International Conference on Environmental Remediation and Radioactive Waste Management
ICEM2023
International Conference Centre Stuttgart,
October 3-6, 2023, Stuttgart, Germany

ICEM2023-111101

TAILORING NUCLEAR WASTE GLASS PROPERTIES FOR JOULE HEATED CERAMIC MELTER TECHNIQUE WITH BOTTOM DRAIN GLASS POURING

Martin Weiser
Kraftanlagen Heidelberg (KAH)
Heidelberg, Germany

Christian Willberger
Kraftanlagen Heidelberg (KAH)
Heidelberg, Germany

Nicolas Finck
Karlsruhe Institute of Technology (KIT)
Karlsruhe, Germany

Meng Xiangda
China Nuclear Power Engineering (CNPE)
Beijing, China

Qu Xiaorui
China Nuclear Power Engineering (CNPE)
Beijing, China

Zhao Jing
The 404 Company Limited, CNNC (404)
Diwopu, China

Siegfried Weisenburger
Karlsruhe Institute of Technology (KIT)
Karlsruhe, Germany

ABSTRACT

Detailed investigations during the glass formulation development for the future Diwopu plant are described. Three different glass formulations were developed including two base glasses for the different waste streams present at Diwopu site and a corresponding Start Glass that allows commissioning of the LFCM and later switch-over from glass production operation of the melter to idling mode for maintenance. The waste glasses have to possess similar physical properties to be processed within the same LFCM. Therefore, all three developed glasses were tailored to lie within given margins for rheological and electrical resistivity data as well as to allow a high waste glass loading and high chemical durability. Further in-depth research was conducted to clarify the crystallization behavior of the waste glasses as it is known that the crystallization tendency has to be minimized to exclude relevant impacts on the viscosity. Increase of the viscosity due to crystallization might otherwise lead to unfavorable conditions for the bottom drain up to blockage in the worst case.

Keywords: HLLW, vitrification, ceramic melter, crystallization, Rietveld, glass development

1. INTRODUCTION

Development of waste glasses for vitrification of high-level liquid waste (HLLW) by Joule heated liquid-fed ceramic melters (LFCM) requires a number of specific physicochemical and technical issues to be considered. Former projects (PAMELA, VEK, VPC) have shown that the waste glass must be tailor-made not only for the waste composition to be processed but also for details of the applied vitrification technology as for instance LFCM with bottom drain glass pouring technique. For new projects the focus has been directed to a high waste glass loading and particularly to a low waste glass crystallization tendency in addition to the primary waste glass parameters, i.e., chemical durability, and rheological and electrical properties.

A low waste glass crystallization in the glass pouring channel of a LFCM bottom drain glass pouring system is required. It is to assure that the glass viscosity vs. temperature characteristic of the waste glass is maintained for safe and smooth glass pouring and not impacted by glass crystallization. A low crystallization tendency is of particular importance for LFCM with bottom pouring technique because the glass pouring into stainless steel canisters takes place discontinuously every 10 to 25 hours (dependent on the glass production rate) when about a quarter of the glass pool inventory of the melter is poured out. The glass in the pouring channel of the melter is heated to pouring temperatures of about 1000 °C by mean frequency induction and Joule heating.

In times without pouring, the glass in the pouring channel is maintained at temperatures in the range of 600 – 900 °C where the waste glass can be sensitive to crystallization processes. They could increase glass viscosity depending on the waste glass composition and time. Crystallization can impact the start of the glass flow and the glass flow rate. In the worst-case scenario it can cause blockage of the bottom drain. For this purpose, the glass development must consider waste glass compositions which limit the potential formation of crystalline phases under the described temperature conditions of 600 – 900 °C. In the lab scale work, it is necessary to investigate the formation and concentration of crystalline phases in the waste glass under different temperature levels and times.

The determination of the crystalline content in the waste glass was performed by the Quantitative Phase Analysis (QPA) according to the Rietveld method [1, 2]. It required X-ray diffraction measurements of waste glass samples mixed with a crystallographically known oxide added to the powdered sample as internal standard.

The two waste streams to be vitrified by the Diwopu project differ greatly in their chemical composition, in the radioactivity level and in the waste oxide yield.

The first stream designated Pilot Waste (PW) has a high concentration of noble metals partly due to the fines added to the PW. It has also a high radioactivity level and high contents of Na_2O (30.5 wt.%), U_3O_8 (11.9 wt.%), oxides of rare earth metals (12.3 wt.%), but a low total oxide yield of 57.5 g/L. As the oxide yield of the PW is rather low and the specific activity very high, there was no need to maximize the waste glass loading. With the planned and achieved waste oxide loading of 18 wt.% the radiological inventory of the glass canisters can be kept at a moderate level and the processability of the glass melt is also given despite large contents of noble metals that have to be drained with every glass pouring operation.

The second waste stream to be vitrified is the Legacy Waste (LW). Its oxide yield is dominated by Na_2O (36.2 wt.%), Al_2O_3 (25.9 wt.%) and Fe_2O_3 (10.2 wt.%). The total oxide yield is 196.7 g/L. Due to this high value it was of utmost importance to realize a high waste glass loading by suitable glass formation development to allow a good processability within the planned waste glass production line. The focus in this paper is laid on development of the Legacy Waste glass formulation which turned out to be the more challenging one during its development.

2. MATERIALS AND METHODS

Glass samples fabricated in the lab were analyzed by ICP-OES measurements using a 7500 Optima by Perkin Elmer. SEM-EDX analysis was performed using a QUANTA 650 FEG from FEI combined with a Thermo Scientific NORAN System 7 equipped with UltraDryTM silicon drift X-ray detector.

2.1 Viscometry

For the viscosity measurements of the glass, a rotational viscosimeter type VIS 403 (TA Instruments, USA) was used.

