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ABSTRACT

Leachabilities of cesium and strontium from the glass matrices were correlated with the microstructures of glasses containing waste sludge from two SRP waste tanks. All sludge components, except mercury which volatilized, were completely soluble in the melt, but small amounts of crystalline iron oxide precipitated during cooling. These precipitates were less leachable than the glass matrix. Even though the compositions of the two sludges that were tested were similar, glass containing one of the sludges devitrified during heating at 600°C; glass containing the other sludge did not devitrify. Leachability of the devitrified glass was as much as 100 times greater than that of nondevitrified glass, but still very low, $<10^{-6}$ g/(cm^2)(day).

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INTRODUCTION

Glass is being studied as a possible matrix for long-term storage of Savannah River Plant (SRP) high-level waste.[1,2] Properties of glass that make it attractive for this purpose are its low leachability and high strength.

Previous studies[1,2] identified an acceptable glass composition, designated Glass Mix 18 (Table 1), that allowed incorporation of 25 to 40 wt % SRP waste sludge into high quality waste forms. Those studies also included measurements of volatility of radionuclides during melting and of leachabilities of radionuclides from the waste glasses. This report presents results of analyses of the microstructures of glasses made with actual waste sludges from two SRP waste tanks. X-ray analyses of the glasses and differential thermal analyses (DTA) of glasses containing simulated sludges are also presented.

The power density of aged SRP waste sludge is low (~0.001 W/g), and the storage temperature of glass waste forms is expected to be much less than the temperature at which devitrification occurs (~600°C).

This work included a study of the compatibility of SRP waste with glass and analyses of devitrification products that would be formed under unusual conditions.

TABLE 1

Composition of Glass Frit (Glass Mix 18)

Component	*Wt %*
SiO_2	52.5
Na_2O	22.5
B_2O_3	10.0
TiO_2	10.0
CaO	5.0

DESCRIPTION OF SRP WASTE

At SRP, high-level waste is presently stored in underground tanks. The waste consists of an alkaline salt solution, a solid salt cake, and an insoluble sludge layer that contains iron, aluminum, manganese, uranium, and many other elements. In the conceptual process for solidification, the waste for longer-term storage would be removed from a tank by dissolving the salt cake with water and sluicing the slurry of sludge and solution from the tank. Sludge and solution would be separated by centrifugation and filtration. Cesium-137, the principal biological hazard in solution, would be removed by an ion exchange process and sorption on zeolite. Sludge would be washed to remove salts, dried, and blended with the cesium-zeolite for solidification into either concrete or glass.

Approximately 25 liters (total) of sludge, varying in age from 3 to 6.5 years, was collected from 3 SRP waste tanks (Tanks 5, 13, and 15). The sludge was washed to remove soluble salts and then dried to obtain a free-flowing powder. Details of sludge collection and processing are discussed elsewhere. Table 2 shows only major elements of the chemical composition of the three sludges, which vary widely in composition. Tank 5 is rich in uranium, and Tank 15 contains mainly Al_2O_3. Table 3 shows the radiometric composition of the sludge. The principal radionuclide component is ^{90}Sr, although ^{144}Ce is present in a substantial amount.

TABLE 2

Chemical Composition[a] of Washed, Dried Sludges

Element	*Tank 5* *wt % (mole %)*	*Tank 13* *wt % (mole %)*	*Tank 15* *wt % (mole %)*
Fe	27.5 (39.6)	27.9 (39.9)	3.1 (3.9)
Mn	10.8 (15.9)	8.8 (12.8)	2.3 (2.9)
Al	1.5 (4.6)	7.1 (21.0)	33.5 (86.2)
U	15.4 (5.2)	4.0 (1.3)	0.9 (0.3)
Na	6.1 (21.6)	3.1 (10.7)	1.2 (3.6)
Ca	0.6 (1.3)	2.3 (4.7)	0.2 (0.4)
Hg	0.1 (-)	2.1 (0.8)	0.9 (0.3)
Ni	5.1 (7.1)	0.5 (0.7)	0.5 (0.6)

a. Major elements only.

