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EVALUATION OF THE TiO_2 LIMIT FOR DWPF GLASS

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Executive Summary

The titanium dioxide (TiO_2) solubility limit for Defense Waste Processing Facility (DWPF) glass is evaluated in this report. Based on the analyses of existing data, the solubility limit can be raised from 1 wt% to 2 wt%, and the existing liquidus temperature (T_L) model currently in use in the DWPF Product Composition and Control System (PCCS) should be used for process control.

The T_L model has only been validated over a TiO_2 concentration range of 0-2 wt%. The substitution of the T_L model for an absolute solubility limit is based on the fact that not all of the literature glasses surveyed for this study with TiO_2 levels <2 wt% satisfy the currently implemented T_L constraint. Since the impact of the TiO_2 content of a glass on the T_L is not linear (e.g., there are interactive effects from other components such as Cr_2O_3, Fe_2O_3 and MnO), the use of the T_L model up to a TiO_2 solubility limit of 2 wt% is the only validated approach that can be used for processing in the DWPF.

This work has been prepared to address technical issues discussed in Technical Task Request SP-TTR-2003-00004 (Lilliston, 2003) and in accordance with the Task Technical and Quality Assurance Plan (Lorier, 2003).

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Acronyms

CBU	Closure Business Unit
CCC	canister-centerline cooling
CST	Crystalline Silicotitanate
DWPF	Defense Waste Processing Facility
HLW	high-level waste
MAR	Measurement Acceptable Region
MST	Monosodiumtitanate
PAR	Property Acceptable Region
PCCS	Product Composition Control System
PCT	Product Consistency Test
SB2	Sludge Batch 2
SB3	Sludge Batch 3
SRS	Savannah River Site
SRTC	Savannah River Technology Center
T_L	liquidus temperature
TTR	technical task request
TTT	time-temperature-transformation
WL	waste loading

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1.0 Introduction

Approximately 130M L of sludge / supernate high-level radioactive waste (HLW) is currently stored in underground carbon steel tanks at the Savannah River Site (SRS) in Aiken, South Carolina. The Defense Waste Processing Facility (DWPF) began immobilizing the sludge fraction of the waste in borosilicate glass in 1996. Currently, the radioactive glass is being produced as a "sludge-only" composition by combining washed high-level sludge with glass frit and melting. The molten glass is poured into stainless steel canisters that will eventually be disposed of in a permanent geological repository.

The vitrification process is controlled using model-based algorithms and other compositional constraints (e.g., single component solubility limits) to assure processability of the sludge/frit blend through the melter as well as the durability of the final product. The DWPF process control system (the Product Composition Control System (PCCS)) imposes several constraints on the composition of the contents of the Slurry Mix Evaporator (SME) to define acceptability. The primary constraints relate process or product properties to composition via predictive models. In addition, single component constraints (e.g., TiO_2, NaCl, and Na_2SO_4) are also used to assure processability and/or product quality. Samples of the sludge/frit blend are taken from the SME, the compositions are determined, and properties are predicted from the measured compositions and are verified to a high confidence level to be within an acceptable processing window. A batch is deemed acceptable (or processable) if its composition measurements lead to acceptable property predictions after accounting for modeling, measurement, and transfer uncertainties. The baseline document guiding the use of these data and models is Revision 4 of "SME Acceptability Determination for DWPF Process Control" by Brown, Postles, and Edwards (2002). If a given feed is acceptable in terms of the property predictions, then it is transferred to the melter, converted to molten glass, and poured into canisters.

As previously mentioned, one of the single component constrains in PCCS is associated with TiO_2. The current solubility limit for TiO_2 in glass is restricted to 1 wt% (Bickford, 1990). This limit was based on studies performed by Plodinec (1979, 1980) on DWPF-type glasses in which the effect of TiO_2 on the crystalline content of glass at 1000°C was analyzed. It was stated that >1 wt% TiO_2 in the glass provided the potential to crystallize ~2 volume% ferrite if the melter temperature fell below the DWPF liquidus temperature constraint of 1050°C. This 2% ferrite precipitation in the presence of TiO_2 was deemed an acceptable risk and the 1 wt% TiO_2 limit for the DWPF was set upon that basis. A more detailed discussion on the technical basis for this limit is provided in Section 2.0.

