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LA-UR--89-1041

DE89 009346

TITLE EXTRACTION OF PLUTONIUM FROM LEAN RESIDUES BY ROOM TEMPERATURE FLUORIDE VOLATILITY

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SUBMITTED TO AMERICAN CHEMICAL SOCIETY, 1989 I&EC DIVISION
SPRING SYMPOSIUM - ATLANTA, GA

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FORM NO 836 R4
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EXTRACTION OF PLUTONIUM FROM LEAN RESIDUES BY ROOM TEMPERATURE FLUORIDE VOLATILITY

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ABSTRACT

The use of dioxygen difluoride (FOOF) and KrF_2 for the recovery of Pu from lean residues by conversion to gaseous PuF_6 is being investigated. The greater stability of PuF_6 at room temperature allows much more extensive removal of Pu from contaminated wastes, when compared to the high temperature fluoride volatility process. The process also requires fewer additive chemicals than aqueous processes, thus minimizing the amount of material that must be disposed of as radioactive waste. The transportability of gaseous PuF_6 allows much of the process to be automated, reducing operator exposure to radiation. Removal of PuF_6 decomposition product is easily facilitated by the use of these fluorinating agents.

INTRODUCTION

The high cost and political sensitivity associated with the disposal of radioactive waste makes it imperative that the quantity of waste generated be kept at the lowest reasonable level. The processing of Pu waste by direct conversion to PuF_6, that can be easily separated as a gas, was examined many years ago.[1] The process was limited then to reaction of residues with F_2 at elevated temperature. Because of the corrosive nature of hot F_2, there was a significant materials compatibility problem. Also, because PuF_6 becomes increasingly unstable at temperatures above 170 K, there was reduced reaction efficiency, and PuF_6 decomposition product deposits outside of the reaction zone. To some, the advantages of the process, including the reduction of the number of processing steps, space requirements, and the need for fewer chemical additives, outweighed the disadvantages. As the cost of waste disposal has sharply increased in recent times, the fluoride volatility process has gained new significance.

To compliment the high temperature process and overcome some of the perceived shortcomings, we have been examining the possibility of room temperature fluoride volatility. The compound FOOF and its gas phase equilibrium product FOO have had the most emphasis in this study because of the potential for making it in sufficient quantity economically. They have been shown to be powerful fluorinating agents for the

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(1) Jonke, A.A. *Reprocessing of Nuclear Reactor Fuels by Processes Based on Volatilization, Fractional Distillation and Selective Adsorption*, *At. Energy Rev.* **March 1965**, 3, 1.

actinides.[2,3] The compound KrF_2 is believed to have desirable chemical properties,[4] but is more difficult to produce in sufficient quantity at this time. We have found that the KrF_2 reaction with Pu residues has a half time greater than 5 h and a reaction efficiency at least as good as FOOF.

The chemical reactions of interest in the FOOF process are:

$$F_{2(g)} + O_{2(g)} \rightarrow FOOF_{(g)} \qquad (1)$$

$$3\ FOOF_{(g)} + PuR_{(s)} \rightarrow PuF_{6(g)} + 3\ O_{2(g)} + R_{(s,g)} \qquad (2)$$

$$6\ FOO_{(g)} + PuR_{(s)} \rightarrow PuF_{6(g)} + 6\ O_{2(g)} + R_{(s,g)} \qquad (3)$$

where $R_{(s)}$ is a solid residue. The first reaction requires the input of energy. The others proceed spontaneously at room temperature.

Kinetic studies[5,6] of the FOOF, FOO, O_2 system showed that there was an equilibrium ($2FOO = FOOF + O_2$) that produced FOO in the gas phase. The reaction rate was very temperature sensitive with an activation energy of 13 kcal/mole. It was found that FOO reacted to produce PuF_6 much more efficiently when the Pu residue was spread over a metal

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(2) Malm,J.G.;Eller,P.G.;Asprey,L.B.*J.Amer Chem.Soc.***1984**, *106*, 2726 .

(3) Kim,K.C.;Campbell,G.M.*Appl.Spect.***1985**,*39*,625.

(4) Asprey,L.B.;Eller,P.G.;Kinkead,S.A.*Inorg.Chem.***1986**,*25*,670.

(5) Campbell,G.M.*J.Mol.Structure*,**1988**,*189*,301.

(6) Campbell,G.M. to be published.

surface. The life time of FOOF at room temperature was a few seconds.

The first gas circulating loop was designed to optimize the fluorination reaction in light of the information gained from the kinetic studies. It was operated at a high flow rate so that FOOF passed quickly from the supply reservoir to the gas-solid reactor. The gas-solid reactor had a large volume so that the gas reactant remained in contact with the solid residue for several seconds. The solid residue was spread over a metal surface (metal matrix).

After demonstrating that the metal matrix reactor operated efficiently, the information obtained was used to adapt the reaction to a fluidized bed, that was believed would be more convenient for use in a production mode. To compensate for the slower flow rate used in fluidization, and the lack of a metal catalyst, the amount of FOOF (as opposed to FOO) reaching the reaction zone was optimized. This required additional cooling of the gas stream and control of the O_2 pressure.

A severe test of Pu extraction was made by removing it as PuF_6 from incinerator ash. Fluorination of the ash at elevated temperature was shown to result in the formation of nonvolatile fluorides. When the untreated ash was fluorinated at room temperature, volatile PuF_6 was formed.

EXPERIMENTAL

APPARATUS

The apparatus used in carrying out the gas-solid reactions involving the fluorination of Pu residues was enclosed in a glove box designed for the safe handling of Pu. Fig. 1 is a simplified schematic of the equipment used. Although Ni or Al were the preferred materials of construction for handling fluorinating agents, stainless steel was found to be perfectly adequate for many uses at room temperature.

The FOOF was made outside of the glove box and cryopumped to a receiving reservoir inside the glove box. The receiving reservoir was one component of a gas circulating loop.

