

HEAVY METAL ISOTOPIC FRACTIONATION EFFECTS LINKED TO ACID LEACHING OF DOPED POLYMERIC MATRIX: A STUDY BY HYPHENATED MASS SPECTROMETRY

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ABSTRACT

Fractionation effects associated with heavy metal isotopes leached from a doped polypropylene matrix was studied. The matrix itself was doped with oxides of Mg, Ti and Zn at levels of 3% and 10%. Acid leaching was investigated at pH3 and pH10. The leachates were analyzed by high performance ICP-MS and the results showed that normal natural abundances were recorded for Mg and Zn. However, depletion of Ti-48 and enrichment of Ti-46 were observed at statistically significant levels. At pH3, Ti-46 and Ti-48 displayed cycles of decay and growth with leaching over time for both the 3% and 10% doped polymeric materials. Such growth and decay were less pronounced for pH10, but the existence of enriched and depleted levels persisted. These data are interpreted in terms of the extraordinary crystal structure of TiO₂, and mechanisms relating to the crystal lattice arrangement of TiO₂. The mechanistic aspects were corroborated by TEM imaging. The fundamental application of our work lies in the discovery of a facile process for preparation of enriched Ti-46 solutions and depleted Ti-46 polymers.

Keywords: ICP-MS, isotopic fractionation, Ti-46/Ti48, polypropylene.

INTRODUCTION

The significance of an investigation of this nature is twofold: (i) to delineate the behavior of polymeric materials under conditions of chemical stress; and (ii) to discover new processes of enriching/depleting metal isotopes (Niederer *et al.*, 1980; Kung, 1989; Victor and Cox, 1996; Williams *et al.*, 2003; Häusser *et al.*, 1970) in polymers. The present study focused on subjecting metal-doped polymeric matrices (Pillay *et al.*, 2010) to acid leaching and observing the levels of isotopic fractionation in the leachates. There were sporadic attempts to study fractionation of metal isotopes using techniques other than ICP-MS (Jouvin *et al.*, 2012; Fujii *et al.*, 2011; Williams *et al.*, 2014). However, research of this caliber has not been previously accomplished where fractionation effects were monitored using high-performance Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS is a notable mass-analytical technique for measurement of ultra-low levels of metal isotopes. The technique is highly sensitive, quick and accurate. Polymeric material (polypropylene) used in this study was specially doped with major concentrations of Mg, Ti and Zn at levels of 3% and 10%. These particular doping levels were selected for clear observation of fractionation processes; and to study the effects of leaching on the stability of the polymeric material. Polymer stability can be adversely affected by unabated leaching; this is of high

significance in conducting polymers used in applications such as fuel cells (Mondal *et al.*, 2011).

Heavy-metal isotopic leaching studies of polymeric material are relatively unexplored because these effects are usually not appreciable and can only be detected by highly sensitive instruments. Regular mass spectrometry could be employed for such studies, but hyphenated mass spectrometry (ICP-MS) is a more powerful tool because of successful elimination of matrix effects. Clearly, one novel aspect of this research is the observation of these fractionation effects, especially in titanium isotopes; and proposal of a mechanism associated with such heavy-metal fractionation. TiO₂ is particularly prone to such effects because it can exist in various metastable phases such as β metastable Ti (Chang *et al.*, 2014) (unlike Mg and Zn) (Kung, 1989; Victor and Cox, 1996; Häusser *et al.*, 1970). Therefore, a second novel area of this study uncovers the facile capability to deplete polymeric material and concurrently enrich solutions with Ti-46. For the treatment of cancer by radioactivity (Ragde *et al.*, 2000; Maria *et al.*, 2008) titanium capsules are used but Ti-46 tends to create a problem because of the formation of unwanted radioactive Sc-46. Practical depletion techniques for Ti-46 are therefore, useful. In addition, enriched solutions (Stephen *et al.*, 2014) of Ti-46 can be used to abstract the isotope in question and convert it to Sc-46, which can be used as a tracer in oil refineries (Schweitzer, 1991). This work, therefore, has high potential for application in the oil and gas sector. Our

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technique at varying pHs could possibly be applied to deplete the Ti-46 in such applications.