A Pt crucible (inner diameter of 19 mm) was filled with a sample volume of 13.8 cm^3 which corresponds approximately to 35 g of glass sample to yield a filling level of 33.5 mm. At the maximum temperature a Pt rotor was lowered into the sample melt while rotating with 30 min^{-1}. The rotor has a diameter of 9 mm and a measuring length of 24.5 mm. The temperature program was as follows:

Heating to 1250 °C at a rate of 10.0 K min^{-1}
Holding at 1250 °C for 15 min
Cooling to the desired lower boundary temperature at a rate of 5.0 K min^{-1}

The viscosity measurements were performed continuously during the cooling segment. The rotational speed of the Pt rotor was adjusted as a function of the corresponding torque. Starting with a rotational speed of 160 min^{-1} at 1200 °C this value was halved each time a torque limiting value of 45 mN m^{-1} was reached with decreasing temperature.

2.2 Specific electrical resistance

The equipment used for the measurement of the specific electrical resistance of waste glass melts was developed by Karlsruhe Institute of Technology (KIT) in the nineties. A scheme is shown on the right side of Figure 1. The measurements are conducted between 600 and 1200 °C in a small measurement cell made of Al_2O_3 having two cavities. One contains the glass melt to be investigated. Inside this cavity two oppositely located Pt-plate electrodes 1 cm × 1 cm with a distance of 1 cm are arranged. The two electrodes are connected to a LCR Bridge (Rhode & Schwarz, Munich, Germany) by which the specific electric resistance of the glass melt is measured at a 1000 Hz voltage frequency. In the second cavity the temperature is measured with a Pt/Pt10Rh thermocouple (Type S). The second cavity serves also for collecting the glass when the glass melt expands at higher temperatures and causes an overflow from the glass-containing cavity.

The device is operated in a tube furnace (Nabertherm, Lilienthal, Germany). The temperature of this furnace is electronically controlled, and different heating/cooling programs can be realized. No calibration of the described device is required.

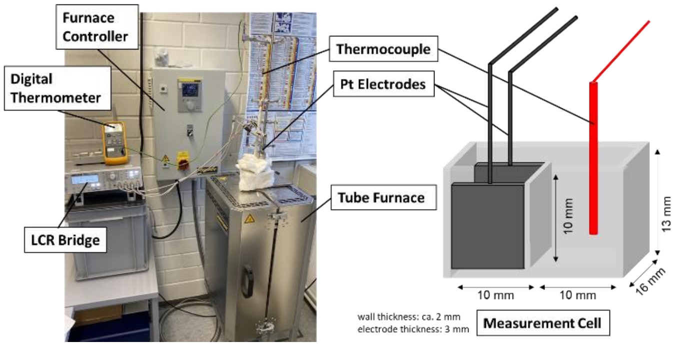


FIGURE 1: PICTURE OF THE MEASUREMENT INSTALLATION OF THE SPECIFIC ELECTRICAL RESISTANCE APPARATUS AND SCHEME OF THE AL_2O_3 MEASUREMENT CELL.

The recordings of the specific electrical resistance by the LCR bridge and of the temperature of the sample by the Temp101A Temperature Data Logger (MadgeTech, USA) were started as soon as the furnace was turned on and heated up to 1250 °C within 2 h. While maintaining this temperature for 1 h the glass sample temperature reached values of 1150 to 1200 °C. When the glass sample temperature became constant with at least 1150 °C (maximum 1200 °C), the temperature program was started, and the furnace cooling rate was controlled at 5 K/min. Specific electrical resistance vs. temperature was recorded continuously during this cooling procedure.

2.3 Chemical durability

The chemical durability was assessed following the ASTM C 1220 standard (MCC-1 test [3]). The sample, typically 16 × 13 × 1 mm^3 in size, is exposed to 90 °C hot deionized water. Only leaching pots made of PTFE are required as well as a well controllable drying cabinet into which the leaching pots are placed for 28 d.

The evaluation of the MCC-1 test results requires the chemical analysis of the glass specimen to determine the elemental fractions f_i and of the element concentration of Si, B, Na, Cs and La in the leachant at the end of the MCC-1 test. The analytical methods used were AAS for Cs and ICP-OES for all other elements.

The Soxhlet test is a dynamic chemical durability test and is operated at 98 – 99 °C. The equipment consists of a glass flask in which approximately 100 ml of deionized water are boiled with a heating mantle. On top of the glass flask with the boiling water, a glass column is mounted which contains in its upper section a reflux condenser. The generated steam from the deionized water in the glass flask is cooled in this section and forms a condensate which flows down into the sample cavity, i.e., into the location of the monolithic glass sample (5 × 5 × 10 mm^3). The liquid with a temperature of 98 – 99 °C leads to corrosion of the glass sample submerged in the liquid. Due to the syphon effect the accumulating condensate exchanges automatically from time to time and realizes the dynamic nature of this test method. The liquid flows down the tube into the glass flask under the pull of gravity and discharges frequently a portion of the accumulating condensate. By means of the initial mass determined before the test, the mass at the end and the initial surface of the specimen, the normalized overall mass loss was calculated for each of the specimen.

2.4 Crystallization

Crystallization conditions

The Legacy Waste Glass with 25 wt.% loading (LWG25) was ground to a homogeneous powder and filled into an Al_2O_3 crucible (approximately 2/3 of the total volume was filled). The crucible was then put into a muffle furnace which was afterwards heated from 25 to 1150 °C in 4 hours. After the final temperature of 1150 °C was reached the glass sample was held at this temperature for 1 h. This is to remelt all crystalline phases possibly present in the sample before the experiments. The temperature of the furnace was then adjusted to the defined crystallization conditions, i.e., 700, 725 or 750 °C. The test duration, i.e., 3, 7, 14 or 28 days, started when the furnace was at the target crystallization temperature. After the test, the Al_2O_3 crucible containing the heat-treated glass sample was put into a pre-heated second furnace and allowed to cool down at 2 K/min to room temperature.

XRD sample preparation

The heat-treated sample was cut with a low-speed saw (Buehler, Esslingen, Germany) in a way to ensure that all zones that have been in contact with either Al_2O_3 or air are excluded. Afterwards, at least 1 g of the sample was powdered. After the addition of 1.5 wt.% ZnO as internal standard, this powder was used for XRD measurements with the aim to determine quantitatively crystalline phases formed in the LWG25 waste glass during heat treatment [4].

