Sulfur incorporation in high level nuclear waste glass: A S K-edge XAFS investigation

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Sulfur incorporation in high level nuclear waste glass: a S K-edge XAFS investigation

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Abstract. We perform X-ray absorption fine structure (XAFS) spectroscopy measurements at the sulfur K-edge to elucidate the electronic and geometric bonding of sulfur atoms in borosilicate glass used for the vitrification of high level radioactive liquid waste. The sulfur is incorporated as sulfate, most probably as sodium sulfate, which can be deduced from the X-ray absorption near edge structure (XANES) by fingerprint comparison with reference compounds. This finding is backed up by Raman spectroscopy investigation. In the extended XAFS data, no second shell beyond the first oxygen layer is visible. We argue that this is due to the sulfate being present as small clusters located into voids of the borosilicate network. Hence, destructive interference of the variable surrounding prohibits the presence of higher shell signals. The knowledge of the sulfur bonding characteristics is essential for further optimization of the glass composition and to balance the requirements of the process and glass quality parameters, viscosity and electrical resistivity on one side, waste loading and sulfur uptake on the other side.

1. Introduction

Borosilicate glass is widely used for the immobilization of high level radioactive liquid waste (HLLW) originating from spent nuclear fuel reprocessing due to its remarkable chemical, especially radio-chemical and thermal properties [e.g., 1-3]. The Institut für Nukleare Entsorgung (INE) at Forschungszentrum Karlsruhe (FZK) has developed such a vitrification technology to convert high level liquid wastes to glass by a single-stage process [1]. HLLW from the 1960s to 1970s often contains significant amounts of sulfur. A typical sodium borosilicate glass composition for nuclear waste vitrification does not dissolve sulfur in higher concentrations than 0.4 to 0.5 wt% in terms of sulfate. Higher amount causes oversaturation of the glass with sulfur, resulting in the occurrence of a separated, undesired yellow phase. The chemical composition of such a phase depends on the glass and mainly on waste composition but is usually dominated by sodium sulfate, Na_2SO_4. The yellow phase has unfavorable properties like high water solubility. In particular, it extracts radionuclides like Cs and Sr. In order to avoid sulfur becoming the limiting factor of the waste glass loading, which directly impacts the overall economics of the waste vitrification plant including HLLW throughput, glass production rate, operation time and amount of glass to be produced, an attempt is undertaken to develop a waste glass composition with enhanced sulfur incorporation capacity. In the conventional glass industry sulfur is used for two purposes: to aid the fining of the glass melt by adding sodium

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sulfate to the glass batch, which decomposes gradually from 1250 to 1450 °C producing large bubbles of gaseous SO_2, which in turn will sweep smaller bubbles from the glass melt [4] and to accelerate the kinetics of dissolution of the glass batch [5]. In contrast, the task in the nuclear waste vitrification field is not to expel the sulfur as gaseous SO_2 or SO_3 into the environment but to keep the sulfur in the glass during processing of the HLLW.

This problem has been extensively addressed in the literature for the past three decades. Schreiber et al. [4] described the basis of the sulfur chemistry in borosilicate glasses in detail (redox equilibrium, kinetic properties, sulfur interaction with glass constituents). Based on laboratory-scale results Schreiber and Stokes [5] reported that increased concentration of the oxides of elements like Na, Ca and Mg can significantly enhance the sulfur incorporation capacity of a borosilicate waste glass. Kaustik et al. [6] described a solution of the problem based on barium borosilicate glass with typically more than 20 wt% of BaO. An incorporation capacity of about 1.5 wt% of sulfur in terms of SO_4^{2-} was reported. The high BaO content, however, decreases the glass viscosity to levels inacceptable for operation and glass pouring of a large-scale liquid-fed ceramic-lined nuclear waste glass melter. Holmquist [7] performed a classical experiment demonstrating that the activity of free oxide ions O^{2-} in sodium silicate melts impacts strongly the sulfur solubility. More recently, Manara et al. [8] studied the sulfur behavior in silicate glasses and the implications for sulfur incorporation in nuclear waste glasses as a function of the content of alkali cations and of vanadium pentoxide V_2O_5 in the glass. The general objective was to find a waste glass composition with a sulfur incorporation capacity of at least 0.9 to 1.0 wt% in terms of SO_4^{2-}, which also meets specified properties related to processing, melting and chemical/physical quality requirements.

Our study aims at gaining knowledge of the chemical form of the sulfur in the glass, in order to adjust the glass composition to completely dissolve the sulfur into the glass structure. X-ray absorption near edge structure (XANES) is widely used as a tool to reveal the formal oxidation state of sulfur in a variety of materials [9]. The onset of the excitation of 1s inner shell sulfur electrons serves as a fingerprint for the sulfur species present. The energy position of the main XANES feature, the so-called white line (WL), is observed to shift over 10 eV with increasing formal oxidation state from S^{2-} to S^{6+}. Data evaluation is extended to the EXAFS region and backed up by Raman measurements.