MATERIALS AND METHODS

Sample preparation/ leaching study/ICP-MS

The sample preparation and instrumental technique associated with this work have been reported previously (Stephen *et al.*, 2014). The homopolymer HE445FB was used as base material to prepare the compounded materials, which were doped with 3% and 10% Mg(OH)₂, TiO₂ and ZnO (as reported earlier Stephen *et al.*, 2014). Each sample (1cm x 1cm) was kept individually in the leaching solvent of pH3 and pH10 for 24 weeks. Isotopic measurements of the leachates were undertaken at specific intervals with a Perkin Elmer SCIEX DRC-e ICP-MS. The analytical capability of the instrument was satisfactory producing relative standard deviations (RSD) <5% for repeated measurements on a certified standard (Stephen *et al.*, 2014).

Slicing polymers for TEM imaging

Thin slivers were “carved” from polymer plaques using an Ultra microtome facility (Power Tome PC, RMC Products, Boeckeler, model CRX). The microtome was equipped with a glass knife for coarse chopping and shaping prior to the final slicing. The final slices of 100 nm thickness and 4x4 mm sections were produced by employing a diamond knife. The cutting chamber was maintained at the appropriate temperature by circulating liquid nitrogen through it. The resultant thin slice of the sample was attached to a stainless steel loop dipped in 2 M sucrose solution. Sucrose solution helped to uncurl the sliver and to attach it to the steel loop. Once the slice was attached to the loop, sucrose was rinsed off using deionized water. The sliced sample was then carefully transferred to a tiny copper mesh 3.06 mm in diameter for imaging.

TEM and imaging

The grid along with the polymer slice was inserted into the electron beam path, which was guided down the vertical tubing by an accelerating voltage of 200 kV. An FEI Tecnai (model G2 20S-Twin EDAX) electron microscope was used for this study. The entire TEM was supported on a pneumatic suspension to minimize vibrations.

RESULTS AND DISCUSSION

TEM Study/Mechanism

The TEM study revealed that acid degradation of the TiO₂ bulk crystal structure leads to production of “smaller particles” suggesting that the ordered structure is broken down along planes into diminished entities. There is evidence (Kung, 1989; Victor and Cox, 1996; Häusser *et al.*, 1970) in the documented literature to indicate that

when the crystal is cleaved along a plane, the new surface will be reconstructed, involving atomic rearrangement, to produce a thermodynamically stable surface (Niederer *et al.*, 1980; Kung, 1989; Victor and Cox, 1996). Evidence of atomic rearrangement cannot be deduced from the images but can be inferred from the ICP-MS data below. Crystal stability and rearrangement suggests lighter Ti-46 atoms on the surface with the heavier Ti-48 atoms supporting the interior bulk of the crystal (Kung, 1989; Victor and Cox, 1996; Häusser *et al.*, 1970). The TEM images in figures 1-4 tend to support the theory (Niederer *et al.*, 1980; Kung, 1989; Victor and Cox, 1996; Häusser *et al.*, 1970) that constant crystal cleavage and rearrangement takes place breaking down the bulk structure into minute components. Figures 1 and 2 represent the unleached and leached images of 3% dopant. A comparison of figures 1 and 2 shows the intact bulk structure at the 3% dopant level degrading into myriad constituents at pH3. It is clear from the unleached image (Fig. 1) that the bulk composite ultimately erodes to a more “grainy” conglomerate structure (Fig. 2) with time. The graininess is attributed to the cycle of cleavages followed by atomic rearrangement and formation of new peripheral boundaries (Kung, 1989; Victor and Cox, 1996; Häusser *et al.*, 1970). Figures 3 and 4 represent the unleached and leached images of 10% dopant. The depth of colour in figure 3 reflects the higher dopant concentration. Here again, we observe from these images that acid degradation leads to more grainy formations, corroborating the premise that under acid attack the crystal structure is subjected to cycles of cleavages and re-formation of stable surfaces with atomic rearrangement (Niederer *et al.*, 1980; Kung, 1989; Victor and Cox, 1996; Häusser *et al.*, 1970).

