

# BULK SOLUBILITY AND SPECIATION OF PLUTONIUM(VI) IN PHOSPHATE-CONTAINING SOLUTIONS

H. T. Weger\*, S. Okajima, J. C. Cunnane and D. T. Reed., Argonne National Laboratory, 9700 South Cass Ave., Argonne, IL 60439

\* The research was performed under appointment to the Civilian Radioactive Waste Management Fellowship program administered by Oak Ridge Associated Universities for the U.S. Department of Energy and supported, in part, by developmental funds at Argonne National Laboratory.

DEC 23 1992

## ABSTRACT

The solubility and speciation of Pu(VI) with phosphate as a function of pH was investigated to determine the ability of phosphate to act as an actinide getter. The general properties were first investigated and are reported here with the goal of performing more quantitative experiments in the future.

Solubility was approached from oversaturation at initial pH = 4, 10 and 13.4. Absorption spectra were recorded, the solution filtered and the filtrate counted. Absorption spectra were obtained at varying phosphate concentrations and at pH of 2.7 to 11.9. The effect of complexation on the 833 nm Pu(VI) band was characterized. Evidence for three phosphate complexes was obtained for pH < 10 which have absorption bands at 842, 846 and 849 nm. Evidence for colloid formation was observed but is not conclusive. The possibility of colloids prevents accurate analysis of the solubility experiments. A concentration of 10<sup>-5</sup> to 10<sup>-6</sup> M Pu(VI) was measured in the filtrate at pH ≤ 10 that were passed through a 50 nm filter. Pu(VI) complexes with phosphate over hydroxide at pH ≤ 11.6, but at pH ≥ 11.9, only hydrolyzed Pu(VI) was detected. At pH = 12, the concentration of Pu(VI) was as high as 10<sup>-4</sup> M.

## BACKGROUND

MASTER

An understanding of the solubility and migration behavior of actinides is needed to help determine the suitability of various nuclear waste management options under consideration by the U.S. Department of Energy. This includes the suitability of the potential Yucca Mountain site as a high-level nuclear waste repository, land-fill disposal strategy and LLRW/TRU waste sites currently being evaluated. Solubility limits are needed to set the upper limit of actinide concentration should groundwater come in contact with the wasteform. These data will help determine the source term concentration of actinides to help predict the long-term performance of the waste disposal option.

A potential consideration in the design of either the waste package or the wasteform is the placement of actinide getters, in this case species that result in the formation of insoluble radionuclide phases, in close proximity to the wasteform. This will lower the overall solubility of the radionuclide and improve overall site performance. This getter material can

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ds

## **DISCLAIMER**

**This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.**

be placed in either the waste container or in the backfill surrounding the container. One such material under consideration are phosphate-bearing cements, ceramics, and minerals. These can provide a durable source of phosphate that may help decrease migration of actinides in the near field.

It is generally conceded that the solubility of phosphate phases is exceedingly low. Although phosphate is a relatively common constituent of groundwater, there is surprisingly little data on its interaction with actinide species. Only three papers were found concerning Pu(VI) in phosphate solutions [1-3]. The lowest concentration reported in the undersaturation experiments were of the order of  $10^{-5}$  M. Complexes with all three anionic phosphate species were reported. The  $\text{PO}_4^{3-}$  complexes were stronger by 13 orders of magnitude over  $\text{HPO}_4^{2-}$  complexes and the  $\text{HPO}_4^{2-}$  complexes were stronger by 4 orders of magnitude over  $\text{H}_2\text{PO}_4^-$  complexes.

In this context we plan to look at a wide variety of actinide-phosphate systems to establish general solubility trends and provide data to help evaluate the overall feasibility of the use of phosphate as an actinide getter. We began our analysis with Pu(VI) which is an oxidation state of plutonium expected in oxidizing groundwaters. Preliminary results are reported herein. These data were generated to focus future emphasis of the research.

## EXPERIMENTAL APPROACH

Pu-239, as an oxide, was originally obtained from Oak Ridge National Laboratory. This had been stored for a period of years in 4 M nitric acid. The Pu-239 was taken to dryness, redissolved in 8 M nitric acid, and run through a 1 cm by 10 cm column filled with Bio-Rad MP-1 resin that had been reconditioned with 8 M nitric acid solvent.

