . The Y-Pm separation coefficient is significantly smaller than the Sm-Pm or Pm-Nd separation coefficients; as a result, the Y-Pm binary mixture zone contains a larger fraction of the total promethium than does the Pm-Nd binary zone. This causes an increase in the percent of promethium that must be recycled from each run.

The second problem relates to the elution time required to reach the maximum degree of separation allowed by thermodynamics and the physical geometry of the processing equipment. To achieve a given optimum separation, a mixture of absorbed ions must be displaced or eluted through a specific length or volume of resin beds. The rate at which the band of absorbed ions can be moved through that length is controlled by the kinetics of the various processes required for separation. As the rate of band advance is increased (by increasing the concentration or flow rate of the eluting solution), a point is reached beyond which the degree of separation achieved decreases as the kinetic factors of the

process become dominant. From a practical point of view, then, the rate of production for a given size of equipment is controlled by the magnitude of the thermodynamic separation factors between the ions involved (this defines the elution distance needed) and the kinetics of the processes (the time required to achieve a given distance). With the DTPA flow-sheet currently being used for promethium purification, the separation efficiency decreases rather rapidly when the rate of advance of the absorbed band is increased beyond 0.36 milliequivalent/min-cm².

Recent laboratory experiments have shown that when NTA is substituted for DTPA in a typical promethium purification flowsheet, the elution position of yttrium is moved to a place ahead of samarium. In one typical experiment, an absorbed mixture containing the ions Ho^{+3} , Y^{+3} , Gd^{+3} , Sm^{+3} , Pm^{+3} , and Nd^{+3} was eluted down a column of Dowex 50W, X-8(50-100 mesh) resin in the Zn^{+2} cycle with 10 gms NTA/liter, adjusted to pH 6.00 with NH_4OH . When separation was achieved, the elution order was found by analysis to be holmium, yttrium, gadolinium, samarium, promethium, neodymium; thus removing yttrium from the critical Sm-Pm-Nd zone of the rare earth spectrum.

In previous publications, a standardized ion-exchange elution procedure is described in which a 100 ml bed of resin is completely saturated with equivalent amounts of Sm^{+3} , Nd^{+3} , and Pr^{+3} , then eluted down a 200 ml column of the same resin under standardized conditions.⁽³⁾ (Neodymium serves as a convenient stand-in for promethium in these laboratory experiments.) A graphical integration of the various areas of the elution curves obtained from the analysis of such an experiment permits an accurate comparison of the relative effectiveness of two or more eluting agents. One often used comparison is the ratio of the amount of neodymium obtained 100% pure

divided by the amount of neodymium present in the experiment. This criterion provides a valid basis for estimating the effectiveness of several eluting agents for promethium separation if the Sm-Nd separation is similar to the Nd-Pr separation. Such is true with EDTA and DTPA. However, the results obtained with NTA show that the Sm-Nd separation is dramatically superior to the Nd-Pr separation. Since the separation achievable in the Sm-Nd region should be more representative of promethium purification efficiency (since promethium lies between samarium and neodymium in the periodic table), the ratio of the quantity of material contained in the intermediate zone of binary mixing, divided by the quantity of neodymium present in the experiment is felt to be a more valid basis for comparison of eluting agents for use in promethium purification. Such a ratio, F, is obtained from the graphical integration of the lettered areas of the elution curve (Figure 2) and may then be calculated from the following equation:

$$F = \frac{E + D + C + B}{D + C + B + A + B' + C' + D'} \times 100 \quad .$$

The smaller this quantity, the better the separation, i.e., a value of zero would imply perfect separation.

Six sets of separation experiments have been performed: two with DTPA and four with NTA. In each experiment, the Sm-Nd-Pr feed composition and quantity, the elution distance, and the temperature were held constant. Concentration of eluting agent, pH, and solution flow rate were varied in a programmed manner to provide data at various eluant pH values as a function of mass flow rate. Figure 3 presents the experimental data thus obtained. Examination of Figure 3

FIGURE 2. Typical Elution Curve

FIGURE 3. *Sm-Nd Separation Efficiency*

reveals essentially no change in separation efficiency in the vital Sm-Nd region with increased mass flow rates with 20 gm/l NTA, and it shows only a slight change with 25 gm/l NTA. This is in sharp contrast with DTPA. Such data strongly imply that the use of NTA for promethium processing would allow a 50 to 100% increase in the mass flow rate (over the 0.36 milliequivalent/min-cm² currently being used). This should reduce the process time cycle by a corresponding amount and make it possible to complete a purification run (from raw feed to purified promethium nitrate product solution) in less than five days, thereby eliminating the need for weekend shift coverage. Use of 25 g/l NTA (vice 20 g/l NTA or 20 g/l DTPA) would also reduce eluate waste volumes by about 20%--an important consideration for 300 Area operation.