TABLE 3

Radionuclides in Washed, Dried Sludges[a]

	Tank 5	*Tank 13*	*Tank 15*
^{90}Sr	74.7	15.5	25.6
^{144}Ce	4.8	2.0	16.9
^{106}Ru	2.7	0.4	1.7
^{154}Eu	0.5	0.3	1.2
^{137}Cs	1.3	0.3	0.1
^{125}Sb	0.4	0.1	1.3
Gross α	0.1	0.3	0.1

a. mCi/g

GLASSES CONTAINING ACTUAL SRP SLUDGE[2]

Glasses were made with the glass frit (Glass Mix 18) and the actual sludges. When this glass was heated to 1150°C, 40 wt % of either Tank 5 or Tank 13 sludges could be incorporated into good waste forms. With Tank 15 sludge, which is rich in aluminum, a glass containing only 25 wt % sludge could be vitrified. In one test, 30 wt % Tank 13 sludge and 10 wt % cesium-zeolite were vitrified. In all of the tests, the glasses were melted at 1150°C for 3 hours in alumina crucibles. The molten glasses were then poured into graphite molds and annealed at 500°C for 1 hour. During melting, approximately 3% of the ^{106}Ru, 0.3% of the ^{137}Cs, and all of the mercury volatilized.

Some of the product glasses were leached in stagnant, distilled water at ambient temperature, and the leachabilities determined as previously described.[2] Other glasses were heated for 1 month at either 500°C or 600°C, and then leached as before. Both as-cast and heated glasses were also immersed in boiling water to accelerate leaching and define the relative solubilities of the phases present.

Since the sludge collected from Tank 15 was probably not representative of the entire tank contents, no heating tests or microstructural analyses were made on glass containing this sludge.

RESULTS OF LEACH TESTS

Leachabilities of the glasses at ambient temperatures, based on the entire leach period of 84 to 100 days, are shown in Table 4. Heating the glasses at 500°C or 600°C increased the ^{90}Sr leachability by approximately a factor of 10; however, the final product still had a leachability of $\sim 10^{-6}$ g/(cm^2)(day), which is considered low for waste forms.

Heating Glasses 18-40-5 and 18-30-13/Z* at 500°C did not significantly affect the ^{137}Cs leachability. However, heating Glass 18-40-13 at 600°C increased the ^{137}Cs leachability by a factor of 100 [from 10^{-8} to 10^{-6} g/(cm^2)(day)] probably because of devitrification. Glass 18-40-5, having the same treatment, increased in ^{137}Cs leachability by only a factor of 2 [from 6×10^{-8} to 1×10^{-7} g/(cm^2)(day)]. Heating at 500°C and 600°C did not affect leachability of alpha activity.

TABLE 4

Comparison of Leachabilities of Heated and Unheated Waste Glasses

Sample	*Unheated*	*500°C*[a]	*600°C*[a]
	^{90}Sr Leachability, g/(cm^2)(day)		
18-40-5	2.2×10^{-7}	7.0×10^{-6}	5.0×10^{-6}
18-40-13	4.4×10^{-7}	6.4×10^{-6}	4.3×10^{-6}
18-30-13/Z	1.2×10^{-7}	2.1×10^{-6}	-
	^{137}Cs Leachability, g/(cm^2)(day)		
18-40-5	5.9×10^{-8}	1.7×10^{-8}	1.0×10^{-7}
18-40-13	3.5×10^{-8}	3.1×10^{-7}	4.8×10^{-6}
18-30-13/Z	5.6×10^{-8}	2.7×10^{-8}	-
	Gross Alpha Leachability, g/(cm^2)(day)		
18-40-13	1.3×10^{-7}	6.0×10^{-8}	2.7×10^{-7}
18-30-13/Z	-	6.1×10^{-8}	-

a. Heated 1 month.

* 18 is Glass mix number; 30 is wt % sludge; 13 is Tank 13 sludge; Z signifies 10 wt % cesium-zeolite.

GLASSES CONTAINING SIMULATED SLUDGES

Glasses containing 35 wt % Tank 5 and Tank 13 simulated sludges, and 25 wt % Tank 15 simulated sludge were prepared by the technique described above. These glasses were analyzed by Differential Thermal Analysis (DTA) to determine the temperature of maximum crystal growth (temperature of maximum devitrification rate). The glass containing Tank 13 simulated sludge devitrified with a maximum rate of crystallization at 610°C. Glasses containing simulated Tank 5 and Tank 15 sludges did not devitrify on heating to ~900°C. These results corroborate the leach test results which indicated that the 600°C heat treatment of Glass 18-40-13 caused devitrification.

