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**TIME-TEMPERATURE-TRANSFORMATION-DIAGRAMS FOR DWPF
PROJECTED GLASS COMPOSITIONS**

by

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TIME-TEMPERATURE-TRANSFORMATION-DIAGRAMS FOR DWPF PROJECTED GLASS COMPOSITIONS

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ABSTRACT

The Department of Energy's Waste Acceptance Product Specifications (WAPS) require that time-temperature-transformation diagrams be developed for each of the DWPF high-level waste glass compositions. This information will be useful in understanding the crystallization behavior during melter idling, accident scenarios, and storage. Simulated high level waste glass samples were annealed at temperatures varying from 400-1100°C for times varying from 45 minutes to 32 days. The glasses were characterized by x-ray diffraction to identify and quantify the crystalline phases present. The results were used to construct the diagrams.

INTRODUCTION

Approximately 130 million liters of high-level radioactive waste are currently stored in underground carbon steel tanks at the Savannah River Site (SRS). This high-level radioactive waste will be immobilized in a durable borosilicate glass and poured into stainless steel canisters in the Defense Waste Processing Facility (DWPF). The canistered waste forms will eventually be sent to a repository for final disposal. The Department of Energy has defined requirements, the Waste Acceptance Product Specifications (WAPS)¹, which these canistered waste forms must meet to be acceptable for disposal. Specification 1.4 of the WAPS requires that time-temperature-transformation (TTT) diagrams be developed for each of the DWPF projected high-level waste glass compositions. The TTT diagrams identify temperatures and the duration of exposure at these temperatures that cause significant changes in phase structure and phase composition of the glass waste form in order to provide guidance about conditions to be avoided during shipping, handling, and storage of DWPF canisters.

Seven DWPF glass compositions have been projected and are described in the DWPF Waste Form Compliance Plan (WCP).² Four of these compositions

(Batches 1, 2, 3, and 4) have been projected from existing high-level waste inventory while three of them are hypothetical glass compositions. The three hypothetical glasses are the Blend waste which represents the design-basis, high aluminum (HM) waste which represents the upper design limit of glass viscosity, and Purex (high iron) waste which represents the lower design limit of glass viscosity.² The Purex composition is based on: maximum precipitate feed rate, minimum sludge feed rate and minimum removal of soluble salts during sludge processing. Thus, the Purex represents a possible worst-case composition.

In order to provide the necessary information required by the WAPS, Corning Inc. was contracted to supply large quantities of the seven simulated waste glasses from the WCP.² Corning Inc. was unable to handle uranium containing glasses and so the U_3O_8 component of the WCP glasses was omitted and the glass compositions renormalized. Reference amounts of the minor Ru component were added as RuO_2 . The Corning analysis of the seven glass compositions as fabricated is shown in Table 1.

Table 1. DWPF Projected Compositions

Glass Components Wt %	Blend	HM	Purex	Batch #1	Batch #2	Batch #3	Batch #4
Al_2O_3	4.16	7.15	2.99	4.88	4.63	3.44	3.43
B_2O_3	8.05	7.03	10.33	7.78	7.88	7.69	8.14
BaO	0.18	0.11	0.20	0.15	0.16	0.18	0.25
CaO	1.03	1.01	1.09	1.22	1.08	0.99	0.84
Cr_2O_3	0.13	0.09	0.15	0.11	0.13	0.14	0.14
Cs_2O	0.08	0.06	0.06	0.06	0.02	0.06	0.09
CuO	0.44	0.25	0.42	0.40	0.42	0.40	0.45
Fe_2O_3	10.91	7.78	13.25	12.84	11.12	11.71	11.71
K_2O	3.68	2.21	3.41	3.33	3.38	3.40	3.86
Li_2O	4.44	4.62	3.22	4.43	4.50	4.51	4.29
MgO	1.41	1.49	1.41	1.42	1.42	1.42	1.43
MnO_2	2.05	2.15	2.07	2.11	1.73	1.87	3.11
MoO_3	0.15	0.22	0.08	0.11	0.17	0.12	0.20
Na ₂ O	9.13	8.56	12.62	9.00	9.21	9.01	9.16
Nd_2O_3	0.22	0.55	0.06	0.15	0.26	0.17	0.39
NiO	0.89	0.41	1.19	0.75	0.90	1.05	1.06
RuO_2	0.03	0.04	0.01	0.02	0.04	0.03	0.05
SiO_2	51.90	55.80	46.50	50.20	52.10	52.60	50.10
TiO_2	0.89	0.56	0.68	0.68	0.69	0.68	1.03
ZrO_2	0.14	0.33	0.05	0.10	0.17	0.12	0.22
Total	99.91	100.42	99.79	99.74	100.01	99.59	99.95