At current prices, NTA costs only half as much per pound as DTPA. The use of NTA rather than DTPA would, therefore, reduce chemical costs for the complexant by about 50% since their concentration in the eluting solution is the same on a weight basis.

The above work was performed with "cold" and tracer-level solutions in the laboratory. An early hot-cell test is planned.

References

1. E. J. Wheelwright and F. P. Roberts. Development and Demonstration of an Ion-Exchange Process for Kilogram-Scale Production of High Purity Promethium, HW-78651 REV. General Electric Company, Richland, Washington, October, 1963.
2. P. B. Orr. Ion-Exchange Purification of Promethium-147 and its Separation from Americium-241, with Diethylene-triaminepentaacetic Acid as the Eluant, ORNL-3271. Oak Ridge National Laboratory, Oak Ridge, Tennessee, June, 1962.
3. E. J. Wheelwright, et al. Ion-Exchange Separation of Kilocurie Quantities of High Purity Promethium, BNWL-318. Pacific Northwest Laboratory, Richland, Washington, December, 1966.

PROMETHIUM OXALATE SOLUBILITY STUDIES

F. P. Roberts

Promethium oxide is prepared by precipitation of promethium oxalate from slightly acid solution, followed by calcination at about 1000 °C. Usually, no difficulties are encountered in the precipitation step; but when an unusually high acid concentration occurs in the feed, incomplete precipitation results. A study of the precipitation behavior of promethium oxalate was accordingly undertaken to develop a better understanding of the process and to find optimum conditions for high recovery.

Experimental Procedure

Freshly purified promethium oxide dissolved in perchloric acid was used as the starting material for all of the experiments. The oxide, which had been freshly purified at the start of the study to $>99\%$ Pm_2O_3 , had decayed 45 days at the end of the study; at that time it contained 3.2% Sm_2O_3 .

The procedure used for most of the experiments consisted of equilibrating 3 mg of promethium with 20 ml of the solution to be tested for 8 to 24 hr in a glass thermostated vessel with constant agitation. After equilibrium had been reached, the promethium and the oxalate concentrations in the supernate were determined and the pH was measured. Promethium determinations were by beta proportional counting; the oxalate was measured by titration with 0.01M potassium permanganate. For those experiments at high acid content, the acid was determined by titration with standard sodium hydroxide.

Equilibrium was usually reached in 8 hr at low pH's, but at pH's above 4.5, 16 to 24 hr were required. Tests for equilibrium were made by sampling periodically and observing the change. Equilibrium was approached from both sides and similar results were obtained.

No evidence of colloid formation was observed at pH's lower than 7. In this pH region, the precipitate was crystalline and settled rapidly. A short centrifugation gave a solution free of particles; at pH higher than seven, the precipitate was very finely divided and difficult to separate.

Effect of Acid Concentration

The results of a series of equilibrium solubility measurements in oxalate solutions of widely varying nitric acid

concentration are shown in Figure 4. These data show the importance of acid concentration. Above about 0.5M acid, the logarithm of the solubility increases in direct proportion to the logarithm of the nitric acid concentration. Equilibrium solubilities over the pH range of 0 to 9.8 are shown in Figure 5. The minimum solubility occurs in the pH region 1.0 to 1.5. The data in both these tables were obtained from experiments carried out at 25 ± 0.2 °C in 0.10M total oxalate solutions.

Effect of Excess Oxalate Concentration

Table II gives the results of a series of experiments where the solubility of promethium was measured in solutions with varying concentrations of excess oxalic acid at a constant pH of 1.5 and at a constant temperature of 25 ± 0.2 °C. A small excess of oxalic acid can be tolerated, but a large excess will increase promethium losses.