The eluent was taken to dryness, redissolved in 4 M nitric acid and reanalyzed for actinide content. A small amount of concentrated perchloric acid was added and slowly taken to near-dryness. This oxidized the Pu in the solution to the +6 state. The stock solution was made by adding high purity water and had a pH = 1.08 and a concentration of  $3.2 \times 10^{-2}$  M. No Pu(V) was noted in the spectra of the stock solution, indicating that the solution was >98% Pu(VI).

### Solubility

Three stock solutions of 0.01 M phosphate were prepared at pH = 4, 10, and 13.4. The pH was chosen so that one phosphate species is dominant; at pH = 4,  $\text{H}_2\text{PO}_4^-$  is the dominant species; at pH = 10,  $\text{HPO}_4^{2-}$  is dominant; and at pH = 13.4,  $\text{PO}_4^{3-}$  is dominant.

The pH of the Pu(VI) stock solution was adjusted from 1.08 to 3.70 by adding sodium hydroxide. An aliquot of 0.3 ml of the Pu(VI) stock solution was then added to 15 ml of each phosphate stock solution. The initial concentration of Pu(VI) in the phosphate solution was  $4.8 \times 10^{-4}$  M. The phosphate concentration, therefore, was approximately twenty times greater than the plutonium concentration.

The composition of the atmosphere was not controlled. The Pu(VI)-phosphate

solutions were stored in polypropylene (PP) bottles at room temperature. Spectra were recorded (350-850 nm or 800-1100 nm) over the span of the experiment. Solution was removed from the PP bottle and placed in a cuvette for spectroscopy, and then the solution in the cuvette was disposed.

The solutions were filtered at the end of the experiment. The solutions at  $\text{pH} \leq 10$ , 51 days old, were filtered first with a 200 nm polyvinylidene fluoride (PVDF) disposable filter and then with a polycarbonate (PC) 50 nm filter. The phosphate solution at  $\text{pH} = 13.4$ , 77 days old, was filtered with a 450 nm and a 200 nm polytetrafluoroethylene (PTFE) membrane. The filtrate were counted using low-level alpha counting techniques and concentrations were calculated from the results.

### Absorption Spectroscopy

Absorption spectroscopy was used to determine concentration and oxidation states of the plutonium throughout the experiments. The values found in [4] for the absorption coefficients were used.

Pu(VI) was analyzed spectroscopically in the near infrared (NIR) region of 800 to 950 nm. The 833 nm band of Pu(VI) was chosen for analysis due to its large absorption coefficient ( $\epsilon = 550 \text{ M}^{-1} \text{ cm}^{-1}$ ) and significant shift in wavelength when complexed. The stock solution of Pu(VI) was diluted by addition of high purity water until the concentration was  $1.4 \times 10^{-3} \text{ M}$  and the  $\text{pH} = 2.7$ . The oxidation state and concentration was determined spectroscopically. The only oxidation state detected was +6.

Phosphate or hydroxide solution was added to the plutonium solution in a glass vial. Pu(VI) solution was transferred between the glass vial and the cuvette when spectra were recorded. Throughout the experiment, when the solution was in the glass vial, argon gas was bubbled through the solution and the pH was monitored. No other control of the atmosphere was performed. Phosphate was added in concentration steps of 20% to 40% of the plutonium concentration. Spectra of hydrolyzed Pu(VI) were recorded up to  $\text{pH} = 10$  and used to separate the absorption of hydrolytic from that of phosphate complexes.