EXPERIMENTAL

In order to develop TTT diagrams, samples of the WCP glasses were exposed to various times and temperatures. Approximately 70 grams of glass were placed in covered high purity (99.8%) alumina crucibles. The crucibles were placed in a Lindberg programmable furnace and melted at the DWPF melt temperature of 1150°C for four hours. The glasses were heat treated at temperatures of 500, 600, 700, 800, 900, 1000, or 1100°C for times of 0.75, 3, 12, 48, 192, or 768 hours. For heat treatment at temperatures of 900°C and below, the crucibles were transferred to preheated Thermolyne muffle furnaces. For heat treatment at temperatures above 900°C, the crucibles remained in the Lindberg. Each glass sample was heat treated at a unique time and temperature. The 500 and 1100°C temperatures were chosen for conservatism. The 1100°C temperature being just below the melting temperature and the 500°C temperature being just above the glass transition temperature. Some samples were heat treated at 400°C to serve as controls. Additional samples were heat treated at 650°C to provide more information. In some instances, glasses were not heat treated for the full length of time so additional points were available for developing the TTT diagrams. The upper time limit of 768 hours was chosen to maximize crystallization. After a given time period the crystallization reaches a maximum and then remains constant with time.

Quantitative x-ray diffraction was performed on all glass samples to determine the type and amount of each phase present. Previously developed calibration curves³ were used for the quantitative examination. Scanning electron microscopy (SEM) coupled with energy dispersive analysis by x-ray (EDAX) was used on several of the glass samples to confirm the x-ray identification and chemical composition of the crystalline phases present in the glasses. SEM analysis was also used to verify the presence of RuO₂ and its role in nucleating crystalline phases.

RESULTS

Trevorite, acmite, lithium metasilicate, and nepheline crystals were found by x-ray diffraction in all of the glass compositions except for Purex which did not contain lithium metasilicate. In the glasses heat treated at 400, 500, 1000, and 1100°C, very few crystals were detected. In those samples where crystals were detected, a maximum of 1.5% trevorite was the only phase found in all compositions except Purex. The Purex glasses contained nepheline in the 768 hour heat treated glasses at 500 and 1000°C, and the quantity of crystals was as much as 3.5%. Two other exceptions to this generalization were found. The Blend glass heat treated at 500°C for 768 hours contained 0.8% acmite instead of the trevorite found in the other glasses, and the Batch 3 glass heat treated at 500°C for 768 hours contained 0.1% nepheline in addition to the trevorite. Trevorite was also the only phase found in the 900°C heat treated glasses except for Purex, which once again contained nepheline. Various combinations of trevorite, acmite, nepheline, and lithium metasilicate in much larger quantities were found in the

600°, 700°, and 800°C heat treated glasses, with the majority of the trevorite present in the 800°C glasses. The 600°C heat treated glasses contained the largest quantities of crystals for all compositions except Purex, which contained the largest quantity of crystals in the 700°C heat treated glasses.

SEM results, along with the qualitative x-ray diffraction results are presented in Table 2. Acmite, trevorite, traces of nepheline, and RuO₂ were detected using SEM. The presence of lithium metasilicate can not be determined since SEM can not detect lithium. Only trace amounts of nepheline were found since nepheline is harder to detect due to the small amounts present and the difficulty in distinguishing it from other phases and the glass matrix.