GAS-SOLID REACTORS

METAL MATRIX REACTOR

To take advantage of the effect of a metal surface, the first reactor used was a 13 liter stainless steel cylinder filled with compacted Al foil balls, Fig. 2. These balls formed a matrix for support of the solid reactant.

The solid reactant was distributed evenly throughout the reactor. The 13 liter volume of the reactor was the largest component of the 18 liter gas circulating system. At a circulation rate of one liter per second, the gas entered the reactor about 2 seconds after vaporization in the FOOF reservoir and then spent 13 seconds in the reactor. The circulation rate was controlled by throttling a bypass valve around the bank of three model 601 Metal Bellows compressors. The rate of FOOF addition to the F_2 and O_2 carrier gas mix was controlled by adjusting the temperature of the FOOF reservoir.

FLUIDIZED BED

The fluidized bed reactor consisted of a tapered Al cylinder with a 1.9 cm diameter base opening to a 3.8 cm diameter at the top of the 30.5 cm long reaction cylinder. The reaction cylinder opened into a 10 cm diameter filter assembly. The gas entered through a Ni frit at the base of the reactor, mixed with the solid reactant in a fluidized state and exited after passing through particulate filters. The optimum circulation rate was about 1 slm. The linear gas velocity through the bottom frit was 30 cm/s. The pressure drop across the bed was nominally the weight of the solid reactant per unit cross sectional area.

The FOOF reservoir was located as close as possible to the entrance of the fluidized bed to minimize the gas travel time. At liquid N_2 temperature no FOO was present under the conditions used, but was formed in the gas phase after evaporation of FOOF. The rate at which FOO was formed increased with temperature. In order to maintain a high ratio of FOOF to FOO in the fluidized bed reactor, the carrier gas stream was precooled by a second liquid N_2 trap before it entered the FOOF reservoir. In addition to retarding the formation of FOO from FOOF (as a consequence of the lower temperature), precooling the gas limited the O_2 pressure in the gas stream since an equal mixture of O_2 and F_2 has a vapor pressure of only about 160 torr at liquid N_2 temperature. This favorably effects the equilibrium.

CHEMICAL REACTANTS

The FOOF was prepared in a separate operation by reacting thermally excited F atoms with O_2 at a cold interface. Within a year we expect to have the capability of producing a kilogram of FOOF per day by this method.

The PuF_4 used in these experiments was the unreacted portion of the material used for the thermal generation of PuF_6 for another project. The powder density was about 1.3 g/cm^3. Particle size ranged from 25 to 125 microns.

The PuO_2 (not generated by the incineration of contaminated waste) was produced by the calcination of $Pu(C_2O_4)_2$ precipitate.

PROCEDURE

At liquid N_2 temperature the FOOF is a solid with very low vapor pressure. The physical properties of FOOF have been reviewed by Streng[7]. A carrier gas was introduced to the gas circulating part of the loop not including the ballast tank. The carrier gas was F_2 initially, but became a mixture of F_2 and O_2 as FOOF was introduced. This gas was circulated so that the vapor from the FOOF receiving reservoir was carried first to the gas-solid reactor, then through the infrared diagnostic cell, cold traps, compressor then back to the reservoir. The PuF_6 generated in the gas-solid reactor was condensed in the cold traps at a temperature of about 190 K. The vapor pressure of FOOF in the reservoir, and therefore the rate of addition, was controlled by adjusting the temperature of the FOOF reservoir. Adjusting the height of the liquid N_2 Dewar provided adequate temperature control for these experiments. The pressure in the circulating portion of the loop could be controlled by bleeding gas into the ballast tank. In the fluidized bed experiments the circulating gas pressure was maintained by condensing the gas (at liquid N_2 temperature) into a trap located between the compressor and the FOOF reservoir. The flow rate was monitored by measuring the calibrated pressure drop across an orifice before the gas entered the FOOF reservoir.

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(7) Streng,A.J.*Chem.Rev.***1963**,*63*,607.

All experiments were done in a batch mode. The FOOF was maintained at liquid N_2 temperature until introduction to the gas-solid reaction loop. The progress of the reaction was followed by monitoring pressures and by Fourier transform infrared spectroscopy (FTIR).

RESULTS

METAL MATRIX REACTOR EXPERIMENTS

The chemical reaction efficiency of the oxygen fluorides (FOOF and FOO) with PuF_4 varied from about 12% at a loading of 82 g PuF_4 to 24% with a loading of 400 g. Fig. 3 shows the amount of PuF_6 generated as a function of FOOF used. At the lower loading, the presence of FOO at the FTIR cell, downstream from the reactor, could easily be observed at moderate addition rates. At loadings of 400 g only a trace was observed at the highest rate that could be achieved by allowing the FOOF reservoir to warm in ambient air after having removed the liquid N_2 Dewar. In one experiment 51 g of PuF_6 was generated by the addition of 44 grams of FOOF in about 20 min.

A graph of the PuF_6 generated versus the amount of FOOF used during the fluorination of PuO_2 is shown in Fig. 4. In this case the curve is concave upward rather than downward as was the case during the fluorination of PuF_4. This reflects the fact that there are intermediate stable compounds such as $PuOF_2$ generated before PuF_6 can be produced. By using ultra violet light absorption to monitor the amount of F_2 used during the run, it was determined that the heat generated by the reaction of FOOF with PuO_2 was sufficient to activate a reaction of F_2 with PuO_2 during the early stages of the fluorination. When this factor was excluded, the reaction efficiency was found to approach that of PuF_4 with FOOF.

A comparison of the fluorination of PuF_4 when the supporting material was Teflon instead of Al is shown in Fig. 5. Although the PuF_4 loading, as well as the total surface area was slightly greater when Teflon was used, it is clear that the reaction efficiency has greatly decreased. We feel at this time that, at room temperature, the metal surface enhances the reaction of FOO but may not be necessary for the FOOF reaction because it is more chemically reactive.

