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LEACHING OF DEVITRIFIED GLASS CONTAINING SIMULATED SRP NUCLEAR WASTE

by

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The canister centerline cooling curves can be superimposed on the time-temperature-transformation curves. For each waste glass composition, the cooling curve crosses the noses of the C-shaped transformation curves at less than 24 hours [4]. Simulated centerline cooling of SRL glasses represents worst case crystallization of the glass during canister cooling. The data from duplicate experiments is given in Table I.

TABLE I
Volume Percent Devitrification of Simulated Centerline Cooled Glasses* Determined by Quantative X-ray Diffraction

	High Al	Composite	High Fe
SRL 165	5 spinel	5-8 spinel 10-20 acmite	8-12 spinel 18 acmite
SRL 131	35-40 nepheline	6 spinel 4 nepheline 13 acmite	10 spinel 14-16 nepheline

* error \pm 2% spinel, \pm 5% acmite, \pm 10% nepheline; all data confirmed by optical microscopy and scanning electron microscopy.

RELATIVE DURABILITY OF DEVITRIFIED AND QUENCHED SRL WASTE GLASSES

Quantitative Durability: CGW Leach Tests

The CGW leach test of powered devitrified glass was used for the determination of differential leaching as a function of phase development. Values of pH, Si, Na, and B were contoured on the TTT diagrams but consistent trends were only observed for the release of the glass matrix element boron (Figures 1 and 2). Since boron is the most leachable species in defense waste glass [8], monitoring this element evaluates worst case leachability for devitrified glasses. The poor correlation of phase development with Si and Na may be due to their dual role in both the glass matrix and in the crystallization of acmite. The poor correlation with pH was due to the small range of values observed.

The boron release (in ppm) into solution from the quenched glasses is represented by the data points at 400°C and zero annealing time in Figures 1 and 2. The shaded region corresponds to any devitrified samples releasing more than twice the boron of the as-quenched sample for that composition. For example, the as-quenched sample of SRL-165 high alumina waste glass releases 1 ppm boron to the leachate during the CGW test. The shaded region on the corresponding TTT diagram, therefore, represents all devitrified samples releasing 2 or more ppm boron to the leachant.

A comparison of the boron release values for the as-quenched SRL-165 waste glasses shows a variation from 1 to 3 ppm, a factor of 3X. Likewise, the variation for the SRL-131 based waste glasses show a variation from 4 to 20 ppm boron, a factor of 5X. The effects of devitrification on the durability of the SRL-165 and SRL-131 waste glasses, therefore, demonstrates that devitrification has less effect than compositional changes.

