

## **New Insights into the Radiolytic Stability of Metal(IV) Phosphonate Adsorbent Materials**

### ***Supporting Information***

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## Experimental Methodology

### *Adsorbent Synthesis*

Mesoporous Zirconium Titanium Mixed Oxide: Mesoporous zirconium titanium oxide xerogel powders (MZT) with monomodal porosity and composition  $Zr_{0.33}Ti_{0.66}O_2$  were prepared using palmitic acid as the template, as previously described.<sup>1-2</sup>

Polyphosphonate Functionalization of MZT: Grafting of PIDC or ATMP to the pore surfaces of MZT was achieved by loading 2.5 g of the MZT xerogels into a Schlenk tube followed by out-gassing using a two-stage rotary vane pump. The xerogels were then contacted with an excess of a 41 mM solution of the phosphonic acid by injection into the tube fitted with a septum and left for 24 h with occasional agitation. The pH of the mixture was not adjusted. After contact of the xerogels with the phosphonic acid solution for 24 h, the solution was removed and the xerogels washed thrice with a solution having a water-to-ethanol ratio of one. This washing was then continued with de-ionised water until the filtrate was neutral. The xerogels were dried in air at 80 °C for 24 h and then at 50 °C in a vacuum oven (10 mmHg) for 12 h to afford PIDC-MZT and ATMP-MZT.

Zr-ATMP Coordination Polymers: The Zr-ATMP coordination polymer was prepared with a P/(Zr+P) mole ratio of 0.8 as previously described.<sup>3</sup> Briefly, aqueous ATMP (50 wt%) was mixed with ultrapure water and Zr(IV) propoxide (70 wt% in 1-propanol) was then added. The pH of the resulting precipitate was adjusted to between 4 and 5 by addition of potassium hydroxide solution (2.0 M). The resulting suspension was then stirred at room temperature for 1 h in a plastic beaker before being treated hydrothermally at 160 °C for 24 h. The product was isolated by vacuum filtration, washed with ultrapure water, air-dried and ground to a fine powder in a mortar and pestle.

### *Adsorption Experiments*

Radiotracer Adsorption Experiments: Batch radiotracer adsorption experiments were undertaken to assess sorption properties of the functionalized MZT materials. Approximately 40 mg ( $\pm 1$  mg) of the sorbent and 4.0 mL of nitric acid solution (0.00001-6 M;  $V/m = 100$ ) were mixed in polyethylene vials (5 mL) and spiked with 20  $\mu$ L of  $^{153}\text{Gd}$  radiotracer (>99%, Perkin Elmer Life Sciences), adjusted to roughly 20000 counts per minute (cpm). The activity levels of the tracer used corresponds to sub nano molar concentrations.

The vials were placed on a rotary shaker (40 rpm) and agitated continuously for 3 h at room temperature (25 °C). After contact, three individual 1 mL aliquots of supernatant from each vial were removed and analyzed in triplicate using a Wallac 1480 Wizard 3" gamma counter in which each sample was counted for 60 seconds. Averaged values of the triplicate samples were used to determine the final activities and standard deviations. The distribution coefficient ( $K_d$ ) for the metal cation with respect to the adsorbent was calculated using equation 1:

$$K_d = \frac{A_i - A_f}{A_f} \cdot \frac{V}{m} \quad (1)$$

Where  $A_i$  is initial radiotracer activity,  $A_f$  is final radiotracer activity,  $V$  is the volume of solution contacted with adsorbent,  $m$  = mass of adsorbent employed. Controls were prepared in the same fashion but without a solid adsorbent. The filtrates from the controls were analyzed against the starting solutions to ensure precipitation did not occur.

Macroscopic Adsorption Experiments: Adsorption experiments were undertaken for Zr-ATMP utilizing macroscopic concentrations of f-elements. Specifically, mixed cation solutions containing  $Y^{3+}$ ,  $La^{3+}$ ,  $Ce^{3+}$ ,  $Pr^{3+}$ ,  $Nd^{3+}$ ,  $Sm^{3+}$ ,  $Eu^{3+}$ ,  $Gd^{3+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ ,  $Ho^{3+}$ ,  $Er^{3+}$ ,  $Tm^{3+}$ ,  $Yb^{3+}$ ,  $Lu^{3+}$ ,  $Th^{4+}$ ,  $UO_2^{2+}$  (approx. 2 mg/L each) were used. Quantification of the cation concentrations was performed by the Total Reflection X-ray Fluorescence (TXRF) technique utilizing a Bruker S2 Picofox instrument and using Ga as an internal standard. Typical uncertainties in concentration measurements using this technique are of the order of 5%, as determined by performing five repeat analyses with reference solutions.