FLUIDIZED BED REACTOR EXPERIMENTS

The fluidized bed reactor has been the gas-solid reactor of choice for many chemical reactions in industry. Heat is usually added to drive the reaction. The solid powder can be easily loaded and unloaded. We have not found a convenient way to use a metal catalyst to assist the reaction of FOO in the fluidized bed. To improve the reaction efficiency, we have concentrated our effort toward increasing the ratio of FOOF to FOO. This has been accomplished by precooling the gas, minimizing the travel volume between the FOOF reservoir and the fluid bed reactor, and by controlling the O_2 pressure. Another alternative would be to increase the O_2 pressure to drive the equilibrium (2 FOO = FOOF + O_2) to increased concentration of the more stable FOO. The temperature of the fluid bed could then be raised slightly to activate the FOO reaction.

A comparison of the PuF_6 generated versus the FOOF used, in the fluid bed and in the Al matrix reactor is shown in Fig. 6. The conditions used (except for the PuF_4 loading) were chosen to optimize the reaction efficiency in each case. In this example, the flow rate of the carrier gas through the fluidized bed was about 5 actual l/min. The carrier gas flow rate through the Al Matrix reactor was about 60 actual l/min. The operating pressure was about 150 torr in both experiments. The rate that the reservoir temperature was increased was about the same in each case. The over all reaction efficiency was slightly higher (15% vs 12%) in the Al matrix reactor. A second generation fluidized bed that will allow for higher flow rates and larger sample loading is in the design stage.

FLUORINATION OF Pu CONTAMINATED INCINERATOR ASH

One of the Pu containing residues being stored at DOE Pu facilities is the ash generated from the incineration of combustible materials that accumulate in the process glove boxes. The typical composition of such ash in order of abundance is K, 20% Ca,20% Cl,17% Pu,13% Na,5% Mg,5% Fe,4% P,3% Cr,2% Si,2% Ni,1% C, 0.9% H, 0.5% Cu,0.5% Al, 0.5%. It is well known that alkali metal fluorides can form double salts with Pu fluorides.[8,9] If this happens it could prevent the formation of gaseous PuF_6. To test the severity of this at room temperature, a preliminary experiment was run in which 15 g of PuF_6 was mixed with 85 g of NaF in the fluidized bed. Fig. 7 shows a comparison of the PuF_6 produced versus the FOOF used when fluorinating the mixture and when fluorinating a load of 15 g PuF_4 only. It was found that double salt formation was not a factor in this relatively mild reaction. Further study of this problem will be made using other surrogates.

In order to conserve FOOF and prevent high temperatures from the fluorination reaction energy, the ash was pretreated

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(8) Katz,S.;Cathers,G.I.*Nuclear Applications* **July 1968**,5,5.
(9) Galkin,N.P.;Veryatin,U.D.;Bagryantsev,V.F.;Gusev,V.F.*Radiokhimiya*,**1975**,*17*,604.

with F_2. It was found that ash prefluorinated at temperatures of 520 K did not produce PuF_6. An experiment in which the untreated ash was added to the fluidized bed and pretreated with F_2 at room temperature did produce PuF_6 however. Fig. 8 shows the amount of PuF_6 generated versus the FOOF used. X-ray analysis indicated that the Pu was present in the form of PuO_2. Other substances in the ash may help to occlude the PuO_2, decreasing the reaction efficiency.

At the start, 67% of the particles in the sample were larger than 90 microns, 43% were larger than 180 microns and 25% were larger than 350 microns. No attempt was made to reduce the particle size except the mixing associated with the fluidization process in the bed. We are currently experimenting with simple ways of pretreating the sample to reduce particle size as well as fluorinate most of the oxides before using FOOF. We are optimistic that practical reaction efficiencies will be obtained.

The ash represents the most stringent application of the process. There seems to be no severe problems associated with processing residues rich in Pu.

ACKNOWLEDGMENTS

We wish to acknowledge the contribution of H. J. Newman and H. E. Martinez for the design and fabrication of the fluid bed. E. A. Trujillo and R. M. de Duval were very helpful in materials preparation and characterization. T. R. Mills and R. J. Kissane produced most of the FOOF used in these experiments.

Titles to Figures.

Fig. 1. Simplified Fluorination Loop Schematic.

Fig. 2. Metal Matrix Gas-Solid Reactor.

Fig. 3. Effect of Loading on Fluorination in Al Matrix Reactor.

Fig. 4. Fluorination of PuO_2 in Al Matrix Reactor.

Fig. 5. Fluorination of 400 g PuF_4 on a Al Matrix Compared to Fluorination of 446 g PuF_4 on a Teflon Matrix.

Fig. 6. Comparison of the Fluorination of PuF_4 in the Al Matrix and the Fluid Bed Reactor.

Fig. 7. Fluorination of PuF_4 in Fluid Bed.

Fig. 8. Fluorination of Incinerator Ash Lean in Pu.