XRD measurements

X-ray powder diffractograms were recorded with a D8 Advance (Bruker AXS, Karlsruhe, Germany) equipped with a Cu Kα source operated at 40 kV and 40 mA and a LynxEye XE-T detector. Measurements were performed in continuous scan mode from 5° to 80° 2θ, with a step size of 0.011° per step and counting time of 0.20 second per step. The illuminated sample surface was kept constant by using variable divergence and detector slits.

For the measurements low-background sample holders (high index Si wafer) with a hole (10 mm diameter) at the center were used. Glass powder was mounted on the sample holder and care was taken to minimize preferred orientation X-ray measurement effects during the glass powder preparation.

Evaluation of XRD measurements

The nature of the crystalline phases present in the sample were first identified using the DIFFRAC.EVA software (Bruker AXS, Karlsruhe, Germany). Standard ICDD-PDF (International Centre for Diffraction Data - Powder Diffraction Files) were used to identify the nature of the crystalline material.

Quantitative information was provided by modeling of the experimental powder diffractograms by application of the Rietveld refinement procedure using the DIFFRAC.TOPAS software (Bruker AXS, Karlsruhe, Germany) ([5] and references therein). The Quantitative Phase Analysis (QPA) by the Rietveld method [6] is nowadays a standard technique to determine the concentrations of crystalline phases present in an amorphous material like a multicomponent nuclear waste glass. It is an important precondition of the Rietveld method to find out which crystalline phases are to be modelled for the QPA.

For determination of the concentration of a crystalline phase p in a highly amorphous multicomponent waste glass, a suitable crystalline standard (e.g., ZnO) must be used to quantify each absolute crystalline phase concentration in the amorphous environment of the glass. The crystalline standard to be selected must not be a member of the waste glass constituents (base glass and waste) and must be crystallographically well characterized. It is mixed with a known quantity (e.g., 1.5 wt.% ZnO) as powder to the powdered waste glass sample prior to the XRD measurement (internal standard method). It is treated in the Rietveld procedure as an additional crystalline phase in the waste glass. A crystalline structure model data set is to be used for the standard like those for the crystalline models and taken from a data bank.

Uncertainties for this method are affected by the sample and information is provided by the analysis software. Care was always taken to minimize the R_{wp} value, i.e., the difference between experimental and modeled data.

3. RESULTS AND DISCUSSION

3.1 Glass Formulation

The glass development work for the Legacy Waste had the major objective to obtain a qualified waste glass with a waste oxide loading as high as possible. A high loading contributes significantly to the reduction of the glass production rate of the melter, to the reduction of the total number of glass containers to be produced and disposed of, and to the reduction of the total plant operation time and costs.

During the development work small-scale glass samples (benchmark 100 g) for each investigated glass composition were fabricated for testing major property data (viscosity, specific electrical resistance, chemical durability). By systematic variation of the glass composition – based on the measured data and on general rules of glass science – the development work for the Legacy waste resulted in the base glass composition shown Table 1.

TABLE 1: BASE GLASS COMPOSITION FOR THE LEGACY WASTE.

oxide	wt.%
SiO_2	61.20
B_2O_3	15.60
Na_2O	3.67
Li_2O	2.67
CaO	9.96
BaO	4.50
V_2O_5	1.80
Sb_2O_5	0.60

As shown in the following, the Legacy Waste Glass with 25 wt.% waste oxide loading (LWG25) meets all requirements referred to Joule heating in the melter (specific electrical resistance vs. temperature curve), to glass melting and pouring (viscosity vs. temperature curve) and referred to chemical durability (Soxhlet test and MCC-1 test). The waste glass was also optimized regarding a low crystallization tendency in the glass pouring channel of the melter in the relevant temperature range of 600 – 900°C. This may have been achieved due to the absence of MgO in the base glass to avoid crystallization of diopside (prototype $CaMgSi_2O_6$) as experienced in a former project where the level of Ca and MgO was nearly equal.

The relatively high waste oxide loading is justified for reducing the glass production rate of the plant with all other associated benefits. The target and measured (by ICP-OES) compositions of LWG25 are shown in Table 2.

TABLE 2: TARGET AND MEASURED COMPOSITIONS OF LWG25.

Oxide	Target (wt.%)	Measured (wt.%)
SiO_2	45.90	46.81
B_2O_3	11.70	11.36
Na_2O	11.80	12.05
Li_2O	2.00	2.00
Al_2O_3	6.48	6.38
CaO	7.47	7.32
MgO	0.23	0.22
BaO	3.39	3.30
V_2O_5	1.35	1.38
Sb_2O_5	0.45	0.46
SO_3	0.72	0.41
P_2O_5	1.15	0.98
Fe_2O_3	2.55	2.52
Others	4.81	4.81

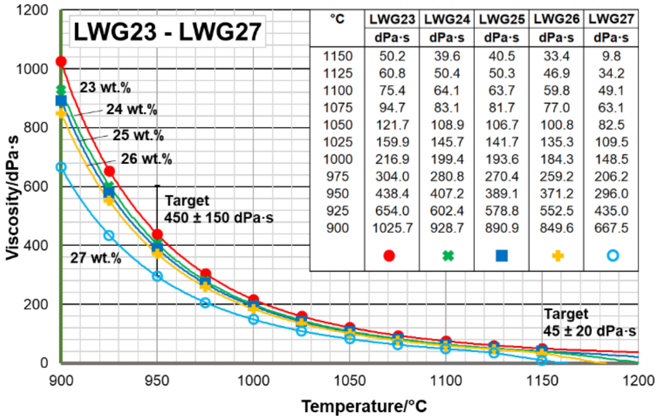
To meet the key operational properties, i.e., viscosity and specific electrical resistance, the waste oxide loading was systematically altered during laboratory investigations. To keep exactly 25 wt.% waste oxide loading is unlikely in an active plant due to impacts like inhomogeneities between or within the HLLW storage tanks, or due to differences of the recycled scrub solution. Scrub solution from offgas components is fed back into the feeding vessel from time to time. Therefore, waste oxide loadings from 23 up to 27 wt.% were screened. The following changes of the most influencing oxides and expected impacts on process parameters (Table 3).