TABLE II. Solubility of Promethium Oxalate in the Presence of the Excess Oxalic Acid

<u>Excess Oxalic Acid</u> <u>Acid, M</u>	<u>Promethium in</u> <u>Solution, mg/l</u>
0	0.12
0.010	0.13
0.10	0.25
0.25	0.44
0.50	0.69
1.00	1.22

FIGURE 4. Solubility of Promethium Oxalate in Nitric Acid

FIGURE 5. Solubility of Promethium in 0.1M Oxalic Acid as a Function of pH

Effect of Ammonium and Sodium Ions

Frequently, promethium solutions containing high concentrations of nitric acid must be processed. The acid concentration must be reduced to obtain high recoveries by oxalate precipitation. This can be done by partial neutralization with sodium or ammonium hydroxide but, of course, adds extraneous cations to the system. The effect of these cations on the promethium oxalate solubility was therefore measured. The results of a series of experiments with solutions containing high concentrations of sodium nitrate or ammonium nitrate are shown in Table III. The data were obtained at pH 1.35 to 1.40 and at 25 °C in 0.10M oxalic acid. The effect of 0.5M ammonium nitrate was to increase the promethium oxalate solubility somewhat less than a factor of two. Increasing the amount of ammonium nitrate over 0.5M had little effect. Sodium nitrate was only slightly different in that the solubility goes through a maximum at about 2M sodium nitrate.

TABLE III. Solubility of Promethium Oxalate in the Presence of Monovalent Cations

<u>Salt Concentration,</u> <u>M</u>		<u>Promethium in</u> <u>Solution, mg/l</u>
NH ₄ NO ₃	0	0.23
	0.5	0.42
	1.0	0.43
	2.0	0.45
	3.0	0.45
NaNO ₃	0.5	0.44
	1.0	0.57
	2.0	0.61
	3.0	0.46

Effect of Temperature on Promethium Oxalate Solubility

Measurements were made of the solubility of promethium oxalate in 0.1M oxalic acid at 15, 25, 30, and 40 °C. The results given in Table IV show the solubility increases with increasing temperatures.

TABLE IV. Temperature Effects on Promethium Oxalate Solubility

<u>Temperature, °C</u>	<u>Promethium in Solution, mg/l</u>
15	0.168
25	0.239
30	0.262
40	0.365

Effect of Complexing Agents

The effect of DTPA and NTA, the two eluting agents used in the ion-exchange purification process, was tested by equilibrating solutions containing 0.05M of the complexant, 0.01M promethium, and 0.1M oxalic acid over the pH range of interest. Little effect was noted below a pH of about 3.5. Above this pH, the promethium is very soluble because of the formation of DTPA or NTA complexes.

Process Implications

Promethium oxalate exhibits a minimum solubility of 0.12 mg/liter at a pH in the range of 1 to 2. For optimum recovery, the pH should be in this range, and large excesses of oxalate or of other complexants (such as DTPA or NTA) should be avoided. Since monovalent cations (Na^+ and NH_4^+) have only a slightly adverse effect on promethium oxalate solubility, highly acidic solutions of promethium (such as result from dissolving promethium scrap or from nitric acid

stripping of ion-exchange product) can be simply neutralized to the proper pH with ammonia or sodium hydroxide prior to precipitation. Ammonia is preferred since it is decomposed on subsequent calcination of the oxalate. The proper pH is readily measured and controlled by use of a pH meter or with color indicating paper.

PROPERTIES OF PROMETHIUM OXIDE

Properties of promethium oxide that are important to potential users are being measured as a part of PNL's program to develop promethium for isotopic heat source use. Results of recent measurements follow.

THERMAL DIFFUSIVITY OF $^{147}\text{Pm}_2\text{O}_3$

R. L. Gibby

The thermal diffusivity of $^{147}\text{Pm}_2\text{O}_3$ was measured as a function of the concentration level of the decay product ^{147}Sm . Measurements were made on a sample when daughter ^{147}Sm concentration levels of 12, 16, and 20 wt% had been formed due to radioactive decay. In addition, a second sample containing 12 wt% Sm was run to check the reproducibility of the data.