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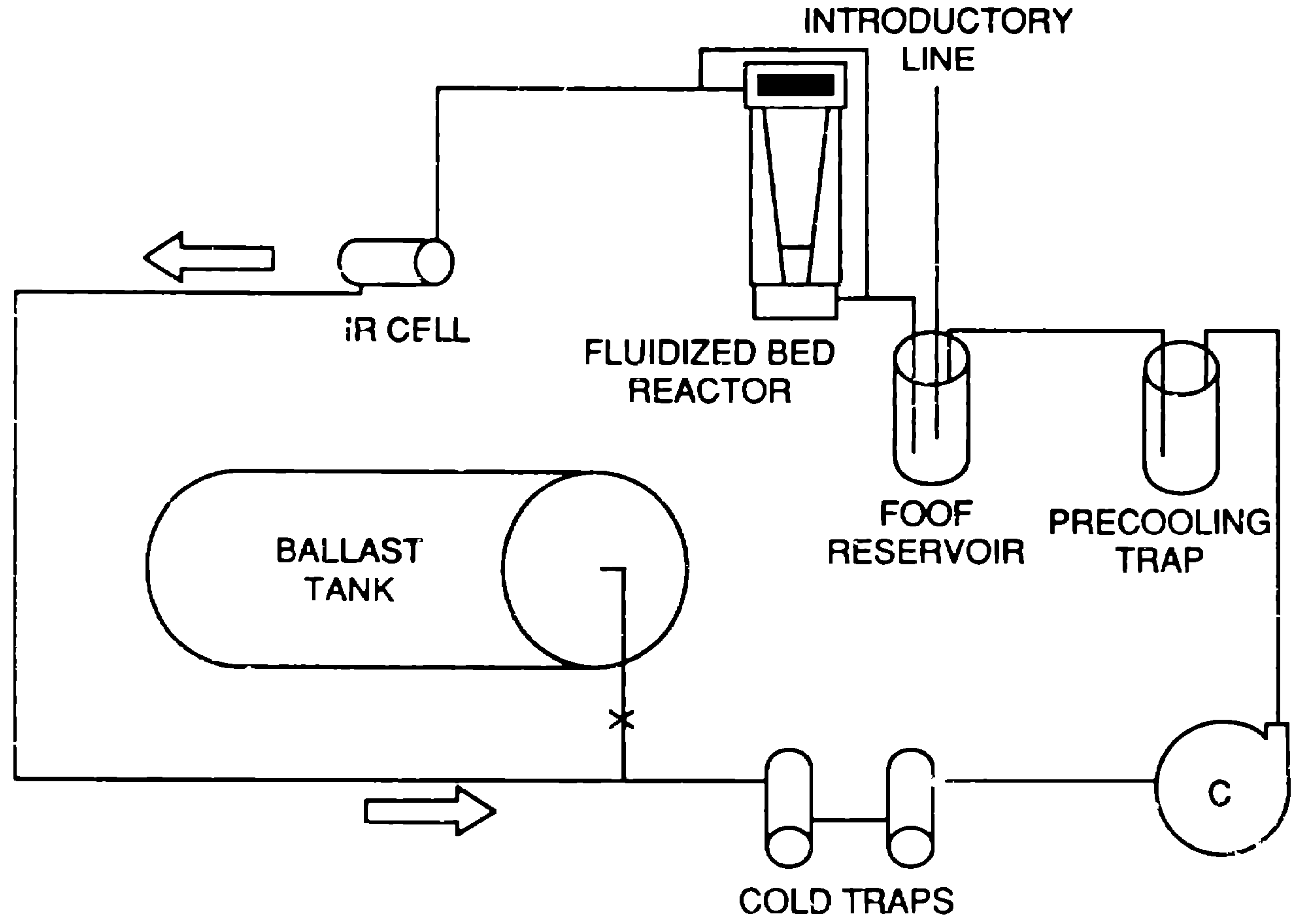