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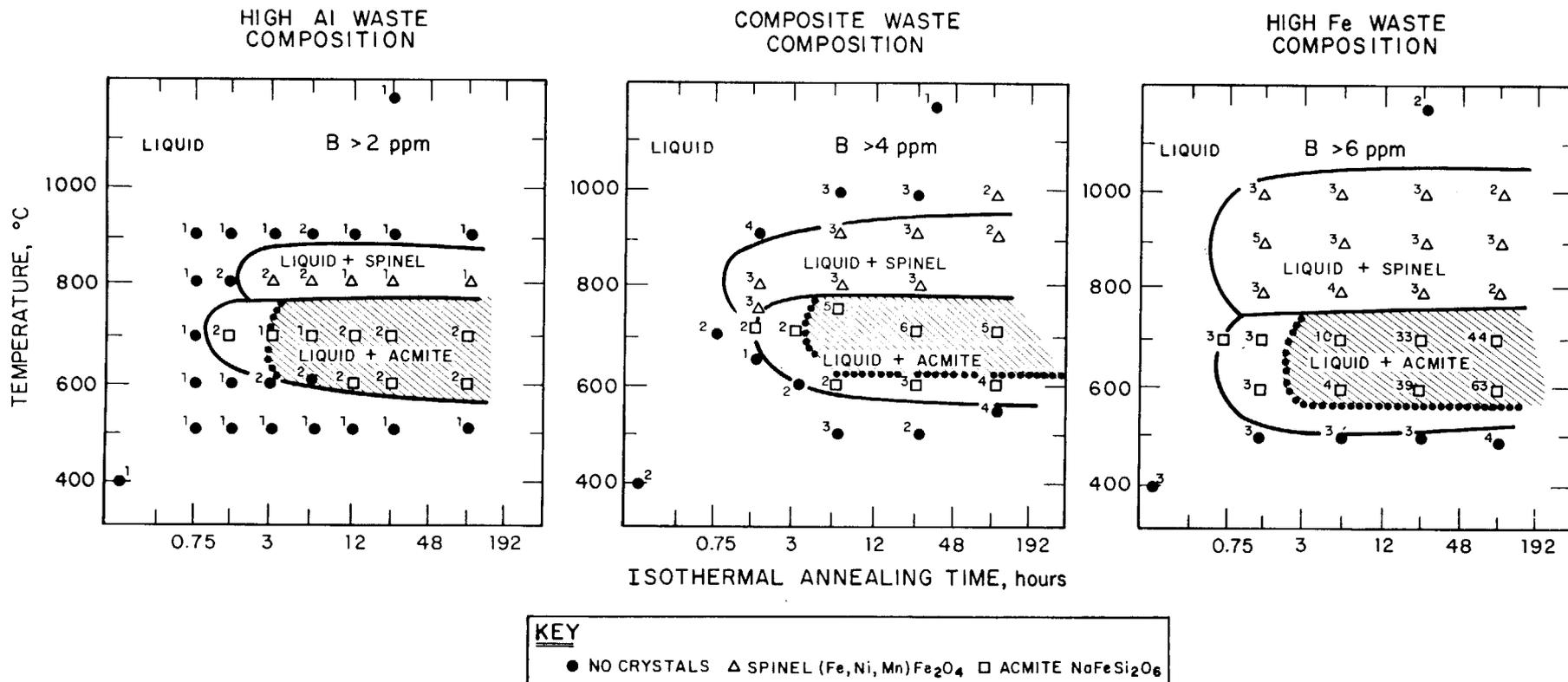


FIGURE 1. Time-temperature-transformation diagrams for SRL-165 waste glasses. Shaded area represents devitrified glasses which cause boron release rates in deionized water greater than twice the as-quenched boron release rate at zero time.

