Iron Phosphate Glass Waste Forms for Vitrifying Hanford AZ102 Low Activity Waste (LAW), Part I: Glass Formation Model.

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Abstract

A methodology for determining glass formation in a 5-component iron phosphate base glass system that contained P_2O_5 , Fe_2O_3 , Al_2O_3 , Na_2O and SO_3 has been developed using a standard 5- component D-Optimal Statistical Mixture Design procedure. This compositional system was selected in order to study the feasibility of vitrifying a high soda (~ 80 wt%), a high sulfate (~ 17 wt%) containing Hanford AZ102 LAW in iron phosphate glasses with waste loadings much higher than the currently reported values. The statistical analysis was designed to develop a series of initial compositions (total 28), nearly half of which formed glass upon melting and cooling. After separating the compositions that formed glass from those that crystallized, three molar ratios, namely, (O/Na), (Na/Al) and (Na/P), were identified as potential parameters for defining glass formation (or crystallization). The (O/Na) molar ratio had the greatest effect. Melts whose (O/Na), (Na/P) or (Na/Al) molar ratios were ≤ 4.35 , ≥ 1.13 , or ≥ 2.56 , respectively, had the highest likelihood to form glass when cooled. The melts crystallized completely when the values of these three molar ratios were, respectively, ≥ 6.02 , ≤ 0.77 or ≤ 1.92 . For the compositions that formed glass, the waste loadings as defined by the sum of Na_2O and SO_3 , the two major components comprising > 90 wt% of the Hanford AZ102 LAW, ranged from 25 to 33 wt%.

A glass formation-composition model that formalized the above findings was developed using the Classification and Regression Tree (CART) analyses. The CART model was validated by testing the glass formation characteristics of several additional compositions whose (O/Na) molar ratio was maintained ≤ 4.35 , i.e., the compositions were expected to form glass. This model is expected to identify similar molar ratios for predicting glass formation/crystallization of iron phosphate based compositions containing not only other Hanford LAW streams, but high level wastes as well. Using the compositions that formed glass, property-composition statistical models for the waste forms were also developed and will be reported in a second paper.

Key words: Iron phosphate glass, Nuclear waste, AZ102 LAW, Glass formation, Statistical models

1. Introduction

Among the high priority nuclear wastes awaiting disposal at Hanford is the high sulfate (~ 17 wt%), high alkali (~ 80 wt%) containing AZ102 low activity waste (LAW). Immobilizing the high and low level nuclear wastes in glassy media, a process known as *vitrification*, is currently considered as the most

viable technology for nuclear waste remediation. In general, a cost effective vitrification process requires the waste to be mixed with common and commercially available glass forming additives (GFA) in the proper proportions to obtain suitable glass compositions that, when melted and cooled, must have specified properties within acceptable limits. The solidified melt of GFA and waste components is known as the glass *waste form*, which must be chemically durable, mechanically strong, and thermally stable to meet the criteria for long-term storage. Currently, borosilicate glass compositions have been chosen internationally as the accepted media for waste immobilization [1 - 4], since borosilicate (BS) glasses have a high chemical durability, especially, in aqueous solutions, and the industrial processing technology for these glasses is mature.

The sulfates present in the AZ102 LAW are known to be poorly soluble in borosilicate glasses [5, 6] and can form a salt layer on the surface of the melt. This fluid molten salt layer can rapidly corrode the ceramic liner in the melter and cause other operational problems [5 – 7]. These include, among others, (1) increased corrosion of the melter components and the off-gas treatment system, which decreases the overall melter life, (2) increased volatility of the sensitive radioactive elements like Tc and Cs, and (3) disruption of the heat flow pattern in the melt by creating low resistance current paths, leading to a possible shut down of the melter. A large number of studies have been made [5 - 12] to determine the sulfate tolerance of silicate melts with the aim to developing borosilicate glass waste forms loaded with sulfur-containing nuclear wastes. For the Hanford LAW glass melts, Pegg et al. [11] suggested a relationship between Na_2O and SO_3 , known as the rule-of-five, as a means of achieving a minimum waste loading as;

$$g_{\text{Na}_2\text{O}} \times g_{\text{SO}_3} \leq 5 \quad \dots \quad \dots \quad \dots \quad \dots \quad (1)$$

where, g_i is the wt% of the i th component. It has been shown that to meet the minimum acceptable chemical durability requirement, a borosilicate glass waste form should have a combined $\text{Na}_2\text{O} + \text{K}_2\text{O}$ content between 20 and 23 wt% [12, 13]. This means that for a Na_2O content of 20 wt%, the amount of SO_3 would be limited to about only 0.25 wt%. More recently, Vienna et al. [7, 10], using a modified glass formulation approach, was able to increase the SO_3 concentration to between 1 and 2 wt%. Even at the highest concentration of 2 wt% SO_3 , a waste loading of no more than 12 wt% was possible for the AZ102 LAW waste form. Such low waste loadings increase the overall volume and cost of the vitrified waste form. A way of overcoming these shortcomings is to develop alternative glass matrices, which have a higher solubility of SO_3 and, thus, higher waste loading while maintaining, at the same time, the required processing conditions and waste form properties such as a high chemical durability.