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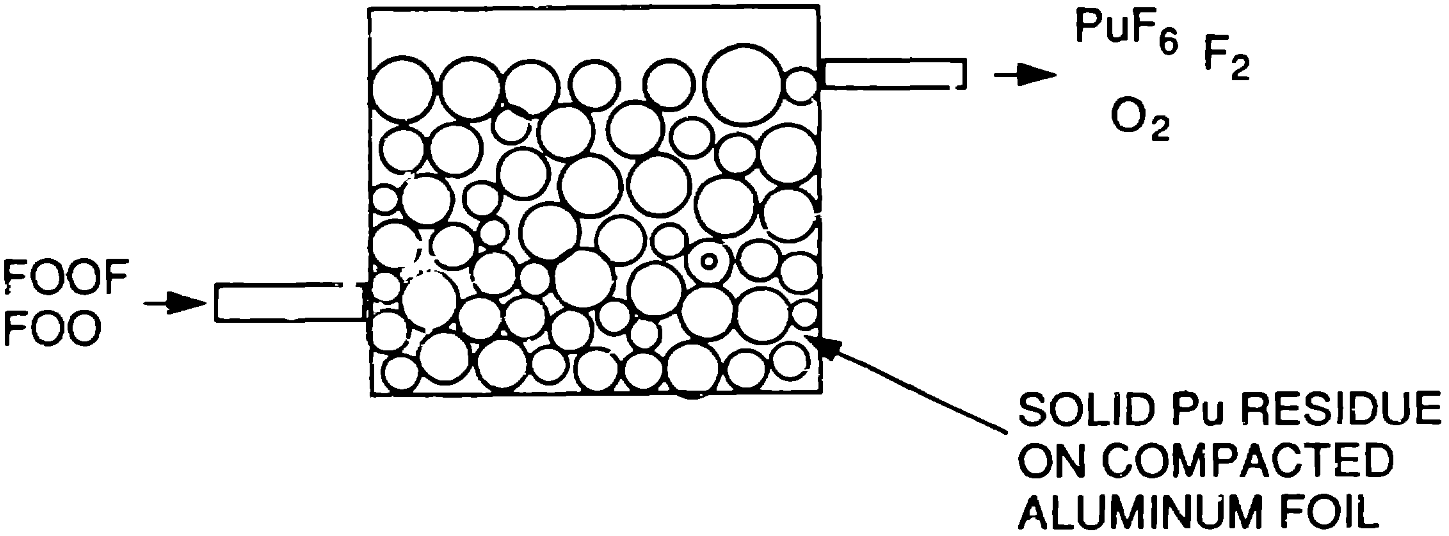
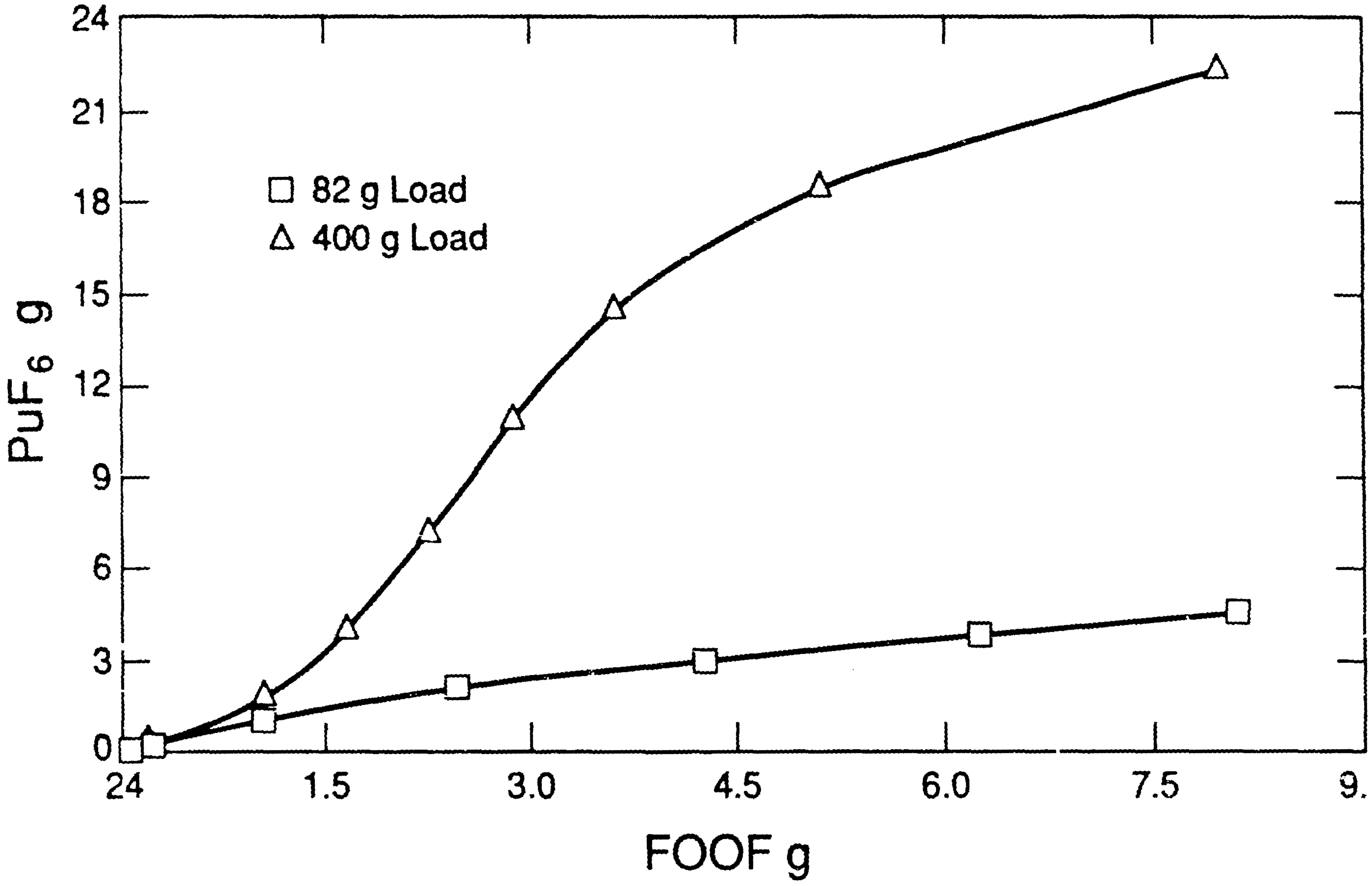

FOOF
FOO
PuF6
F2
O2
SOLID Pu RESIDUE
ON COMPACTED
ALUMINUM FOIL

89051837-1



24
21
18
15
12
9
6
3
0
PuF$_6$ g
☐ 82 g Load
△ 400 g Load
24
1.5
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4.5
6.0
7.5
9.
FOOF g

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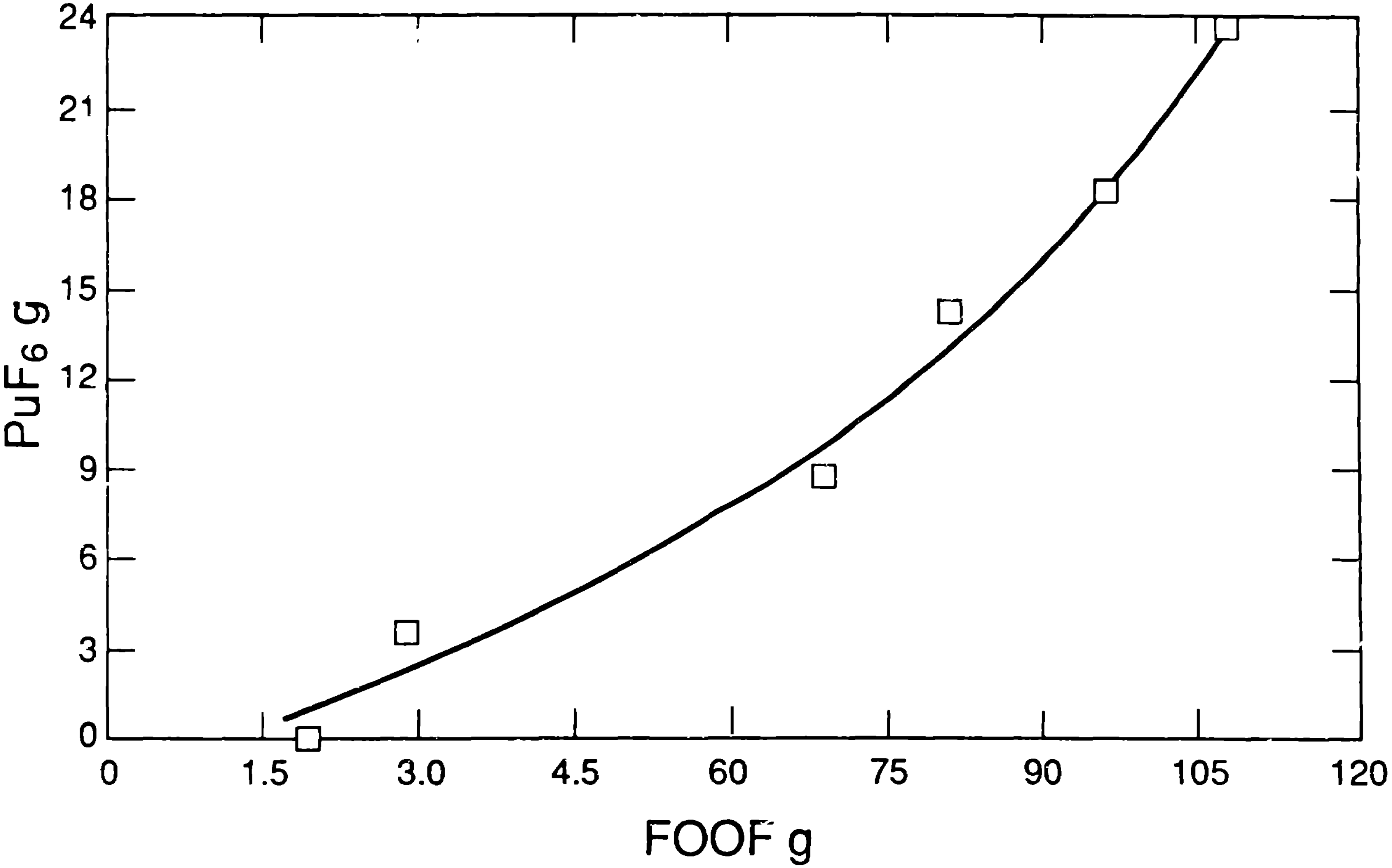