TABLE 3: INVESTIGATED WASTE OXIDE LOADINGS AND EXPECTED IMPACTS ON PROCESS PARAMETERS.

wt.%	Na_2O	Li_2O	SiO_2	impact on viscosity/specific electrical resistance
23	11.15	2.05	47.1	more increasing
24	11.47	2.03	46.5	increasing
25	11.80	2.00	45.9	normal (target)
26	12.12	1.98	45.3	decreasing
27	12.45	1.95	44.7	more decreasing

3.2 Viscometry

While Legacy Waste will be processed, the process control system will be adjusted in such a way that the nominal waste glass loading of 25 wt.% is achieved. In the reality of plant operation, it must be considered that some deviations from the nominal loading may occur, e.g., due to the variation in waste compositions taken over from the storage tanks. It may vary to some extent from batch to batch or due to unintended deviation of the nominal ratio of melter feed to amount of base glass fed into the melter. Therefore, it was investigated what deviations in waste glass loading can be tolerated. Referred to the viscosity vs. temperature of the nominal LWG25 waste glass, the resulting viscosity of underloading of the glass with 23 wt.% and 24 wt.% waste oxides and the overloading of the waste glass with 26 wt.% and 27 wt.% of waste oxides were measured. The results of these investigations are shown in Figure 2.



°C	LWG23 dPa·s	LWG24 dPa·s	LWG25 dPa·s	LWG26 dPa·s	LWG27 dPa·s
1150	50.2	39.6	40.5	33.4	9.8
1125	60.8	50.4	50.3	46.9	34.2
1100	75.4	64.1	63.7	59.8	49.1
1075	94.7	83.1	81.7	77.0	63.1
1050	121.7	108.9	106.7	100.8	82.5
1025	159.9	145.7	141.7	135.3	109.5
1000	216.9	199.4	193.6	184.3	148.5
975	304.0	280.8	270.4	259.2	206.2
950	438.4	407.2	389.1	371.2	296.0
925	654.0	602.4	578.8	552.5	435.0
900	1025.7	928.7	890.9	849.6	667.5
	●	✖	■	✚	○

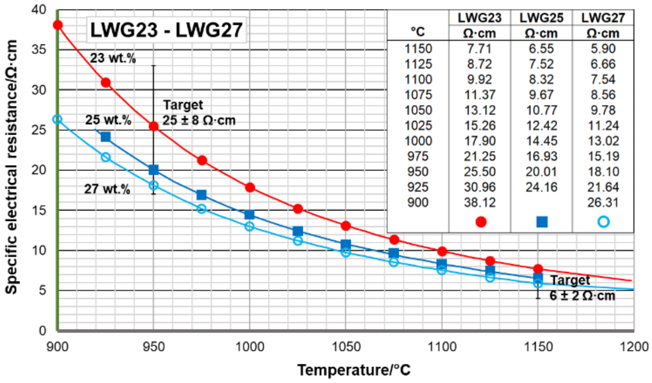
FIGURE 2: VISCOSITY VS. TEMPERATURE OF LWG23 AND LWG24 WITH LOWER LOADING AND LWG26 AND LWG27 WITH HIGHER LOADING COMPARED TO THE NOMINAL LOADING OF 25 WT.%.

The data show that an underloading of the LWG up to 23 wt.% would be tolerable in respect to the resulting viscosity vs. temperature curve. The viscosity increases slightly with the lower loadings but remains well within the processable ranges. In contrast, an overloading up to 27 wt.% would not be tolerable. The viscosity decreases significantly in the high temperature region, especially around 1150 °C. The LWG27 waste glass would adopt at 1150 °C very low viscosity values in the range of 10 dPa s only, whereas the LWG 26 values are still within the required range. Based on these data the tolerable band width of scatter of waste glass loading of the LWG is limited to the range of 25 ± 1 wt.%.

3.3 Specific Electrical Resistance

As waste glass loading deviations can occur due to the reasons mentioned above the tolerable deviation to keep the specific electrical resistance within the processable range was also investigated (which is related to the release of required power in the glass pool). Referred to the specific electrical resistance vs. temperature of the LWG, the data in case of underloaded waste glass with 23 wt.% and in case of overloaded waste glass with 27 wt.% of waste oxides were recorded. The results of these investigations are shown in Figure 3.

The data show, that the specific electrical resistance of the LWG increases when the waste oxide loading is lowered from nominal 25 to 23 wt.%. The data show, additionally, that an underloading would be tolerable with respect to the resulting specific electrical resistance vs. temperature curve. The increase of the specific electrical resistance curve over the entire temperature range remains at 950 °C and 1150 °C well inside the required ranges and could thus be tolerated. A similar situation is valid for the opposite case of overloading the LWG waste glass from nominal 25 to 27 wt.% waste oxides. The data lie also within the specified ranges at 950 °C and 1150 °C. In Figure 3, the specific electrical resistance data curve for the nominal loading of the LWG with 25 wt.% is plotted for comparison.



°C	LWG23 Ω·cm	LWG25 Ω·cm	LWG27 Ω·cm
1150	7.71	6.55	5.90
1125	8.72	7.52	6.66
1100	9.92	8.32	7.54
1075	11.37	9.67	8.56
1050	13.12	10.77	9.78
1025	15.26	12.42	11.24
1000	17.90	14.45	13.02
975	21.25	16.93	15.19
950	25.50	20.01	18.10
925	30.96	24.16	21.64
900	38.12		26.31
	●	■	○

FIGURE 3: SPECIFIC ELECTRICAL RESISTANCE VS. TEMPERATURE OF LWG23 AND LWG27 COMPARED TO NOMINAL WASTE OXIDE LOADING OF LWG25.