### Characterisation

The  $^{31}\text{P}$  Magic Angle Spinning (MAS) Nuclear Magnetic Resonance (NMR) spectra were recorded at room temperature using a Bruker Avance II-300 (7 Tesla) spectrometer equipped with a 4 mm MAS probe. Each spectrum was acquired with 128 scans, with a recycling time of 30 s. The spinning rate for all the samples was 10 kHz. The  $^{31}\text{P}$  MAS NMR data were acquired using a single-pulse (Bloch decay) experiment with and without strong  $^1\text{H}$  decoupling ( $B_{1\text{H}} \sim 80$  kHz) during acquisition. The measured  $^{31}\text{P}$  chemical shifts were referenced to ammonium dihydrogen phosphate  $(\text{NH}_4)\text{H}_2\text{PO}_4$ .

Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were conducted on a Setaram TAG24 (France) with high purity instrument air carrier gas. Simultaneous TGA and differential scanning calorimetry (DSC) were conducted DT Instruments Q600 also using high purity instrument air carrier gas.

Nitrogen adsorption-desorption porosimetry data were measured at 77 K either using a Micromeritics ASAP 2010 or ASAP 2420 instrument. Samples were outgassed at between 120 and 150 °C.

### Gamma Irradiation

For the  $\gamma$  irradiations, air-dried samples (equilibrated at ambient humidity of 50-75% RH) were irradiated in stoppered standard soda glass vials using a  $^{60}\text{Co}$  source at the PISI facility at the Centro Atómico Ezeiza in Buenos Aires, Argentina. The  $^{60}\text{Co}$  source emits gamma radiation with energies 1.173 and 1.332 MeV. The PISI facility conveyor system served to automatically move the samples in and out of the irradiation chamber. The samples passed through the irradiation field within the chamber at a precisely controlled rate to absorb the amount of energy required for treatment. The dose rate within the chamber was 20.525 kGy/h and the samples were irradiated for varying amounts of time to provide the required amount of dose, as specified below:

- 14 h 40 min to provide 301.03 kGy absorbed dose
- 30 h to provide 615.75 kGy absorbed dose
- 141 h 32 min to provide 2904.97 kGy absorbed dose

As is standard for high dose dosimetry performed at gamma irradiation facilities, the dose measurements refer to the absorbed dose to water. Dose was not corrected for the electron density and fractions of the investigated materials, as these are preliminary experiments and we have applied a basic protocol.

### Adsorption

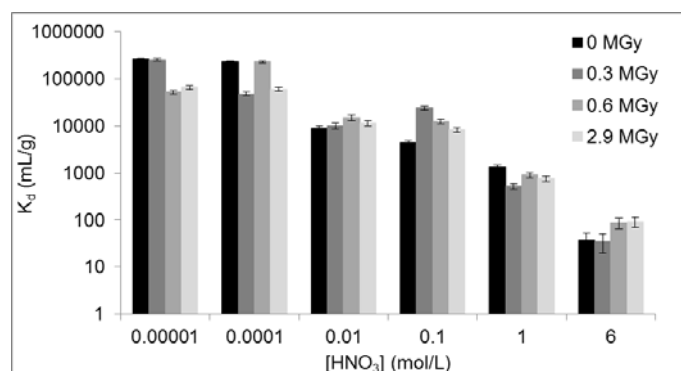


Figure S1. Extraction of Gd by Zr-ATMP from solutions with varying  $\text{HNO}_3$  concentration as a function of radiation dose in the range 0 – 2.9 MGy.

Unlike the ATMP-MZT material for which only weak extraction of  $^{153}\text{Gd}$  was observed at  $\text{HNO}_3$  concentrations greater than 0.01 M (Figure 1 in main manuscript), the Zr-ATMP coordination polymer showed quantitative extraction of all LN up to a  $\text{HNO}_3$  concentration of 0.1 M (Figure S1). Notwithstanding the use of tracer (microscopic) versus macroscopic LN concentrations in the two experiments, it would seem that the Zr-ATMP coordination polymer and phosphonate functionalised porous zirconium titanate ATMP-MZT had different dependencies on acid concentration. This is most

likely a result of the substantially higher capacity of the Zr-ATMP relative to ATMP-MZT. Specifically, the fact that Zr-ATMP had a higher density of phosphonate groups, so enough remain deprotonated to effectively sorb LN from solution even at lower pH values. However, it cannot be excluded that the difference in metal composition may have some influence.

