

MS23 O1

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

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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 Q² (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.

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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. Fábrián^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

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Alkali borosilicate based glasses are of significant current interest as suitable materials for isolating host media for radioactive waste material storage (i.e. UO₃ or PuO₂) [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)SiO₂·xB₂O₃·25Na₂O·5BaO·5ZrO₂ (x=5, 10, 15 mol%). The samples were prepared by melt-quenched technique [2]. For sample preparation isotopically enriched ¹¹B (99.6%) was used to avoid the high neutron absorption of natural boron containing ¹⁰B.

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].

RMC simulation of the experimental structure factor was successfully applied to generate a reliable 3-dimensional atomic configuration. Several partial atomic pair correlation functions, like the $g_{\text{SiO}}(r)$, $g_{\text{BO}}(r)$, $g_{\text{OO}}(r)$, $g_{\text{SiSi}}(r)$, $g_{\text{SiB}}(r)$, $g_{\text{NaO}}(r)$, $g_{\text{BaO}}(r)$, and $g_{\text{ZrO}}(r)$ and most of the corresponding coordination number distributions has been revealed providing information on the short and intermediate range order.

The Si-O network proved to be highly stable consisting of slightly modified SiO_4 units. The B-O surrounding proved to be more complex. We have found that two characteristic well resolved first neighbour B-O distances are present at 1.40 Å and 1.60 Å. The latter agrees with the Si-O first neighbour distance, which is also at 1.60 Å. From the detailed analyses of the B-O and O-B coordination number distributions we have established that both 3- and 4-fold coordinated boron atoms (denoted as $^{[3]}\text{B}$ and $^{[4]}\text{B}$) are present.

We suppose that the boron atoms partly form a mixed continuous network with Si-O network, where several different mixed $^{[4]}\text{B-O-Si}$ and $^{[3]}\text{B-O-Si}$ linkages are present in agreement with the findings of NMR [4,5] and Raman spectroscopy [6].

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MS23 O4

Magnetic phase transition of FeS at high pressures
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According to the cosmochemical arguments and the seismological data, the Earth's core must contain some light elements. However, the nature of the light element is still uncertain, and the major proposed candidates have been C, Si, O, H, or S. Therefore, it is important to understand the phase relationships of iron alloys at high pressures and high temperatures. In this study, we conducted high-pressure experiments and ab initio calculations to investigate the phase transitions and the physical properties of iron sulfide. In the case of high-pressure experiments, the laser-heated diamond anvil cell combined with the synchrotron X-ray diffraction technique was used [1]. We also used the first-principle calculations to investigate the magnetic property of high-pressure phase, which was discovered in the high-pressure experiments [2]. According to previous studies at ambient temperatures, FeS exhibits the following sequence of high-pressure phase transitions: troilite (FeS-I), low-P MnP phase (FeS-II), monoclinic phase (FeS-III). In our high-pressure experiments, we confirmed that the monoclinic phase was stable up to 40 GPa. Above 40 GPa, the sample

was heated to 1000-2000 K to induce the phase transition. After heating, a new high-pressure phase (high-P MnP phase) was observed. This high-P MnP phase (FeS-VI) remained stable at pressures higher than 120 GPa. We found a significant discrepancy between low-P MnP and high-P MnP phases. The discontinuities for the unit cell volume and the cell parameters between two phases were observed. As the structure of low-P MnP phase is identical to that of high-P MnP phase, these discontinuities indicated that an unknown type of phase transition must occur. Next, we investigated the magnetic properties and the spin configurations of these phases using the ab initio calculations. Previous study [3] confirmed that the low-P MnP phase was antiferromagnetic state. The same results were confirmed in our calculations. We also calculated the non-magnetic state for the MnP structure. The calculated results showed that the non-magnetic MnP structure was more stable than anti-ferromagnetic MnP structure at high pressures. The volume and cell parameters of non-magnetic MnP structure were in good agreement with those of high-P MnP phase observed in our experiments. Therefore, the magnetic transition of the MnP structure occurred at high pressures. The high-pressure stability limit of the high-P MnP phase was also investigated. We found that the phase transition from the high-P MnP phase to the CsCl-type phase occurs at about 300 GPa. Thus, the high-P MnP phase is stable at pressures corresponding to the lower mantle and the outer core. In contrast, the CsCl-type phase is stable in the inner core. Our new findings can contribute to the understanding for the nature of the Earth's core.

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MS23 O5

Sound velocities of MgSiO_3 perovskite and post-perovskite: A constraint on the D'' discontinuity
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Keywords: Brillouin scattering, elasticity, post-perovskite, D'' discontinuity

Recent discovery of post-perovskite phase transition has important implications for interpretation of the D'' layer at the base of Earth's mantle. Knowledge of the pressure dependence of acoustic wave velocities of post-perovskite phase provides essential and direct constraints for the seismic wave velocity profile at the D'' region. In this study, we report the aggregate shear wave velocities in MgSiO_3 post-perovskite phase by Brillouin spectroscopy in a diamond anvil cell (DAC) up to 173 GPa, in combination with infrared laser annealing of the samples. High-pressure Brillouin scattering measurements of sound velocities were carried out at room temperature in a symmetric diamond anvil cell with a 60-degree angular aperture. An argon-ion laser at a wavelength of 514.5 nm and 25-150 mW of power was used as a probe beam. The incident laser was focused to a beam size of ~30 µm in diameter on the sample. The scattered light was analyzed by a six-pass tandem Fabry-Perot interferometer. All measurements were performed in a platelet scattering geometry. Polycrystalline samples were synthesized in situ