For immobilization of many nuclear wastes containing problem components, iron phosphate glasses can be advantageous for several reasons. These glasses have [14 - 18] (1) higher solubility limits for many of the nuclear waste components including SO_3 , which prevents the formation of sulfate salt layers on the melt surface, (2) low melting temperature ($< 950^\circ\text{C}$) and a low viscosity (200 to 400 cP) at the melting temperature, which ensures faster melting and more rapid homogenization of the melt, and (3) excellent chemical durability that is comparable or better than that of the borosilicate glasses. A lower melting temperature and shorter melting time also help retain volatile components (S, Cl, F, Cs, Tc) and other long lived radioactive elements in the glass waste form. These unique features of iron phosphate melts offer a way of vitrifying many different types of nuclear wastes [14 and references there in], especially at Hanford and Idaho, at waste loadings ranging from 30 to 75 wt%.

Previous studies for vitrifying Hanford LAW, including AZ102, in iron phosphate glasses show [17 - 19] a waste loading of up to 30 wt% can be easily achieved in homogeneous glass waste forms when melted between 1000 and 1050°C in air for 3 to 5h. The SO₃ content of these waste forms, which met the DOE chemical durability requirements, ranged from ~ 3.8 wt% (86% retention) when melted for 3h to 2.1 wt% (48% retention) when melted for 10 days. These percentages are ~ 2 to 4 times higher than those reported for borosilicate glass waste forms. The final optimum compositions in these studies were developed on a purely experimental basis using intuition based on the existing knowledge of glass compositions. This process is arbitrary and, hence, time consuming.

The use of mathematical models, based on statistical analysis, to design suitable glass compositions that must be optimized with a set of relevant properties by developing appropriate property-composition models should be a rational and practical approach. Such mathematical models for glass formulation for several waste streams like Hanford HLW/LAW, Spent Nuclear Fuel (SNF), INL Zirconia high-activity waste and INL SBW have been developed [20 – 24 and references there in] for borosilicate (BS)-based glass as the host matrix. Similar glass formulation models using iron phosphate glass as the host matrix have not been developed up to this time.

The work described herein (Part I) is the first attempt to develop suitable glass formulation models for iron phosphate glass using a waste composition similar to that of the Hanford AZ102 LAW, which has been simplified to a 5-component system consisting of P₂O₅, Fe₂O₃, Al₂O₃, Na₂O and SO₃ for the purpose of simplifying the mathematical analyses and data interpretation. Developing a suitable glass composition model must be supported by optimizing glass compositions with critical waste form properties, which will be described separately in Part II of this paper, by developing useful property-composition models.

The glass formulation effort in the present work utilizes statistical modeling and analysis based on a standard five component statistical D-Optimal Mixture design technique [25] to generate initially a set of 28 glass compositions in the system P₂O₅ - Fe₂O₃ - Al₂O₃ - Na₂O - SO₃. A set of boundary conditions for the range of each component estimated from earlier work [17 - 19] was imposed as input parameters in the calculations. One obstacle to utilizing data from the D-Optimal mixture design is that the compositions suggested by the design do not all form glass. Thus a model that predicts the probability that a given composition will form glass would be of high utility. After separating the compositions that formed glass upon melting and cooling from those that crystallized, three molar ratios, namely, (O/Na), (Na/Al), and (Na/P) were identified as potential parameters for determining glass formation and crystallization. A glass forming ability-composition model that formalized the above findings was developed using the Classification and Regression Tree (CART) analyses [26]. Several additional compositions that satisfied the model-identified glass formation condition for the molar ratio (O/Na) were developed for the purpose of testing the model.

2. Experimental Procedures

2.1 Composition Formulation using Statistical Modeling

A 5-component iron alumino phosphate system consisting of P₂O₅, Fe₂O₃, Al₂O₃, Na₂O and SO₃ was used in the present work for formulating waste form compositions and developing property-composition models for selected properties of the waste form. The selection of this compositional system stems from the fact that it represents, as a first approximation, the vitrification of the Hanford AZ102 LAW which

contains Na₂O and SO₃ as the major components in an iron phosphate glass (P₂O₅ + Fe₂O₃). See Table 1 for a simplified average composition of AZ102 LAW as provided by Hanford.