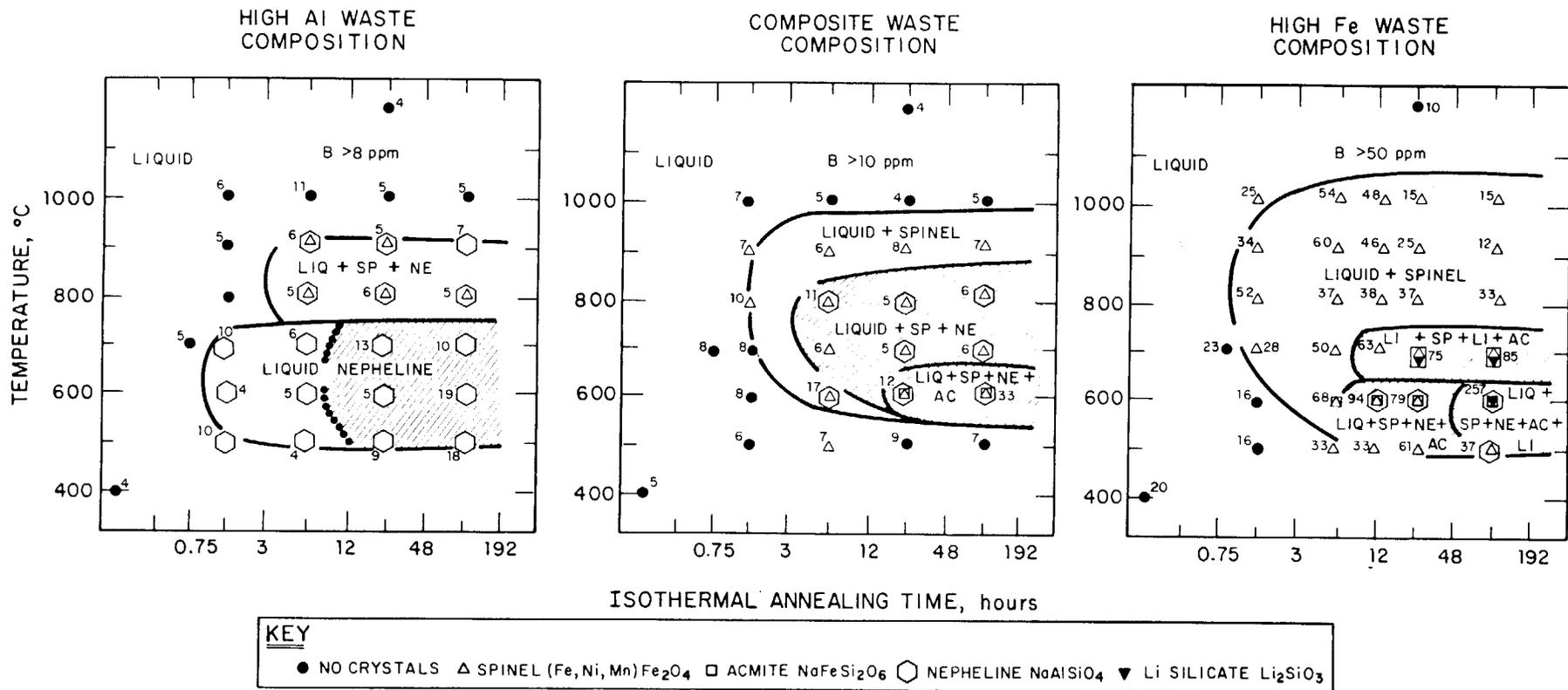


FIGURE 2. Time-temperature-transformation diagrams for SRL-131 waste glasses. Shaded area represents devitrified glasses which cause boron release rates in deionized water greater than twice the as-quenched boron release rate at zero time.

Crystallization of spinel does not affect glass durability. Crystallization of alkali silicate phases correlates with the time-temperature regions of increased leachability. SRL-131 waste glasses are less durable than SRL-165 waste glasses in the as-quenched state (Figures 1 and 2) even when normalized to the differing amounts of boron in the parent glass (Table II). The devitrification of three different alkali silicate phases in SRL-131 glasses causes additional loss of durability.

TABLE II
Relative Durability for Quenched and
Devitrified SRL Waste Glasses

<u>Waste Glass</u>	<u>Baron Release (PPM)*</u>	
	<u>Quenched</u>	<u>Devitrified at 700°C >24 hours</u>
SRL-165 High Al	1	1-2
SRL-165 Composite	2	5-6
SRL-165 High Fe	3	33-44
		<u>Devitrified at 600°C >24 hours</u>
SRL-165 High Al	3	3-13
SRL-131 Composite	3	9-22
SRL-131 High Fe	17	18-65

* Normalized to Wt % B in the different glasses

The maximum rate of devitrification occurs at 700°C for SRL-165 glasses and at 600°C for SRL-131 glasses. Release rates corresponding to a transportation/fire accident scenario, e.g. 790°C for 30 minutes, would be the same as the as-quenched values shown in Figures 1 and 2 since these conditions are coincident with the region where no devitrification occurs. The values shown can also be applied to worst case conditions of canister heating in the repository environment.

