Investigating the Effect of Protonation on Disorder and Multiple Scattering in Phosphate Solutions and Solids Using XAFS

Ashaki A. Rouff*, Stefan Rabe, Maarten Nachtegaal and Frédéric Vogel

General Energy Research (ENE), Laboratory for Energy and Materials Cycles
Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

PAUL SCHERRER INSTITUT

INTRODUCTION

MOTIVATION To detect phosphate precipitation and speciation in biomass slurries during hydrothermal gasification. This process is an efficient means of producing synthetic natural gas (SNG) from biomass, a renewable resource and viable alternative to fossil fuels. As the solubility of salts is reduced under hydrothermal conditions, nutrients such as P can be recovered and recycled.

TECHNIQUE X-ray absorption fine structure spectroscopy (XAFS) can be used in-situ to detect changes in phase and speciation of an element by probing its local coordination environment. For P, data collection and analysis is challenging as low-energy x-rays are required for measurements. Thus the suitability of XAFS for P systems needs to be assessed.

QUESTIONS
1. Can differences between aqueous and solid-phase phosphate species be detected using XAFS?
2. Is this technique sensitive to changes in phosphate speciation?

METHODS Solutions (Fig.1) and solids (Fig. 2) of phosphates in different protonation states were studied at 25 ℃ and 1 bar. Data was collected at the P K edge at 2.15 keV at the LUCIA beamline (X07A), Swiss Light Source (SLS), Villigen-PSI, Switzerland.
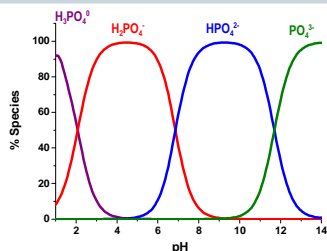
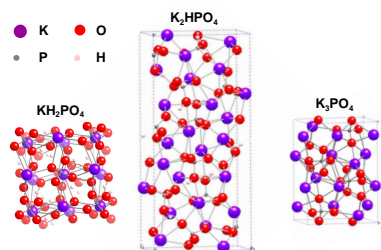**Figure 1. Phosphate speciation with pH. Solutions were prepared at pH 1.5, 4.5, 9.0 and 13.**

K : K O : O P : P H : H

Figure 2. Crystal structures of studied solids

RESULTS

XANES Solids exhibit more structure in the X-ray absorption near edge (XANES) region relative to solutions. There are no differences in solution spectra based on speciation. The spectrum for each solid is unique, reflective of differences in crystal structure. All solids have a distinct shoulder at ~4.5 eV above the edge due to backscattering from the K site.
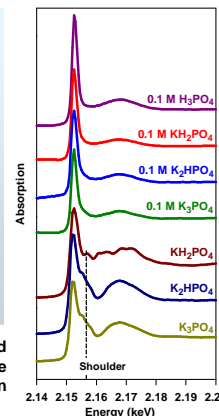
Figure 3. XANES spectra for solids and solutions with different phosphate speciation

EXAFS In the extended region of the fine structure (EXAFS), chi spectra (Fig. 4) are dominated by backscattering from an O shell. Multiple scattering (MS) within this shell (Fig. 5) contributes significantly to the beat pattern of the first oscillation in the chi. The O and MS shells are represented by a primary and secondary peak in the Fourier transform (FT), respectively (Fig. 4). Fitting these peaks to a model gives structural information including coordination number (N), distance from core (R) and structural disorder (Debye-Waller, DW) for the two shells (Table 1.).
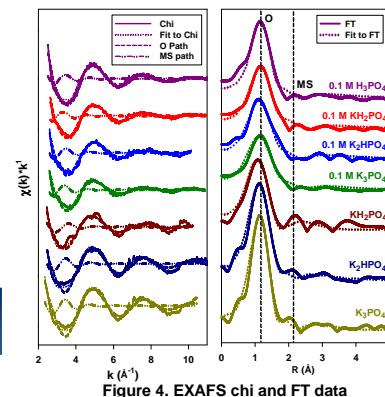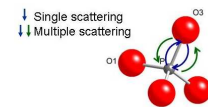
Figure 4. EXAFS chi and FT data

↓ Single scattering
↓↓ Multiple scattering

Figure 5. MS in phosphate tetrahedron

	Sample	Shell	CN	R	DW
Solutions	0.1 M H3PO4	O	4	1.55	0.005
		MS	2.8	3.21	0.005
	0.1 M KH2PO4	O	4	1.55	0.009
		MS	3	3.25	0.009
	0.1 M K2HPO4	O	4	1.55	0.01
		MS	3.4	3.20	0.01
	0.1 M K3PO4	O	4	1.55	0.013
		MS	3.2	3.23	0.013
Solids	KH2PO4	O	4	1.53	0.007
		MS	3.3	2.94	0.007
	K2HPO4	O	4	1.54	0.003
		MS	2.9	3.16	0.003
	K3PO4	O	4	1.54	0.002
		MS	2.2	3.18	0.002

Table 1. EXAFS fit results

EFFECT OF PROTONATION Addition of protons to phosphate primarily affects disorder within the P-O shell:
- For solutions disorder decreases due to reduced P-OH interaction with solvating waters relative to P-O units (chaotropic behaviour).
- For solids disorder increases due to elongation of P-OH relative to P-O bonds resulting in greater bond length distribution.

CONCLUSIONS

FINDINGS Though challenging, it is possible to collect P XAFS for both aqueous and solid samples:
- XANES can be used to distinguish between aqueous and solid phosphate species and different solid phases.
- EXAFS is sensitive to changes in protonation state of phosphate species.

IMPLICATIONS Excellent XAFS data at low T and p increases the likelihood of collecting data under hydrothermal conditions. Phosphorus XAFS can be a useful tool in many chemical, biological and geochemical systems.

QUEENS COLLEGE