3.4 Chemical Durability

The MCC-1 Test as static chemical durability test was performed with LWG25. The data are presented in Table 4. They contain on the right side some specific information concerning the surface of each individual sample (three parallel samples were measured). Then the total mass loss in g after 28 days exposure time is given. Furthermore, the normalized mass loss (referred to the total surface of the sample) in g m^{-2}, the ratio of the sample surface S to the volume V of the leachant being deionized water, the volume of the leachant in ml, the volume of the blank in ml, and finally the pH value of the leachant after the respective exposure time.

On the left side of Table 4, the measured and subsequently calculated data of the five elements under investigation are shown. For each of the elements there is given the measured concentration C_i in the leachant in mg L^{-1}, the measured concentration B_i in the blank in mg L^{-1}, the mass fraction f_i of the element in the respective glass obtained by the glass analysis of the samples prior to leaching. Finally, the normalized elemental mass losses NL_i (after 28 days) in g m^{-2} and the normalized elemental mass loss rate NL_i in g m^{-2} d^{-1} after 28 days exposure time are shown. The latter is required to be ≤ 1 g m^{-2} d^{-1}. Table 4 shows that for all LWG25 samples the normalized elemental mass loss rate was found to be well below 1 g m^{-2} d^{-1}.

TABLE 4: RESULTS OF MCC-1 TEST OF LWG25.

MCC-1 calculations, LWG25 (sample 1, exposure time 28 days)

Elements	**B**	**Na**	**Si**	**Cs**	**La**	**Surface:**	4.766 cm^2
C_i/mg L^{-1}	2.9650	7.3400	16.3100	0.0230	0.0190	**Total mass loss:**	0.0033 g
B_i/mg L^{-1}	0.0000	0.0700	0.0410	0.0080	0.0020	**NL_{total}:**	6.92 g m^{-2}
f_i	0.0364	0.0837	0.2103	0.0003	0.0098	**S/V:**	9.35 m^{-1}
NL_i/g m^{-2}	8.5790	9.1422	8.1464	5.9810	0.1813	**Leachant:**	51.0 mL
NL_i/g m^{-2} d^{-1}	0.3064	0.3265	0.2909	0.2136	0.0065	**Blank:**	54.0 mL
Method	ICP-OES	ICP-OES	ICP-OES	AAS	ICP-OES	**pH:**	9

MCC-1 calculations, LWG25 (sample 2, exposure time 28 days)

Elements	**B**	**Na**	**Si**	**Cs**	**La**	**Surface:**	4.980 cm^2
C_i/mg L^{-1}	3.0750	7.2380	16.6100	0.0260	0.0090	**Total mass loss:**	0.0037 g
B_i/mg L^{-1}	0.0000	0.0700	0.0410	0.0080	0.0020	**NL_{total}:**	6.62 g m^{-2}
f_i	0.0364	0.0837	0.2103	0.0003	0.0098	**S/V:**	9.79 m^{-1}
NL_i/g m^{-2}	7.5689	7.6679	7.0578	6.1357	0.0628	**Leachant:**	51.0 mL
NL_i/g m^{-2} d^{-1}	0.2703	0.2739	0.2521	0.2191	0.0022	**Blank:**	54.0 mL
Method	ICP-OES	ICP-OES	ICP-OES	AAS	ICP-OES	**pH:**	9

MCC-1 calculations, LWG25 (sample 3, exposure time 28 days)

Elements	**B**	**Na**	**Si**	**Cs**	**La**	**Surface:**	5.149 cm^2
C_i/mg L^{-1}	3.4230	7.5090	18.5700	0.0250	0.0050	**Total mass loss:**	0.0035 g
B_i/mg L^{-1}	0.0000	0.0700	0.0410	0.0080	0.0020	**NL_{total}:**	6.80 g m^{-2}
f_i	0.0364	0.0837	0.2103	0.0003	0.0098	**S/V:**	9.90 m^{-1}
NL_i/g m^{-2}	9.3418	8.8253	8.7517	6.4825	0.0295	**Leachant:**	52.0 mL
NL_i/g m^{-2} d^{-1}	0.3336	0.3152	0.3126	0.2315	0.0011	**Blank:**	54.0 mL
Method	ICP-OES	ICP-OES	ICP-OES	AAS	ICP-OES	**pH:**	9-10

Two individual Soxhlet Tests as dynamic chemical durability tests were performed. The data are plotted in Figure 4 and compared with values of the simulated VPC (Vitrification Plant China) waste glass from earlier investigations. The comparison shows that the chemical durability of the final Legacy Waste Glass with 25 wt.% waste oxide loading is in the same range as for the VPC waste glass. Soxhlet data of waste glasses (VPC, VEK, from France, UK) are known to be (after 30 d exposure time) in the mass loss range of around 130 – 170 g m^{-2}. Therefore, maximum 140 g m^{-2} as determined for LWG25 after 30 d exposure time is well within the expected ranges.

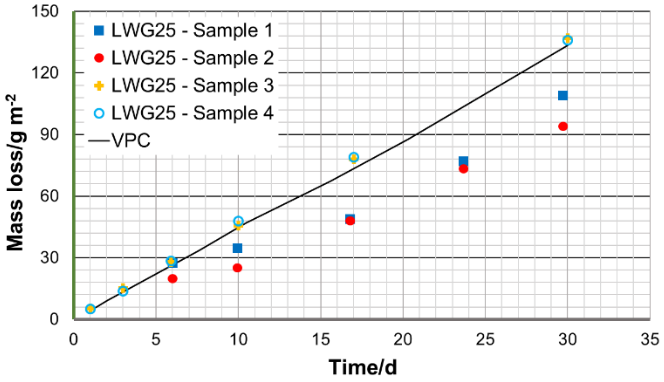


FIGURE 4: RESULTS OF SOXHLET TESTS IN COMPARISON WITH KNOWN RESULTS FROM VPC WASTE GLASS SIMULANT.

3.5 Crystallization

Undesired partial crystallization in nuclear waste glasses can occur in distinct temperature ranges from 600 – 1000 °C. Depending on the extent of such crystallization, key properties of the waste glass for processing and glass pouring from melter like the glass viscosity can be unfavorably changed. Such changes should be limited by limiting the amount of crystalline phases in the waste glass to a low level, usually a few vol.% of the waste glass. During the waste glass development, it was therefore necessary to avoid chemical waste glass compositions which are susceptible to such partial crystallization processes at the relevant temperature range of the waste glass in the bottom drain glass pouring channel.