2. Experimental
2.1. Sample preparation
The standard preparation of the glass frit consists of mixing the oxides SiO_2, B_2O_3, MgO, TiO_2 in the appropriate ratio and adding Na_2O, Li_2O, Al_2O_3, CaO as the respective compounds Na_2CO_3, Li_2CO_3, $Al(OH)_3$ and $CaCO_3$. Fine powder of the glass frit is sieved through a 280 μm mesh and premelted at 1250 °C for 20 min. The frit is then cooled, ground and remelted for 2 h at 1250 °C. After cooling and grinding again it is used as the glass matrix powder for preparation of the glass batch, i.e., mixing of the glass frit with the waste oxide residue and with additives. Glass loading is set up at 16 wt% waste oxide residue. Excess sulfur is used in the glass batch sample, i.e., 1.5 wt% SO_4^{2-}. Then the glass batch is converted to waste glass at about 1100 °C and 2 h melting time. The composition of the candidate waste glass is given table 1. Detailed studies with varying waste oxides compositions and preparation routes are presented elsewhere [10].

The sulfur content of the glass samples is determined by ion chromatography, which proves to be superior over ICP-OES and XPS. After fabrication, glass samples with promising high sulfur content are investigated using SEM, Soxhlet, X-ray, viscosity, as well as electrical resistivity measurements.

Pieces of the waste glass samples are ground and the powder fixed onto self-adhesive Kapton-tape for the XAFS or pressed on a piece of indium foil for the Raman investigation, respectively. Crystalline Na_2SO_4, K_2SO_4, $MgSO_4$, $CaSO_4$ and $BaSO_4$ powder samples are prepared in the same way and measured as reference compounds.

Table 1. Candidate waste glass composition.

| Oxide	wt%
Glass frit oxides	
SiO_2	42.550
B_2O_3	12.260
Na_2O	5.880
Li_2O	2.180
Al_2O_3	3.700
CaO	6.720
MgO	4.370
TiO_2	0.840
BaO	5.000
Waste oxide residue	
SrO	0.037
Y_2O_3	0.016
MoO_3	0.194
MnO_2	0.013
Cs_2O	0.120
BaO	0.021
La_2O_3	2.031
Cr_2O_3	0.298
Fe_2O_3	3.238
NiO	0.592
Na_2O	7.011
Al_2O_3	1.450
K_2O	0.094
TiO_2	0.150
SO_3	0.664
P_2O_5	0.071
Additive to waste (Sb_2O_3)	0.500
Σ	**100.000**

2.2. XAFS measurements

XANES spectra are recorded at the XAS-Beamline [11] of the synchrotron source ANKA, Forschungszentrum Karlsruhe, Germany. The storage ring operates at 2.5 GeV with electron currents between 100-200 mA. The Si(111) crystals of the fixed-exit double-crystal monochromator are used to produce a monochromatic photon beam. Energy calibration is done with respect to the WL maximum of a $ZnSO_4$ powder sample, defined as 2481.44 eV. The spectra are recorded at a step width of 1 eV in an energy interval from 2455 to 2465 eV, thereafter a step width of 0.2 eV until 2520 eV. Ionization chambers filled with N_2 at 80 mbar pressure are used for detection. The reference samples are measured in transmission mode; five spectra are averaged to increase the signal-to-noise ratio. Ten spectra of the glass sample are recorded in fluorescence mode using a silicon drift detector (Vortex, SII NanoTechnology, USA). Data treatment is done using standard techniques described elsewhere [12]. The ATHENA program [13] is used to extract the EXAFS $\chi(k)$-function, the UWXAFS program package [14] for fitting. Single-scattering paths are calculated with FEFF8 [15] using the respective crystal structures of the reference compounds.

2.3. Raman investigation
Raman measurements are performed on a SENTERRA dispersive Raman microscope (Bruker, Germany). The excitation wavelength is set to 532 nm, a power of 10 mW is used for the waste glass sample and 5 mW for the reference compounds. Each spectrum is an average of two data sets, each collected for 60 s.