Plodinec (1979, 1980) also indicated that the TiO_2 content of DWPF-type glasses was also shown to impact the amount of devitrification anticipated to occur in a DWPF canister, as TiO_2 is a known nucleating agent in glass (Volf, 1984). The research performed by Plodinec indicated that 5 wt% TiO_2 in a DWPF glass could form as much as 50 vol% devitrification in a canister. This amount of devitrification may lead to an unacceptable durability (e.g., exceeding the glass durability limit set by the Environmental Assessment (EA) glass) when glasses undergo canister centerline cooling (CCC). A crystallized glass can exhibit an unacceptable durability based on the fact that as a new phase precipitates in a previously homogeneous glass, it affects the glass matrix, in which it is embedded, both chemically and mechanically. These changes may impact the rate of glass dissolution in water and thus change its chemical durability (Jantzen and Bickford 1985; Cicero et al. 1993; Kim et al. 1995). Though it is recognized that durability was only a secondary concern in the establishment of the 1 wt% TiO_2 limit, it is initially assessed with available data (Edwards et al., 1999) in Section 3.0.

Other studies such as the study by Langowski (1994) set a TiO_2 limit at <4 wt% with the recognition that the solubility is highly dependent upon the overall glass composition. The glass compositions used to evaluate TiO_2 solubility by the Langowski (1994) study are listed in Table 1. As shown, the TiO_2 concentration in these glasses ranged from 1.0 to 10.0 wt%.

Table 1. Glass Compositions Evaluated in Langowski (1994) for the Effects of TiO_2.

Component	HEWC[a] Glass Composition (wt%)	SRL-21 (base composition) (wt%)	SRL-131 (base composition) (wt%)
SiO_2	38.75	52.5	57.9
TiO_2	1.55	10.0	1.0
B_2O_3	21.7	10.0	14.7
Na_2O	8.64	18.5	17.7
Li_2O	3.10	4.0	5.7
CaO	3.88	5.0	---
Al_2O_3	20.68	---	---
MgO	---	---	2.0
La_2O_3	---	---	0.5
ZrO_2	---	---	0.5
SO_3	0.9	---	---
Others	0.8	---	---

[a] Highly Enriched Waste Concentrate (HEWC).

Langowski (1994) indicated that the TiO_2 solubility was highly influenced by the Al_2O_3 concentration in glass (i.e., if Al_2O_3 was not present, the TiO_2 limit increased). In addition, the TiO_2 solubility increases in silica glasses as the amount of alkali and alkaline earth metals are increased – K_2O is particularly effective. However, Zn, Mg, Al, and B decrease the solubility of Ti in silicate glasses – microcrystallinity forms as these components increase (Langowski, 1994; Volf, 1984). Liquidus temperature measurements indicated that TiO_2 may also increase T_L by acting as a nucleating agent. The Langowski (1994) and Volf (1984) studies also caution about the behavior of titania during melting – due to its density of 4.26, Ti-rich spinels may separate during melting and settle to the bottom of the melter. Based on the analyses of the solubility tests, the interactions of TiO_2 with Al_2O_3, and T_L measurements performed by Langowski (1994), it was determined that levels of TiO_2 greater than 4 wt% in glass (for the compositions listed in Table 1) may hinder waste processing. Results presented by Langowski (1994) indicate that higher TiO_2 levels in glass can be achieved that exceed the 1 wt% limit as currently defined in PCCS.

The Closure Business Unit (CBU) of the Westinghouse Savannah River Company (WSRC) has indicated that it is desirable to obtain a TiO_2 loading in glass of at least 2 wt% if possible (Lilliston, 2003). The recent development of a new liquidus temperature (T_L) model (Brown et al., 2001) and work performed by Edwards et al. (1999) on glasses containing Crystalline Silicotitanate (CST) and Monosodiumtitanate (MST), provided new data that indicated the TiO_2 limit in DWPF glasses should be reevaluated.

2.0 Basis for Original DWPF TiO_2 Limit

The objective of this task is to review the recently generated data and the new T_L model to evaluate if the TiO_2 solubility limit in DWPF glass may be revised. As stated earlier, the current solubility limit of TiO_2 in glass is restricted to 1 wt% or less. This limit was based on experiments that demonstrated that 1 wt% TiO_2 in the glass provided the potential to crystallize ~2 volume% ferrite if the melter temperature fell below the DWPF T_L constraint of 1050°C – a concern which has been recently addressed via implementation of the new T_L model.