To facilitate interpretation of leach-test results and identification of precipitated phases, a similar glass sample was cast containing 35 wt % simulated Tank 13 sludge and 1 wt % each of cesium and strontium. The microstructure of the glass was examined by optical and scanning electron microscopy, and the elemental compositions of the precipitates were determined by both microprobe and energy-dispersive x-ray analyses. As with samples containing actual sludge, this simulated sludge-glass matrix contained a uniform distribution of dendritic particles; this shape indicates that they precipitated from the melt during cooling. These particles contained principally iron with some manganese, nickel, and titanium. The concentrations of cesium and strontium were not measurably different in both precipitate and matrix; there was no obvious preferential segregation. When the sample was leached in boiling water, the glass matrix was attacked preferentially. These results suggest that the precipitates are possibly beneficial in that some of the cesium and strontium are contained in a less-leachable form (precipitates).

MICROSTRUCTURES OF GLASSES CONTAINING ACTUAL SLUDGES

Six glass samples, three that were heated and three as-cast, were examined by optical microscopy. Glass 18-40-13 consisted of a matrix in which particles and clusters of particles were distributed uniformly (Figure 1a). Although these particles were not analyzed, they probably contained iron, manganese, nickel, and titanium, as was found in particles of similar appearance in glass containing 35 wt % simulated sludge. Heating at 600°C for 1 month devitrified the glass matrix, as evidenced by the formation of small crystallites (Figure 1b). During leaching for 96 hours in boiling water, the glass matrix leached faster than the particles in both the as-cast and devitrified glasses. The shape of holes that developed in the devitrified glass during leaching suggests that leaching occurred along crystallite boundaries (Figure 1c).