The glass formulation effort utilizes statistical modeling and analysis within the following boundary conditions (in wt%);

$$42 \leq \text{P}_2\text{O}_5 \leq 60, \quad 4 \leq \text{Fe}_2\text{O}_3 \leq 15, \quad 10 \leq \text{Al}_2\text{O}_3 \leq 18, \quad 15 \leq \text{Na}_2\text{O} \leq 28, \quad \text{and} \quad 2 \leq \text{SO}_3 \leq 5, \quad \dots \quad (2)$$

$$\text{where, } \text{P}_2\text{O}_5 + \text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3 + \text{Na}_2\text{O} + \text{SO}_3 = 100, \text{ wt\%} \quad \dots \quad \dots \quad \dots \quad \dots \quad \dots \quad (3)$$

The above boundary conditions were chosen based on our experience and literature data for iron phosphate compositions that are likely to form glass when melted at temperatures below 1200°C and cooled in air.

A standard five component statistical D-Optimal Mixture design technique was used to generate 23 initial compositions and an additional replication (duplicate run) for each of 5 selected compositions for verifying the reproducibility of the results and calculating experimental error. Thus, a total of 28 compositions were generated and investigated for glass formation and developing property-composition models. These compositions are shown in Table 2 where the duplicate compositions are highlighted in color.

The statistical design technique is aimed at generating a sufficiently wide range of compositions that cover the entire compositional space defined by the above conditions, eqns 2-3, with uniform scatter. Figure 1 shows a scatter matrix plot of the 28 compositions generated using this statistical approach. It is clear that the compositions are well distributed, as intended, over the entire compositional space defined by eq. 2.

2.2 Glass Melting/Glass Formation

The compositions in Table 2 were melted using well-mixed batches of appropriate raw materials (> 99.0% purity) that yielded ~200g of melt. The melting was conducted in air between 1000 and 1200°C for 3 h in alumino-silicate refractory crucibles (DFC 83 wt% SiO₂, 17 wt% Al₂O₃). The melting characteristics were observed at frequent intervals, and the temperature at which the batch melted completely was taken as the melting temperature, T_m, as shown in Table 2 for each composition. The melts were stirred four times using a fused silica rod before being cast directly onto a steel plate. In general, these iron phosphate melts were highly fluid at the melting temperature, with negligible corrosion of the refractory crucible, see Figure 2. Figure 2, which is a typical example for all the melts, shows the vertical cross section of the crucible wherein glass #1 (Table 2) was melted at 1050°C for 3 h. No corrosion of the crucible by the melt is visible.

The solidified melts that appeared glassy on visual examination were annealed at 450°C for 1h and then cooled to room temperature overnight inside the furnace. Considering the duplicate compositions as independent, fifteen of the 28 compositions in Table 2 formed glass as confirmed by the absence of any peaks in the x-ray diffraction (XRD) patterns. The XRD patterns for glasses #5 and 25 are shown in Figure 3 as typical examples. The compositions that formed glass or which crystallized are indicated in the right hand column of Table 2.

3. Results and Discussion

3.1 Glass Formation

As shown in Table 2, 15 of the 28 compositions formed glass when melted and cooled in air in the manner described herein. Due to some interesting observations that were noted for the glass forming ability of these compositions, the compositions in Table 2 have been rearranged in Table 3 according to the increasing molar ratio of oxygen to sodium (O/Na), from top to bottom (set A), and to the decreasing molar ratio of (Na/Al) and (Na/P) (sets B and C). Rearranging the compositions in this way, with the exception of one or two outliers, the compositions fall into two distinct groups for each set; one whose melts formed glass (shaded green), and a second set whose melts crystallized on cooling (shaded red).

Table 3 also includes a composition designated as MS26, yellow boxes, which is an iron phosphate composition that contains 26 wt% of the Hanford AZ102 LAW given in Table 1. This composition has been reported [18, 19] to form glass when melted at 1030°C and cooled in air. As expected, the MS26 composition falls within the glass forming green zone in all three sets (A, B, and C) in Table 3.

The duplicate compositions in Table 2 are grouped together as one composition in Table 3. Thus, the total number of independent compositions, including MS26, is 24 (Table 3); over half (13) of these compositions formed glass (green) and a nearly equal number of compositions (11) crystallized (red) during cooling in air. Although, this number of melts is not statistically optimal for model development, still the data in Table 3 suggests that these three parameters, namely, the (O/Na), (Na/Al) and (Na/P) molar ratios are useful in predicting the glass forming (or non-glass forming) tendency of these alkali-alumino-iron phosphate melts. Glass formation becomes highly likely when the molar ratios (O/Na) < ~4.40 (Set A, Table 3), (Na/Al) > ~2.15 (Set B, Table 3), and (Na/P) > ~0.84 (Set C, Table 3). The exact reason(s) why glass formation depends upon these ratios is not fully known, at this time, nor is it known whether these conditions must be satisfied simultaneously. In any case, it is believed that any dependence of glass formation upon these ratios is related to the atomic structure of the melt/glass.