Table 2. Phase Identification by SEM and XRD

<u>Comp.</u>	<u>Temp.</u>	<u>Time</u>	<u>SEM</u>	<u>X-ray diffraction</u>
Batch 1	600	48	Acmite	Acmite, Li ₂ SiO ₃
Batch 1	700	48	Acmite	Acmite, Li ₂ SiO ₃
Batch 1	800	48	Trevorite + Acmite	Trevorite, acmite
Batch 1	900	48	Trevorite + RuO ₂	Trevorite
Batch 2	600	12	Acmite	Acmite
Batch 2	600	48	Acmite + RuO ₂ + Trev.	Acmite, Li ₂ SiO ₃
Batch 2	600	192	Acmite + RuO ₂	Acmite, Li ₂ SiO ₃ , Neph.
Batch 2	600	768	Acmite + trace Nepheline	Acmite, Li ₂ SiO ₃ , Neph.
Batch 3	700	48	Acmite + RuO ₂	Acmite, Li ₂ SiO ₃
Batch 3	700	768	Acmite + RuO ₂	Acmite, Li ₂ SiO ₃ , Neph.
Batch 3	800	192	Trevorite + RuO ₂	Trev., acmite
Batch 4	500	192	RuO ₂	Trevorite
Batch 4	800	768	Trev. + Acmite + RuO ₂	Trev., acmite, Li ₂ SiO ₃
Batch 4	1000	768	Trevorite + RuO ₂	Trevorite
Batch 4	1100	192	Trevorite + RuO ₂	Trevorite
Blend	600	48	Acmite	Acmite, Li ₂ SiO ₃
Blend	600	192	Acmite	Acmite, Li ₂ SiO ₃ , Neph.
Blend	700	48	Acmite	Acmite, Li ₂ SiO ₃
Blend	700	192	Acmite + RuO ₂	Acmite, Li ₂ SiO ₃ , Neph.
Purex	600	48	Trace Nepheline	Nepheline
Purex	600	192	Acmite	Acmite, nepheline
Purex	700	48	Acmite	Acmite, nepheline
Purex	700	192	Trevorite + Acmite	Acmite, nepheline
HM	600	192	Acmite + RuO ₂	Acmite, li ₂ SiO ₃
HM	700	48	Acmite + RuO ₂	Acmite, Li ₂ SiO ₃ , neph.
HM	700	192	Trevorite	Acmite, Li ₂ SiO ₃ , neph.
HM	800	192	Trev. + RuO ₂ + Acmite	Trevorite

The trevorite detected in most glasses was the NiFe₂O₄ composition and tended to be enriched in chromium and manganese. It was detected in some glasses by SEM where it was not with XRD, probably due to the acmite peak interference. The acmite detected by SEM was composed mostly of calcium, iron, and silicon, not sodium. RuO₂ was detected in all glass compositions, except Purex, with SEM, but when XRD was used it was only detected in the HM glasses. In most of the glasses, individual and clustered RuO₂ particles seemed to serve as nucleating sites. The RuO₂ not only served as a nucleating site for trevorite, but also for an

acicular nickel-rich iron silicate compound, which seemed to act as a host nucleus for massive acmite formation.

The results from the quantitative x-ray diffraction analyses were used to construct parabolic curves for each of the seven waste glass compositions to monitor the maximum crystallization at a given temperature over time. It has been shown that crystallization reaches a maximum and remains constant over time, after reaching a given time period at a specific temperature. The parabolic curves developed for Batches 1 and 2 are presented in Figure 1. Only the data from the 600, 700, and 800°C heat treated glasses were plotted, since they contained the most significant amounts of crystals. As shown in the graphs, the volume percent crystals increased with time, reached a maximum, and then remained constant. This maximum point of crystallization occurred between 192 and 768 hours for all waste glass compositions.