The high iron TTT diagrams represent worst case boron releases to the solution because microcracking is induced during the quenching from the isothermal annealing temperature. The boron release rates directly correlate with the volume percent acmite present. One potential explanation of this data could be thermal expansion mismatch caused by the growth of very large acmite crystals in these iron rich compositions. Subsequent experiments which slowly cooled the isothermally annealed samples, devitrified to the same extent but had leach rates comparable to non-devitrified samples of the same composition. Thus, fresh waste glass will not experience microcracking, due to the low volume percentage acmite and the slow cooling in the canister region of maximum devitrification.

SRL-165 and SRL-131 waste glasses devitrified during cooling simulating canister centerline temperatures yielded 23-25 volume percent crystallization. Only spinel and acmite crystallized in SRL-165 glasses while spinel, acmite, and nepheline crystallized in SRL-131 glasses. For SRL-165 glasses, this only increased the boron release by 2-3X relative to the boron release of the nondevitrified, (i.e. quenched) glass. For SRL-131 glasses, the more complex devitrification of the additional alkali silicate phase, nepheline, caused a 5X increase in the boron release relative to a non-devitrified glass of the same composition.

Monolithic samples of devitrified glass are difficult to obtain due to sample cracking and crystal plucking during preparation. Since the monolith surface is representative of only a small volume of the sample, the MCC-1 test is more sensitive to sample inhomogeneities, e.g. non-uniform devitrification. Samples were, therefore, run in triplicate or quadruplicate.

The results of the static MCC-1 leach test in deionized water for 28 days demonstrate that the non-devitrified samples give reproducible boron releases but the devitrified samples do not (Table III). Variations of up to 2X can be observed for the boron releases of devitrified samples.

TABLE III
Comparative MCC-1 Leach Rates for SRL Glasses

Glass Composition	Condition Of Glass	Volume Percent Crystals	Leach Rates (N _{Li} , g/m ²)		
			Boron	Silicon	Lithium
165 High Alumina	Quenched	None	8.39	7.81	9.36
			9.06	7.22	8.56
			7.94	9.78	11.71
			8.16	8.61	10.32
	Centerline Cooled	8 Spinel	11.46	8.41	10.59
			16.03	11.11	19.51
			25.17	24.25	37.86
			27.12	24.45	38.29
165 Composite	Quenched	None	15.30	14.23	17.21
			9.86	10.07	13.73
	Centerline Cooled	5 Spinel 20 Acmite	15.34	10.32	18.16
			24.37	12.33	17.96
			15.23	14.05	18.01

Comparing the MCC-1 leach data for SRL-165 glasses in the quenched and devitrified states shows that no more than a factor of 1-3X release of boron or silicon occurs due to devitrification. Leach rates for the more mobile alkali element lithium indicate no more than a factor of 4X increase. Comparative durability of quenched and devitrified glass by MCC-1 procedures confirms the results of the 24-hour CGW leach test.

Validation of CGW Leach Test Results

Comparison of leach data using the CGW method and the MCC-1 test method is given in Table IV. The data for Si and B release were compared for samples in the as-quenched, canister centerline cooled, and devitrified states. The leach rates were compared in units of g/m²-day. Both tests showed that leach rates of the as-quenched and the centerline cooled glasses were similar, while extreme devitrification increased the leach rate of Si and B by only a factor of 2 to 3 times (Table IV). The MCC-1 leach test is more sensitive to small percentages of devitrification such as observed in the centerline cooled samples, but is more subject to error due to inhomogeneous devitrification. For rapid determination of the effects of devitrification, the CGW 24-hour test provides an accurate determination of leach rate enhancement.

TABLE IV
Comparative Leach Rates for SRL-165 Composite Glass

Condition	Volume Percent Crystallinity	Leach Rate (g/m ² -d)			
		Silicon		Boron	
		MCC-1**	CGW*	MCC-1	CGW
Quenched	0	0.45	0.24	0.48	0.28
Simulated Canister Centerline Cooling	5 Spinel 20 Acmite	0.63	0.22	0.75	0.28
Heat Treated 24 hrs at 700°C	20 Acmite	0.79	0.40	1.25	0.74

* CGW is a 24-Hr Test of about 10g powdered waste glass sieved between 100 and 200 mesh to about 2g with an effective SA/V of about 4.3 cm⁻¹.