3.2. Modeling Glass Formation

The experimental results in Table 3 were used to develop glass formability-composition models using a statistical analysis approach based on the Classification and Regression Tree (CART) algorithm (JMP Pro 10 Statistical Software package) [26]. The CART procedure provided a simple but mathematically systematic way to determine the ability of each of the molar ratios (Na/P, O/Na, and Na/Al) in predicting glass formation through a “tree-structured” decision model. The models were obtained through a sequence of steps, each step splitting the data in to two sub-sets based on the value taken by a specific molar ratio so that each sub-set of the split contained “mostly glass” or “mostly crystal” region. Each step refined the model further by increasing the predictive ability of the model.

The rationale for using the CART procedure is two-fold. First, the results from the model are easily interpretable. Second, it introduces an objective way to identify the glass forming region. While a careful inspection of Table 3 may suggest that compositions with (O/Na) molar ratios <4.35 would produce glass, one can also argue that a cut-off criteria of <4.59 would be equally appropriate since none of the compositions at or above 4.59 (#7, column 1, Table 3) formed glass. The use of CART algorithm removes this subjectivity by obtaining the cut-off value through a mathematical criterion that minimizes the residual log-likelihood chi-square value (this is equivalent to 2* entropy, note that a smaller entropy

means a better model fit, see reference [27]). An additional advantage is that the procedure allows the simultaneous inclusion of more than one molar ratio into the model, even though in the current context the inclusion of additional ratios did not improve the prediction accuracy of the model.

The CART procedures as applied to the 24 compositions in Table 3 used each of the three molar ratios separately as an input variable, and the “glass formation” or “crystallization” was expressed as a binary variable with “0 = crystal” and “1 = glass”. The results for the step by step CART analysis using the (O/Na) molar ratio are shown in the tree diagram in Figure 4 as an example. Also included in the figure is the Receiver Operating Characteristics (ROC), which predicts the overall accuracy of the model.

The results in Figure 4 identify compositions that are predicted to form glass with a high probability when their (O/Na) molar ratio falls into a certain region. Compositions with an (O/Na) ratio ≤ 4.35 are predicted to form glass (blue bar, Fig. 4) with a probability of 0.9647, while those with a (O/Na) ratio ≥ 6.02 are designated as non-glass forming compositions (red bar, Fig. 4) with a probability of 0.9287. Similar results were obtained for the other two molar ratios, namely (Na/Al) and (Na/P), when the CART procedures were applied to the same 24 compositions in Table 3. The limits that satisfy the “glass formation/crystallization” condition as obtained using the CART procedures are given in Table 4 for all three molar ratios, (O/Na), (Na/Al) and (Na/P). As shown in Table 4, glass formation becomes probable for compositions that have (Na/P) ratio ≥ 1.13 or (Na/Al) ratio ≥ 2.56 .

To the authors’ knowledge, this is the first time that glass formation criteria for iron phosphate compositions have been identified or modeled on the basis of the molar ratio of certain compositional components. However, the reason(s) why glass formation depends upon these particular ratios is not fully understood at this time, nor is it known whether these ratios are of equal importance and whether all three need to be satisfied simultaneously. At this time, it is believed that these ratios are associated with specific atomic arrangements (network structure) in the melt, which favors glass formation (prevents crystallization) on cooling. This fascinating aspect of identifying glass forming compositions on the basis of the molar ratios of a few major components warrants further study to gain a detailed and deeper understanding of the underlying science.

There are three main parameters that can be used to determine the prediction accuracy of the models. These are (1) the area under the glass and crystal ROC (Receiver Operating Characteristics) curves, see Figure 4, (2) the AICC values (top inset in Figure 4) and (3) the R^2 values. The values of these parameters for each model corresponding to the molar ratios (O/Na), (Na/Al) and (Na/P) are given in Table 4. Higher values for the ROC-area curves and R^2 values, and lower AICC-values predict better accuracy of the models. These prediction accuracies were obtained using two splits (groups), see Figure 4 for example. Calculations using more than two splits (3 or 4) did not improve the prediction accuracy. A test was also performed to determine if combining any of the two ratios, such as (O/Na) and (Na/Al), would improve the classification accuracy, but it did not.

As shown in Table 4, the prediction accuracy for the models as determined by the values of R^2 , AICC, and ROC curve-area is very close for the (O/Na) and (Na/Al) molar ratios, and is slightly better

than that for the model for (Na/P). This is also consistent with the experimental results. While the models for (O/Na) and (Na/Al) both miss one (outlier) composition that formed glass (#13 for (O/Na) and #4 for (Na/Al) in Table 1 or 2), the same for (Na/P) miss three compositions (#13, 20 and 25 in Table 1 or 2). The compositions #4, 13, 20 and 25 in Table 1 or 2 are predicted to crystallize by one or more of the three models, while in reality all these compositions formed glass when melted and cooled in air. The limited number of data presented here show that the (O/Na) and (Na/Al) molar ratios are equally important in predicting glass formation/crystallization in these iron phosphate glasses. It is demonstrated later from further studies that the (O/Na) molar ratio is a somewhat better predictor than the (Na/Al).

