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VITRIFICATION OF MIXED WASTE
FROM URANIUM PROCESSING OPERATIONS

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ABSTRACT

Three silos at the Fernald Environmental Management Project (FEMP) in Fernald, Ohio, contain residues from the processing of pitchblende ores. Silos 1 and 2, designated as K-65, contain the depleted ore, while Silo 3 contains calcined residue from processing solutions. Silos 1 and 2 also contain a bentonite clay cap that was added to the silos to reduce the radon emanation from the waste.

Previously, the initial vitrification testing, conducted as a treatability study for the Remedial Investigation/Feasibility Study (RI/FS) being performed at the FEMP, demonstrated the feasibility of vitrifying the silo residues. Various combinations of the waste materials were successfully vitrified at 1350°C with waste loadings ranging from 66 percent to 89 percent. Measured volume reductions ranged from 50 to 68 percent. All of the glasses tested "non-hazardous" by the Toxicity Characteristic Leachate Procedure (TCLP), and Product Consistency Test (PCT) testing showed the durability of the glasses to be equal to or better than typical high-level waste glasses. The radon emanation rate from the glass has been measured at less than 0.1 $pCi/m^2/s$, more than two orders of magnitude below the EPA limit of 20 $pCi/m^2/s$ and about the same level as natural, "non-radioactive" building materials such as brick or concrete. This level represents a reduction in the emanation rate of more than 500,000 times from the non-vitrified residue. Although the initial treatability testing demonstrated the applicability of vitrification to these wastes, some areas requiring further work were identified.

One of the issues concerned the use of a small amount of carbon to reduce the sulfates present in the K-65 residue. In some instances, the carbon addition resulted in over-reduction of the melt and the formation of a reduced metal phase in the bottom of the crucible. Another issue was the presence of microscopic crystals in the Silo 3 glass. Because of the success of the initial work, further development work was authorized by the client to address the identified issues. The initial formulations were modified, and all of the issues were successfully resolved. For example, a different approach to the sulfate issue resulted in a formulation that did not require the use of a reductant. Consequently, the formation of a reduced metal phase by over-reduction was no longer a problem. This work demonstrates the applicability of vitrification to not only a typical siliceous material like the K-65 residue, but also to the Silo 3 residue which is high in sulfates and phosphates and low in silica.

BACKGROUND

Three silos at the Fernald Environmental Management Project (FEMP) in Fernald, Ohio, contain residues from the processing of pitchblende ores. Silos 1 and 2, designated as K-65, contain the depleted ore, while Silo 3 contains calcined residue from processing solutions. Silos 1 and 2 also contain a bentonite clay cap that was added to the silos to reduce the radon emanation from the waste. The K-65 residue is a siliceous material containing uranium and thorium with high levels of radium and lead, while the Silo 3 residue is lower in silica and consists largely of metal oxides and salts (sulfate, phosphate, nitrate, carbonate) containing uranium and thorium. The K-65 residue tests hazardous for lead by the Toxicity Characteristic Leachate Procedure (TCLP), while the Silo 3 residue tests hazardous for arsenic, cadmium, chromium, and selenium. Due to the high radium concentration of the K-65 residue, radon emanation from the waste is also a significant concern.

Previously, the initial vitrification testing, conducted as a treatability study for the Remedial Investigation/Feasibility Study (RI/FS) being performed at the FEMP, demonstrated the feasibility of vitrifying the silo residues (1,2). Various combinations of the waste materials were successfully vitrified at 1350°C with waste loadings ranging from 66 percent to 89 percent. Measured volume reductions ranged from 50 to 68 percent, and all of the glasses tested "non-hazardous" by the TCLP. Product Consistency Test (PCT) results showed the durability of the glasses to be equal to or better than typical high-level waste glasses and more than an order of magnitude better than the Defense Waste Processing Facility-EA glass, which is commonly viewed as the lower limit of acceptable durability for high-level waste glasses. The radon emanation rate from the glass has been measured at less than 0.1 $pCi/m^2/s$, more than two orders of magnitude below the EPA limit of 20 $pCi/m^2/s$ for radon emanation from uranium mill tailings and about the same level as natural, "non-radioactive" building materials such as brick or concrete. This level represents a reduction in the emanation rate of more than 500,000 times from the non-vitrified residue. Although the initial treatability testing demonstrated the applicability of vitrification to these wastes, some areas requiring further work were identified. These are as follows:

1) Small amounts of carbon added to the K-65 melts were found to prevent the formation of a conductive sulfate scum; however, in some instances, the addition of carbon resulted in over-reduction of the melt and

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the formation of a reduced metal phase in the bottom of the crucible. Additionally, the amount of carbon which successfully eliminated the salt layer in small crucible melts was not always successful in larger crucible melts. Careful control of the sulfate layer with the addition of carbon might be possible; however, a better solution would be to develop glass formulations that do not require such control to prevent sulfate separation.

2) The vitrified product from the Silo 3 residue, although durable and homogeneous on a macroscopic scale, had microscopic crystals. Behavior of the melt during viscosity measurements indicated crystallization was occurring at melt temperatures. A formulation that resulted in a more vitreous product with greater resistance to crystallization was needed.
3) Melts which included the bentonite clay material were too viscous due to the increased alumina content. Formulations needed to be developed that ensured either a reasonable viscosity was maintained over a range of K-65/bentonite mixtures, or determined the amount of additives necessary to keep the viscosity in the correct range.
4) Although the leach testing showed the glasses to be durable and non-hazardous, potential improvements in durability of the K-65 glasses were desired to further reduce the leaching of radionuclides from the waste. Additionally, the Silo 3 glass showed a degree of selective leaching of some of the elements in the waste. Changes in the formulations to address these issues of durability needed to be investigated.

Because of the success of the initial treatability work, further development work at PNL was authorized to first address the above issues by modifying the initial treatability study formulations, and then to develop the glass formulations for application in pilot-scale vitrification testing. Numerous melts were carried out using both simulants and the actual residue. The use of simulants for this work was necessitated by the shortage of actual residue available. Some additional reasons for using simulants are the much greater ease of working with non-radioactive materials, and the ability to obtain substantially more data through the use of simulant melts because of the additional cost and time requirements of radioactive work. The simulant compositions were qualitatively validated by repeating the treatability study formulations with simulants rather than the real residue. The melts with simulants were observed to be comparable to the melts previously performed with the actual waste material. Later, scanning electron microscopy (SEM) testing of melts using both simulants and actual wastes found the melts to be similar on a microstructural basis. The following sections discuss glass development in general, the approach for the initial treatability work, and the successful resolution of all of the above issues.

GENERAL APPROACH TO GLASS DEVELOPMENT

When developing a glass formulation for a given waste stream, the usual objective is to obtain a single-phase glass that is stable and vitreous and has high durability, high waste loading, and high robustness (i.e., a low sensitivity to compositional variations). Often specific performance criteria for the waste must be met (such as testing non-hazardous by the TCLP). When dealing with wastes, robust formulations are important because they allow for variability in the waste without impacting the process or waste form, and they do not require extensive analysis and formulation as the waste changes. To ensure that the continuous processing of the actual waste can be implemented, a compromise between the objectives of high waste loading and high robustness is often required.

Another compromise that is often required is a balance between a detailed, scientific characterization of the glass and a practical, objective oriented engineering approach. With the application of vitrification to many wastes other than high-level wastes, care must be taken to avoid over characterization of the glass, or in other words, obtaining large amounts of data (at great expense) which are of little or no benefit to meeting the treatment objectives. Sufficient data must be obtained to ensure that the glass formulation will be processable and will meet the performance criteria; nevertheless, one of the great benefits of vitrification is that it can be very robust and can be applied to many wastes without the time and expense of detailed characterization of the waste or the waste form. This practical approach is a simple and effective way to develop glass formulations for many waste streams.

The first step in developing a glass formulation is to determine the composition of the waste and asses the potential variability in the waste stream. After the composition of the waste is determined, potential limiting components (phosphate, chromium, or other compounds with limited solubility in glass) are identified. A search of the available literature and databases including the International Glass Database (INTERGLAD), the PNL glass database, and standard literature sources is conducted. The goal of the search is to identify reported glass compositions which allow high waste loadings of the identified limiting constituents. Then drawing on the decades of experience of waste glass development at PNL and using principles of glass chemistry, potential glass formulations for the waste are determined.