3. Results and Discussion

Sulfur dissolves in borosilicate glass melts either as ion SO_4^{2-} under oxidizing conditions or as the sulfide ion S^{2-} under reducing conditions [4]. XANES is strongly sensitive to the oxidation state and coordination chemistry of the absorbing atom. Fingerprint comparison of XANES spectra show that in the glass sample investigated the sulfur is in the oxidation state S^{6+} and appears to be present as the anion SO_4^{2-} (see figure 1). No significant contribution is seen below the WL maximum at 2482 eV, typical for compounds with oxidation state S^{6+}. The broad resonance at approximately 2498 eV in all spectra is due to multiple scattering of the outgoing electron wave at the first oxygen shell around the sulfur ions. Small deviations in the peak position result from slightly different sulfur-oxygen distances and/or distortion of the sulfur-oxygen tetrahedron.
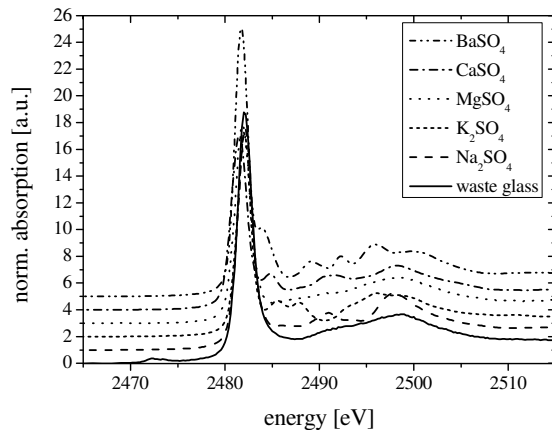

Figure 1. XANES spectra of the waste glass sample compared to reference compounds.

The sulfate ion needs electrical charge compensation by cations in the melt like Na^+, Ca^{2+}, Mg^{2+} and Cs^+. It is therefore assumed that the presence of sulfur in the waste glass melt is governed by the reversible chemical reaction in the waste glass melt:

(1) $SO_4^{2-}{}_{melt} \rightleftharpoons SO_{2,g} + ½ O_2 + O^{2-}{}_{melt}$ $\Delta H < 0$
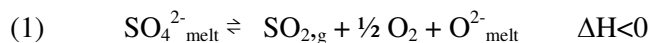
There are several strategies to shift this equilibrium in the waste glass melt to the left side of equation (1), i.e., to the dissolved sulfur in the glass. As for example, the oxygen O_2 or the oxide ion O^{2-} concentration or both could be increased in the waste glass melt to favor the left side of (1). The left side would also be favored by a decrease of the temperature because the reaction enthalpy ΔH is negative. The increase of the free oxide ions O^{2-} in the melt (i.e., increase of the melt's basicity) can be accomplished, e.g., by increasing the alkali or alkaline earth metals content of the glass (Na_2O, K_2O or MgO, CaO, BaO). "Free oxide ions" O^{2-} means that they are exclusively bound to non-network forming cations. They follow an equilibrium given mainly by the chemical composition of the waste glass, being

(2) $O^0 + O^{2-} \rightleftharpoons 2 O^-$
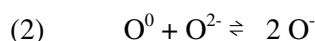
Here, O^0 is the activity (concentration) of the bridging oxygens in the glass network and O^- the activity (concentration) of non-bridging oxygens.

By comparing the XANES spectra in figure 1, it can be deduced that sulfur in the glass is most probably coordinated by Na^+ cations. The spectra of K_2SO_4, $CaSO_4$ and $BaSO_4$ exhibit strong

resonances between 2483 eV and 2490 eV, not seen in the glass spectrum. In fact, the spectrum of Na_2SO_4 is the only one which shows a well defined minimum at 2487.5 eV, as does the glass spectrum. This interpretation is backed up by results obtained from Raman spectroscopy measurements shown in figure 2. The Raman shift of the ν_1 S-O symmetric stretching vibration at 992.5 cm^{-1} in the glass spectrum best matches the peak for pure sodium sulfate Na_2SO_4. Similar findings were reported by McKeown et al. [16]. The brought feature underneath the ν_1 S-O symmetric stretching vibration originates from the borosilicate backbone of the glass. McKeown et al. [16] showed that no dominant feature is visible in Raman spectra without sulfur.
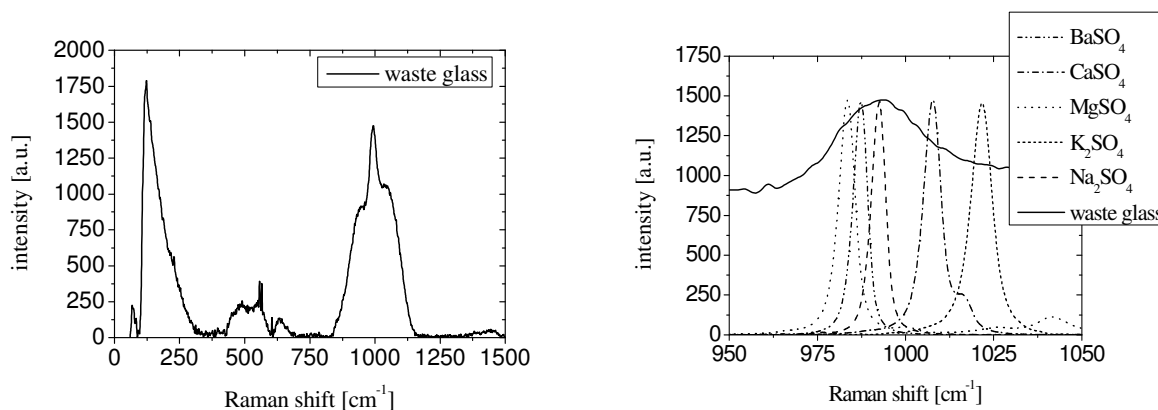
Figure 2. Raman spectra of the waste glass (left) and fingerprint comparison of the ν_1 S-O symmetric stretching vibration at 992.5 cm^{-1} with reference compounds (right).