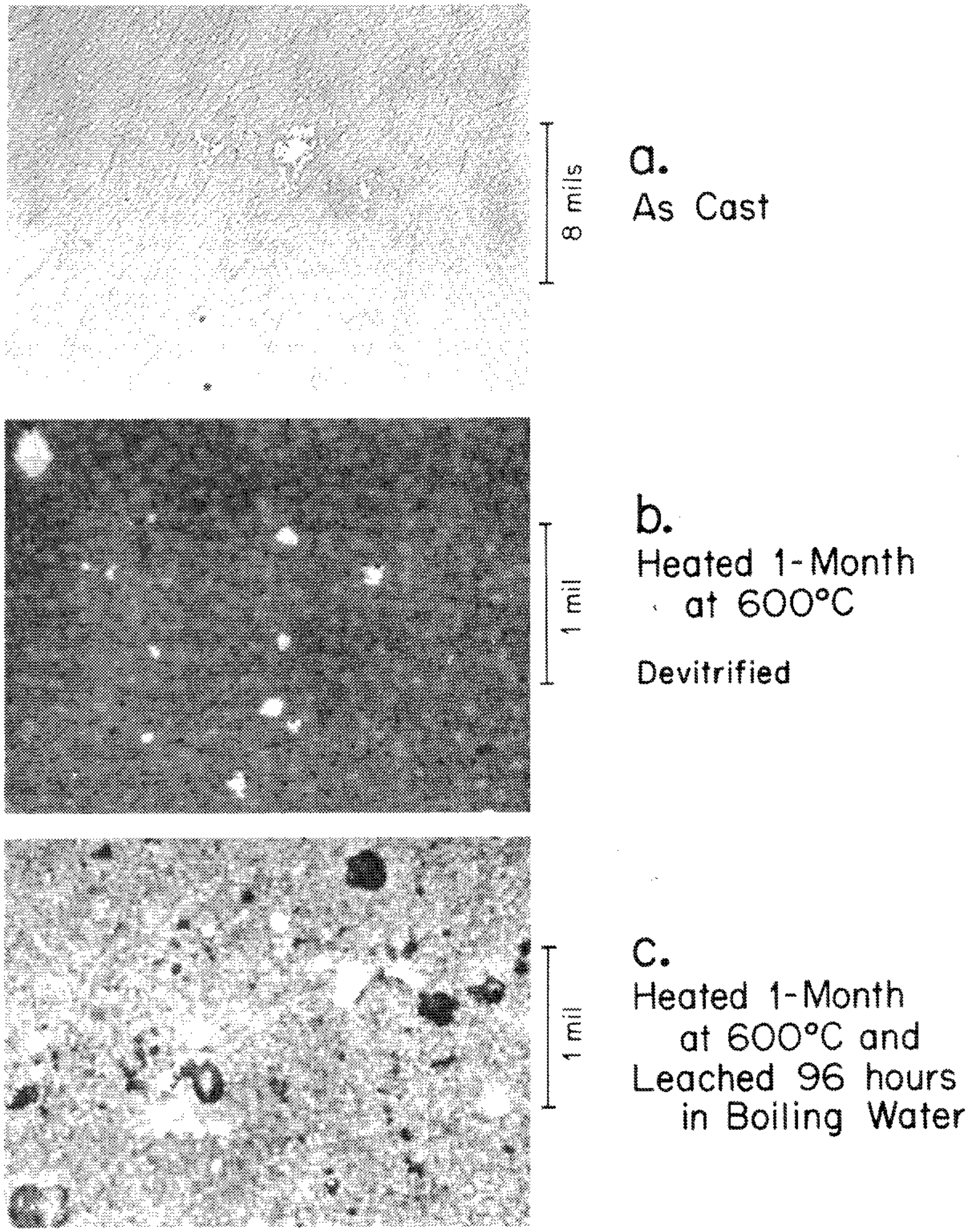

FIGURE 1. Microstructure of Glass 18-40-13

The microstructure of Glass 18-40-5 (Figure 2a) was similar to that of the glass containing Tank 13 sludge except that the Tank 5 glass contained many more precipitated particles, in agreement with the higher total of iron, manganese, and nickel in this sludge (Table 2). Heating for 1 month at 600°C did not appear to devitrify the glass matrix. In both as-cast and heated Tank 5 glasses, the glass matrix was attacked more rapidly than the particles, and no holes formed during leaching; the ^{137}Cs leachability of the heated Tank 5 glasses measured at 25°C was similar to that of the unheated glass.

No particles precipitated in Glass 18-30-13/Z (Figure 3a). The absence of particles indicates that the solubility limit for the metallic constituents (iron, manganese, and nickel) is between 30 and 35 wt %. Heating for 1 month at 500°C had no effect on microstructure or ^{137}Cs leachability. Undissolved zeolite particles were found occasionally (Figure 3c), but these could probably have been eliminated simply by heating longer than 3 hours at the melting temperature (1150°C).

X-RAY ANALYSES OF GLASSES CONTAINING ACTUAL SLUDGES

Four glasses containing actual SRP sludges from Tanks 5 and 13 were analyzed by wide-angle x-ray diffraction. Two of the glasses were as-cast, and two had been heated for 1 month at 600°C.

Glasses 18-40-5 and 18-40-13 as-cast contained both crystalline and amorphous phases. The main crystalline component in both glasses was γ-Fe_2O_3, with an expanded lattice parameter, probably resulting from manganese, nickel, and titanium in solution. Glass 18-40-5 had more γ-Fe_2O_3 in its matrix than had Glass 18-40-13; this was also shown by metallographic examination. Heating Glass 18-40-5 at 600°C for 1 month did not cause devitrification, confirming DTA results. However, the γ-Fe_2O_3 content increased slightly during the heat treatment. Heating Glass 18-40-13 at 600°C did cause devitrification, as expected from the DTA and leach test results. The major crystalline phase formed was nepheline, $NaAlSiO_4$, along with some $Ca_4Fe_{14}O_{25}$. Nepheline was also the major crystalline phase in devitrified glass containing simulated sludge.