The maximum amount of crystallization, or saturation concentration, was determined from the parabolic curves at each temperature. This data was then used to create sigmoidal fractional ingrowth curves for the seven waste glass compositions. Sigmoidal fractional ingrowth curves are developed by plotting fractional ingrowth vs the log of time. The sigmoidal and parabolic curves provide an excellent method for monitoring the heat treatment process because any data that is sufficiently off will appear outside of the expected limits determined from the graphs. The sigmoidal fractional ingrowth curves for the Batch 1 and Batch 2 glass compositions are presented in Figure 2. Once again, only the 600, 700, and 800°C heat treated data were plotted, since the saturation concentration had to be determined from the parabolic curves. The maximum amount of crystallization was determined from the maximum point of the parabolic curves. As can be seen in Figure 2 the data created curves that were "S-shaped", indicating that the data was fairly accurate.

The total volume percent crystals, along with the volume percent of each crystal type, was plotted versus temperature to observe the variation of the rate of nucleation with temperature. In general, a specific crystal type will continue growing

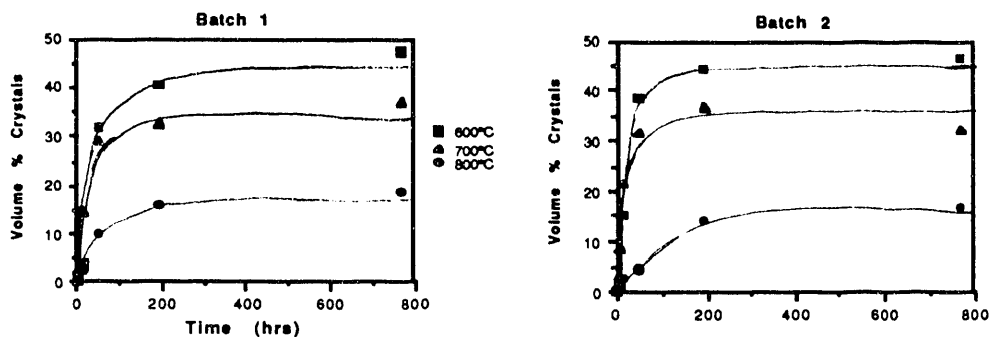


Figure 1. Parabolic curves for Batches 1 and 2.

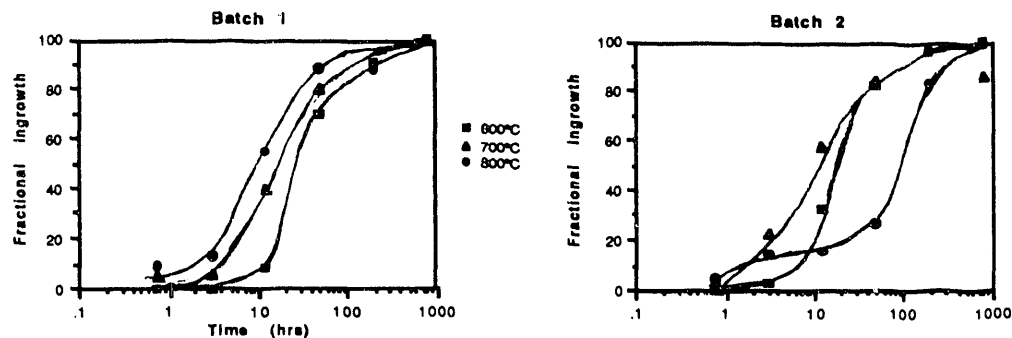


Figure 2. Sigmoidal fractional ingrowth curves for Batches 1 and 2.

until a maximum point is reached, and then the amount of this crystal type will decrease. Since the 768 hour heat treated glasses showed the greatest variety of detectable crystals, this data was plotted for each of the waste glass compositions. The plots for the seven waste glass compositions are shown in Figure 3.

After evaluating the data using the curves discussed above, the time-temperature-transformation diagrams for the seven DWPF waste glass compositions were developed. These TTT diagrams are shown in Figure 4. The liquid phase was present by itself and with all the crystalline phases. For simplification, liquid is not included in the following lists of crystalline phase regions.