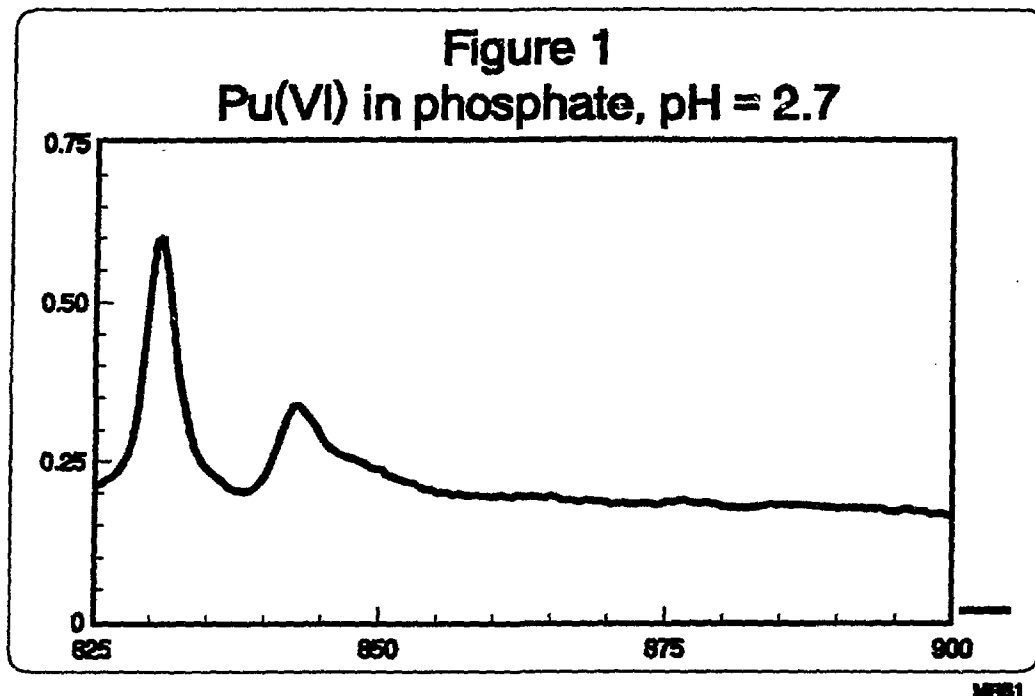
## **RESULTS**

Initial experiments were performed to qualitatively understand the behavior of Pu(VI) in phosphate solution. This information will be used to perform more quantitative experiments. Two sets of experiments were performed: solubility and spectroscopic.

### Spectroscopy

A favorable spectroscopy was observed for the 833 nm band of Pu(VI) in phosphate solutions. Three phosphate bands, at 842, 846 and 849 nm, were found for  $\text{pH} < 10$ . All three bands are present at  $\text{pH} = 2.7$ , which is shown in Figure 1. The 846 and 849 nm bands appear as shoulders of the 842 nm band. Here, the phosphate concentration was  $9.9 \times 10^{-4} \text{ M}$

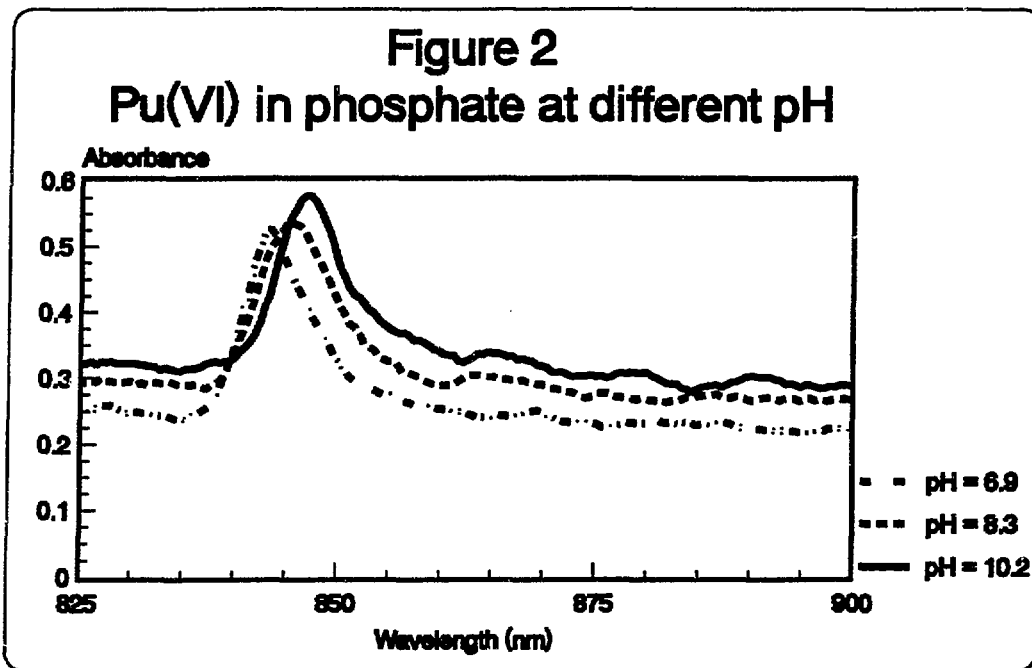
and the Pu(VI) concentration was  $1.3 \times 10^{-3}$  M.