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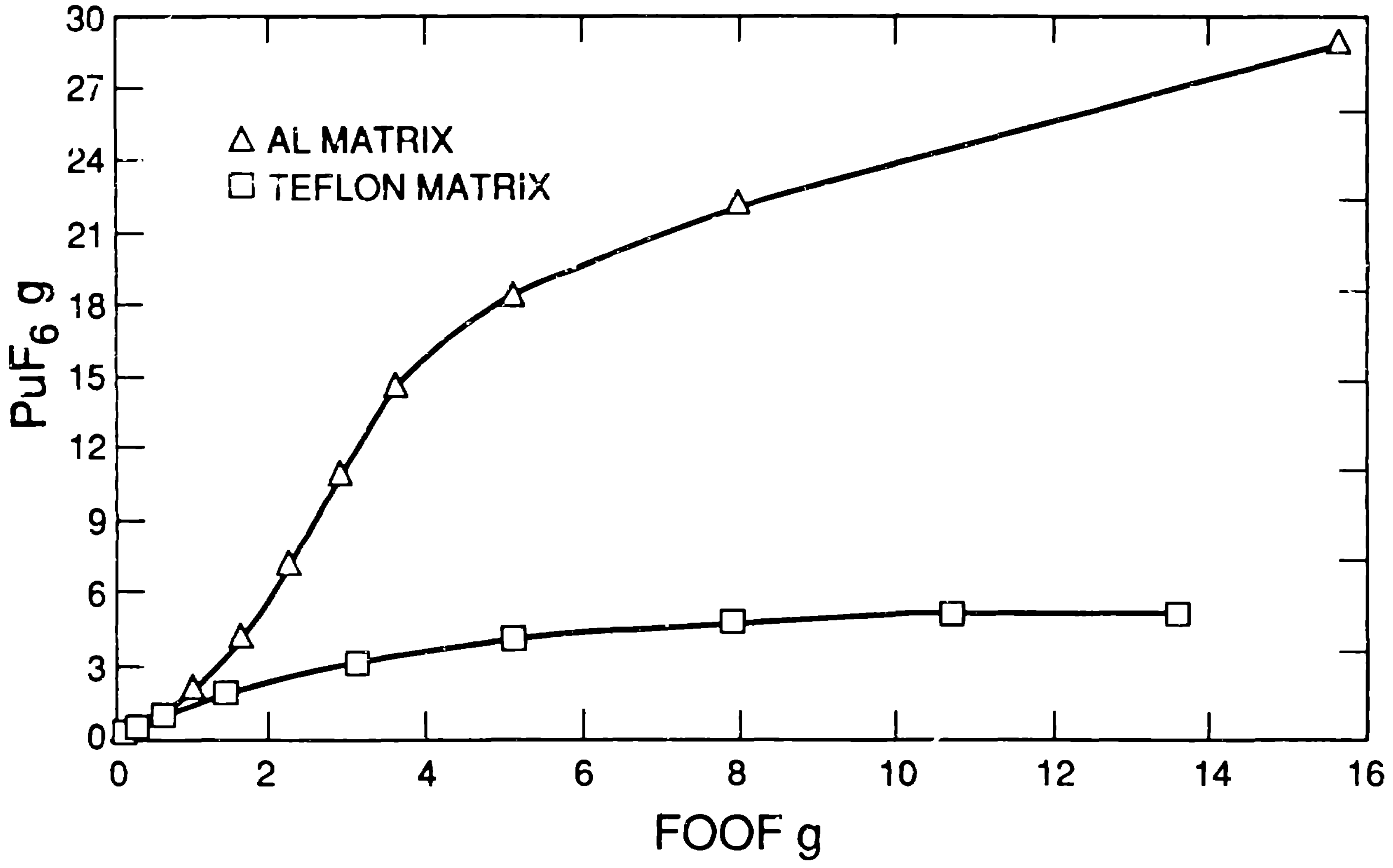