The thermal diffusivity measurements were made from 75 to 1600 °C using a laser heat pulse apparatus.⁽¹⁾ The samples consisted of small wafers (0.63 cm diam x 0.0597 cm) sectioned from a larger sintered pellet. The pellet was sintered at 1450 °C to a density of 6.73 g/cm³ (~90% TD). Since Pm_2O_3 is transformed irreversibly from the cubic C-type rare earth structure to the B-type monoclinic structure at the sintering temperature of approximately 950 °C, it is assumed that the samples were in the monoclinic form after the sintering treatment. The samples were coated with a colloidal graphite suspension to prevent transmission of

the laser beam through the sample. At the higher measurement temperatures, the coating sometimes deteriorated badly, thus affecting the results. In such cases the data were discarded. The results are shown in Figure 6. The data form a normal scatter band which is characteristic of the precision of the method. An increase in ^{147}Sm concentration had no measurable effect on thermal diffusivity in the concentration range investigated. Measurements are now in progress on $^{147}\text{Pm}_2\text{O}_3$ with less than 1 wt% Sm_2O_3 .

References

1. *Pacific Northwest Laboratory Radioisotope Technology Programs Quarterly Report, April-June, 1967, BNWL-570, p. 6. Pacific Northwest Laboratory, Richland, Washington.*

THE HYDROLYSIS OF RARE EARTH OXIDES

H. T. Fullam and F. P. Roberts

In designing an isotopic heat source for space or terrestrial applications, one of the basic requisites of the fuel form is that of low solubility (or slow dissolution) in saline or fresh water. If this prerequisite is not met, then capsule design must be adequate to insure fuel containment upon exposure of the heat source to aqueous media.

For promethium, the sesquioxide, Pm_2O_3 , is currently the preferred heat source fuel form. Experimental work reported previously⁽¹⁾ has shown that the dissolution rate of compacted and sintered Pm_2O_3 is very slow (see Table V) and that the solubility is also very low. However, the work has also shown that compacted and sintered promethium sesquioxide shapes disintegrate quite rapidly when exposed to water. This is shown by the data in Table VI. These data were obtained by exposing cold-pressed and sintered or hot-pressed Pm_2O_3 pellets to a flowing water stream and visually observing the breakup and disintegration of the pellet. The

FIGURE 6. Thermal Diffusivity of $^{147}\text{Pm}_2\text{O}_3$ - $^{147}\text{Sm}_2\text{O}_3$ Solid Solutions

results obtained are rather unexpected in that the hot-pressed pellet, which had a higher density and had been compacted at a higher temperature than the cold-pressed and sintered pellets, disintegrated more rapidly than the sintered pellets.

TABLE V. *Solubility and Dissolution Rate of Pm_2O_3 in Fresh and Saline Water*

Oxide	Water	Water pH	Dissolution Rate $\mu\text{g}/\text{cm}^2$ pellet surface-hr
Pm_2O_3	Distilled	5.9	3.8
Pm_2O_3	Sea	8.2	0.04
			Solubility, g/liter
Pm_2O_3	Distilled	8	0.003

TABLE VI. *The Disintegration of Pm_2O_3 Compacts in Water*

Oxide	Compaction Method	Compaction Temp., °C	Water Temp., °C	Time to Initial Cracking, days
Pm_2O_3 -15% Sm_2O_3	Cold Press and Sinter	1400	38	5
Pm_2O_3 -15% Sm_2O_3	Cold Press and Sinter	1400	38	5
Pm_2O_3 -15% Sm_2O_3	Hot Press	1590	40	2

The implication of these data is that, even though the dissolution rate of the compacted and sintered oxide is low, the rapid disintegration of the fuel can result in widespread promethium contamination if the source cladding is ruptured. The reason (or reasons) for the pellet disintegration is unknown at this time but it appears to be due to hydrolysis of the oxide surface--forming an insoluble but more voluminous hydroxide.

Compacted shapes of neodymium and samarium sesquioxides show a similar tendency to disintegrate in the presence of water. The stability increases, however, with increasing atomic number as evidenced by the data given in Table VII.

TABLE VII. The Stability of Hot-Pressed Pellets in Water

<u>Oxide</u>	<u>Compaction Temperature, °C</u>	<u>Water Temperature, °C</u>	<u>Time to Initial Cracking, days</u>
Nd ₂ O ₃	1590	25	<0.5
Pm ₂ O ₃	1590	40	~2
Sm ₂ O ₃	1590	40	>30

In each case the pellets were prepared by hot pressing the oxides under similar conditions.