All three bands are related to phosphate complexation since hydrolysis of Pu(VI) is insignificant at  $\text{pH} < 4$  [5-6]. In the solubility experiments, all three phosphate bands were observed for solutions at  $\text{pH} \leq 10$ ; but the 842 nm band was predominant in the  $\text{pH} = 4$  phosphate solution and the 846 nm band was predominant in the  $\text{pH} = 10$  phosphate solution. The bands found in the solubility experiments were used to help identify the individual phosphate bands in the spectroscopic experiments.

The relative intensity of the three bands is a function of pH. These spectra for  $\text{pH} \leq 10.2$  are shown in Figure 2. The phosphate concentration is  $1.2 \times 10^{-3}$  M and the Pu(VI) concentration is around  $9.3 \times 10^{-4}$  M. Since the three bands are close to each other, the change in the absorbance of the three bands appears as a gradual shift in wavelength. At  $\text{pH} < 6.9$ , the 842 nm band is favored over the 846 nm band but at  $\text{pH} > 8.3$ , the 846 nm band is favored over the 842 nm band. The 842 nm band is no longer detected at  $\text{pH} = 9.4$ . The 849 nm band is relatively small compared to the other two bands at  $\text{pH} < 10$ , but as pH approaches 12, the 846 and 849 nm bands are approximately equal in absorbance.

Absorption bands due to hydrolysis also exist at 846, 852 and 870 nm. In the absence of phosphates, hydrolysis becomes significant at  $\text{pH} > 4.2$ . In the presence of phosphate, however, it was observed that hydrolysis first becomes significant at  $\text{pH} > 10$ . Analysis of



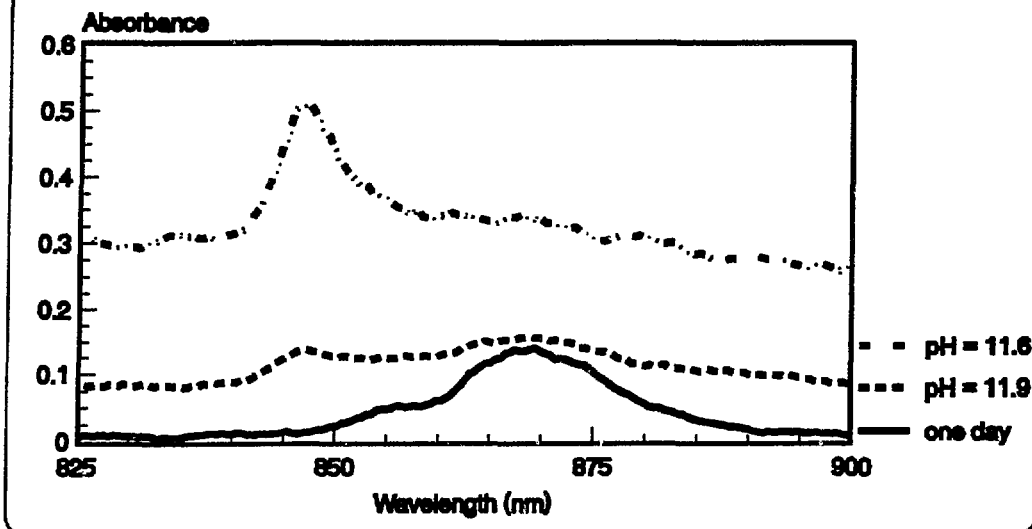
MF82

spectra at  $\text{pH} > 10$  is obscured by possible interference from the 846 and 852 nm hydrolysis bands.