Isotopic fractionation

TiO₂ has an anomalous crystal structure (Kung, 1989; Victor and Cox, 1996), resulting in extraordinary phases and metastable phases during chemical and physical stress (Niederer *et al.*, 1980). Thus its crystal structure is prone to effects unseen in other crystal structures – such as those of Mg and Zn. Figure 5a-d represents isotopic abundances of the metals of interest under leaching conditions of pH3 and pH10. Clearly, from the plots in figure 5, significant levels of enriched/depleted Ti-46/Ti-48 were observed. It is equally clear that these plots depict cycles of growth and decay. For pH3 and dopant levels of 3% and 10% (Figs. 5a,c) Ti-46 decays sharply with corresponding growth of Ti-48. This suggests that the crystal surface is optimized (maximized) with Ti-46 at lattice points, which is gradually degraded by acid attack showing a decline of Ti-46 levels. As the acid penetrates the bulk, the Ti-48 grows. After 12 weeks the data suggest “disintegration” of the bulk crystal structure (throughout the sample, from persistent attack) into grainy formations – as supported by the TEM images – leading to atomic rearrangement and

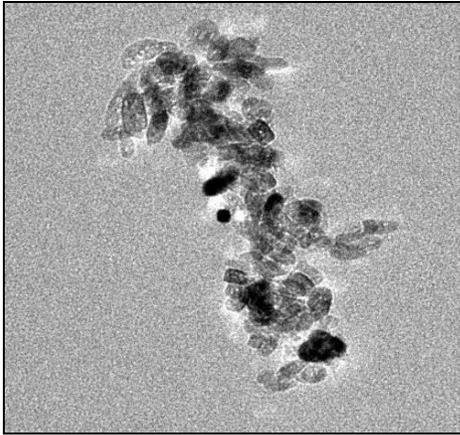


Fig. 1. Unleached 3%.

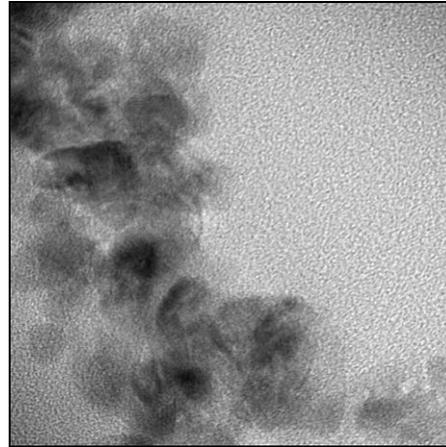


Fig. 2. Leached, 3%, pH3, 12 weeks.

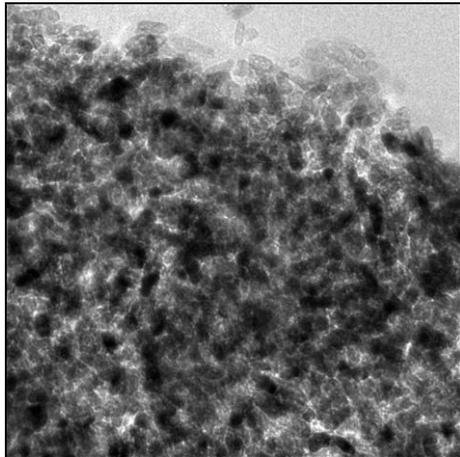


Fig. 3. Unleached 10%.

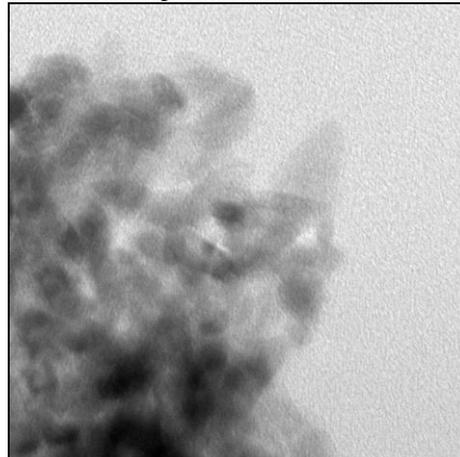


Fig. 4. Leached, 10%, pH3, 12 weeks.

resulting in new cycles of growth and decay (Niederer *et al.*, 1980; Kung, 1989; Victor and Cox, 1996).

