MS23 O1

Calcium silicate hydrates: Importance in disposal of nuclear wastes Peter Stemmermann[a], Krassimir Garbev[a], Biliana Gasharova[b] [a]*Institut für Techische Chemie (ITC-TAB), Forschungszentrum Karlsruhe.* [b] *Institut für Synchrotronstrahlung (ISS), Forschungszentrum Karlsruhe.* E-mail: peter.stemmermann@itc-tab.fzk.de

Keywords: cement hydration, microstructure, carbonate formation

One of the key issues in predicting the suitability of cementitious waste forms for safe disposal of radioactive wastes is the long-term stability of the strength dominating cement hydrate, the calcium silicate hydrate gel (C-S-H). Its microstructure not only determines physical characteristics like mechanical strength and microporosity, but also heavily influences chemical parameters, especially the pH, which is essential in preventing corrosion of reinforced materials [1]. The C-S-H structure and the structural changes caused e.g. by carbonation in air are still not well known. The principal reason is the poor crystallinity, the difficulties in preparing homogeneous samples and the poor stability during analysis. Raman spectra of a series of mechanochemically prepared C-S-H samples with C/S ratios from 0.2 to 1.5 reveal changes in structure with changes in the C/S ratio. Samples with C/S ratios from 0.66 to 1 are dominated by Q^2 (chain elements). At C/S > 1 dimers are the main building unit [2]. Exposure to air results in very fast surface carbonation. Amorphous calcium carbonate is formed within minutes. Type and extent of carbonation is very sensitive to the C/S ratio of the primary phase. In experiments, which lasted up to 6 month, most spectra showed broad bands of amorphous silica. However, C-S-H with a C/S ratio of 0.66 and 0.75 showed only minor carbonation. Amorphous carbonate crystallizes over time to give primarily vaterite at C/S > 0.67 and aragonite at C/S<= 0.5. Calcite was not observed as a principal carbonation product [3]. With respect to carbonation the results suggest the addition of silica fume to cementitious waste forms.

[1] Galle, C.; Peycelon, H.; Le Bescop, P.; Bejaoui, S.; L´Hostis, V.; Bary, B.; Bouniol, P.; Richet, C., *J.Phys. IV France,* 2006, 136, 25.
[2] Garbev, K.; Stemmermann, P.; Black, L.; Breen, C.; Yarwood, J.; Gasharova, B., *J. Am. Ceram. Soc.*, 2007, 90, 900.
[3] Black, L.; Breen, C.; Yarwood, J.; Garbev, K.; Stemmermann, P.; Gasharova, B., *J. Am. Ceram. Soc.*, 2007, 90, 908.

MS23 O2

Wasteform design for nuclear waste immobilisation: one size does not fit all Neil Hyatt, Immobilisation Science University, Department of Engineering Materials, The University of Sheffield, Mappin Street, Sheffield, S1 3JD.

Nuclear power has enjoyed a resurgence of interest in recent years and was described as *"back on the agenda with a vengeance"*, in a recent speech by Prime Minister Tony Blair. This resurgence is motivated by the need to ensure security of energy supply and to reduce dependence on carbon fuels in order to combat global warming. Deployment of nuclear power on a scale to address these issues in the UK, and elsewhere, raises legitimate concerns regarding the production of nuclear wastes proliferation of fissile materials. Over shadowing this debate is the waste legacy of over 50 years of civil (and defence) related nuclear activities, the clean up of which is estimated to be in excess of £70bn in the UK alone.

The eventual fate of all nuclear waste is disposal in an appropriate facility, after immobilisation in a suitable matrix or *wasteform*. The first defence against release of radioactivity to the environment in this context is the wasteform itself, placing stringent constraints on the chemical and physical properties of such materials. Inorganic materials chemistry therefore has a pivotal role to play in meeting the challenges of legacy waste clean up, the treatment of new nuclear wastes and the safeguarding of fissile materials, through the design of durable wasteform materials.

In this talk I will present an overview of wasteform design applied to the immobilisation of current and future UK nuclear wastes, inspired by archaeology, crystallography and mineralogy. In particular I will focus on three key areas concerning: i) the structure of simulant UK nuclear waste glasses will be discussed, in relation to their processing and chemical durability; ii) the design of ceramic wasteforms for the immobilisation of iodine and caesium radioisotopes for advanced "partitioning and conditioning" fuel cycle flowsheets; and, iii) the design of ceramic wasteforms for the disposition of plutonium. In each case I will attempt to highlight the importance of structural characterisation in understanding wasteform design and performance.

MS23 O3

Short- and Intermediate Range Order in Borosilicate Waste Glasses. E. Sváb[a], M. Fábián[a], E. Veress[b], Th. Proffen[c], [a]*Research Institute for Solid State Physics and Optics, Budapest, Hungary* [b]*Babeş-Bolyai University, Cluj, Romania* [c]*Los Alamos Natl Lab, USA.* Email: svab@szfki.hu

Keywords: borosilicates; neutron diffraction; reverse Monte Carlo
Alkali borosilicate based glasses are of significant current interest as suitable materials for isolating host media for radioactive waste material storage (i.e. UO_3 or PuO_2) [1]. Structural characterization of these glasses is essential for understanding of glass durability. However, due to the high number of contributing elements and the overlapping distances, it is very difficult to derive adequate structural data from diffraction experiments.

Here we present a structure study performed on a 6-component sodium borosilicate host glass system with the composition of $(65-x)SiO_2 \cdot xB_2O_3 \cdot 25Na_2O \cdot 5BaO \cdot 5ZrO_2$ (x=5, 10, 15 mol%). The samples were prepared by melt-quenched technique [2]. For sample preparation isotopically enriched ^{11}B (99.6%) was used to avoid the high neutron absorption of natural boron containing ^{10}B.

Neutron diffraction pattern of the powdered glassy specimens were measured up to high momentum transfer 30 $Å^{-1}$, which made available high *r*-space resolution for the total atomic pair correlation function obtained by direct sine-Fourier transformation. Several characteristic atomic distances were revealed, which served as a priori input constraints for reverse Monte Carlo (RMC) modeling [3].