In 1979, Plodinec tested a range of TiO_2 concentrations from 0 to 10 wt% in the frit to evaluate the effect of TiO_2 on melting. The tested frit compositions are listed in Table 2. Frit 211 was derived from Frit 21 by simply eliminating TiO_2 and renormalizing.

Table 2. Frit Composition, wt% (Plodinec, 1979)

	Frit 21	Frit 211	Frit 131
SiO_2	52.5	58.3	57.9
B_2O_3	10.0	11.1	14.7
Na_2O	18.5	20.6	17.7
Li_2O	4.0	4.4	5.7
CaO	5.0	5.6	---
MgO	---	---	2.0
TiO_2	10.0	---	1.0
ZrO_2	---	---	0.5
La_2O_3	---	---	0.5

The influence of TiO_2 was found to greatly impact the T_L, viscosity, crystalline content (after heat treatment at 1000°C), and melt rate (see Figure 1, Table 3 and Table 4). Figure 1 summarizes the relative volume percent crystallization as a function of TiO_2 concentration in glass. At 1 wt% TiO_2, 2 volume% crystallization (ferrite) was observed which was ultimately used to establish the current DWPF limit.

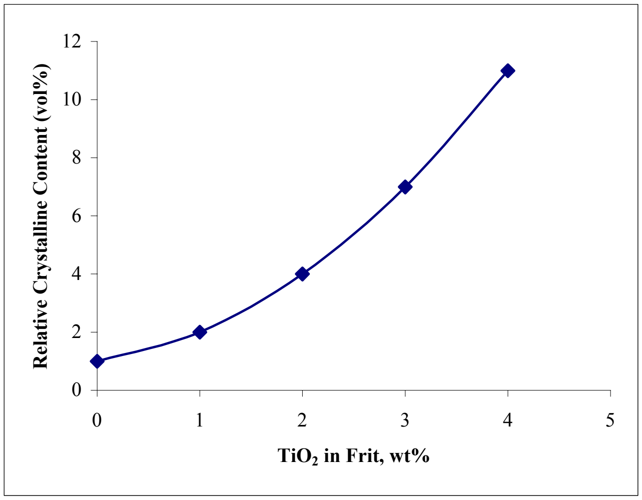

Figure 1. Effect of TiO_2 on the Crystalline Content at 1000°C (Plodinec, 1979)

In addition, the studies by Plodinec (1979, 1980) assessed the impact of TiO_2 on viscosity, melt rate, and devitrification potential of the glass within the canister. With respect to viscosity, Plodinec (1979, 1980) found a significant increase in viscosity with increasing TiO_2 content. Melt rate declined in the presence of TiO_2, as Frit 211 dissolved simulated waste more than twice as fast as Frit 21. The TiO_2 content of a glass was also found to impact the amount of devitrification that could occur in a DWPF canister (Plodinec, 1979, 1980), as TiO_2 is a known nucleating agent in glass (Volf, 1984). Table 2 indicates that 5 wt% TiO_2 in a DWPF glass could form as much as 50 vol% devitrification in a canister. This amount of devitrification may lead to a glass that exceeds the glass durability limit set by the Environmental Assessment (EA) glass when glasses undergoing canister centerline cooling (CCC) are tested.

Moreover, the presence of large amounts of crystalline material can cause glass melts to become non-Newtonian (Plodinec, 1979). Glasses which crystallize become non-Newtonian when the amount of crystalline material exceeds ~3 vol%. If two glasses have essentially the same glassy phase and devitrify to the same crystalline phase, the temperature at which the melts first display non-Newtonian behavior indicates the devitrification rate. The higher this temperature, the greater is the tendency of the glass to devitrify. In Plodinec (1979), melt viscosities were measured as a function of temperature and shear rate. Table 3 lists the temperature at which the measured viscosity began to depend on the rate of shear, i.e. where significant non-Newtonian behavior was first observed. The final entry in Table 4 is melt rate, which was assessed in a small-scale continuous joule-heated melter (Plodinec, 1980).