** MCC-1 is a 28 day test of about 1g monolith of glass with SA/V of 0.1 cm⁻¹.

CHARACTERIZATION OF REACTIONS AT THE GLASS-LEACHED SURFACE LAYER INTERFACE

The morphology of corrosion at the glass-gel reaction zone, e.g. under the leached layer, can be examined when the leached layer is stripped off with adhesive. Examination of the glass gel reaction zone by scanning electron microscopy of the stripped glass surface and comparative microscopy of the leached layer adhering to the adhesive enabled the morphology of the dissolution to be studied. The morphology of the leached layer for quenched glasses was highly structured and the dissolution nonuniform (Figure 3). The glass-gel interface of the SRL-131 glasses were more nonuniform (Figure 4) than the SRL-165 glasses (Figure 3). The nonuniformity of the dissolution has been observed previously for monolithic waste glass samples with rough or scratched surface finishes [9,10].

Examination of devitrified and leached glass surfaces (SRL-165 high alumina, centerline cooled) at the glass-gel interface indicated the same nonuniform dissolution of the glass matrix with some non-uniform dissolution at the crystal grain boundary (Figure 5). However, the non-uniform dissolution is not enhanced in the region around the crystal (Figure 5d) compared to the depth of dissolution along a surface scratch (Figure 5c). It is, therefore, impossible to distinguish whether accelerated attack is the result of grain boundary* dissolution or localized surface damage at the glass/crystal boundary during sample preparation.

Scanning electron microscopy of the leached layer at the gel-solution interface, e.g. with the leached layer intact, shows that the leached layer covers or shields the grain boundaries from dissolution (Figures 5a, and 5b). Examination of the gel layer at the glass gel interface demonstrates this as well. Holes are apparent in the stripped off leached layer where the crystals had higher relief, e.g. were more resistant to leaching than the surrounding glass matrix. Moreover, energy dispersive x-ray analysis of the elements concentrated in the gel at the reaction zone provides microchemical data suggesting that the gel layer is ion-selective [11] and may contribute to the non-uniformity of the dissolution.

* Grain boundary is used synonymously with crystal boundary.