Usually, crystallization processes do not occur in borosilicate glass melts at operation temperatures of 1150 °C. The liquidus temperature T_L of most crystalline phases formed in nuclear borosilicate waste glasses is typically in the range $\leq$ 1000 °C. Above T_L the crystallized phases in the glass can no longer coexist for thermodynamic reasons in the randomly organized glass structure. One task during the waste glass development for Legacy Waste was therefore to identify and quantify crystalline phases – if any – formed at temperatures of 700, 725, and 750 °C within defined times of 3, 7, 14 and 28 days. Both the weight portion and the volume portion of the potential crystalline phases in the glass had to be determined.

The results reported here were obtained on waste glass samples with thermal history detailed in Table 5.

TABLE 5: THERMAL HISTORY OF INVESTIGATED SAMPLES.

20 °C	thermally untreated
700 °C	3, 7, 14, and 28 days
725 °C	3, 7, 14, and 28 days
750 °C	3, 7, 14, and 28 days

After identification of the crystalline phases, the quantitative phase analysis (QPA) according to the Rietveld method has been used for LWG25 to determine its mass and volume concentration in the waste glass.

Results of crystalline material in thermally untreated LWG25

The lower curve in Figure 5 shows the X-ray diffraction patterns of a thermally untreated LWG25 sample. No diffraction peak can be recognized. Only the amorphous glass network is indicated. The upper curve shows the thermally untreated LWG25 sample with the internal standard of 1.5 wt.% ZnO.

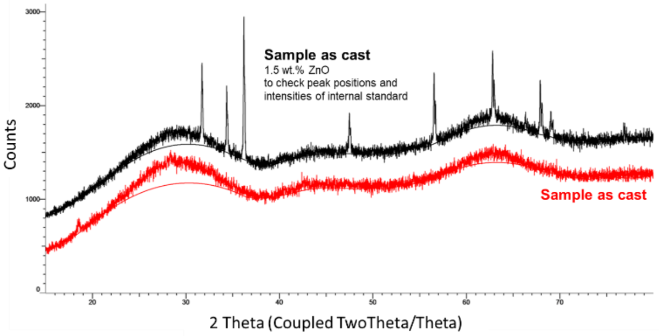


FIGURE 5: X-RAY DIFFRACTOGRAMS OF THERMALLY UNTREATED LWG25 GLASS SAMPLES (SAMPLE AS CAST, AND SAMPLE AS CAST + 1.5 WT.% ZNO).

Results for LWG25 samples heat-treated at 700 °C

Figure 6 shows the XRD results obtained for LWG25 heat-treated at 700 °C for 3 d, 7 d, 14 d, and 28 d. At 700 °C/3 d no peaks are visible for the investigated core sample, except the peaks of cyan color corresponding to internal standard ZnO (1.5 wt.% added to sample). After an isothermal heat treatment time of 700 °C/7 d, additional peaks (purple colored) appeared evidencing the presence of a crystalline phase. Comparison with the database revealed this phase to be hedenbergite (a list of the Miller indices for hedenbergite from the literature [7] was used for identification of the individual peaks from the diffractograms). After 14 d of isothermal heat treatment, peaks of a second phase appeared (magenta colored), identified as calcium phosphate borate. The Rietveld-based QPA with internal standard resulted in a hedenbergite concentration in the LWG25 glass core sample of 4.246 wt.%, corresponding to 3.148 vol.%, in a calcium phosphate borate concentration of 1.579 wt.%, corresponding to 1.380 vol.% and a total crystallinity of 4.528 vol.% after 28 d.

The measured data and the calculated ones are compiled in Table 6 for the 700 °C heat-treated LWG25 samples.

TABLE 6: CONCENTRATION OF CRYSTALLINE PHASES IN THE 700 °C HEAT-TREATED LWG25 SAMPLES.

Crystalline phase	Heat treatment time/d	Concentration wt.%	Concentration vol.%
Hedenbergite	3	0.000	0.000
	7	1.312	0.965
	14	3.268	2.416
	28	4.246	3.148
Calcium phosphate borate	3	0.000	0.000
	7	0.000	0.000
	14	1.352	1.182
	28	1.579	1.380
sum	3	0.000	0.000
	7	1.312	0.965
	14	4.620	3.598
	28	5.825	4.528

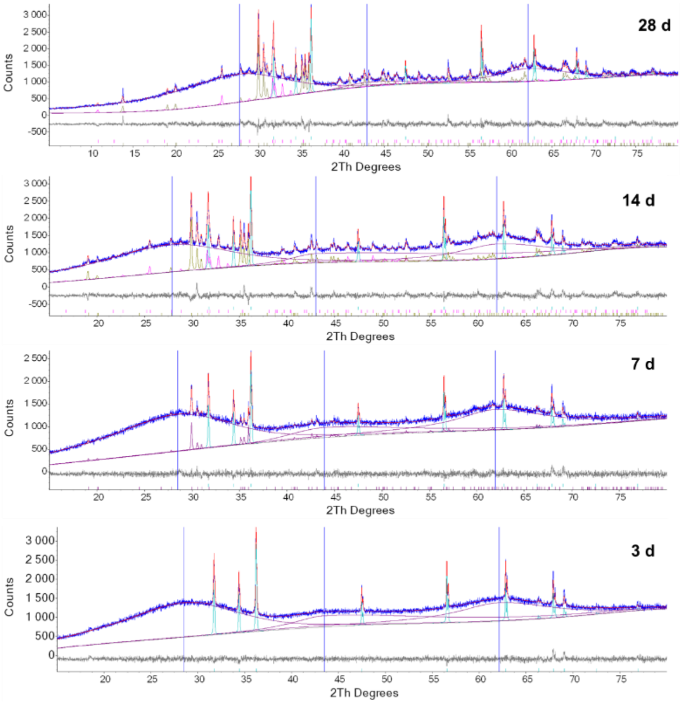


FIGURE 6: XRD OF LWG25 CORE SAMPLES + 1.5 WT.% ZNO AT 700 °C FOR 3 D, 7 D, 14 D AND 28 D. (YELLOW: HEDENBERGITE (PURPLE FOR 7 D), MAGENTA: CALCIUM PHOSPHATE BORATE, CYAN: ZNO)