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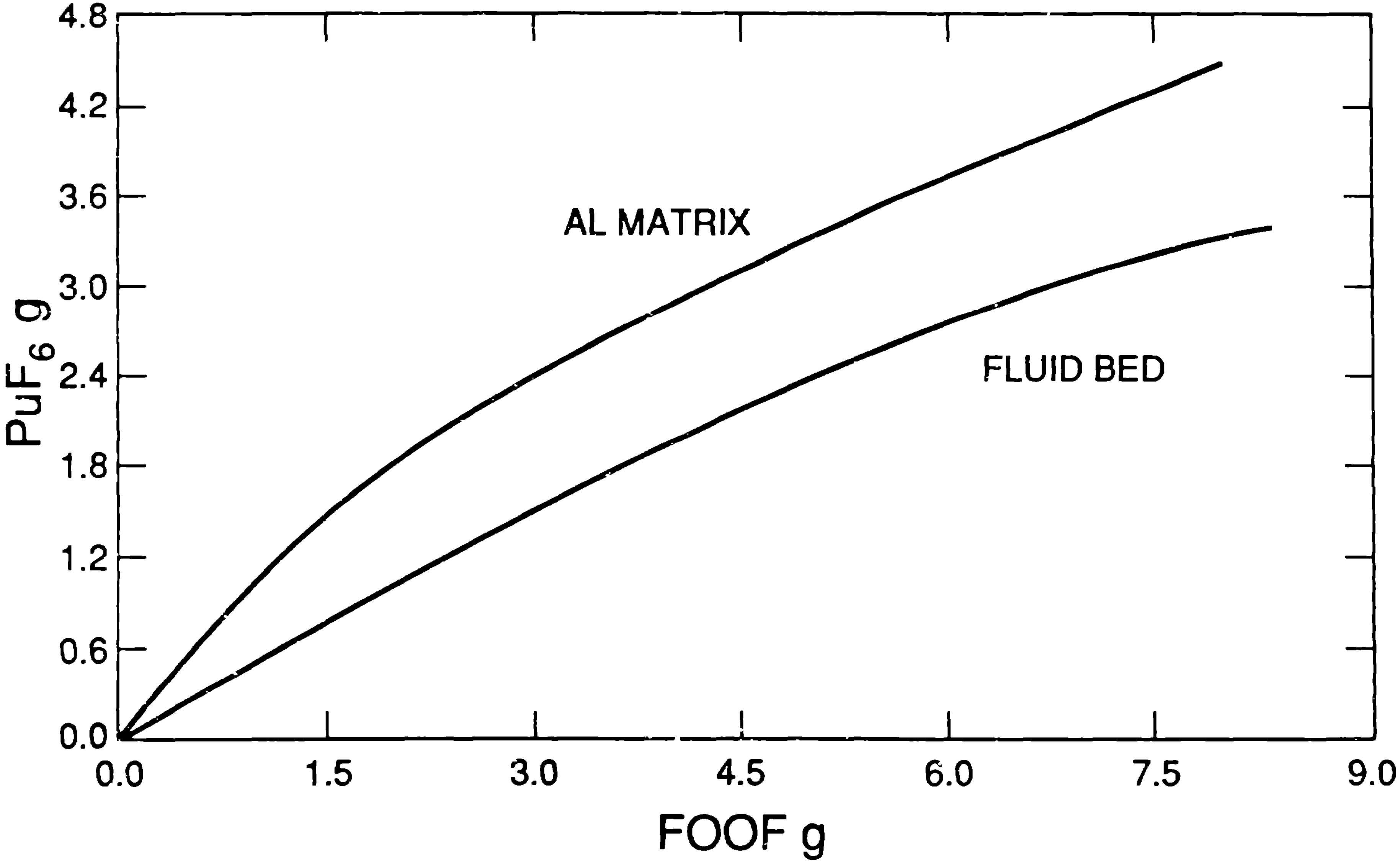

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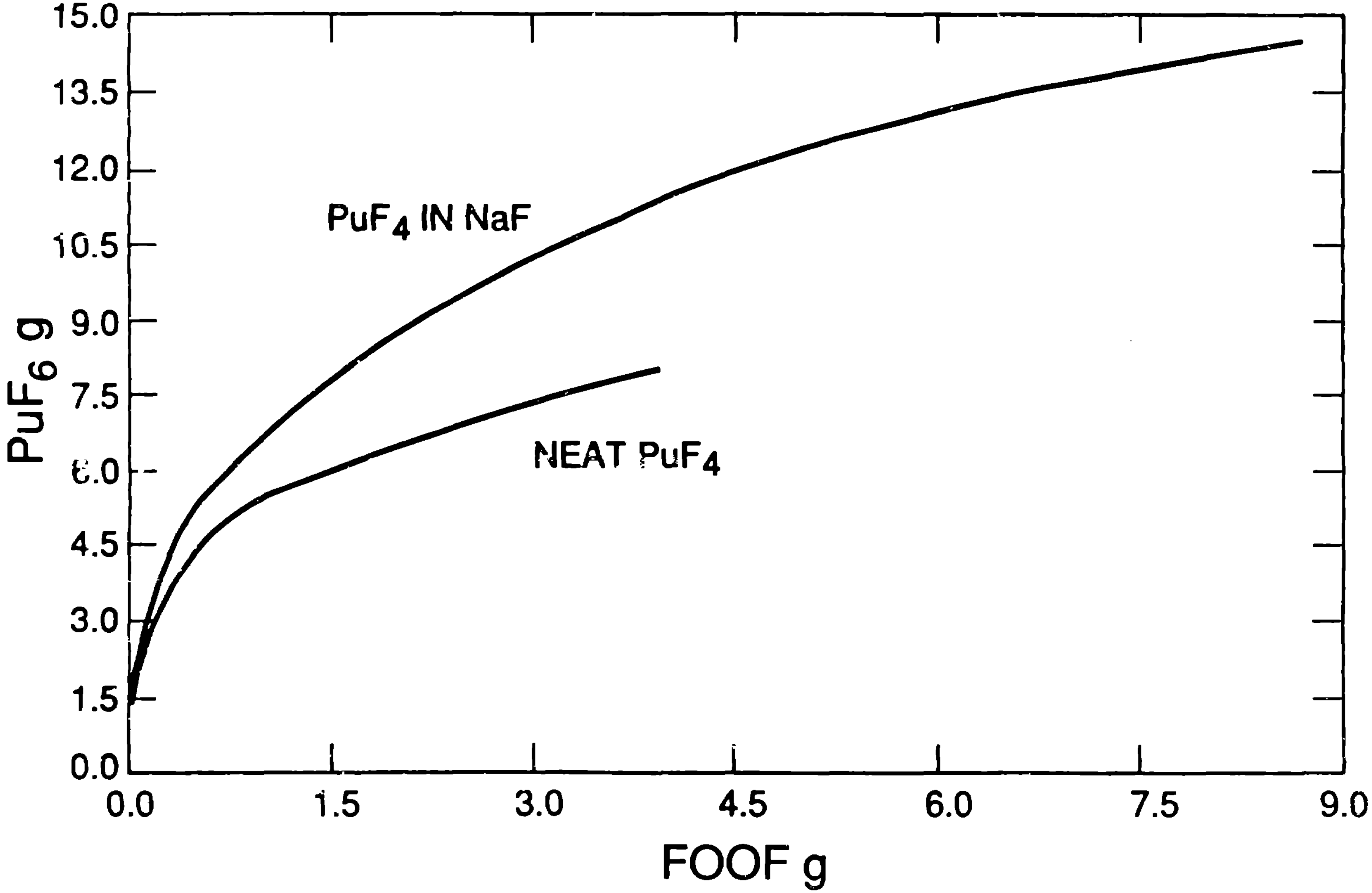