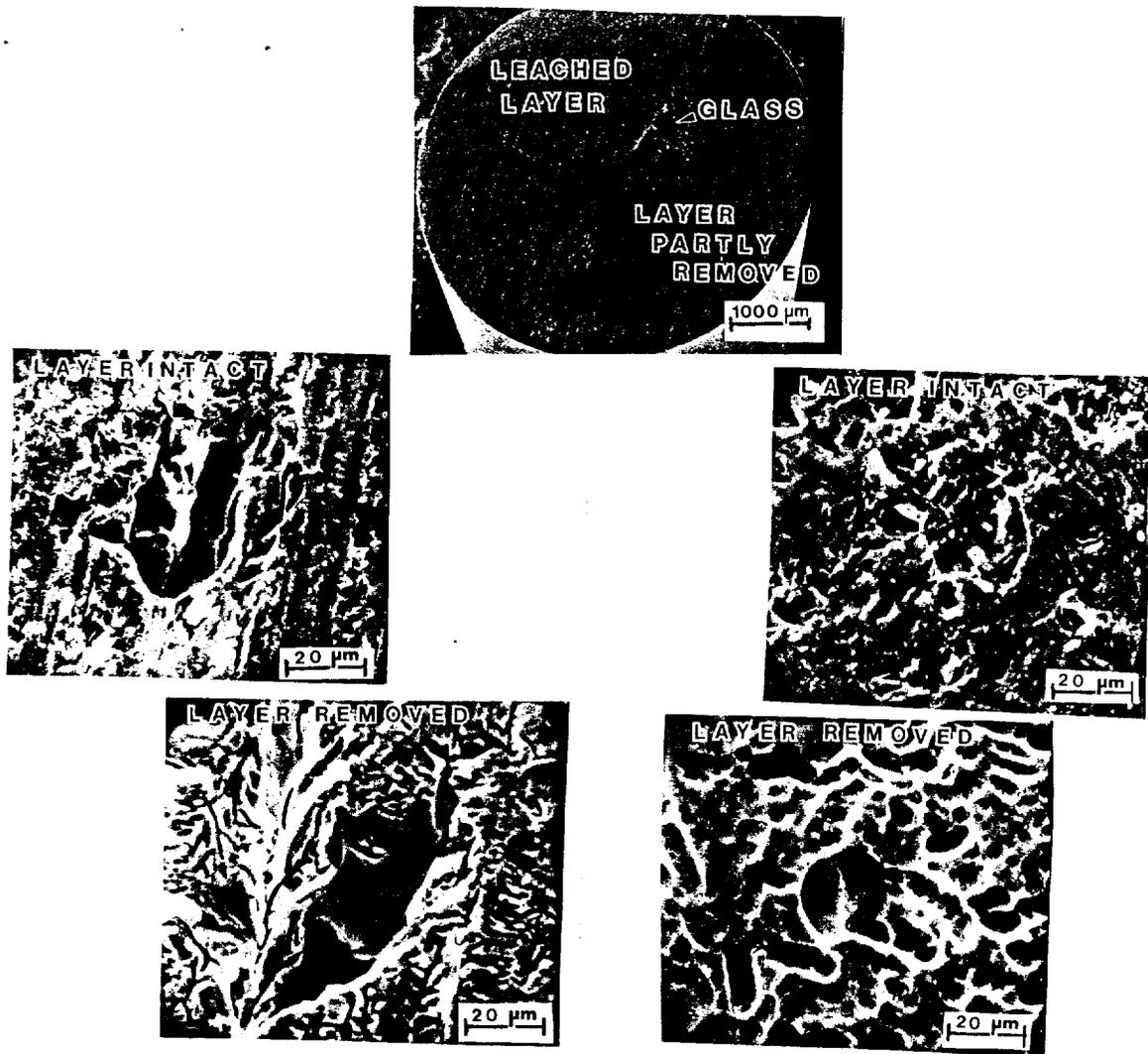


FIGURE 3. Surface morphology of quenched SRL-165 waste glasses (high alumina composition on left and composite composition on right) leached for 28 days in deionized water.