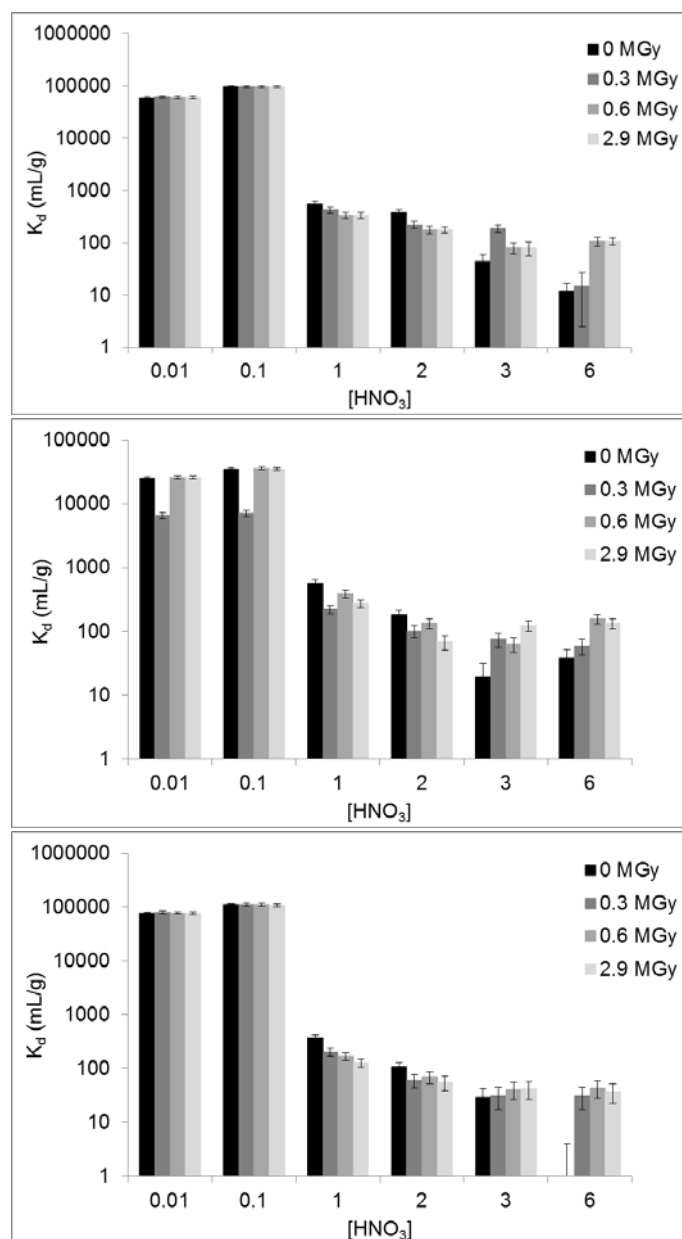


Figure S2. Extraction of Ce<sup>3+</sup> (top), Gd<sup>3+</sup> (middle) and Lu<sup>3+</sup> (bottom) by Zr-ATMP from a mixed cation solution containing a range of LN and actinides as a function of acid concentration.

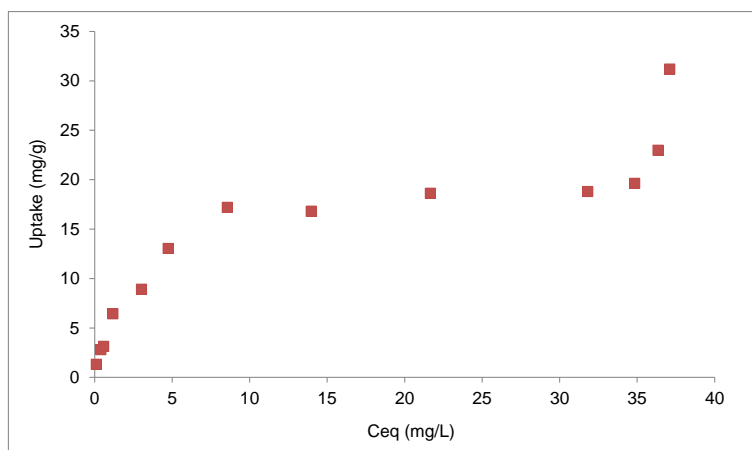


Figure S3. Uranium adsorption measured for Zr-ATMP in 1 M HNO<sub>3</sub>.