Figure 3 shows selected spectra for Pu(VI)-phosphate systems at  $\text{pH} > 11$  with phosphate concentration at  $1.2 \times 10^{-3}$  M and Pu(VI) concentration at  $8.7 \times 10^{-4}$  M. It can be seen that the 846 nm and the 849 nm bands remain up to  $\text{pH} = 11.6$ ; but at  $\text{pH} = 11.9$ , hydrolytic species appear to predominate and the absorption of the 846 nm and 849 nm phosphate bands decrease significantly. A spectrum recorded a day later on the same solution shows that the 846 and 849 nm bands have disappeared.

When phosphate was added in the presence of hydrolyzed Pu(VI), a slow reaction rate was observed as Pu(VI) became complexed with phosphate. In one set of spectroscopic experiments, a plutonium solution free of phosphate was adjusted to  $\text{pH} = 6$ . When phosphate at  $\text{pH} = 4$  was added, the  $\text{pH}$  increased to 7 and the hydrolysis absorption bands decreased while the phosphate bands increased. It is believed that the increase in  $\text{pH}$  resulted from the amount replacement of hydroxide by phosphate as the complexing ligand. A reaction time of up to ten minutes was observed for the  $\text{pH}$  to stabilize.

**Figure 3**  
**Pu(VI) in phosphate at different pH**



MF83

H.T. Weger.  
Page 6 of 8

### Solubility

The initial solubility experiments we performed are difficult to analyze since aggregation (colloids) occurred. The pH = 4 phosphate solution, after 10 days, had white precipitates visible which disappeared upon shaking. The baseline and the absorption of the spectrum increased after shaking the solution. Within the time span of the experiment, no decrease was seen in the absorbance of the 842 nm band for a freshly shaken solution, indicating that the complex formed did not change significantly with time.

The spectrum for the pH = 10 phosphate solution did not change with time. After 10 days, the spectrum did not change when shaken. The filtration results indicated that most of the plutonium in solution was between 200 and 50 nm in size (see Table 1).

The solubility experiment also revealed a preference for hydrolysis over phosphate complexation at pH  $\geq 11.9$ . The phosphate at pH = 13.4 solution in the solubility experiment turned yellow immediately upon plutonium addition. A yellow color is associated with the 870 nm hydrolysis band. The final pH was 12 and the 833 nm absorption band had shifted to 870 nm.

As described earlier, the solutions were filtered and the concentration determined by

alpha counting. The results are shown in Table 1, but since colloids were observed we are not yet convinced that all plutonium in the 50 nm filtrate is truly in solution.

Table 1  
Concentrations of the Pu(VI) Filtrate Solutions.

Solution	Concentration (M) of Pu			
	Unfiltered	450 nm	200 nm	50 nm
Plutonium(VI)				
Phosphate, pH = 4	$4.8 \times 10^{-4}$ *	n/a	$2.4 \times 10^{-5}$	$2.3 \times 10^{-5}$
Phosphate, pH = 10	$4.8 \times 10^{-4}$ *	n/a	$1.5 \times 10^{-5}$	$6.4 \times 10^{-6}$
Phosphate, pH = 13.4	$2.7 \times 10^{-4}$	$2.5 \times 10^{-4}$	$2.2 \times 10^{-4}$	n/a

\* based on initial dilution of stock solution

n/a indicates that filtration at this pore size was not performed

Another interesting observation from the solubility experiments is that immediately following the addition of the plutonium(VI) aliquot to the phosphate stock solutions, a significant drop in pH was observed. The Pu(VI) stock solution, at a pH of 3.7, was added to the phosphate solution at pH = 4 resulting in a final pH of 3.12. This drop in pH cannot be attributed only to the acidity of the Pu(VI) stock solution. The pH of the solubility solutions over time are shown in Table 2.