The TTT diagram for the Batch 1 waste glass composition had six different phase regions: trevorite; trevorite + acmite; trevorite + acmite + lithium metasilicate + nepheline; acmite; acmite + lithium metasilicate; and acmite + lithium metasilicate + nepheline. The trevorite region encompassed the majority of the phase diagram, and was the prevalent crystalline phase at higher temperatures and shorter annealing times. Between 750 and 850°C, acmite began to form with the trevorite. The acmite concentration in this region increased with time, as the trevorite concentration remained constant, until extreme annealing times were reached where lithium metasilicate and nepheline began to grow and replace some of the trevorite. At temperatures from 550 to 750°C and times greater than 3 hours, trevorite no longer formed and acmite became the primary nucleating phase. In addition, as annealing times increased, lithium metasilicate formed and then nepheline at longer annealing times.

The Batch 2 TTT diagram was similar to the Batch 1 diagram and also had six different phase regions: trevorite; trevorite + acmite; trevorite + acmite + lithium metasilicate; acmite; acmite + lithium metasilicate; and acmite + lithium metasilicate + nepheline. Once again, the trevorite region encompassed most of the TTT diagram, but was not found below temperatures of 650°C. The trevorite + acmite region existed at approximately the same time and temperature as the Batch 1 composition. However, this region started at lower temperatures and did not develop any nepheline at the extreme annealing times. The same growth order