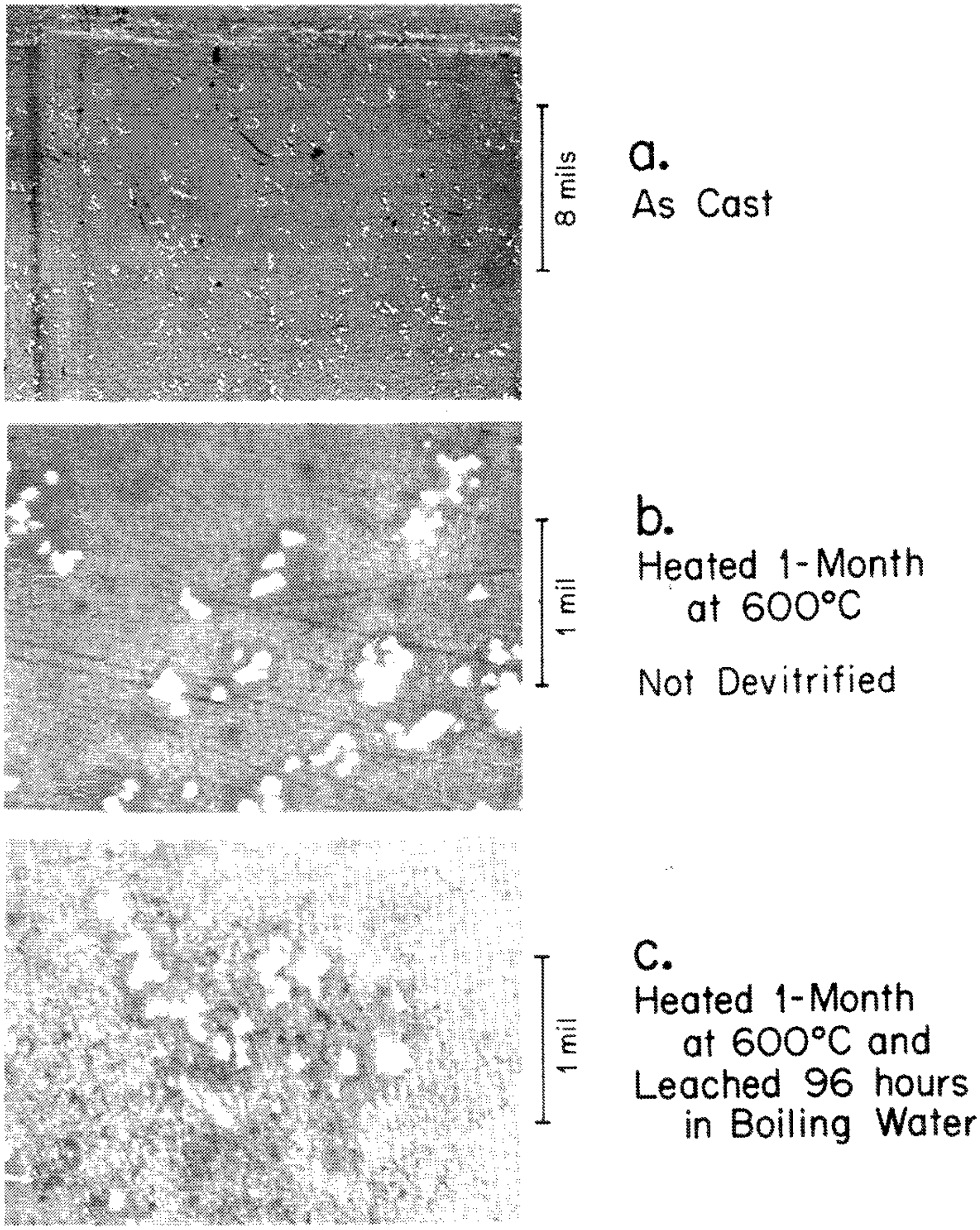

FIGURE 2. Microstructure of Glass 18-40-5

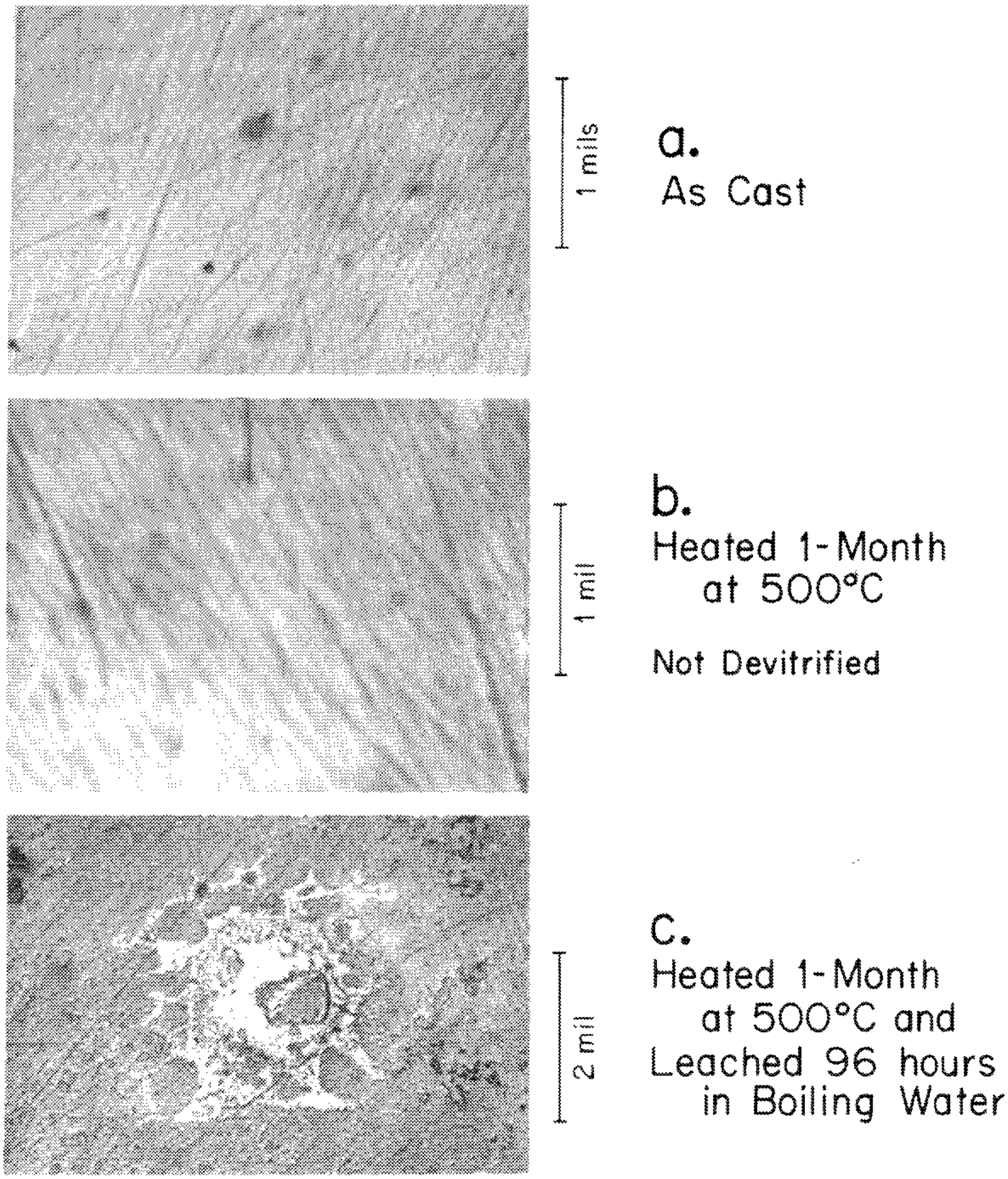

FIGURE 3. Microstructure of Glass 18-30-13/Z

CONCLUSIONS AND FUTURE WORK

This work showed that good glasses can be made with SRP waste sludges. All sludge components, except mercury which is volatilized, can be solubilized in a relatively low-melting glass. Small amounts of crystalline γ-Fe_2O_3, containing some sludge components in solution, precipitate in the glass during cooling from the melt. These precipitates have no adverse effects; their leachabilities are less than those of their glass matrices and they are not enriched in cesium and strontium. The glass containing 40 wt % Tank 13 sludge devitrified when heated at 600°C for 1 month, as shown by DTA, x-ray, and microscopic analyses. Devitrification increased the ^{137}Cs leachability by a factor of approximately 100. The glass containing 40 wt % Tank 5 sludge did not devitrify with the same heat treatment even though the two sludges have similar chemical compositions.

Further work will be directed toward understanding why Tank 5 glass does not devitrify and Tank 13 glass does. Also, glasses containing sludges from other SRP waste tanks will be made in 304L stainless steel tubes to investigate in-can melting of SRP waste sludges. Glass products will be leached and analyzed microscopically and by x-ray diffraction.

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