Table 3. Effect of TiO_2 on Devitrification During Cooling (Plodinec, 1979)

TiO_2 content in frit (wt%)	0	5	10
Temperature to get to 5% crystals (°C)	930	1000	1030
Devitrification after cooling (vol%)	10	50	90

Table 4. Comparison of Frits 21 and 211 (Plodinec, 1980)

Property	Frit 21 (w/ TiO_2)	Frit 211 (w/o TiO_2)
Tendency to devitrify	High	Moderate
Viscosity (poise)	22	13
Waste solubility at 1150°C (max. waste loading)	25	30
Melt rate (g/min)	4.1	9.8

3.0 Basis for New DWPF TiO_2 Limit

3.1 CST Glass Study

The main set of data evaluated in this study was on a variability study for glasses containing CST, MST, and either simulated Purex or HM sludge (Edwards et al., 1999). A total of 25 glasses (22 containing Purex sludge and 3 containing HM sludge) were fabricated and tested in the Edwards study. The glasses were tested for durability using the 7-day Product Consistency Test (PCT) (both quenched and CCC) and characterized by measuring the viscosity at 1150°C and by assessing the T_L in increments of 50°C using isothermal heat treatments. The introduction of CST and MST in this study resulted in a range of TiO_2 in the glasses from ~2 to 5 wt%.

A series of glasses were also fabricated that contained either 22, 26, or 30 wt% oxide Purex sludge, 3, 6, or 9 wt% CST, and 1.25 or 2.5 wt% MST (Edwards et al., 1999). The three glasses fabricated with the HM material were of the same sludge loadings plus 6 wt% CST and 1.25 wt% MST.

The following discussion addresses the impact of higher TiO2 levels on (1) devitrification potential within the canister and subsequent impacts on durability, and (2) the devitrification potential within the melter and subsequent impacts to processability. As previously stated, the current limit was solely defined base on issues associated with melter processability. Although the impact devitrification in the canister and its potential impact on durability is addressed, it is considered a secondary issue.

In the Edwards et al. (1999) study, it was found that all of the glasses (both quenched and CCC) were very durable, as shown in Figure 2. Figure 2 shows how the glasses of the Edwards et al. (1999) study are far more durable than the EA glass based on the normalized release (g/L) for boron. Quenched glasses are represented by the green data points, and the red data points represent CCC glasses. These data indicate that DWPF-type glasses with TiO_2 levels of up to 5.5 wt% can be produced that do not compromise product quality even after an extremely slow cooling cycle. Again, these results address the secondary issues or concerns identified by Plodinec (1979, 1980) associated with the potential negative impacts of devitrification on durability.

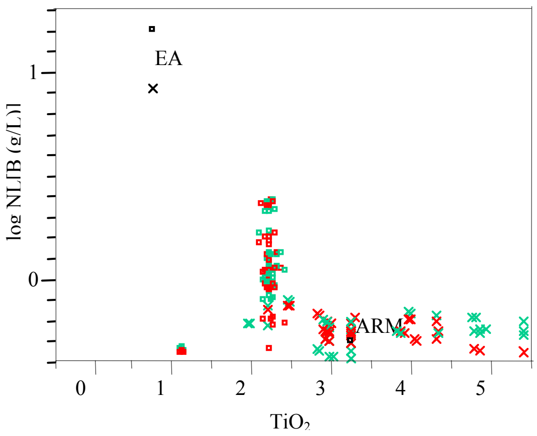

Figure 2. Normalized Release for Boron (g/L) Versus TiO_2 Loading

As previously stated, the primary concern regarding glasses containing high TiO_2 concentrations is the risk of "bulk crystallization" within the melter. From a processing viewpoint, all 25 glasses had a T_L less than 1000°C (Edwards et al., 1999), indicating that DWPF-type glasses can be produced containing up to 5.5 wt% TiO_2 with T_L's less than 1050°C (the current limit in DWPF). It should also be noted that at the time of the Edwards et al. (1999) study, a gradient furnace was not available to measure the T_L on the glasses (per standard ASTM procedure). A decision was therefore made to perform 24-hour isothermal holds at 900°C, 950°C, 1000°C, and 1050°C to assess T_L. X-ray diffraction (XRD) was selected to detect the presence of crystal formation in the glasses after the isothermal hold. The estimated detection limit of the XRD unit under the run conditions was approximately 1 volume%. For this type of measurement, the absence of a crystalline phase by XRD was evidence that the T_L was less than 1050°C. The assessments of T_L for the 25 study glasses are given in Table 5.