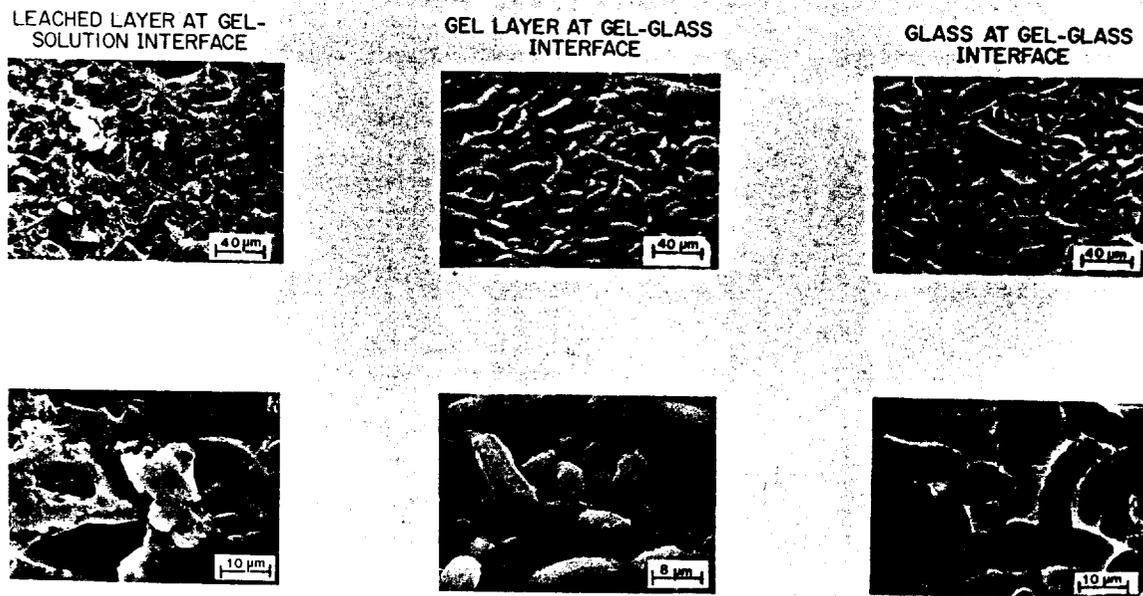


FIGURE 4. Surface morphology of quenched SRL-131 waste glasses (composite composition) leached for 28 days in deionized water.