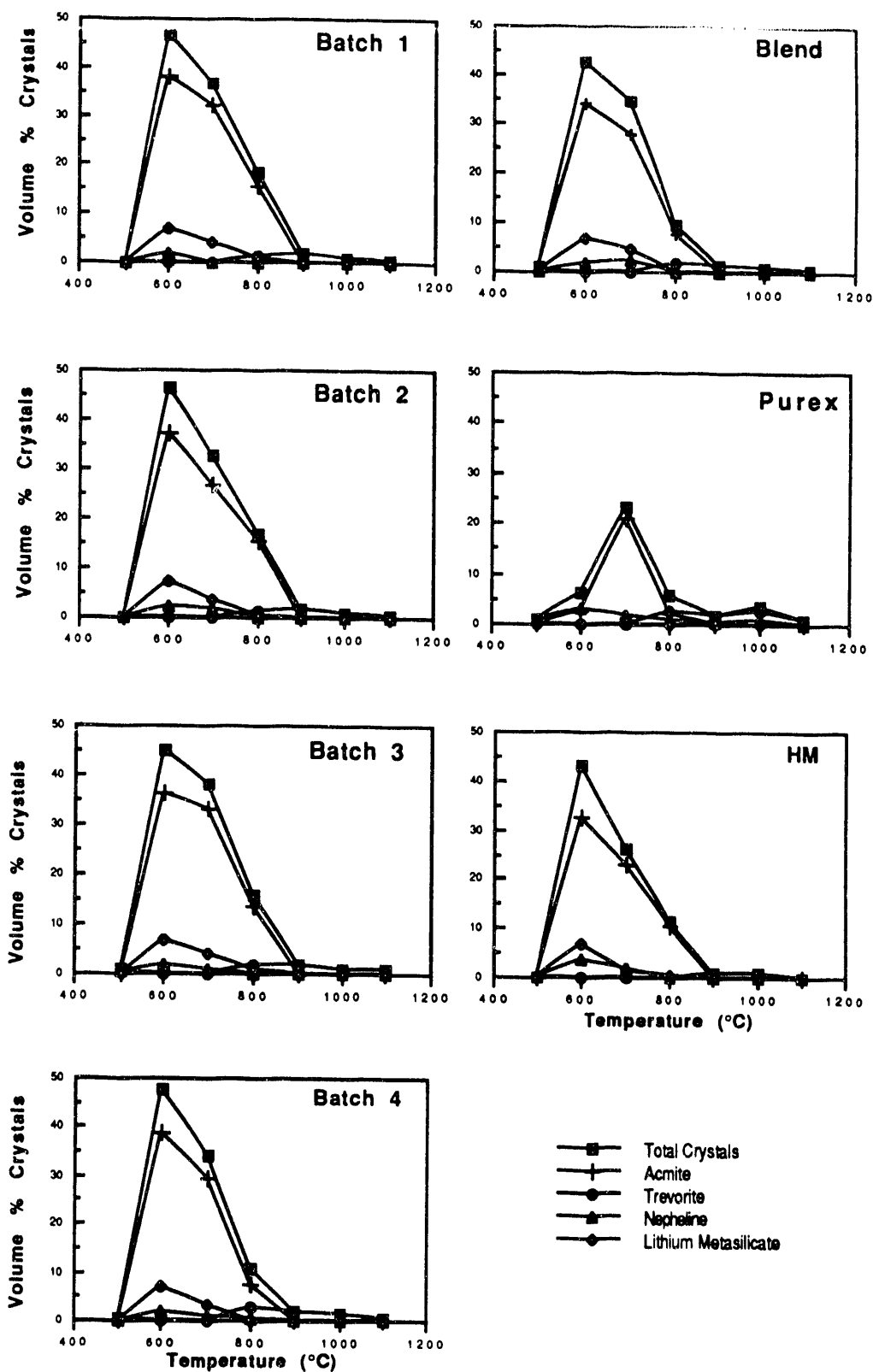


Figure 3. Percentage of Crystals vs Temperature for Heat Treated Samples.