With pH10 (Figs. 5b,d) the cycles of decay and growth are reversed and less pronounced. However, the existence of maxima and minima are apparent with use of higher pH. The data suggest that at pH10 the dual combination of negatively charged hydroxide ion (OH⁻) and H⁺ (at lower concentrations) has the double capability of attacking the crystal surface and the interior bulk structure, more effectively, with minima not as deep as in the case of pH3. Inroads of OH⁻ into the heart of the crystal releases Ti-46 from within and without – hence the plots in figures 5b,d show an initial increase in Ti-46 followed by a decline. The Ti-48, on the other hand shows a decline as these isotopes are abstracted from within the crystal structure, and their corresponding levels decrease. It is interesting to observe that in figure 5d (3% dopant) due to the diminished concentration of TiO₂ the effect is not as pronounced as that shown in figure 5b, but continued cycles of cleavage and reconstruction are still present.

From the mechanistic perspective, the ICP-MS data tend to support the hypothesis proposed by other authors that degradation of the TiO₂ structure is followed by cleavage along the planes of the crystal and atomic rearrangement (Niederer *et al.*, 1980; Kung, 1989; Victor and Cox, 1996; Häusser *et al.*, 1970). The data also support the theory that spatial arrangement of lighter Ti-46 isotopes is more probable as these are maximized on the periphery than in the interior of the bulk structure. This is logical as the heavier isotopes are needed within the crystal to provide support. If instead the interior were composed of mainly Ti-46 the crystal structure would collapse.

Kinetics/Impact of this study

The kinetics of this study is represented in figures 6 a-d and follows the same first-order format described in our previous paper (Stephen *et al.*, 2014). Inspection of figure 6 reveals that at the higher dopant level the rate of Ti-48 leaching increases with pH3 than with pH10. This suggests that at higher dopant levels the cycles of crystal cleavage and atomic re-arrangement are accelerated with higher H⁺ concentration (and infiltration into the crystal bulk) leading to a steeper slope (Fig. 6a). The plot for Ti-