### Thermogravimetric Analysis (TGA)

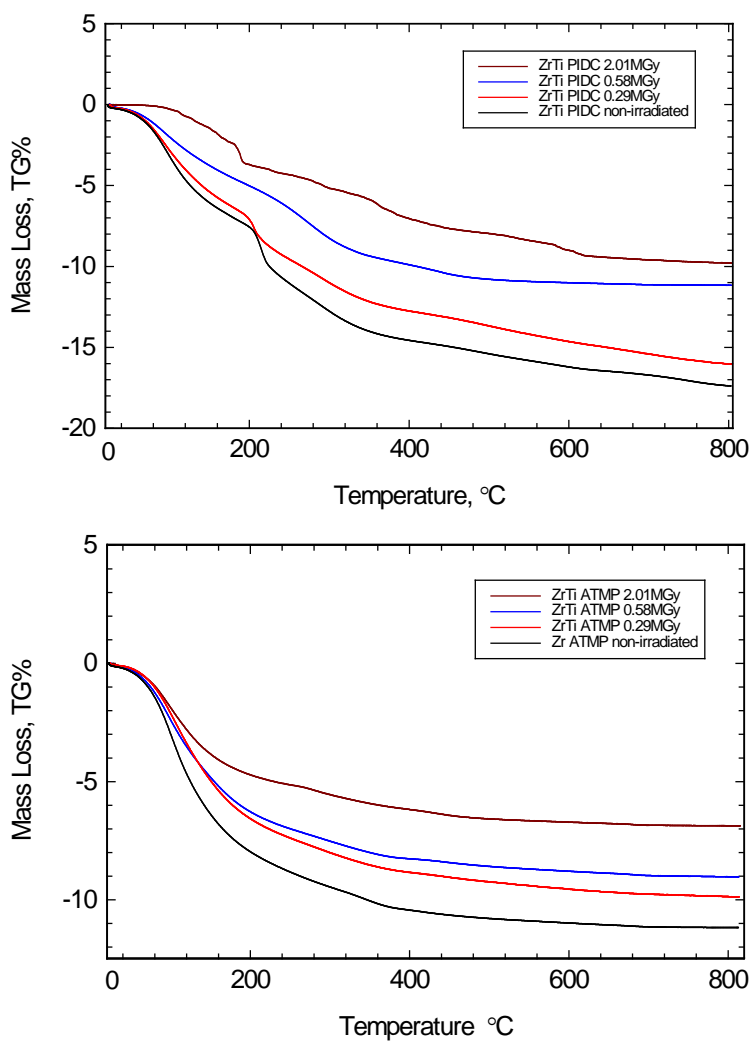


Figure S4. Comparative TGA weight loss curves before and after  $\gamma$  irradiation for PIDC-MZT (top) and ATMP-MZT (bottom). A progressive reduction in weight loss is observed in the temperature range 100 to 800 °C as a function of dose.