The conversion of concentration values of hedenbergite in the waste glass in wt.% to values of vol.% was made by the following equation.

$$\text{vol.\%} = \frac{G_1 \cdot R_2}{G_1 \cdot R_2 + G_2 \cdot R_1} \quad (1)$$

with G_1: wt.% of crystalline phase
R_1: density of crystalline phase
R_2: density of waste glass
$G_2 = 100 - G_1$: wt.% of glass phase

Results for LWG25 samples heat-treated at 725 °C

The X-ray diffractograms of LWG25 waste glass isothermally heat treated at 725 °C are shown in Figure 7 for heat treatment times of 3 d, 7 d, 14 d and 28 d. In contrast to the results for LWG25 heat treated at 700 °C, the crystalline phases hedenbergite and calcium phosphate borate are already present after 3 d. Especially the hedenbergite formation can be well-recognized (yellow peaks in the diagrams). Smaller peaks of the calcium phosphate borate phase can also be recognized in Figure 7. The diffractograms of the LWG25 samples between 7 d and 28 d of isothermal heat treatment show no significant increase in the growth of the crystalline phases. The compilation of crystallization data of heat-treated LWG25 core samples at 3 d, 7 d, 14 d and 28 d are shown in Table 7.

TABLE 7: CONCENTRATION OF CRYSTALLINE PHASES IN THE 725 °C HEAT-TREATED LWG25 SAMPLES.

Crystalline phase	Heat treatment time/d	Concentration wt.%	vol.%
Hedenbergite	3	2.596	1.916
	7	4.608	3.420
	14	4.759	3.533
	28	4.269	3.165
Calcium phosphate borate	3	1.034	0.903
	7	1.255	1.097
	14	1.583	1.384
	28	1.477	1.291
sum	3	3.630	2.819
	7	5.863	4.517
	14	6.342	4.917
	28	5.746	4.456

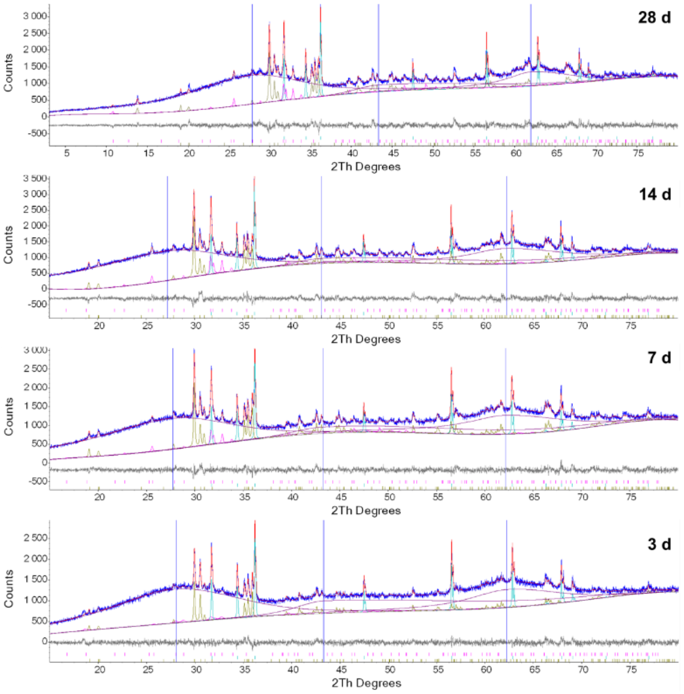


FIGURE 7: XRD OF LWG25 CORE SAMPLES + 1.5 WT.% ZNO AT 725 °C FOR 3 D, 7 D, 14 D AND 28 D. (YELLOW: HEDENBERGITE, MAGENTA: CALCIUM PHOSPHATE BORATE, CYAN: ZNO)

Accordingly, the hedenbergite concentration after 28 d in the sample was 4.269 wt.% (3.165 vol.%), the concentration of the calcium-phosphate-borate 1.477 wt.% (1.291 vol.%) and the total crystallinity is 4.456 vol.%.

Results for LWG25 samples heat-treated at 750 °C

The X-ray diffractograms of LWG25 waste glass samples isothermally heat-treated at 750 °C are shown in Figure 8 for heat treatment times of 3 d, 7 d, 14 d and 28 d. The behavior of crystal growth is rather similar to that observed at 700 °C.

After 3 d of isothermal heat treatment, no peaks are seen in the diffractograms except those of the internal standard ZnO. After 7 d of isothermal heat treatment smaller amounts of hedenbergite are present. After isothermal heat treatment times of 14 d and 28 d both crystalline phases appeared in the diffractograms with clearly recognizable peaks. After 28 d of isothermal heat treatment, the hedenbergite formation resulted in a concentration of 4.867 wt.% (3.614 vol.%) in the LWG25 core sample, the concentration of the crystalline calcium phosphate borate phase resulted to 1.568 wt.% (1.371 vol.%) and the total crystallinity to 4.985 vol.%. The compilation of the crystallization data of heat-treated LWG25 core samples for 3 d, 7 d, 14 d and 28 d at 750 °C both in wt.% and vol.% are shown in Table 8.