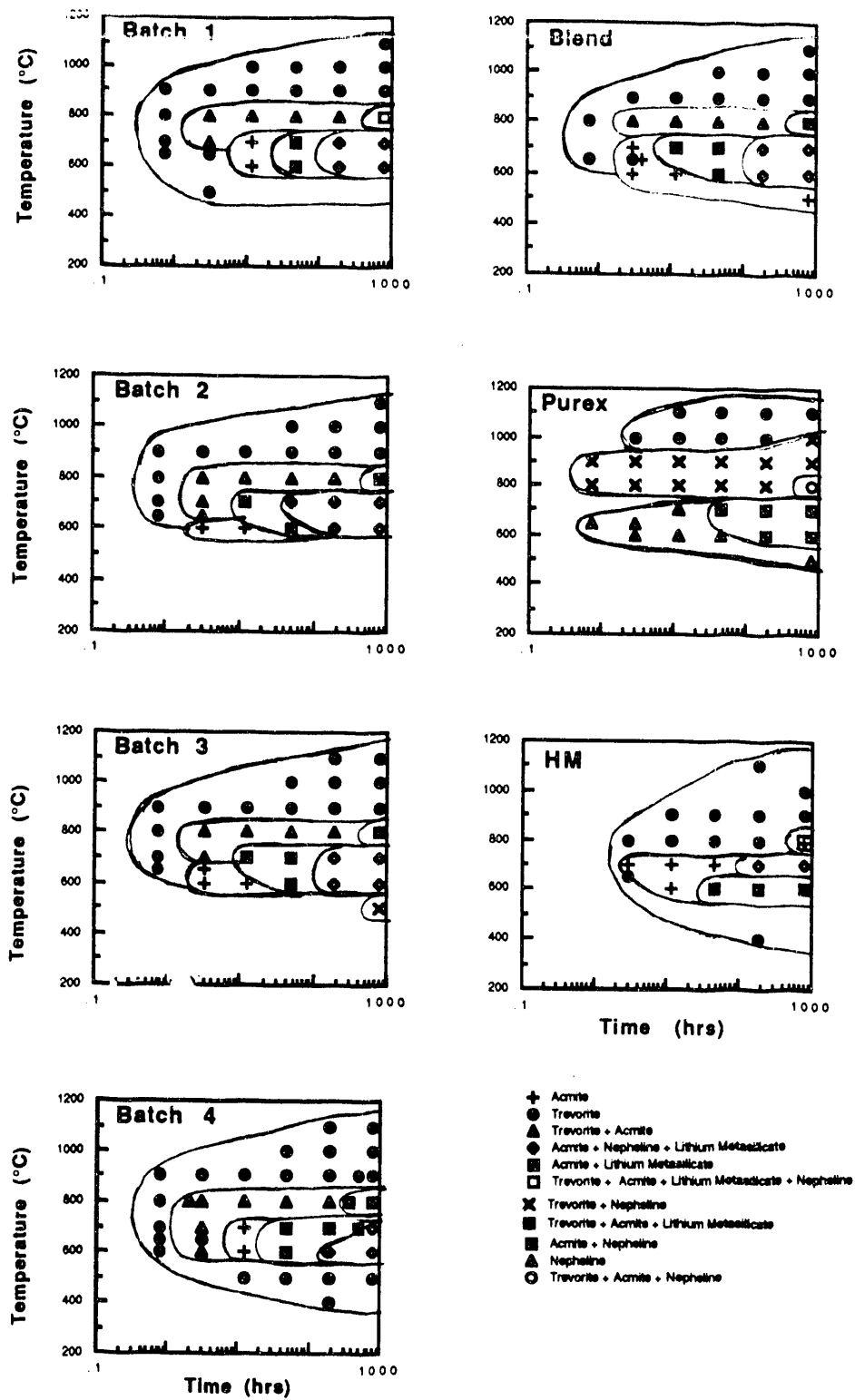


Figure 4. TTT Diagrams for DWPF Projected Glass Compositions.

of acmite, lithium metasilicate, and then nepheline was experienced at temperatures from 550 to 750°C, but they appeared at higher temperatures sooner than they did in the Batch 1 composition.

Batch 3 was also similar to the Batch 1 TTT diagram and produced the same phase regions as Batch 2, plus an additional trevorite + nepheline region. The trevorite region encompassed most of the diagram at higher temperatures and shorter annealing times. The trevorite + acmite region was identical to Batch 1, but as was the case with Batch 2 glasses, the extreme annealing times only produced lithium metasilicate and not nepheline. Both acmite and lithium metasilicate began to appear at shorter annealing times in the 550 to 750°C region, which can probably be attributed to the higher lithium concentration in the waste composition. This higher lithium concentration combined with the lower alumina concentration in the glass composition attributed to the growth of nepheline at lower temperatures and longer annealing times in the trevorite + nepheline region. The acmite + lithium metasilicate + nepheline phase region was the same as Batch 1.

The TTT diagram for the Batch 4 composition was similar to the previous diagrams, but contains a few extra data points which better define the phase regions. The six phase regions found were trevorite, trevorite + acmite, trevorite + acmite + lithium metasilicate, acmite, acmite + lithium metasilicate, and acmite + lithium metasilicate + nepheline. Once again, the trevorite phase region encompassed most of the diagram, and was even detected at lower temperatures for longer times. Its presence at shorter times in the middle temperature range produced a larger trevorite + acmite phase region. However, an extra point for the Batch 4 composition heat treated at 800°C verified that the lithium metasilicate started growing earlier than predicted in other diagrams at these temperatures. The growth pattern of acmite, lithium metasilicate, and nepheline between 550 and 750°C was repeated, except that nepheline did not start growing in the upper temperatures of this region until extreme annealing times had been reached.

The Blend composition TTT diagram was similar to the Batch 1 - Batch 4 diagrams, and also contained six phase regions. These regions are trevorite, trevorite + acmite, trevorite + acmite + lithium metasilicate, acmite, acmite + lithium metasilicate, and acmite + lithium metasilicate + nepheline. As with the Batch 1 - 4 diagrams, the trevorite phase region was the predominant phase of the diagram, but it was only present at higher temperatures. Acmite began to form with the trevorite from 750 to 850°C above 0.75 hour annealing times and lead to the in-growth of lithium metasilicate at extreme annealing times, consistent with the other TTT diagrams. The normal growth procession of acmite, lithium metasilicate, then nepheline occurred in the absence of trevorite at the lower temperatures.