Additionally, the sulfur appears to be completely isolated from the SiO_4/BO_4 tetrahedral glass network. This hypothesis is backed up by EXAFS data shown in figure 3 for the glass sample and Na_2SO_4.
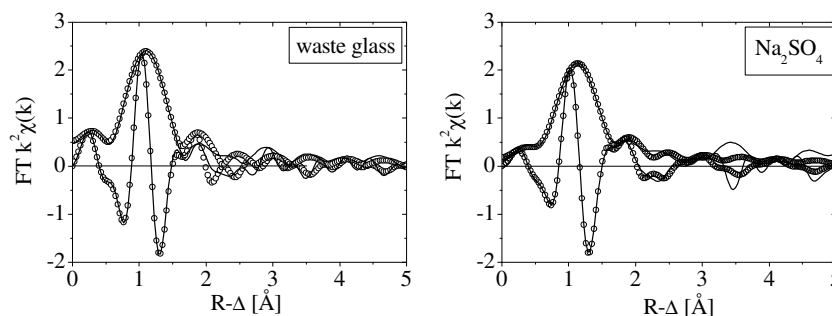
Figure 3. EXAFS evaluation of the waste glass spectrum (left) and Na_2SO_4 (right).

No second shell beyond the first oxygen shell is indicated in the waste glass Fourier transform (FT), in figure 3, whereas the FT of the Na2SO4 spectrum exhibits a broad peak around 3.4 Å. This peak arises from ten sodium neighbors at 3.112 Å, 3.444 Å, and 3.470 Å, and four oxygen atoms at 3.595 Å, respectively [17]. Fitting of this feature is abandoned as the number of independent data points is not sufficient for the number of variable parameters needed. The sulfate in the laboratory-scale waste glass sample investigated may therefore most probably be present in small clusters, or even isolated as anions SO_4^{2-}, together with cations for the compensation of the negative electrical charges and located in voids of the borosilicate glass network. Hence, destructive interferences of the variable environment prohibit the presence of higher shell signals. EXAFS parameters of the oxygen tetrahedron around the absorbing sulfur atoms for Na_2SO_4 and the glass sample are summarized in table 2. Structural parameters of thenardite [17] are fixed when fitting the Na_2SO_4 data to determine the amplitude reduction factor, which results in a rather low value of for S_0^2 of 0.57 and a rather large energy shift ΔE_0 of 17.4 eV. But when keeping S_0^2 fixed at 0.57 for the fitting of the waste glass data, reasonable numbers are gained for the first oxygen shell of the sulfate tetrahedral.

Table 2. EXAFS parameters for sulfur in the waste glass and Na_2SO_4.

	CN	r[Å]	$\sigma^2[Å^2]$	$\Delta E_0[eV]$	r-factor
Waste glass	4.0±0.1	1.45±0.01	0.005±0.001	8.3±0.9	0.0012
Na_2SO_4	4^a	1.479^a	0.003±0.001	17.4±0.1	0.0001

[a] parameters fixed, S_0^2 varied for Na_2SO_4, then set to 0.57 for the waste glass

4. Summary

A candidate borosilicate waste glass composition is found which would take up increased amounts of sulfur. According to laboratory-scale results it may be possible to load the glass at least with 1.0 to 1.1 wt% of SO_4^{2-}. This is mainly accomplished by increasing the basicity of the sodium borosilicate waste glass (i.e., the amount of "free oxide ions" O^{2-} in the glass) due to an increase of alkali-, as well as earth alkali oxides in the waste glass. Simultaneously it is assured that specified waste glass parameters related to glass melting properties, physical and chemical properties, as well as to quality parameters are met. XAFS and Raman spectroscopy studies on a candidate laboratory waste glass sample suggest that the sulfur is present in the glass as sulfate anion SO_4^{2-}, most probably as small Na_2SO_4 clusters in voids of the glass matrix.

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