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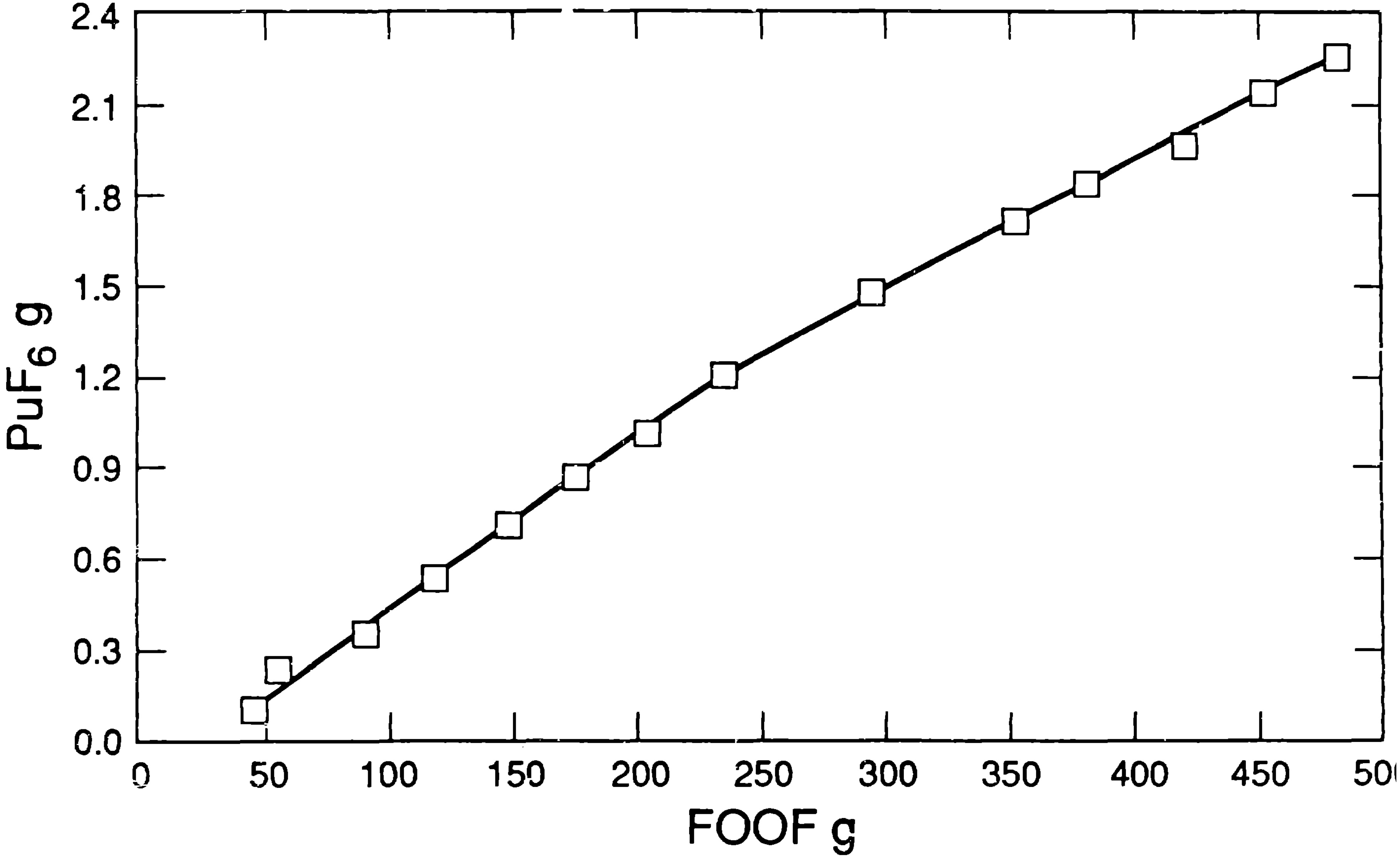
2.4
2.1
1.8
1.5
1.2
0.9
0.6
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PuF_6 g
0
50
100
150
200
250
300
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400
450
50
FOOF g