## Nitrogen Porosimetry

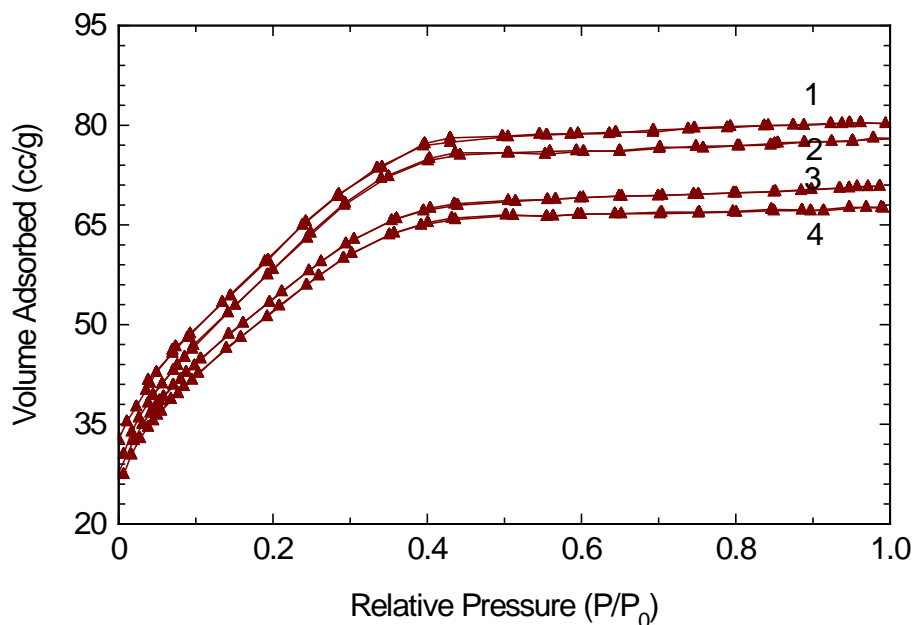


Figure S5. Nitrogen adsorption-desorption isotherms for ATMP-MZT as a function of dose 1 – 0, 2 - 0.29, 3 - 0.58, 4 - 2.9 MGy.

Table S1. Changes in functionalized-MZT average pore diameter and pore volume after varied doses of  $\gamma$ -irradiation

Sample Description	$\gamma$ - dose			
	0 MGy	0.29 MGy	0.58 MGy	2.9 MGy
	<b>Average Mean Pore Diameter (nm)</b>			
ATMP-ZrTi-0.33	2.3	2.3	2.2	2.2
PIDC-ZrTi-0.33	2.2	2.2	2.1	2.1
	<b>Pore Volume (cc/g)</b>			
ATMP-ZrTi-0.33	0.12	0.12	0.11	0.11
PIDC-ZrTi-0.33	0.12	0.12	0.12	0.11

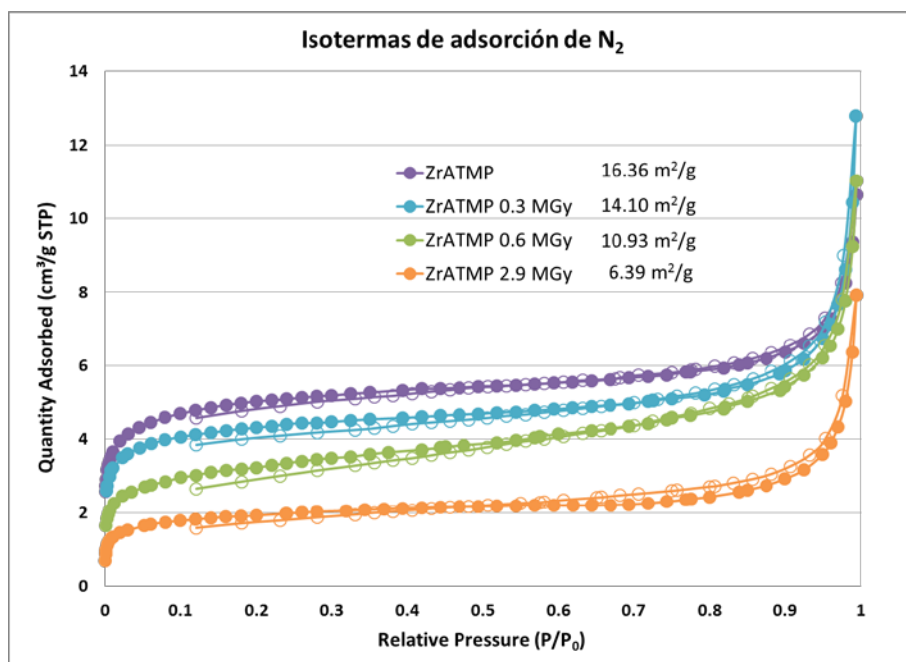


Figure S6. Nitrogen adsorption-desorption isotherms of the Zr-ATMP materials as a function of radiation dose.

## References

1. C.S. Griffith, M. DeLos Reyes, N. Scales, J.V. Hanna, V. Luca, *ACS Appl. Mater. Interfaces*, 2010, **2**, 3436-3446.
2. M. de los Reyes, P.J. Majewski, N. Scales, V. Luca, *ACS Appl. Mater. Interfaces*, 2013, **5**, 4120-4128.
3. J. Veliscek-Carolan, T. Hanley, V. Luca, *Sep. Pur. Technol.*, 2014, **129**, 150-158.