Depending on the availability of the waste material, test melts are performed with simulants and/or the actual material. The initial formulations are modified as needed to reach a durable, stable, vitreous waste form. Emphasis on the glass formulation typically must be for robustness. Developing a formulation to tenths of a percent of various oxides does not make sense from either a full-scale processing standpoint or when the variability of the waste is of the order of several to tens of a percent. The variability of the waste must be considered throughout this process and a determination made as to whether a single formulation is sufficient or if the formulation must be changed based upon analysis of the waste. Some materials are easily vitrified with few or no additives. Other materials may present special problems because of the composition of the waste or its variability. The Fernald silo residues presented some unique challenges as discussed below.

DEVELOPMENT AND USE OF SURROGATES

The surrogates were made from pure chemicals to match the oxide content of the wastes, the sulfate content, and when possible the other anions such as nitrate and carbonate. They included all elements over 0.7 wt% in the waste. Experience has shown this approach to adequately represent the general properties of the glass (viscosity, conductivity, etc.). Among the minor constituents, none were identified in concentrations thought to be sufficient to significantly impact the glass form ing ability of the melt. Surrogate testing was begun after t treatability tests were completed, so melts were made using the treatability formulations and the simulant material. These surrogate glasses were visually compared to the previous melts with the actual residue, followed by a qualitative viscosity comparison. The melts with the simulant were observed to be comparable to the previous melts with the actual residue. After the improved formulations were developed, melts of these formulations were carried out with both simulant and actual waste residue. The melts with the actual residue were visually similar in all respects to the simulant melts. Samples of these melts were analyzed by SEM and the only difference observed between the simulant and actual melts was the presence of a few, very small (100 - 300 nm) noble metal inclusions in the melts with the actual waste. Consequently, the surrogate materials were judged to adequately represent the waste.

CHALLENGES FACED IN THE INITIAL TESTS

Sulfate and Phosphate in the Waste

The sulfate concentration in the K-65 residue is approximately 3 wt%, while the Silo 3 residue contains about 18 wt% sulfate. Only a fraction of this sulfate (typically less than 1 wt%) can be incorporated into the glass, while the rest tends to form a separate phase which floats on top of the dense glass phase (3,4). This sulfate layer is conductive, corrosive to refractories, and, if allowed to accumulate, could interfere with processing the wastes in the melter. Additionally, if the sulfate layer is discharged from the melter as a secondary phase, it would result in a poor-quality waste form.

During the screening tests, a sulfate layer was observed on the K-65 formulations melted at 1150°C. The temperature was raised to 1350°C in an effort to decompose the sulfate. As a consequence, the sulfate layer was reduced to isolated patches. The addition of small amounts of carbon to reduce the sulfate layer was found to eliminate the salt layer completely. However, when the same formulations were melted in larger batches, the carbon was found to reduce much of the lead present in the waste.

The sulfate in the Silo 3 residue was present in much higher concentrations and was expected to pose much more serious difficulties. Initial formulations included carbon in sufficient amount to reduce the sulfate. When a formulation was identified which gave a vitreous product, the melt was repeated without the carbon addition to verify the effect of the carbon. Surprisingly, there was no change in the melt. Many other melts have been performed since, and it has been found that particular formulations for the Silo 3 residue promote the decomposition of the sulfate and prevent the formation of a salt layer, even at temperatures as low as 1200°C. The cause of this effect is still being investigated.

Another unique challenge for vitrification presented by the Silo 3 residue was the high phosphate content of the waste. The Silo 3 residue contains about 16 wt% phosphate on a oxide basis, while the solubility of phosphate in silicate glasses is typically very small, in the range of 1 or 2 wt%. Higher amounts than this may be soluble at higher temperatures, but on cooling, lead to heterogeneous crystallization and the formation of opacity in the glass. A search of the literature indicated that the introduction of large amounts of alumina along with the high phosphate can suppress the tendency for opacity to occur and promote the solubility of phosphate in silicate melts (3). This effect has been explained to be a result of the formation of an alumino-phosphate structure that fits within the silicate network. Therefore, the approach to developing a glass formulation for the Silo 3 residue included the addition of significant amounts of alumina.

