Light absorbing products from aqueous processing of α-dicarbonyls: matrix effects and atmospheric implications

E. Finessi[1*], J.F. Hamilton[1], M.T. Baeza-Romero[2], A.R. Rickard[3], R.M. Healy[4], S. Peppe[5] T.J. Adams[6], M.J.S. Daniels[6], S.M. Ball[6], I.C.A. Goodall[6], P.S. Monks[6], E. Borrás[7] and A. Muñoz[7]

[1]Department of Chemistry, University of York, York, YO10 5DD, UK (*correspond.: emanuela.finessi@york.ac.uk)
[2]Escuela Ingeniería Industrial Toledo, Universidad Castilla la Mancha, Toledo 45071, Spain
[3]National Centre for Atmospheric Science (NCAS), University of York, York, YO10 5DD, UK
[4]Southern Ontario Centre for Atmospheric Aerosol Research, University of Toronto, Canada
[5]School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK
[6]Department of Chemistry, University of Leicester, Leicester, LE1 7RH, UK
[7]EUPHORE Laboratories, Instituto Universitario CEAM-UMH, 46980, Valencia, Spain

Aqueous phase chemistry of glyoxal (GLY) and methylglyoxal (MGLY) in the presence of inorganic salts has been recently identified as an important source of secondary organic aerosol (SOA) and brown carbon. However, the reversibility and the magnitude of the processes involved is still a matter of debate due to the lack of detailed speciation for such dynamic and complex systems.

In this study, a series of on- and off-line mass spectrometric techniques (FTICR-ESI-MS, LC-ESI-MS^n, ATOFMS) have been applied together with comprehensive gas chromatography with nitrogen chemiluminescence detection (GCxGC-NCD) and bi-dimensional nuclear magnetic resonance spectroscopy (2D-NMR) to identify the major organic products formed in bulk lab solutions with an emphasis on light absorbing organonitrogen species (ONs). The change in composition of the lab solutions as a function of different parameters was investigated. Mass spectral ions were identified as tracers for SOA generated from the uptake of gas-phase GLY and MGLY onto ammonium sulphate seeds and detected in chamber experiments conducted at the European PhotoReactor (EUPHORE). A series of light absorbing ONs, detected for the first time in chamber SOA by using off-line analyses, are presented as potential tracers for GLY- and MGLY-SOA in ambient aerosols. The relative potential of GLY and MGLY to form SOA and brown carbon through aqueous chemistry will be discussed.

Dissolution kinetics of ZrO_2 based innovative waste forms

Finkeldei, S.*, Brandt, F., Bukaemskiy, A., Neumeier, S., Modolo, G. and Bosbach, D.

Institute of Energy and Climate Research, IEK-6, Forschungszentrum Jülich, Germany; (s.finkeldei@fz-juelich.de (*presenting author), f.brandt@fz-juelich.de, a.bukaemskiy@fz-juelich.de, s.neumeier@fz-juelich.de, g.modolo@fz-juelich.de, d.bosbach@fz-juelich.de)

Plutonium and the minor actinides (MA = Np, Am, Cm) are the main contributors to the long-term radiotoxicity of spent fuel. As an alternative to the disposal in glass or the direct disposal of spent fuel ceramic waste forms are under consideration [1]. Regarding the long-term safety, zirconia based pyrochlores ($A_2B_2O_7$) have outstanding properties with respect to their high radiation resistance and their high durability in aqueous environments. As a consequence of radiation damage zirconia based pyrochlores undergo a phase transition to the less ordered defect fluorite structure [2]. Recent publications have demonstrated the possibility to include e.g. Cm and Pu on regular lattice sites of the pyrochlore crystal structure [3,4].

In the open literature no systematic study of the dissolution kinetics of ZrO_2 - Nd_2O_3 pyrochlores and defect fluorites is reported. The dissolution rate is an important property of potential host phases because it defines the source term for the radionuclides in the case of water intrusion into a high level nuclear waste repository.

Here, we present new experimental data regarding the influence of the chemical composition and crystal structure on the dissolution kinetics. The dissolution experiments were carried out using a dynamic setup to ensure far from thermodynamic equilibrium conditions. Moreover, the influence of temperature and pH on the dissolution rate was studied for the defect fluorite and the pyrochlore ceramics. An initial incongruent elemental release for Nd and Zr was observed. At steady state conditions and pH = 1, the dissolution rates of pyrochlore and defect fluorite are congruent and in the range of 10^{-5} to 10^{-6} $g□m^{-2}□d^{-1}$.

Further insight into the dissolution mechanism is gained by electron microscopy investigations.

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www.minersoc.org
DOI:10.1180/minmag.2013.077.5.6