Increasing the water temperature greatly accelerates the rate of disintegration of the oxide pellets. This is shown by the data in Table VIII for pressed and sintered samarium oxide pellets. Neodymium sesquioxide pellets showed a similar rapid increase in the disintegration rate as the water temperature was increased. From these results, one would expect promethium sesquioxide to behave in a similar manner.

TABLE VIII. The Effect of Water Temperature on Sm₂O₃ Pellet Stability

<u>Compaction Temperature, °C</u>	<u>Water Temperature, °C</u>	<u>Time to Initial Cracking, hr</u>
1600	25	>500
1600	60	18-24
1600	90	1-4

In an attempt to improve the stability of the promethium oxide to attack by water, a number of mixed oxides were prepared and their stability measured. Sm_2O_3 and Nd_2O_3 were used as stand-ins for Pm_2O_3 ; the mixed oxides prepared included phosphates, vanadates, titanates, and tungstates. The experimental procedures used consisted of pelletizing the mixed oxide, sintering 24 hr at 1300 °C, and then exposing the cold pellet to the atmosphere. The rate of oxide hydrolysis was determined by weight gain as a function of time. Of the mixed oxides tested, only the tungstates appeared to show improved stability as compared to the Sm_2O_3 and Nd_2O_3 standards. To further evaluate the potential of the tungstates, pellets were pressed from various Sm_2O_3 - WO_3 mixtures (from 1 to 40 wt% WO_3), sintered at 1600 or 1800 °C, and then exposed to water at 25, 60 and 90 °C. The tungstate pellets showed a slightly improved stability over the Sm_2O_3 standards but not enough to warrant additional study.

When the rare earth oxides are hydrolyzed by exposure to moist air, the final product appears to be the hydroxide $\text{RE}(\text{OH})_3$ or $\text{RE}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. This is probably the final product formed when the Pm_2O_3 pellet disintegrates in water. Additional studies are underway to verify this assumption.

Reference

1. Pacific Northwest Laboratory Radioisotope Technology Programs Quarterly Report, January - March, 1967, BNWL-466. Pacific Northwest Laboratory, Richland, Washington.

PARTICLE SIZE OF AS-PRODUCED PROMETHIUM OXIDE

F. P. Roberts

The particle size of Pm_2O_3 produced by our standard oxalate decomposition-high temperature treatment process⁽¹⁾ is of interest to some potential users (particularly those who wish to use ^{147}Pm as a beta source and cannot tolerate excessive self-absorption). Microscopic examination of promethium oxide was accordingly carried out to obtain an approximate particle size distribution. The average particle size was found to be less than 5 μ . Very few discrete particles larger than 10 μ were observed. The measurements were made on a sample of promethium oxide prepared in a routine production run. The oxide (which was prepared by ignition of promethium oxalate at 1000 °C) had decayed to 95.6% at the time of the measurement.

About 1 mg of the oxide was slurried with 1 cm^3 of Kel-F stopcock grease. A small amount of the slurry was placed on a microscope slide, and a cover glass was placed over this. Slight pressure applied to the cover glass spread the sample over an area of 2 to 3 cm^2 . Slides prepared in this fashion could be handled in fume hoods with ordinary care without spread of contamination. The particles were measured at a magnification of 1000X with a microscope fitted with a micrometer in the eyepiece ruled to the equivalent of 5 μ .

Measurements were made on a total of ten samples. The results given in Table IX show most particles to be less than 5 μ . No particles were larger than 10 μ .

Reference

1. Pacific Northwest Laboratory Radioisotope Technology Programs Quarterly Report, April - June, 1967, BNWL-385, p. 12. Pacific Northwest Laboratory, Richland, Washington.