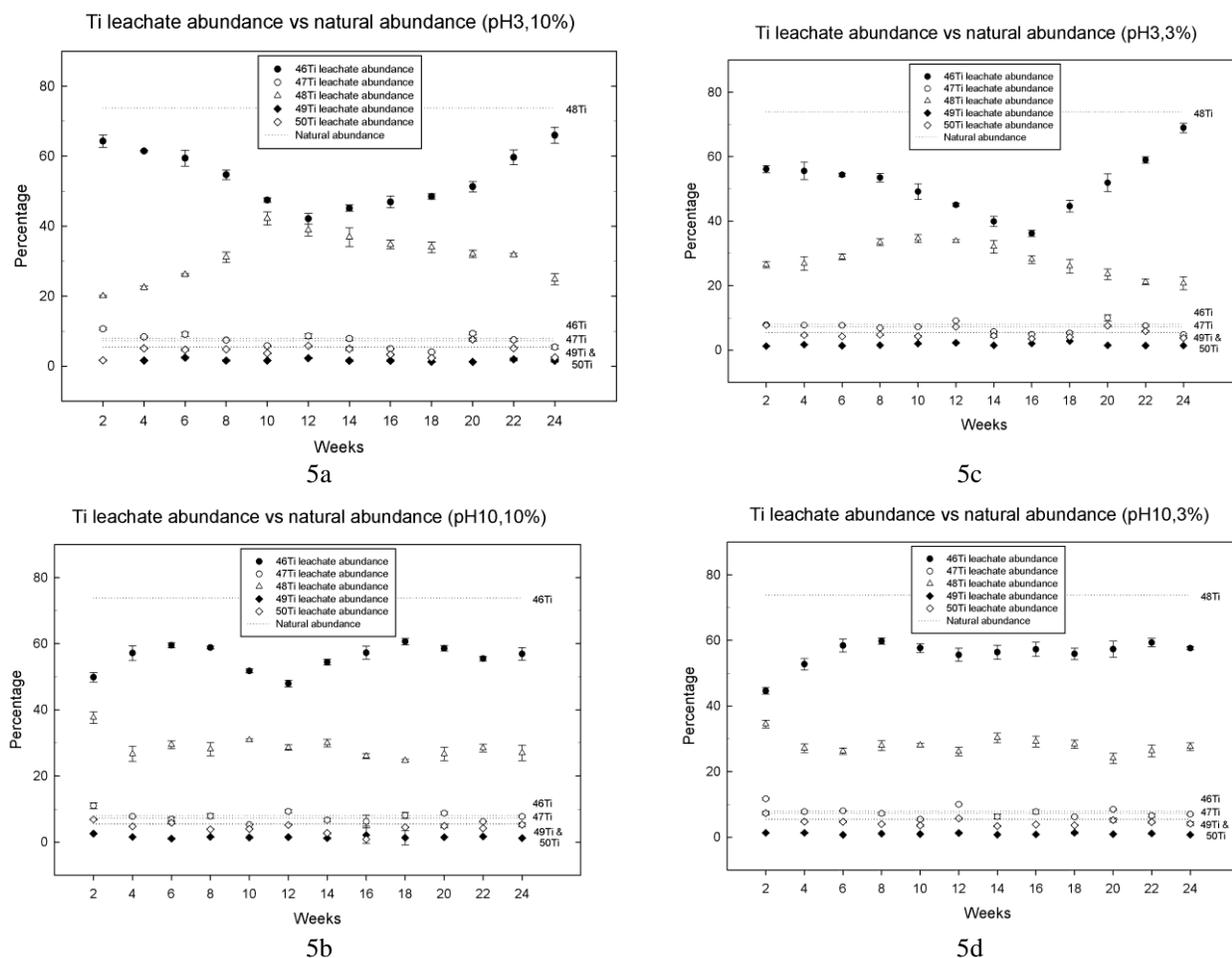


Fig. 5. a-d: Data showing cycles of growth and decay of Ti-46/ Ti-48 at pH3 and pH10.

46 is similar but less pronounced, as expected, due to lower natural abundance of this isotope. However, an interesting observation is that the levels of Ti-48 are consistently lower than those of Ti-46 supporting the theory that leaching of Ti-46 is more pronounced (but virtually constant) with constant re-arrangement of lattice structures composed predominantly of peripheral Ti-46 on the exterior of the bulk structure (Niederer *et al.*, 1980; Kung, 1989; Victor and Cox, 1996). A comparison of pH3 and pH10 (at 10%), figures 6a and 6c, reflects higher levels of Ti-48 at pH10 corroborating the view that combined OH⁻ and H⁺ attack occurs as the bulk structure is infiltrated. It is important to underscore that according to the experimental data, leaching occurs with both H⁺ and OH⁻. However, the rate of leaching could be affected by interfering chemical reactions such as possible formation of titanium complexes from undesirable impurities (Stephen *et al.*, 2014). The impact of the study lies in the development of a novel facile method for production of significant enrichment of Ti-46 in solution. As suggested earlier, this enriched Ti-46 can be converted to radioactive Sc-46 for use as tracers in oil refineries (Schweitzer, 1991). Another practical application of the

technique is discovery of depletion of Ti-46 in polymeric materials. This can be extended to other materials, including biomaterials, which could be used for brachytherapy treatment of prostate cancer (Ragde *et al.*, 2000).