It is of interest to ascertain if the CART procedure would be as efficient when a smaller number of compositions were available for modeling. Such an assessment was carried out using approximately half of the original 24 compositions. The sub-sample of the compositions was randomly selected using the following procedure. Each of the original 24 compositions (Table 3) was assigned a value of either 0 or 1 by generating Bernoulli random variables, which takes values either 0 or 1 with equal probability. Only those compositions associated with the value 1 were then selected for analysis using CART procedure. This process was repeated 10 times, giving us assessment of the performance of the CART procedure under 10 different sets (column 1, Table 5) of randomly selected compositions (column 2, Table 5). The 10 repetitions of this assessment process were considered more than necessary to determine how the CART procedure works when the number of compositions was decreased by approximately one-half. While roughly 12 compositions are expected to be selected for each set, the number of samples ranged from 11 to 15 due to the random nature of the Bernoulli process. The results of this sub-sample analysis using the CART procedure are given in Table 5 for each of the molar ratios (O/Na), (Na/Al) and (Na/P).

The results of CART analysis in Table 5 include the cut-off value for glass formation (and non-glass formation) as predicted by the CART algorithm along with the R^2 -prediction accuracy for each of the three molar ratio. The results show that even with lesser number of samples (10 to 15 compared to 24 in the original data set), the CART algorithm picked up cut-off values for glass formation for the (O/Na) and (Na/Al) molar ratios close to what was picked up when full data set was used (compare results in Table 4 and Table 5), while the same for the (Na/P) molar ratio appeared to be random. In addition, in 6 out of 10 groups (shaded green in Table 5) for both (O/Na) and (Na/Al) molar ratios, the CART procedure yielded perfect separation of glass forming and non-glass forming compositions in the sample data set used to obtain the model. One caveat that should be stressed is that the results of the CART procedure will be only as good as the data presented to it. Groups that lack data near the threshold between glass forming and non-glass forming regions will produce cut-off values that are not as accurate as that produced in groups that straddle this threshold very closely. It is not the size of the group that matter *per se*, but the availability of the data near the boundary of the glass forming region. Thus a two-step procedure in gathering data for CART modeling may be warranted. After the initial fitting of a CART model, more data should be gathered near the estimated cut-off value and the model re-fitted to get a better estimate of the glass forming boundary.

The accuracy of the models (as indicated by the preceding three parameters) for the (O/Na) and (Na/Al) molar ratios for predicting glass formation is so close that it is difficult to conclude which molar ratio is statistically superior to the other, especially in light of the limited number of melts used herein in model building. As described in the following section, additional compositions were investigated and

new data were obtained to determine which molar ratio would be the better predictor for glass formation for these iron phosphate glasses.

3.3 Model Validation and Relative Importance of the Molar Ratios (O/Na), (Na/Al), and (Na/P) on Glass Formation

Further effort was made to validate the glass formation models described in section 3.2, and to determine which of the three ratios, (O/Na), (Na/P), and (Na/Al), is the most important parameter for predicting glass formation for these iron phosphate compositions. Several new compositions in this 5-component system were designed following closely the boundary conditions given in eqns. (1) and (2) with the additional constraint that the (O/Na) molar ratios for all the compositions meet the glass formation criterion (i.e., are ≤ 4.35) as predicted by the model (Figure 4, Table 4). In designing the compositions in this way, not all but only a few of the compositions had a (Na/P) or (Na/Al) ratio that fell within the range for glass formation as predicted by the model (highlighted in yellow, Table 6).

As shown in Table 6, nineteen of the 20 compositions whose (O/Na) molar ratios met the model-predicted condition (< 4.35) for glass formation, formed glass when melted and cooled in air. This is a 95% accuracy of the model using the (O/Na) molar ratio. The one composition shaded yellow (T2) did not form glass.

There are several compositions whose (Na/P) or (Na/Al) molar ratio did not meet the glass formation conditions (i.e., they should crystallize), but their (O/Na) ratio did, e.g., (T2, T3, T4, T5, T9, T11, T19 and T20) for the molar ratio (Na/P) and (T1, T2, T3, T5, T11, T12, T13, T17, T18 and T19) for the molar ratio (Na/Al), see Table 6. According to the model predicted conditions for (Na/P) and (Na/Al), all these compositions should crystallize when melted and cooled. However, with the exception of composition T2, all formed glass in agreement with the glass formation condition predicted by the model for the molar ratio (O/Na). This suggests that among the three molar ratios, the (O/Na) ratio is likely the most important parameter that must be met in designing glass forming compositions in this iron aluminophosphate system.