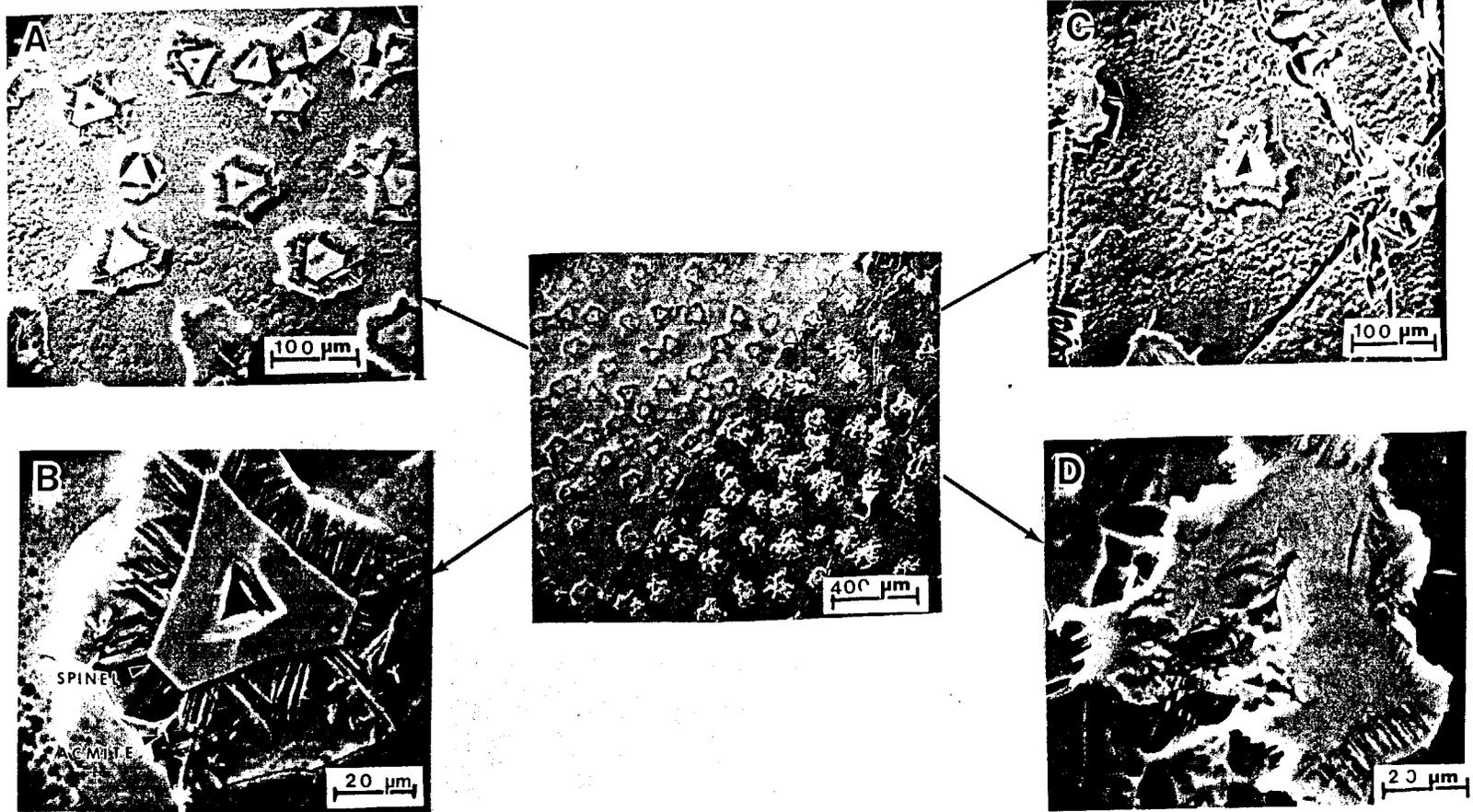


FIGURE 5. Surface morphology of devitrified centerline cooled SRL-165 high alumina waste glass leached for 28 days in deionized water. Note how the leached gel layer "shields" the grain boundary from dissolution (compare 5b to 5d).

CONCLUSIONS

Time-temperature-transformation diagrams for SRL-165 and SRL-131 waste glasses have been completed. The glasses are homogeneous when melted at 1150°C and do not crystallize when air quenched from this temperature, or when isothermally annealed below 500°C. If isothermally treated, all SRL-165 waste glasses form spinel at high temperatures (750-1000°C) and acmite in the lower temperature range (600-800°C). The maximum rate of devitrification occurs at 700°C. All SRL-131 waste glasses form spinel in the temperature range 900-1050°C. Three alkali silicate phases form over both the higher and lower temperature range (500-950°C). Maximum devitrification occurs at 600°C.

Although the waste glasses are complex, the growth kinetics follow the expected trends based on theoretical models of simple glasses, e.g. smooth fractional ingrowth curves are achieved as a function of aging. Comparison of the TTT curves demonstrates that iron in the waste composition promotes spinel formation as suggested by Welch et al [12]. This is especially true for higher temperatures at shorter times, e.g. in the range of melter idling conditions. The liquidus temperature (defined as the highest temperature of appearance of spinel) correlates with increasing Fe₂O₃/SiO₂ content of the glass in mole percent.

The formation of spinel has little or no effect on leachability, while the formation of acmite produces a small but noticeable increase in the rate of dissolution of the matrix glass. Quenched SRL-131 glasses are less durable than the current reference glass, SRL-165, as reported previously [13,14]. The two additional alkali silicate devitrification products in SRL-131 are leachable phases which cause poorer overall durability. Devitrification only increases leachability of a given glass composition by 2-3%. Moreover, devitrification does not produce any significant effect on the leachability of radioactive SRL-165 waste glasses devitrified at higher than normal crystallizations [15]. Thus, leach rates from SRL glass subjected to accident conditions, or moderate temperatures for long time periods will be similar to those of unaged glass of the same composition.

The effects of devitrification on the durability of the SRL waste glasses demonstrates that devitrification has less of an effect than compositional changes. Examination of the glass surface at the glass-leached layer reaction zone of quenched glasses indicates that glass dissolution is non-uniform. The reaction zone in devitrified samples is similar. It is impossible to determine whether accelerated attack is the result of grain boundary dissolution or localized surface damage at the glass/crystal boundary during sample preparation. Further examination of the leached layer at the gel-solution interface indicates that formation of the leached layer shields the grain boundaries from further dissolution. Leach rate enhancement from selective grain boundary attack in devitrified glass does not occur.

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