TABLE IX. *Particle Size of Promethium Oxide*

Measurement Number	% of Particles in Size Range	
	<u>0-5 μ</u>	<u>5-10 μ</u>
1	58	42
2	60	40
3	58	42
4	59	41
5	63	37
6	68	32
7	75	25
8	74	26
9	55	45
10	66	34
Average	64	36

APPENDIX A

CHARACTERISTICS OF RADIOISOTOPIC HEAT SOURCES -

C. A. Rohrmann

CHARACTERISTICS OF RADIOISOTOPIC HEAT SOURCES

	⁶⁰ Co	⁹⁰ Sr	¹⁰⁶ Ru	¹³⁷ Cs	¹⁴⁴ Ce	¹⁴⁷ Pm	¹⁷⁰ Tm	²¹⁰ Po	²³⁸ Pu	²⁴² Cm	²⁴⁴ Cm
1. Watts/Gram (100% Basis)	17.4	0.96	33.1	0.42	25.6	0.33	13.6	141	0.56	120	2.65
2. Half-Life, Years	5.24	28	1.0	30	0.78	2.6	0.35	0.33	87.4	0.45	18.1
3. Estimated Isotopic Purity, %	10 ^(a)	55 ^(b)	3.3 ^(b)	35	4.5 ^(b)	95 ^(b)	10 ^(a)	95	80	90	95
4. Compound Form	Metal	SrTiO ₃	Metal	CsCl	Ce ₂ O ₃	Pm ₂ O ₃ ^(c)	Tm ₂ O ₃	Metal	PuO ₂	Cm ₂ O ₃	Cm ₂ O ₃
5. Melting Point of Compound, °C	1480	1910	2310	646	2190	2130	2375	255	2250	1950	1950
6. Active Isotope in Compound, %	10	23	3.3	28	3.8	82	8.8	95	70	82	86
7. Watts/Gram Compound	1.74	0.22	1.1	0.12	1.0	0.27	1.2	134	0.39	98	2.27
8. Density of Compound, g/cm ³ , actual or 90% TD	8.8	4.6	12.4	3.2	6.2	6.6	8.0	9.3	10	9	9
9. Power Density, W/cm ³ Compound	15.8	1.01	13.7	0.38	6.2	1.8 ^(c)	9.6	1210 ^(d)	3.9 ^(d)	882 ^(d)	20.4 ^(d)
10. Dimension of capsule for 50 W _t , cm, ^(e)	2.2	4.4	2.3	6.1	2.8	3.9	2.5	2.0	3.8	2.0	2.4
11. Availability	Avail.	Avail.	Poten. Avail.	Avail.	Avail.	Avail.	Avail.	Avail.	Avail. ^(f)	Poten. Avail.	Avail. ^(f)
12. Type of Radiation (Major)*	γβ	βx	γβx	βγx	βγx	β	β	α	α	αn	αn
13. Shielding Required ^(g) [MeV of significant β or γ]	Heavy (9.5) [1.33v]	Heavy (6) [2.26β]	Heavy (9) [3.35β]	Heavy (4.6) [1.17β] 0.67γ]	Heavy (10.2) [2.98β] 2.18γ]	Minor (1) [0.23β]	Moderate (2.5) [0.97β]	Minor (1) [0.8γ]	Minor (0.1) [0.04v]	Minor (0.4) [0.04v]	Moderate (2) [0.04v]
14. Biological Hazard, Ci/m ³ MPC, Air, W/m ³ Continuous Exposure g/m ³	3x10 ⁻⁹ 4.6x10 ⁻¹¹ 2.7x10 ⁻¹²	10 ⁻¹⁰ 6.8x10 ⁻¹³ 7x10 ⁻¹³	2x10 ⁻⁹ 2x10 ⁻¹¹ 5.9x10 ⁻¹³	5x10 ⁻⁹ 2.4x10 ⁻¹¹ 5.8x10 ⁻¹¹	2x10 ⁻⁹ 1.6x10 ⁻¹¹ 6.3x10 ⁻¹³	2x10 ⁻⁸ 7.2x10 ⁻¹² 2.2x10 ⁻¹¹	10 ⁻⁸ 2.3x10 ⁻¹¹ 1.7x10 ⁻¹²	7x10 ⁻¹¹ 2.2x10 ⁻¹² 1.6x10 ⁻¹⁴	7x10 ⁻¹³ 2.3x10 ⁻¹⁴ 4.1x10 ⁻¹⁴	4x10 ⁻¹¹ 1.4x10 ⁻¹² 1.2x10 ⁻¹⁴	3x10 ⁻¹² 10 ⁻¹³ 3.7x10 ⁻¹⁴
15. Estimated Future Price \$/g(Pure)[Present price]	280 [452]	20 ^(h) [29]	120 ^(h)	6.5 ^(h) [10.9]	50 ^(h) [477]	75 ^(h) [186]	136	2800 ⁽ⁱ⁾	300 ⁽ⁱ⁾	2000 ^(j)	170 ^(h)
16. Estimated Future Price, \$/W	16	21	5	15.5	2	220	10	20	540	17	64
17. Curies/Gram (100% Basis)	1130	142	3394	87	3180	928	6048	4500	17	3320	81
18. Curies/Watt	65	148	102	207	124	2788	445	32	30	28	29
19. Total kWh _t /initial gram for (yr) mission	575 (5)	74 (10)	210 (1)	33 (10)	150 (1)	6 (3)	33 (0.4)	350 (0.4)	47 (10)	310 (0.4)	190 (10)
20. Minimum Cost, \$/kWh _e ^(k) for (yr) mission	15 (5)	6 (10)	23 (1)	4 (10)	11 (1)	350 (3)	125 (0.4)	235 (0.4)	138 (10)	180 (0.4)	22 (10)
21. Spontaneous Fission Half-Life, Yr	--	--	--	--	--	--	--	--	4.9x10 ¹⁰	7.2x10 ⁶	1.4x10 ⁷
22. Estimated Recovery from Power Reactor Fuels; g/metric ton at 25,000 MWd/ton	--	363	44	880	86	61 (aged)	--	--	(300 Np)	--	6 (200/Pu Recycle)
23. Production in Power Reactors Kg/1000 MWY _e	--	18	2	42	5	3 (aged)	--	--	(18 Np)	--	0.5 (9/Pu Recycle)
24. Availability in 1980, kW _t ^(f)	MWs	1200	11,000	1200	8400	53	MWs	MWs	250 ^(l)	--	93 ₁₅₆ ^(m)