4. Conclusions

The mathematical models developed and used in the present work were successful in predicting the glass forming region for compositions in the $P_2O_5 - Fe_2O_3 - Al_2O_3 - Na_2O - SO_3$ system. This is considered a noteworthy achievement since this important compositional system includes a nuclear waste similar to the high soda, high sulfate waste at Hanford (AZ102 LAW), which is one of the more challenging and difficult wastes to vitrify due to its high sulfate content. The “model formulated” compositions which formed glass had a waste loading that ranged from 25 to 33 wt% and formed a homogeneous melt when melted for only 3 hrs. at $\sim 1050^\circ C$.

Three compositional parameters were identified as being important to the glass forming ability of the iron phosphate compositions in this 5-component system. These are the molar ratios of (O/Na), (Na/P) and (Na/Al) which were found to accurately predict the region of glass formation with the (O/Na) ratio being the most important. Compositions with the values of (O/Na), (Na/P) or (Na/Al) molar ratio as

≤ 4.35 , ≥ 1.13 , or ≥ 2.56 , respectively, are highly likely ($\sim 96\%$) to form glass when melted and cooled in air.

The high waste loadings attained in the iron phosphate glass compositions predicted by the mathematical models developed herein are relevant to the vitrification of not only AZ102 LAW, but also for other Hanford LAW fractions and similar wastes containing Na_2O and SO_3 .

The chemical durability of the glass waste forms prepared for the model predicted compositions has been measured and used to develop chemical durability-composition models. As is described in a second paper, these models can predict optimized glass compositions that meet the DOE requirements for chemical durability.

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C. S. Ray et. al.: Iron Phosphate Glass Waste Forms for vitrifying Hanford AZ102 Low Activity Waste (LAW), Part I: Glass Formation Model.

Figure Captions

Figure 1. Scatter plot of the 28 target compositions in Table 2. The scatter plot as a function of SO_3 is not included as it can be easily deduced from the other plots shown above.

Figure 2: Vertical cross-section of the refractory crucible wherein glass #1 (Table 2) was melted at 1050°C for 3 h. No corrosion of the crucible by the melt is observed

Figure 3: XRD patterns for the glasses (a) #5 and (b) #25. See Table 2 for the composition of these glasses.

Figure 4. CART analysis showing partitioning of glass formation/crystallization of iron phosphate compositions as a function of the O/Na molar ratio. The Receiver Operating Characteristics (ROC) plot that predicts the overall sensitivity of the model is also shown.

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C. S. Ray et. al.: Iron Phosphate Glass Waste Forms for vitrifying Hanford AZ102 Low Activity Waste (LAW), Part I: Glass Formation Model.

Tables

Table 1: Average chemical composition (wt%) of Hanford AZ102 Low Activity Waste (LAW).

Al ₂ O ₃	B ₂ O ₃	Cl	Cr ₂ O ₃	Cs ₂ O	F	K ₂ O	Na ₂ O	P ₂ O ₅	Re ₂ O ₇	SiO ₂	SO ₃	Total
0.27	0.10	0.14	0.81	0.50	0.60	3.01	77.04	0.22	0.10	0.42	16.79	100.01

Table 2. Iron phosphate waste form compositions developed using a 5-component D-Optimal Mixture Design technique

Glass Number	Target Composition, wt%					Melting Temp. °C	Waste Loading *, wt%	Glass or Crystal
	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	SO ₃			
1	45.0	5.0	18.0	28.0	4.0	1050	32.0	Glass
2	45.0	5.0	18.0	28.0	4.0	1050	32.0	Glass
3	45.0	9.0	13.0	28.0	5.0	1050	33.0	Glass
4	45.0	11.0	18.0	23.0	3.0	1050	26.0	Glass
5	45.0	14.0	10.0	28.0	3.0	1050	31.0	Glass
6	45.0	14.0	10.0	28.0	3.0	1050	31.0	Glass
7	45.0	15.0	18.0	19.0	3.0	1100	22.0	Crystal
8	45.0	15.0	14.0	23.0	3.0	1050	26.0	Glass
9	47.0	15.0	18.0	15.0	5.0	1200	20.0	Crystal
10	47.0	15.0	18.0	15.0	5.0	1200	20.0	Crystal
11	48.0	11.0	12.0	24.0	5.0	1050	29.0	Glass
12	50.0	5.0	14.0	28.0	3.0	1050	31.0	Glass
13	50.0	15.0	10.0	20.0	5.0	1050	25.0	Glass
14	51.0	5.0	18.0	21.0	5.0	1100	26.0	Crystal
15	52.0	5.0	10.0	28.0	5.0	1050	33.0	Glass
16	52.0	5.0	10.0	28.0	5.0	1050	33.0	Glass
17	53.0	15.0	14.0	15.0	3.0	1125	18.0	Crystal
18	54.0	10.0	14.0	18.0	4.0	1100	22.0	Crystal
19	54.0	13.0	13.0	16.0	4.0	1125	20.0	Crystal
20	54.0	7.0	12.0	23.0	4.0	1125	27.0	Glass
21	57.0	15.0	10.0	15.0	3.0	1050	18.0	Crystal
22	59.0	4.0	16.0	19.0	2.0	1050	21.0	Crystal
23	59.0	5.0	18.0	15.0	3.0	1150	18.0	Crystal
24	59.0	5.0	18.0	15.0	3.0	1150	18.0	Crystal
25	60.0	5.0	10.0	22.0	3.0	1050	25.0	Glass
26	60.0	5.0	15.0	15.0	5.0	1175	20.0	Crystal
27	60.0	10.0	10.0	15.0	5.0	1050	20.0	Crystal
28	42.0	15.0	16.0	22.0	5.0	1050	27.0	Glass