CONCLUSION

Our study established that TiO₂ is prone to metal isotopic fractionation effects caused by acid percolation of polymeric material. We found the process to be highly pH dependent, and led to enriched Ti-46 solutions. At higher pHs the results suggested combined OH⁻ and H⁺ attack of the crystal structure. Lower pHs tend to induce accelerated rates of percolation, attributed to accelerated atomic re-arrangements of the crystal structure. Cycles of growth and decay of Ti-46/Ti-48 were observed, and attributed to constant cleavage and lattice re-formation with persistent acid attack. These cycles were found to be less pronounced at higher pH due to possible chemical ramifications with dual OH⁻ and H⁺ infiltration. The practical application of our study is facile production of

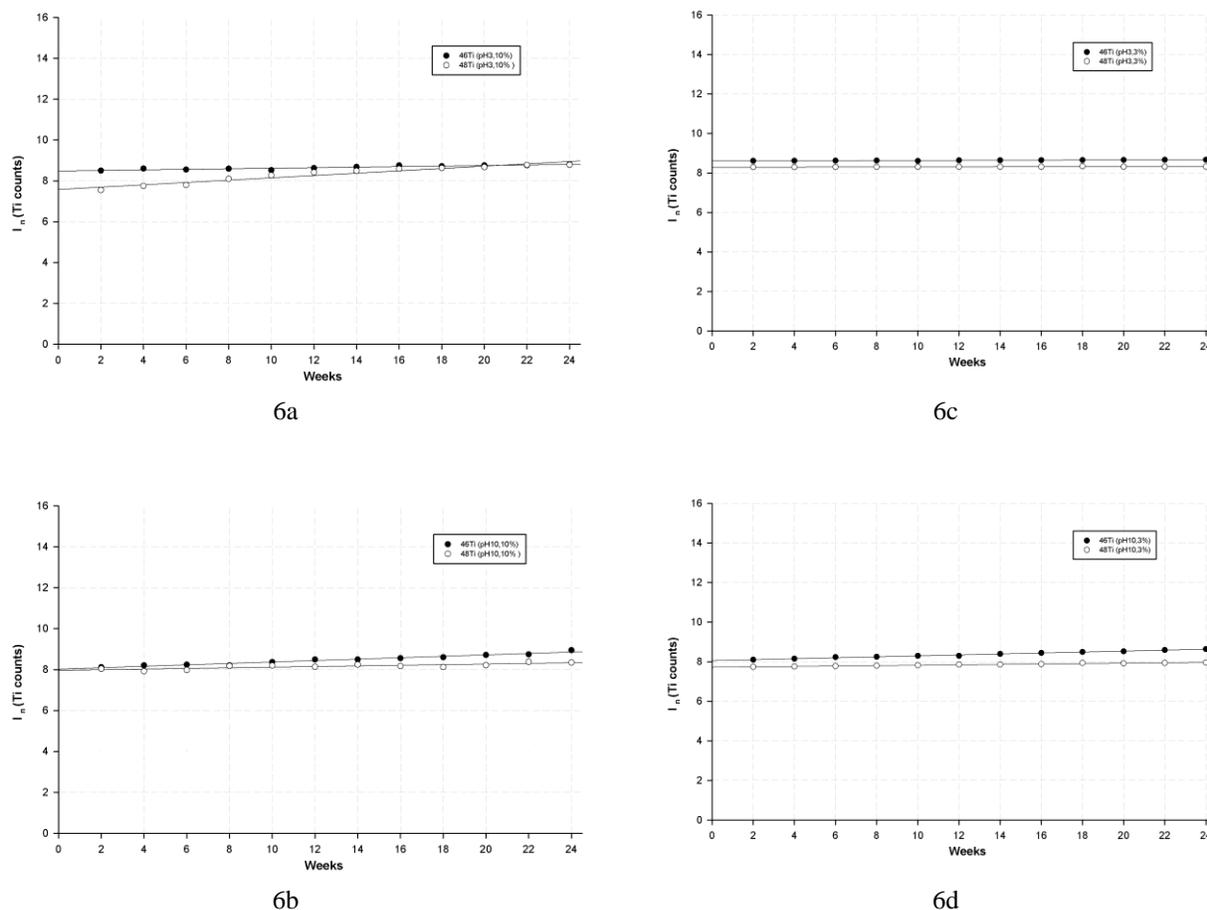


Fig. 6. a-d: Kinetic study of doped polymeric materials at pH3 and pH10.

enriched Ti-46 solutions for conversion into Sc-46 tracers for use in oil refineries (Schweitzer, 1991).

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Received: July 16, 2014; Accepted: Aug 19, 2014