Table 2  
The pH of the Pu(VI) Solutions

Solution	pH		
	20 minutes	28 days	38 days
Phosphate at pH = 4	3.12	3.41	3.35
Phosphate at pH = 10	8.24	7.82	7.86
Phosphate at pH = 13.4	12.04	12.03	11.95

## DISCUSSION

At this initial stage of the work, the evidence is not conclusive. There are, however, some observations that are apparent. There are three spectroscopically distinct species associated with the Pu(VI) phosphate system. Based on pH considerations alone, the 842 nm band may be a  $\text{H}_2\text{PO}_4^-$  complex, the 846 nm band may be a  $\text{HPO}_4^{2-}$  complex, and the 849 nm band may be a  $\text{PO}_4^{3-}$  complex. The pKs of phosphoric acid are 2.1, 7.2 and 12.4; the 842 nm band is favored over the 846 nm band at pH < 7.2 and the 846 nm band is favored over the 842 nm band at pH > 7.2. As the pH approached 12, the 849 nm band increases in absorbance.

These proposed assignments may explain other observations. All three phosphate species are seen at pH as low as 2.7, where  $\text{H}_2\text{PO}_4^-$  is the dominant species. Based on the



literature and the speciation hypothesis, this would be an expected result since  $\text{PO}_4^{3-}$  complexes are more stable than  $\text{H}_2\text{PO}_4^-$  or  $\text{HPO}_4^{2-}$  complexes. Furthermore, this would explain the pH drop observed in the solubility experiments since formation of  $\text{PO}_4^{3-}$  complexes would liberate hydrogen cations by the disassociation of  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  to maintain the equilibrium of the different phosphate species. Further data is needed to test this hypothesis.

It appears that Pu(VI) favors complexation with phosphate over hydrolysis at  $\text{pH} \leq 11.6$ . Hydrolysis, which becomes significant around  $\text{pH} 4.5$  for Pu(VI) in solution with no complexing ligands, did not become significant until  $\text{pH} > 10$  in phosphate solutions. At  $\text{pH} \geq 11.9$ , Pu(VI) is hydrolyzed and no significant complexation with phosphate is seen for solutions where phosphate concentration is equal to the plutonium concentration or when it is twenty times greater than the plutonium concentration.

In the initial solubility experiments, a Pu(VI) concentration of  $10^{-5}$  to  $10^{-6}$  M was observed at  $\text{pH} < 10$ . It is unlikely that these concentrations, even though they correspond to filtered solutions, represent the solubility of Pu(VI)-phosphate phases in the aqueous systems investigated. Both stable (periods of weeks) and unstable Pu(VI)-phosphate colloidal species were noted in almost all the systems investigated. Since many of these were less than 200 nm in size, it is likely that colloidal species smaller than 50 nm also exist in our samples. This limitation in interpreting the data reported herein will be resolved in future work by longer term experiments, more extensive filtration, further characterization of the colloidal species (light scattering and photoacoustic spectroscopy) and undersaturation experiments using solids generated in the various environments of interest.)

The data does not yet enable us to predict phosphate's ability to act as a getter. The complexes formed indicate that phosphate complexes would be formed in the groundwater, but the presence of colloids requires further investigation. The colloids formed, could increase the migration potential of Pu(VI) in groundwater systems.

Future experiments will concentrate on determining the speciation and further characterization of the colloidal properties observed. The spectroscopic features already noted for the 833 nm Pu(VI) band will help in the future analysis planned.

## REFERENCES

- 1 R. G. Denotkina, V. B. Shevchenko and A. I. Moskvina, Russ. J. Inorg. Chem., **10**, 1333 (1965).
- 2 R. G. Denotkina and V. B. Shevchenko, Russ. J. Inorg. Chem., **12**, 1237 (1967).
- 3 A. I. Moskvina, Sov. Radiochem., **11**, 447 (1969).
- 4 J.J. Katz, G. T. Seaborg and L. R. Morss, *The Chemistry of the Actinide Elements*, 2nd. Ed. (Chapman and Hall, New York, 1985), p. 787.
- 5 Initial Hydrolysis of Pu(VI), S. Okajima and D.T. Reed, accepted for publication Radiochimica Acta, 1992.
- 6 Speciation of Pu(VI) in Near-Neutral Solutions via Photoacoustic Spectroscopy, S. Okajima, D.T. Reed, J.V. Beitz, C.A. Sabau, and D.L. Bowers, Radiochimica Acta, **52/53**, 111-117 (1991).