Color shaded cells indicate duplicate compositions.

*Waste loading includes the sum of the wt% Na₂O and SO₃ since they are the predominant components in the Hanford AZ102 LAW

Table 3. Molar ratios of oxygen to sodium (O/Na), sodium to aluminum (Na/Al), and sodium to phosphorus (Na/P) for the compositions in Table 2. A closely similar composition, MS26, reported previously [19, 20] is also included. The (O/Na) ratio has been arranged in increasing order, while the (Na/Al) and (Na/P) ratios have been arranged in decreasing order from the top to the bottom of the table.

Set A for (O/Na) Molar Ratio			Set B for (Na/Al) molar Ratio			Set C for (Na/P) Molar Ratio		
Glass Number as in Table 2	O/Na (molar)	Glass or Crystal	Glass Number as in Table 2	Na/Al (molar)	Glass or Crystal	Glass Number as in Table 2	Na/P (molar)	Glass or Crystal
5, 6	3.00	Glass	5, 6	4.61	Glass	5, 6	1.43	Glass
3	3.06	Glass	15,16	4.61	Glass	3	1.43	Glass
1, 2	3.11	Glass	25	3.62	Glass	1, 2	1.43	Glass
12	3.13	Glass	3	3.41	Glass	12	1.28	Glass
15, 16	3.16	Glass	12	3.29	Glass	MS26	1.26	Glass
MS26	3.50	Glass	13	3.29	Glass	15, 16	1.23	Glass
11	3.66	Glass	11	3.28	Glass	4	1.20	Glass
4	3.70	Glass	20	3.17	Glass	28	1.20	Glass
8	3.72	Glass	8	2.70	Glass	8	1.17	Glass
20	3.89	Glass	MS26	2.61	Glass	11	1.13	Glass
28	3.91	Glass	1, 2	2.56	Glass	20	0.96	Glass
25	4.18	Glass	21	2.47	Crystal	7	0.97	Crystal
14	4.35	Crystal	27	2.47	Crystal	14	0.94	Crystal
13	4.41	Glass	28	2.15	Glass	13	0.92	Glass
7	4.59	Crystal	4	2.15	Glass	25	0.84	Glass
22	4.76	Crystal	22	2.05	Crystal	18	0.77	Crystal
18	5.03	Crystal	18	2.10	Crystal	22	0.76	Crystal
19	5.57	Crystal	19	1.99	Crystal	9, 10	0.73	Crystal
9, 10	5.96	Crystal	14	1.92	Crystal	19	0.69	Crystal
17	6.02	Crystal	17	1.76	Crystal	17	0.65	Crystal
21	6.07	Crystal	7	1.74	Crystal	21	0.60	Crystal
27	6.25	Crystal	26	1.65	Crystal	23, 24	0.58	Crystal
23, 24	6.31	Crystal	9, 10	1.37	Crystal	27	0.57	Crystal
26	6.36	Crystal	23, 24	1.37	Crystal	26	0.57	Crystal

Table 4. Model parameters for glass formation/non-glass formation analysis (Figures 4 to 6) of iron phosphate compositions using molar ratio of (O/Na), (Na/P) or (Na/Al).

Molar ratio	Limit for glass formation with probability (in parenthesis)	Limit for crystallization with probability (in parenthesis)	R squared	AICC	Area under the glass/crystal formation ROC curves
O/Na	≤ 4.35 (0.9647)	≥ 6.02 (0.9287)	0.781	42.44	0.9339
Na/P	≥ 1.13 (0.9618)	≤ 0.77 (0.9438)	0.743	47.70	0.9346
Na/Al	≥ 2.56 (0.9647)	≤ 1.92 (0.9376)	0.793	40.59	0.9398

Table 5. Results of CART analysis using less number of samples selected randomly using Bernoulli random variables from the original larger number (24) of samples.