Table 5. Liquidus Temperature (°C) Assessment for CST Glasses (Edwards et al., 1999)

Glass ID	Estimated T_L	Glass ID	Estimated T_L
cst01	<900°C	cst12	<900°C
cst02	<900°C	cst12c	<1000°C
cst03	<900°C	cst13	<1000°C
cst04	<900°C	cst14	<900°C
cst05	<900°C	cst15	<950°C
cst06	<900°C	cst16	<950°C
cst07	<950°C	cst17	<950°C
cst08	<900°C	cst17c	<950°C
cst09	<900°C	cst18	<1000°C
cst10	<950°C	cst18c	<1000°C
cst11	<900°C	cst20	<900°C
cst11c	<1000°C	cst26	<900°C
		cst32	<900°C

3.2 Liquidus Temperature Analysis

The impact of TiO_2 on T_L was evaluated on the recently developed T_L model (Brown et al., 2001). The data upon which the new T_L model was developed included T_L measurements via two methods: a proposed ASTM isothermal method and the ASTM gradient furnace method. Table 6 provides the pertinent mass oxide component ranges and thus describes the region of applicability of the model (as noted by Brown et al., 2001). With respect to TiO_2, the model applicability only spans a range of 0 to 1.8549 wt%. As such, use of the new model to predict T_L's of glasses with TiO_2 concentrations up to ~2 wt% is acceptable because this model is semi-empirical in nature. Use of the model beyond 2 wt% TiO_2 is not advisable until additional data or assessments of existing data can be performed to validate the model for higher TiO_2 ranges.

Table 6. T_L Data Composition Ranges in Weight Percent (Glass Basis) (Brown et al., 2001)

	Al_2O_3	B_2O_3	CaO	Cr_2O_3	FeO	Fe_2O_3	$(\Sigma Fe)_2O_3$	K_2O	Li_2O
Maximum	14.162	12.652	2.007	0.3008	6.901	16.977	17.60	3.8846	6.1576
Minimum	0.99	4.893	0.3053	0	0.0161	3.427	3.452	0	2.4901

	MgO	MnO	Na_2O	NiO	SiO_2	TiO_2	U_3O_8	ZrO_2	Total
Maximum	2.6502	3.25	14.901	3.045	58.230	1.8549	5.1378	0.97	94.5479
Minimum	0.470	0.7392	5.989	0.0379	41.795	0	0	0	81.5746

The T_L was calculated using the Brown et al. (2001) model for the compositions of the glasses tested in the Plodinec (1979, 1980) study (represented by the solid circles in Figure 3) and Edwards et al. (1999) study (represented by the red x's and o's in Figure 3). Calculations were performed to assess the model's ability to predict T_L's of glasses containing up to 5.5 wt% TiO_2 (recognizing that the use of the T_L model to predict at concentrations above ~2 wt% TiO_2 is essentially an extrapolation beyond the limits of the current model which may not be warranted). The results of the predicted T_L versus TiO_2 loading are shown in Figure 3.