Challenge of Maximizing Waste Loading with a Low-Silica Waste

Achieving high waste loadings with a waste that is low in silica presents a challenge. Typical silicate glasses contain high percentages of silica and other glass formers such as boron. Consequently, the waste loadings for low-silica wastes in these typical silicate glasses are in the range of 20% to 30%. This is the approach used in the high-level waste programs and is essentially one of diluting the waste into a borosilicate glass. Another option, which may be available in some instances, is to blend the low-silica waste with a high-silica waste, thereby achieving a high waste loading. Alternatively, durable glasses may possibly be formulated in composition ranges outside those typical of silicate glasses.

In addition to the high sulfate and phosphate in the Silo 3 residue, another challenge was presented by the low silica content of the waste. The Silo 3 residue is about 15 wt% silica on an oxide basis. In order to achieve high waste loadings, low-silica glass formulations were sought. A search of the literature identified several potential glass compositions which were modified to more closely match the composition of the waste. Several melts were performed using a surrogate for the actual radioactive waste, and a formulation which yielded a homogeneous, vitreous product was identified. This was confirmed with melts using the actual residue; however, when this formulation was cooled more slowly in a different furnace, the glass devitried. Further development in the treatability study showed that the durability of the devitrified waste form was adequate; however, viscosity measurements on the glass indicated that crystals were forming in the glass at typical processing temperatures. This issue was later addressed in further development work and its resolution is discussed in the next section.

RESOLUTION OF ISSUES ARISING FROM INITIAL TESTS

Issue: Formation of Reduced Metal Phase/Molten Sulfate Layer

One approach to dealing with the sulfate problem is to dilute the waste to a point that the sulfate would be soluble in the melt; however, this is contrary to the objective of a high waste loading. Previous screening melts indicated that some formulations with very high sulfate did not form a sulfate layer, even without the addition of a reductant. So, another approach was to develop a formulation that eliminated the need to add a reductant. Information presented by Volf (4) indicates that a higher calcium content tends to suppress the separation of a molten sodium sulfate phase. Since the initial K-65 melts included only soda as an additive and were low in calcium, a number of melts using the non-radioactive simulant were carried out which substituted CaO for Na_2O in the formulation.

The melts showed evidence of a salt layer on the surface when the additive was mainly soda. As the amount of calcia was increased and soda decreased (while maintaining constant waste loading), the salt on the surface decreased and then disappeared. No evidence of sulfate was observed on the surface of the glass when the ratio of CaO to Na_2O was approximately 1:1 or greater. Also, without the addition of the carbon reductant, the reduction of metals observed in the previous tests will not occur.

The formation of a salt layer in a blend of the K-65 and Silo 3 residues was more significant due to the higher sulfate concentration in the blended waste stream. The substitution of calcium for soda was not effective in preventing the separation of a salt phase, so it was determined to pursue a formulation more like that for the Silo 3 glass alone where here was not a problem with the sulfate. When the K-65/Silo 3 blend was vitrified with a formulation similar to that of Silo 3, no salt layer formed on the melt.

The behavior of sulfates was further investigated by perorming melts as a function of time and by performing cold-op crucible melts. Samples were melted at 1350°C for times anging from one to thirty minutes. No separate salt phase was observed in the K-65 residue at any time during the melting process, indicating that a sulfate layer does not form and then olatilize during the two hour duration of the typical crucible melt. Rather, the sulfate appears to be soluble in the melt or eadily decomposed. For the Silo 3 residue, sulfate was observed on the melt surface up to about fifteen minutes, after which it was not present. The foaming observed in the Silo 3 melts is thought to result from the sulfate decomposition.

Cold-top crucible melts were performed by heating the ower portion of a crucible to the melting temperature while insulating the remainder of the walls and keeping the top urface open to ambient conditions. Material was regularly dded to the crucible, simulating for a short time actual processing conditions in the cold-cap of a continuous melter. Melts were performed with both K-65 and Silo 3 simulants sing both dry and slurry feed. As expected, some sulfate was present at the interface of the cold-cap and the molten glass; owever, for both the K-65 and Silo 3 simulants, the amount f sulfate on the glass surface was a small fraction of the total which had been added. This provides evidence that even the igh amounts of sulfate in the Silo 3 residue will be decomposed and driven off from the melter during continuous proessing. The accumulation of molten salts does not appear to be a problem with these formulations.