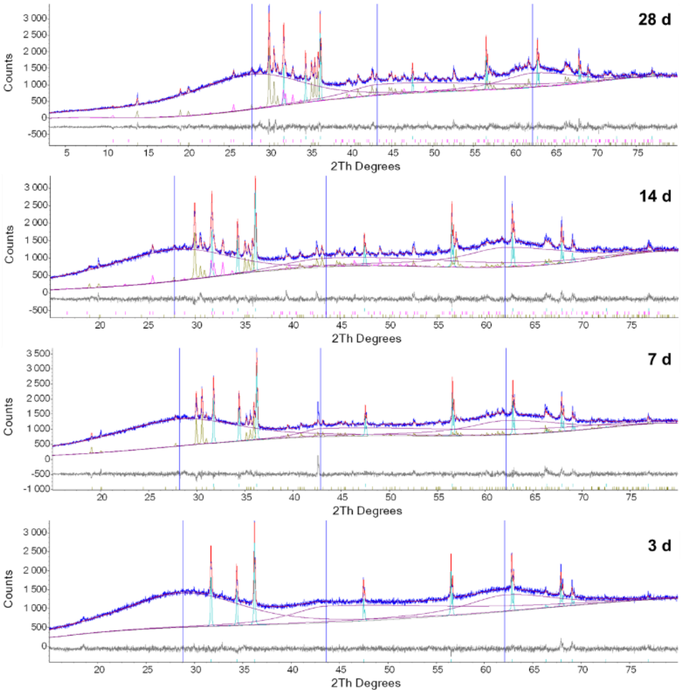


FIGURE 8: XRD OF LWG25 CORE SAMPLES + 1.5 WT.% ZNO AT 750 °C FOR 3 D, 7 D, 14 D AND 28 D. (YELLOW: HEDENBERGITE, MAGENTA: CALCIUM PHOSPHATE BORATE, CYAN: ZNO)

TABLE 8: CONCENTRATION OF CRYSTALLINE PHASES IN THE 750 °C HEAT-TREATED LWG25 SAMPLES.

Crystalline phase	Heat treatment time/d	Concentration wt.%	vol.%
Hedenbergite	3	0.000	0.000
	7	2.013	1.483
	14	2.669	1.970
	28	4.867	3.614

Crystalline phase	Heat treatment time/d	Concentration wt.%	vol.%
Calcium phosphate borate	3	0.000	0.000
	7	0.000	0.000
	14	1.384	1.210
	28	1.568	1.371
sum	3	0.000	0.000
	7	2.013	1.483
	14	4.053	3.180
	28	6.435	4.985

Reliability of the results

The results obtained by the Quantitative Phase Analysis (QPA) using the Rietveld method with internal standard are not easy to evaluate. The calculation procedure is a complex process. Today the Rietveld method is used as a standard technique not only for crystal structure determination from powder or single crystals XRD but also for the opposite purpose (i.e., to use available crystal structure data from data bases as model structures to calculate for the QPA the associated XRD of the crystalline phases present in the sample). One of multiple preconditions for an accurate QPA is that the starting crystalline models are good approaches of the real crystalline phases present in the sample. This is to get realistic minimum approach residuals R of the measured and the calculated XRD of the sample.

In the present investigations of LWG25 waste glass two crystalline phases were identified from measured XRD profiles of isothermally heat treated LWG25 samples. These are hedenbergite (prototype $CaFeSi_2O_6$) and calcium phosphate borate (prototype Ca-Phosphate Apatite $Ca_{10}(PO_4)_6Z_2$). The crystalline model structures used for the Rietveld refinement with QPA for hedenbergite and calcium phosphate borate are given in the following. The reliability of the results gained with the QPA of the Rietveld method is strongly influenced by the good approach of the model crystal structures.

Crystalline hedenbergite model structure

The formula of the crystalline hedenbergite model structure is $Ca(Fe_{0.821}Al_{0.179})(SiAl_{0.822}Fe_{0.178}O_6)$ and crystallographic data have been published by [7] and correspond to the ICSD collection code 62718. The unit cell volume is 443.69376 $Å^3$ and Z = 4. The crystalline density is 3.697 g cm^{-3}, the cell mass is 987.830 g.

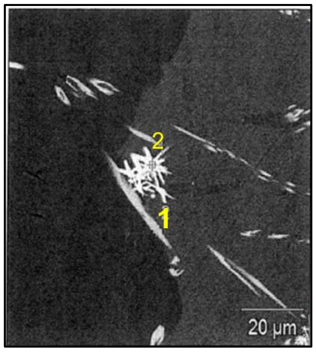
Crystalline calcium phosphate borate model structure

The crystalline calcium phosphate borate model structure data originates from ICSD collection code 68336 [8]. The formula is $Ca_{9.93}(P_{5.84}B_{0.16}O_{24})(B_{0.67}O_{1.76})$, having a unit cell volume of 534.69884 $Å^3$ and Z = 1. The crystalline density is 3.106 g cm^{-3}, the cell mass is 1000.301 g.

ZnO model structure

ZnO serves as internal standard. The crystalline material data originates from ICSD collection code 26170 [9].

The chemical composition of the crystalline phase calcium phosphate borate in LWG25 was determined by SEM-EDX analysis as depicted in Figure 9. Besides the usual composition with Ca cations and phosphate anions additionally small amounts of Na, Al, Si, V and La as foreign constituents were found. The B content cannot be measured by EDX.



Element	wt.%	at.%
B	-*	-*
O	45.9	64.2
Na	2.1	2
Al	1.5	1.2
Si	5.8	4.6
P	10.8	7.8
Ca	28.7	16
V	1.5	0.7
La	2	0.3
* not measurable by EDX		

FIGURE 9: SEM-EDX OF GLASS SAMPLE LWG25. (POINT 1: CALCIUM PHOSPHATE BORATE, SHORT PRISMATIC, POINT 2: OTHER SMALL PARTICLES, CONTAINING MOSTLY CR, NI)

4. CONCLUSION

The waste glass formulation for processing the Diwopu Legacy Waste solution to glass meets all requirements concerning high waste glass loading of 25 wt.%, rheological and electrical properties for use in a Joule heated ceramic melter, and the chemical durability requirements measured by MCC-1 test method. The high waste glass loading contributes significantly to the possibility of limiting the melter size, the glass production rate, the canister pouring frequency, and the glass canister handling frequency. The low crystallization tendency of the LWG25 waste glass along with the reliable quantitative determination of the crystallization by the QPA/Rietveld method supports the safe and effective operation of the mature bottom draining system of the LFCM melter.

ACKNOWLEDGEMENTS

We thank Dieter Schild (KIT-INE) for SEM-EDX analyses.

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