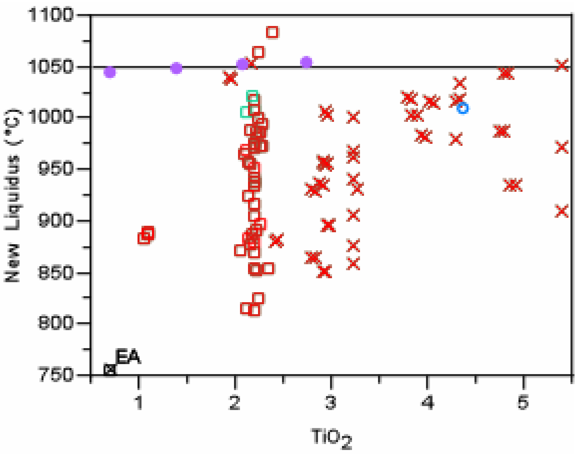

Figure 3. Plot of Calculated T_L Versus TiO_2 Loading

A horizontal line is shown for reference in Figure 3 that represents the DWPF T_L limit of 1050°C, a limit that does not account for prediction or measurement uncertainties. In general, the majority of the glasses have predicted T_L's less than the 1050°C limit – this includes glasses containing up to 5.5 wt% TiO_2 supporting the experimental T_L assessments by Edwards et al. (1999) as previously discussed. Glasses as high as 5.5 wt% TiO_2 have predicted T_L's less than 950°C. Some of the glasses from the Plodinec (1979, 1980) study on which the current TiO_2 limit was based, had a predicted T_L slightly less than 1050°C and some had a predicted T_L of just over 1050°C (see Table 7) which was driven primarily by the Cr_2O_3 concentrations of these glasses (~0.27 wt% Cr_2O_3).

Table 7. Relation of TiO_2 Content to DWPF Processing.

TiO_2 wt% in Plodinec (1979, 1980) glasses	Predicted T_L (°C)	Predicted PAR T_L (°C)	Predicted MAR T_L (°C)	Pass PCCS criteria of T_L < MAR T_L?
0	1040.4	1036.3	1019.2	NO
0.7	1044.9	1036.4	1019.8	NO
1.4	1049.4	1036.4	1020.3	NO
2.1	1053.2	1036.3	1020.6	NO
2.8	1054.8	1036.1	1020.8	NO

Though all of the Plodinec (1979, 1980) glasses failed the T_L criteria at the MAR of ~1020°C and the PAR of ~1036°C (see Table 7), most of glasses shown in Figure 3 had T_L's well below the limits. Not using the MAR T_L limit is not conservative for DWPF processing, and not using the MAR could result in bulk crystallization within the melter.

However, it should be cautioned that use of the T_L model to predict the T_L of glasses with greater than 2 wt% TiO_2 is questionable since there were only six high-TiO_2 validation points in the T_L validation database (some at 2.49 wt% and some at 4.99 wt% TiO_2). Of the six high TiO_2 validation data points, four were not well predicted by the new T_L model. Several of these high TiO_2 glasses contained no Al_2O_3 or B_2O_3 – out of the DWPF composition range. However, with only two of the six high-TiO_2 validation points being predicted by the T_L model, an extrapolation beyond the limits of the current model is not warranted or substantiated. Thus, if the TiO_2 content of the glass is less than or equal to 2.0 wt%, then the T_L model may be used for process control. Because the T_L model is a mechanistic model, it is not a large extrapolation from 1.85 wt% TiO_2 to 2.0 wt%. If the TiO_2 content of the glass is within the range of 0-2 wt% but the T_L constraint is violated, then the material may not be processed. If the T_L constraint is satisfied and the TiO_2 content of the glass is within the range of 0-2 wt%, then the melter feed may be processed (given all other SME acceptability criteria are satisfied).

4.0 Recommendations

The original TiO_2 limit of <1 wt% in glass set for the DWPF was based on data generated by Plodinec (1979, 1980) to avoid spinel crystallization in the DWPF melter at 1050°C. However, HLW pretreatment strategies have indicated a need to reassess this limit. Based on the evaluations discussed in this report, the following recommendations are made:

- Raise the TiO_2 concentration limit in glass from 1 wt% to 2 wt% (the upper limit of the current T_L model database) AND use the PCCS liquidus temperature model for process control.

- Continue to use the MAR T_L limit. Failure to do so greatly increases the risk of "bulk" crystallization occurring within the DWPF melter.

- Evaluate the effects of higher TiO_2 contents on T_L. This may be performed via several methods. First, reevaluate the current T_L model and develop using a larger range of TiO_2 content (develop new model data). Second, generate new validation data by fabricating glasses with higher amounts of TiO_2 (outside the current composition region limit), determine the T_L, and compare to what is predicted.

- It was found that increased TiO_2 levels may have a detrimental effect on melt rate, (Plodinec, 1979, 1980), and thus waste throughput. If TiO_2 levels higher than 1 wt% are desired, tests utilizing the current SRTC melt rate equipment should be performed with sludge batch simulants at the desired waste loadings (and TiO_2 levels). That is, although raising the TiO_2 limit to 2 wt% and using the T_L model to demonstrate acceptability via PCCS, there is no model assessment of melt rate in PCCS. Therefore, assessment of melt rate should be performed to ensure that what appears attractive on paper does not result in a difficult feed to process.

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