ssue: Crystalline Silo 3 Formulation

Using the general approach to glass development described earlier, a further search of the database for approprite compositions was performed. Several new formulations were identified. By performing several melts and modifying he formulation based upon observed results, a suitable glass was developed with somewhat decreased waste loading comared to the treatability study glass. This new glass formulaon remained vitreous, even with the relatively slow ool-down rate of the furnace. The durability of this formulaon was found to be equal to or better than typical high-level waste glasses. The amount of alumina was varied in these melts. Melts with 10 wt% alumina or less were typically paque, but when the amount of alumina was increased to 15 wt% to 20 wt%, glasses free from opacity were formed. A ample of the new glass formulation made from the actual waste residue was analyzed by SEM and found to be homogeeous, and leaching of the glass found no selective leaching to indicate a phase separation had occurred. Therefore, it apears that amounts of phosphate significantly in excess of that ypically soluble in silicate glasses may be successfully incororated by including high amounts of alumina in the glass ormulations.

Issue: Decrease the Viscosity of K-65 Glasses Blended with Bentonite

The initial treatability study restricted our tests on the bentonite/K-65 mixture to a 50:50 blend. A preliminary review had indicated that this would be the maximum expected ratio. For simplicity in processing, it was desirable to develop a single formulation that would be suitable for the entire range of waste compositions expected (pure K-65 to a 50:50 mixture of K-65/bentonite). A number of melts were carried out and it was determined that the amount of flux necessary to give a proper viscosity for a 50:50 mixture with bentonite resulted in a glass with greatly reduced durability for the pure K-65 residue.

The next approach was to develop a simple relationship for the amount of additives based upon the amount of bentonite in the waste mixture. The main effect of bentonite on the waste composition is to increase the alumina content, so based upon the results of the previous tests, a simple formula was developed relating the necessary additives to the wt% alumina in the final glass. This formula was tested and found to be applicable to the bentonite/K-65 mixture. Vitreous melts with processable viscosities were obtained for waste ranging from pure K-65 to pure bentonite. This sliding-scale formulation will be easy to apply in the batch slurry feed tanks planned for the vitrification plant.

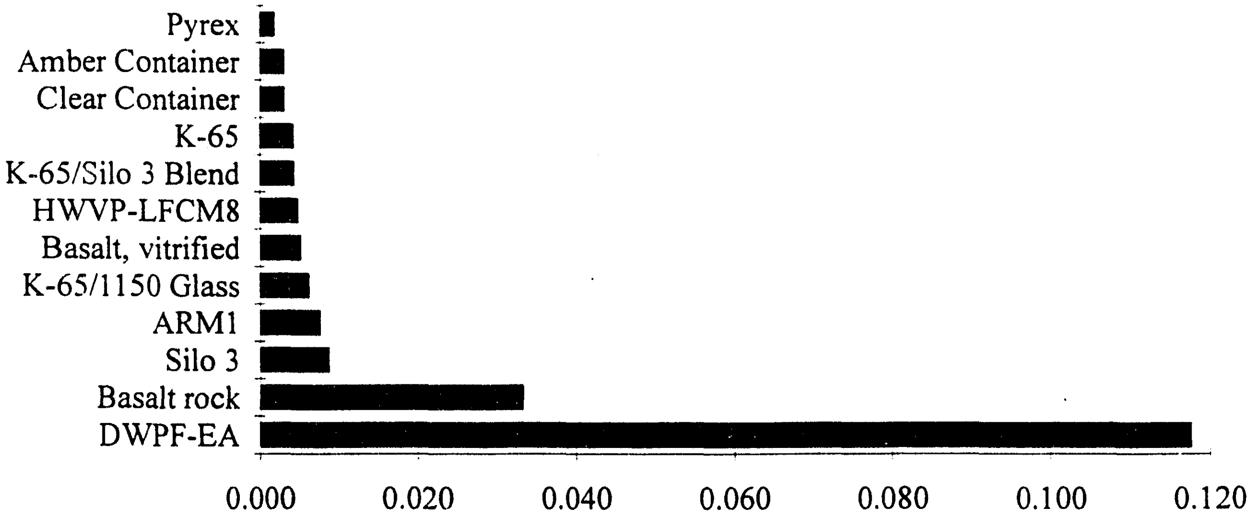
Issue: Increase the Durability of K-65 Glasses

Because of the high lead and radium concentrations present in the waste and the very stringent on-site disposal criteria, the client requested further investigation to explore the practical limits of increased durability. The first approach was the addition of TiO_2 and/or ZrO_2 in amounts up to 5 wt%. These elements are known to improve the resistance of glasses to acid leaching. Test results indicated that additions of these compounds at levels up to 5 wt% could improve the durability by up to a factor of two. Substituting titania for calcia or soda has the advantage of affecting the viscosity to only a small extent, while zirconia significantly increases the viscosity.