(a) Could be produced at higher concentrations, at least double this value, with higher neutron flux and longer exposures.

(b) From U.S. power reactor fuels, 1 year after discharge (one half life for Pm).

(c) Metal may be preferred; m.p. = 1080°C (F. Weigel, Angew. Chem. 75 451 (1963); expected power density = 2.3 W/cm³.

(d) Does not include the usual 1:1 void volume allowance for helium pressurization with this and all other encapsulated alpha emitters.

(e) Capsule is a right cylinder with diameter = height; ²¹⁰Po and ²⁴²Cm assumed to be diluted to 50 W/cm³. Capsule wall thickness is 0.3 cm.

(f) From spent fuels from civilian power reactors (150,000 MW_e in 1980), except for ⁶⁰Co, ¹⁷⁰Tm, ²¹⁰Po which could be produced in megawatt quantities via neutron irradiation of targets.

(g) Except for shielding against neutrons. Number in parentheses indicates approximate inches of lead shielding required for 1 kW source for 10 mR/hr at 1 m. (See ORNL-3576 except for promethium.)

(h) From large, civilian, power reactor, spent fuel processing and isotope recovery facility, after 1970 (see BNWL-25).

(i) Upward revision of minimum costs shown in "Holsted-Albaugh Hanford Diversification Report," 1/15/64, p. 13.

(j) Anticipated price with large scale reactor fueling with plutonium (Pu at \$10/g), and ²⁴¹Am recycle.

(k) At terminal or lowest specific power (W/g); at 5% thermal-to-electrical conversion efficiency. For comparison, power from chemical batteries (specifically flashlight batteries) is calculated to cost \$100/kWh_e.

(l) From accumulated ²³⁷Np from spent fuels from civilian power reactors (550 kg neptunium recoverable in the year 1980).

(m) With recycle of plutonium and americium.

(n) This chart is an extension of Table VI, page 52, HW-76323, Rev 1, "Radioisotopic Heat Sources," 10/15/63. C. A. Rohrmann, Battelle-Northwest, Richland, Washington. Re-issues are made about twice a year to include most current data. Users of previous issues will note the omission of ¹⁷¹Tm, ²⁰⁴Tl, ²²⁸Th, ²³²U and ²⁴¹Am which are not expected to be available in kW or Kg quantities because of large investments required for R&D and production.

(*) α = Alpha
β = Beta
γ = Gamma
n = Neutron
x = Penetrating
bremsstrahlung

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