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DP-MS-83-61X

STABILITY OF RADIOACTIVE WASTE GLASSES ASSESSED FROM HYDRATION THERMODYNAMICS

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by

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A paper proposed for presentation
and for publication in the proceedings
1983 Annual Meeting of the Materials Research Society
Boston, Massachusetts.
November 14-17, 1983

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Assessment of the geologic performance of radioactive waste glasses requires extrapolation of finite tests to very long times. Hydration thermodynamics provides a means to compare the stability of waste glasses to natural analogues and to ancient synthetic glasses. The glass composition is separated into structural components of known free energy of hydration. These are then summed to provide a discrete measure of the stability of a given glass to aqueous attack. Application of hydration thermodynamics to a wide variety of glasses and glass-ceramics leads to the prediction that Savannah River waste glass should be as stable toward aqueous attack as natural basalt.

The information contained in this article was developed during the course of work under Contract No. DE-AC09-76SR00001 with the U.S. Department of Energy.

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SUMMARY

Assessment of the durability of radioactive waste glasses requires extrapolation of finite tests to geologic times. Hydration thermodynamics provides a means to compare waste glass durability to that of natural analogues and to ancient or medievial synthetic glasses.

The thermodynamic basis of glass hydration[1] treats any glass or glass-ceramic as a homogeneous mixture of structural units or species, e.g. Na_2SiO_3, SiO_2, Fe_2O_3, $FeSiO_3$. The reaction of each of these species with water has an associated standard free energy which can be calculated from available data. The stability of the glass is then assumed to be the sum of these component hydration stabilities (G° values), weighted by the fraction of that component in the glass. Glasses with more positive free energies are found to be more durable (Figure 1).

The hydration free energy was plotted against the release of elemental Si from a 28 day MCC-1 static leach test (Figure 1) for the following reasons: (1) All the glasses and glass-ceramics examined contained silica as a structrual component, (2) silica is involved in back reactions (condensation of silanol groups) as well as in ion exchange, and (3) evidence suggests that release of many other elements may be matrix-dissolution controlled. The resulting straight line fit of the data is related to the activity of silicic acid in the leachate and is proportional to the ratio of the rate constants for network hydrolysis and network condensation at saturation, as well as to the pH of the leachant.

Hydration thermodynamics demonstrates that waste glasses are more durable than the medieval glasses tested and are as durable toward aqueous attack as natural basalt. This approach can also be utilized to maximize waste loadings and for optimization of waste glass compositions.

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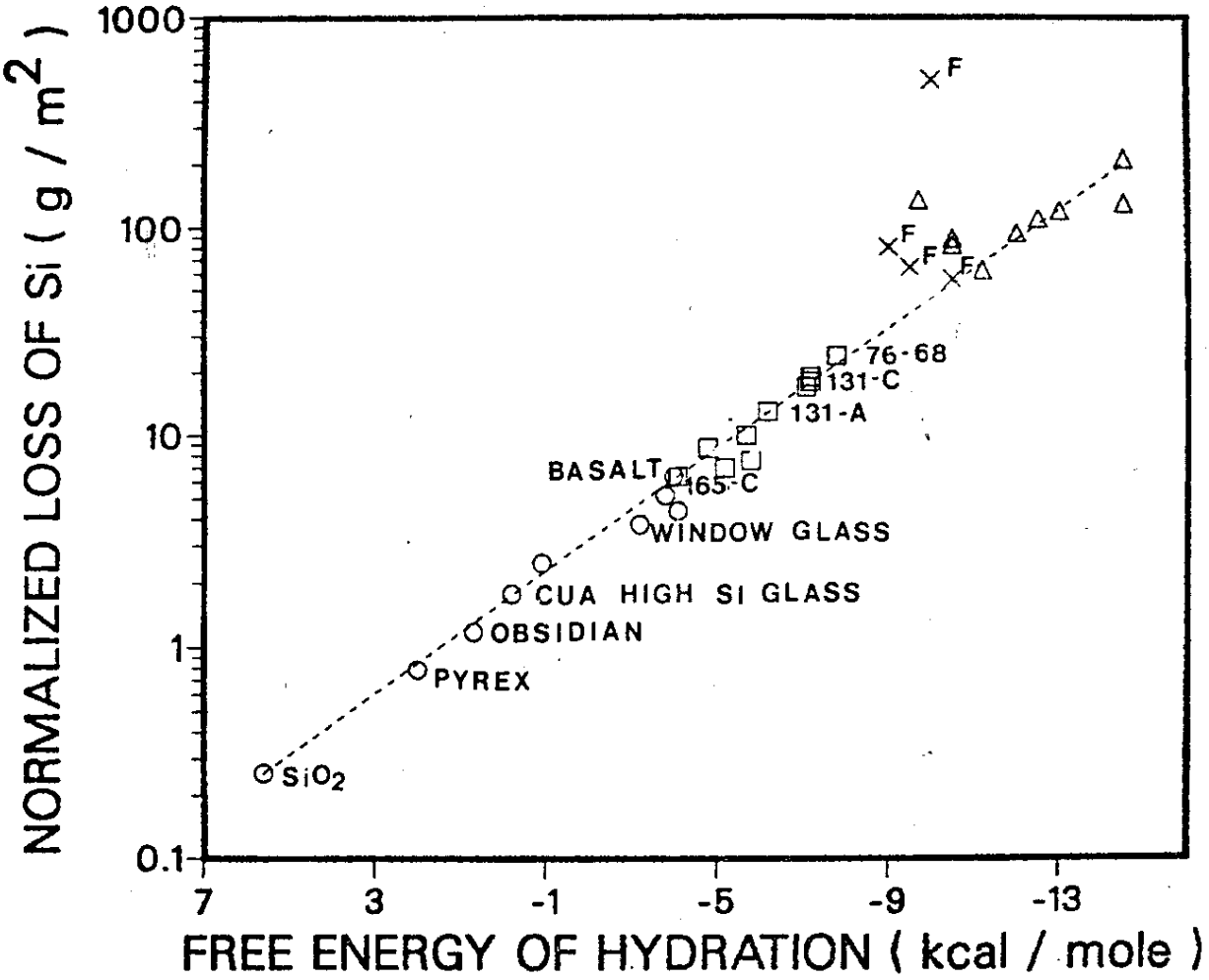

FIGURE 1. **Free Energy of Hydration Versus Release of the Glass Structural Element Silicon**
The X denotes pure glass frits, the triangles are medieval window glass from the European Science Foundation, the squares represent a variety of US and European waste glasses, and the circles represent durable glasses which have high formation temperatures.