

Vanadium Valence and Local Environment in Borosilicate Waste Glasses

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Introduction: The chemical and structural role of vanadium in borosilicate glasses is of interest with regard to the process of vitrifying radioactive wastes for long-term storage, and the incorporation of sulfur from the waste into the borosilicate melt. Recent investigations have shown that adding V_2O_5 to borosilicate formulations may significantly improve the low sulfur solubility in borosilicate melts.

Methods and Materials: XANES data of the vanadium K-absorption edge were collected in transmission mode for a variety of vanadium-sulfide, oxide, and silicate crystals, as well as for eight vanadium and sulfur containing borosilicate glasses produced in various melter environments.

Results: Comparisons of the XANES data for the glasses with the standards indicate that all glasses investigated contain predominantly V^{+5} in tetrahedral coordination with oxygen atoms. However, some V^{+4} (most likely in five-fold coordination) can exist in these glasses, from very small percentages to mixtures up to approximately 20% V^{+4} and 80% V^{+5} . Valence mixture variations in these glasses determined from V XANES data correlate to the amount of reductants added to the corresponding borosilicate melt in the melter environment.

Conclusions: XANES data indicate that the vanadium environments in borosilicate glasses are dominated by fully oxidized V^{+5} in tetrahedral coordination with oxygen atoms. There is no evidence from the spectra that vanadium is providing additional sulfur bonding sites in the glass structure in the form of V-S bonds; however, vanadium bonding to SO_4 tetrahedra cannot be ruled out.

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