Due to the fact that Purex composition glasses tend to crystallize nepheline at lower temperatures, its TTT diagram was different than any of the diagrams discussed earlier. This tendency to crystallize alkali silicate phases (nepheline) at lower temperatures can be correlated to the increase in $(\text{Li}_2\text{O} + \text{Na}_2\text{O})/(\text{SiO}_2 + \text{Al}_2\text{O}_3)$ ratio compared to the other compositions. The five phase regions dis-

covered in the Purex TTT diagram were trevorite, trevorite + nepheline, trevorite + nepheline + acmite, acmite + nepheline, and nepheline. The trevorite region was the predominant phase at higher temperatures, while the nepheline region was the predominant phase at lower temperatures. A combination of the phases, trevorite + nepheline, existed in the middle temperature range. At extreme time durations in the 750 to 850°C temperature range, acmite began to grow with the trevorite and nepheline to form the trevorite + nepheline + acmite region. Acmite was also present when the glasses were heat treated for longer times in the lower temperature region, but only with nepheline and not trevorite or lithium metasilicate.

The HM composition produced a TTT diagram which varied even more than the previous diagrams, partly because no crystals of any type were detected at 0.75 hour annealing times. It contained five phase regions, which were trevorite, trevorite + acmite + lithium metasilicate, acmite, acmite + lithium metasilicate, and acmite + lithium metasilicate + nepheline. The largest region was the trevorite region, which was the predominant phase at temperatures above 750°C. Acmite was not found coexisting with the trevorite in the 750-850°C range, as it had been with the other compositions. The trevorite + acmite + lithium metasilicate region was similar to that found in Batch 2 - 4, and was the only other region where trevorite was detected. Acmite formed between 550 and 750°C at times greater than 0.75 hours, but was only found above this temperature at extreme annealing times. The lithium metasilicate and nepheline still followed the same growth pattern as with the other glasses, but the acmite + lithium metasilicate + nepheline phase region was larger than in the other diagrams and also started to form at shorter annealing times. The acmite + lithium metasilicate phase region was only found in the 550-650°C range, not from 650-750°C as in the other diagrams.

CONCLUSIONS

The TTT diagrams for the seven waste glass compositions have been constructed. All glass compositions contained trevorite, acmite, lithium metasilicate, and nepheline in various amounts and combinations, except for the Purex glasses which did not contain any lithium metasilicate. Trevorite was the predominate phase for all times at temperatures from 850-1100°C and for shorter times at temperatures from 650-850°C for most compositions. For the Purex glasses, the trevorite phase existed only from 950-1100°C and was not found by itself at temperatures below 950°C. The trevorite phase in the HM glasses extended to 750°C, not 850°C as with the other compositions. A combination of acmite and trevorite was the predominant phase for most glass compositions from 750-850°C, except for the Purex and HM waste glasses. For the Purex glasses, trevorite and nepheline were the predominant phases from 750-950°C and for the HM glasses, acmite was the lone phase from 650-750°C at shorter heat treatment times. At temperatures from 550-750°C, acmite, along with some combination of lithium metasilicate and nepheline, was the predominant crystalline species, except for in the Purex glasses. Nepheline was the predominant phase in this temperature range in these glasses. These alkali silicate phases were also present in

the 750-850°C range at longer heat treatment times. The largest amounts of crystals were found when the glasses were heat treated for extremely long times in the 600°C and 700°C temperature range. Purex glasses had the lowest volume percent crystallization over all glass compositions. This can be partly attributed to the small amounts of alumina and lithia present in the glass, which tend to increase the rate of devitrification.

From the SEM results, it appears that all crystallization was heterogeneous with RuO₂ serving as the principal nucleating agent. At temperatures above 850°C, the RuO₂ served as a host site for trevorite nucleation, while at temperatures below 850°C, it served as a host site for massive acmite formation. In the 500-700°C range, acicular acmite began nucleating on the RuO₂ sites, which lead to the massive acmite formations.

ACKNOWLEDGMENT

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