A number of other formulations were investigated which were made to match compositions reported to be resistant to acids and acid hydrolysis. In none of these instances was the resulting glass found to be significantly increased in durability. Lowering the waste loading and/or blending with site soil (simulant) typically decreased the leachate concentrations due to the lower concentration of waste in the glass, but the actual durability of the glass was usually not improved. Substitution of titania for soda in these soil-blended formulations was found to have a similar effect to that previously described.

The conclusion derived from all these tests is that the original glass formulations were very durable and that it is not practical to greatly increase their durability. Titania was shown to have a significant effect (reduced leachate concentrations to half of previous values), but much less than the order of magnitude decrease desired by the client.

To demonstrate this point, the TCLP fractional release of the Fernald waste glasses are compared to a number of waste glasses and other common materials in Fig. 1. The fractional release is a measure of the fraction of an element which is leached from the sample; for silica reported here it is a measure of the glass dissolution rate. The data show the Fernald glasses to be slightly less durable than Pyrex and typical container glasses, and more durable than other waste and natural glasses under the conditions of the test. The data



Fractional Release % for Si

Fig. 1. TCLP leaching of Fernald glasses compared to other glasses.

also indicate that even Pyrex glass could not meet the desired release criteria for the Fernald wastes if loaded with the lead and radium that the waste glasses contained.

Comment: Glass Formulations for 1350°C versus 1150°C

Processing at temperatures above 1300°C is a standard practice in the glass industry. Because the expected radiation doses from the waste will allow contact maintenance of the equipment, standard furnaces with consumable electrodes and higher operating temperatures (greater than 1150°C) can be used. Higher temperature glasses offer many advantages over lower temperature glasses. These advantages include higher waste loadings, reduced quantities of additives, lower total volume of glass, higher durability, and higher processing rates. For the K-65 and Silo 3 residues, the higher temperature glasses offer the additional advantages of minimizing problems with the sulfate by removing it from the melter and producing a waste form that does not leach sulfur.

For the Fernald residues, the higher temperature (1350°C) glasses resulted in a 10% reduction in the total glass volume compared to the lower temperature (1150°C) glass. Based on the TCLP leachate concentration of heavy metals, the durability was observed to be about three times higher for the 1350°C glass formulations. Additionally, glass formulations melted at 1150°C formed a significant sulfate layer on the surface of the glass, while melts carried out at 1350°C did not show such behavior. Finally, the sulfur is selectively leached out of the 1150°C glasses, but not out of the 1350°C glasses.

Pilot-Plant Testing and Future Work

This paper has focused on the initial phase of glass development work: crucible melt tests. Proper use of these tests results in the generation of a large database of information at very little expense. Once a glass formulation is sufficiently developed in crucible melts (i.e., proper viscosity and electrical conductivity, adequate durability, phase stability), pilot-scale tests should be performed in a continuous melter before moving on to full-scale waste processing. The behavior of waste materials continuously fed into a glass furnace can differ from that observed in crucible melts, and the pilot-scale tests may indicate a need for additional modifications to the glass formulation. These changes may be simple enough to investigate in the pilot-scale tests or may require further investigation at the crucible level before returning to the pilot plant. Pilot-scale testing, therefore, provides both a final refinement of the glass formulations and the design and operating data for the full-scale system.

CONCLUSIONS

Without wading through the data, the work described in this paper presents a successful application of a practical, engineering oriented approach to developing glass formulations. The Fernald wastes presented significant challenges, all of which were successfully addressed. The robust formulations developed are suitable for pilot-scale vitrification testing. The success is attributed to use of the right approach, knowledge of glass chemistry principles, extensive experience with vitrification of numerous wastes, and the wide applicability of vitrification technology in general.

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