Set Number	Selected Glass Samples (Glass numbers as in Table 2)	O/Na Molar Ratio for Glass Formation		Na/Al Molar Ratio for Glass Formation		Na/P Molar Ratio for Glass Formation	
		Split Criteria	Model R ²	Split Criteria	Model R ²	Split Criteria	Model R ²
1	2, 4, 5, 6, 8, 9, 10, 13, 14, 16, 18, 21, 26	<4.35	0.628	≥ 2.56	0.628	≥ 1.17	0.628
2	1, 3, 5, 7, 10, 12, 14, 17, 19, 23, 25	<4.35	0.874	≥ 2.56	0.874	>0.97	0.268
3	1, 3, 5, 6, 7, 8, 9, 12, 14, 17, 21, 23, 24, 26, 27	<4.35	0.910	≥ 2.56	0.910	≥ 1.17	0.910
4	1, 5, 6, 7, 9, 10, 12, 14, 15, 16, 17, 21, 24, 26	<4.35	0.906	≥ 2.56	0.906	≥ 1.23	0.906
5	2, 3, 5, 6, 7, 14, 16, 18, 19, 23, 25, 27	<4.35	0.893	≥ 2.56	0.893	≥ 1.23	0.597
6	1, 4, 8, 9, 13, 15, 16, 17, 21, 23, 25, 26	<5.98	0.900	≥ 2.56	0.628	≥ 0.84	0.900
7	3, 6, 7, 8, 13, 14, 15, 18, 21, 23, 24, 27,	<4.59	0.615	≥ 2.7	0.891	≥ 0.92	0.439
8	2, 3, 4, 8, 9, 14, 15, 16, 17, 21, 24, 25, 26, 27	<4.35	0.907	≥ 2.56	0.638	≥ 0.84	0.638
9	1, 2, 3, 6, 13, 14, 15, 17, 21, 23, 25, 27	<4.35	0.615	≥ 2.56	0.891	≥ 1.23	0.439
10	1, 4, 7, 9, 11, 12, 13, 14, 17, 21, 23, 26, 27	<4.59	0.639	≥ 2.15	0.474	≥ 0.92	0.474

Criteria highlighted in green yielded perfect separation of glass forming and non-forming compositions in the sample data set used to obtain the model.

Table 6. Iron phosphate compositions (wt%) designed for testing the relative importance of the molar ratios of (O/Na), (Na/P), and (Na/Al) on glass formation. “T” in serial number stands for test samples.

Serial #	Nominal Composition, wt%					O/Na molar ratio	Na/P molar ratio	Na/Al molar ratio	Waste Loading, wt%
	P ₂ O ₅	Fe ₂ O ₃	Al ₂ O ₃	Na ₂ O	SO ₃				
T1	41.90	14.98	15.72	22.00	5.41	3.91	1.20	2.30	27.41
T2	53.36	4.59	18.15	21.21	2.69	4.30	0.91	1.92	23.90
T3	43.79	10.49	19.73	20.58	5.42	4.30	1.08	1.72	26.00
T4	49.12	16.34	8.98	20.36	5.21	4.30	0.95	3.73	25.57
T5	47.98	12.56	15.29	20.50	3.67	4.30	0.98	2.21	24.17
T6	42.82	17.26	9.65	27.52	2.75	3.00	1.47	4.69	30.27
T7	44.20	4.97	16.36	28.65	5.82	3.04	1.48	2.88	34.47
T8	45.00	13.54	9.13	27.49	4.84	3.08	1.40	4.95	32.33
T9	49.51	14.98	9.99	22.87	2.64	3.78	1.06	3.76	25.51
T10	42.30	16.97	11.95	23.36	5.41	3.63	1.26	3.22	28.77
T11	44.54	16.40	16.40	20.05	2.62	4.30	1.03	2.01	22.67
T12	44.17	11.71	19.05	22.37	2.71	3.88	1.16	1.93	25.08
T13	45.61	6.38	20.33	24.88	2.79	3.53	1.25	2.01	27.67
T14	47.13	7.60	13.77	28.66	2.84	3.00	1.39	3.42	31.50
T15	43.47	14.60	13.18	26.00	2.75	3.24	1.37	3.24	28.75
T16	49.31	9.20	13.60	25.05	2.84	3.49	1.16	3.03	27.89
T17	42.04	12.56	16.78	24.82	3.80	3.44	1.35	2.43	28.62
T18	47.82	4.81	17.62	25.41	4.34	3.49	1.22	2.37	29.75
T19	48.53	4.72	18.95	22.27	5.52	4.07	1.05	1.93	28.09
T20	47.43	10.32	13.78	23.01	5.45	3.83	1.11	2.75	28.46