DELIVERABLE REPORT

Thermal treatment for radioactive waste minimisation and hazard reduction

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Executive Summary

This work was performed within "Thermal treatment for radioactive waste minimisation and hazard reduction" (THERAMIN) project. In WP3 the application of selected thermal treatment technologies to radioactive waste management is demonstrated and evaluated. The THERAMIN project has identified a range of waste streams across the EU that are potentially suitable for thermal treatment. There are a wide range of technologies which could be utilised to demonstrate the thermal treatment of such waste streams. The streams selected for demonstration from Slovakia was chrompik.

The vitrification technology as a method for fixation of liquid radioactive waste (chrompik III) into boron-silicate glass matrix is describen. Chrompik, has been used as a heat-transfer medium for cooling off fuel assemblies at the A1 NPP, has ^{137}Cs activity ~ 100 GBq/dm^3. Vitrification technology has been chosen for treatment and conditioning of this liquid radioactive waste.

Samples of active and inactive glass preparations, the effect of additives on the vitrification process are also evaluated.

The trials with inactive surrogate solution of chrompik III and trials with real chrompik III were performed. VICHR facility operation with chrompik III treatment is currently in progress. The VICHR facility is owned and operated by JAVYS, Inc.

Keywords

Thermal treatment, Vitrification, Waste Processing, Vitrification facility, Chrompik, Additives

Acknowledgement

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THERAMIN Project Partners

Andra	Agence nationale pour la gestion des déchets radioactifs – France
AREVA	AREVA – France
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
GSL	Galson Sciences Limited – UK
FZJ	Forschungszentrum Juelich GmbH – Germany
LEI	Lithuanian Energy Institute – Lithuania
NNL	National Nuclear Laboratory – UK
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
SCK•CEN	The Belgian Nuclear Research Centre – Belgium
USFD	University of Sheffield – UK
VTT	Teknologian Tutkimuskeskus VTT Oy (VTT Technical Research Centre of Finland Ltd)
VUJE	VUJE a.s. – Slovakia

THERAMIN End User Group

Andra	Agence nationale pour la gestion des déchets radioactifs – France
CEA	Commissariat à l'énergie atomique et aux énergies alternatives – France
EDF	Electricité de France – France
Fortum	Fortum Oyj – Finland
IGD-TP	Implementing Geological Disposal of Radioactive Waste Technology Platform
Nagra	Die Nationale Genossenschaft für die Lagerung Radioaktiver Abfälle – Switzerland
ONDRAF/NIRAS	Organisme National des Déchets RAdioactifs et des matières Fissiles enrichies – Belgium
RWM	Radioactive Waste Management Ltd – UK
Sellafield	Sellafied Ltd – UK
TVO	Teollisuuden Voima Oyj – Finland

List of Acronyms

EC	European Commission
HST	Handling and Storage Tank
CHR	Chrompik- inorganic liquid radioactive waste
ILW	Intermediate Level Waste
LLW	Low Level Waste
MRB	main reactor building
NRI	Nuclear research institute
LTSC	Long-term Storage Case
LTSP	Long-term Storage Pool
NPP	Nuclear Power Plant
SFA	Spent Fuel Assemblies
SFS	Spent Fuel Storage
STS	Short-term Storage
RAW	Radioactive Wastes
WP	Waste Package

1 Introduction

The Thermal treatment for radioactive waste minimisation and hazard reduction (THERAMIN) project is a European Commission (EC) programme of work jointly funded by the Horizon 2020 Euratom research and innovation programme and European nuclear waste management organisations (WMOs). The THERAMIN project is running in the period June 2017 – May 2020. Twelve European WMOs and research and consultancy institutions from seven European countries are participating in THERAMIN.

The overall objective of THERAMIN is to demonstrate the efficancy of thermal treatment in providing improved safe long-term storage and disposal of intermediate-level wastes (ILW) and low-level wastes (LLW). The THERAMIN project is being carried out in five work packages (WPs). This document reports the output of the WP3 demonstration trials carried out using vitrification technology at NPP A1 in Jaslovské Bohunice, Slovakia. Owner of vitrification facility is JAVYS, Inc.

This document is elaborated with kind permission of JAVYS for publishing information on waste processed in JAVYS, Inc.- especially chrompik, as well as information on the vitrification facility for the purpose of cooperation on the THERAMIN project.

1.1 VICHR technology

Vitrification technology has been chosen for treatment and conditioning of liquid radioactive waste - chrompik, which has been used as a heat-transfer medium for cooling off fuel assemblies at the A1 NPP after their removal from the reactor. The original chrompik had been 1-3 % $K_2Cr_2O_7$ solution (with 0.5 % of KF addition) or 1-3 % K_2CrO_4 solution.

Due to defects on the fuel rod cladding, this cooling medium was contaminated significantly during storing the spent nuclear fuel. Depending on defect sizes and duration of storing the spent nuclear fuel in given cooling medium, the whole inventory of the "chrompik" cooling medium stored at A1 NPP was divided into three categories:

- chrompik I with ^{137}Cs specific activity at level of 10^9 Bq/dm^3,
- chrompik II with ^{137}Cs specific activity at level of 10^{10} Bq/dm^3
- chrompik III with ^{137}Cs specific activity at level of 10^{11} Bq/dm^3

Chrompik I, the entire volume of chrompik I - 18.5 m^3 was conditioned by vitrification technology on VICHR facility in 1996-2001.

Volume of chrompik II was significantly lower than volume of chrompik III, all LTSP (containing chrompik II as well as chrompik III) were finally discharged together to the handling and storing tank (HST) and this mixture was called chrompik III. Its ^{137}Cs activity is 100 GBq/dm^3, solution's pH is 9.5, it mainly contains K, HCO_3^-, CO_3^{2-} and the Cr content in the soluble form is 1 % from its original amount. The reduction of chromate anions was caused by radiolysis of water and content of dowtherm during storage of Chrompik III and thus a significant amount of chromate was reduced into insoluble compounds of Cr (III), which settled in sludge phase at the bottom of the HST tank.

The original vitrification technology was designed for chrompik I treatment as batch and discontinuous technology: 50 dm^3 of chrompik was concentrated in an evaporator to a volume of 3-5 dm^3 and was then discharged into a crucible on the layer of glass frit with weight 7.5 kg. The crucible was heated up and water was evaporated. When the water was evaporated and salts were dried, the temperature in the crucible has been increased and the glass frit were remelted with the salts. The maximum temperature in the crucible was given by high-temperature structural characteristic of the crucible material and it was not allowed to exceed 1050°C. The vitrified product was discharged into steel containers from the crucible by opening of a plunger after remelting. The drying and melting process in the crucible has taken 2.5-3 hours.

Chrompik III treatment meant increasing of the specific activity of processed radwaste by 2 orders, and this fact has required the modification of the vitrification facility technologically and technically.

Some modifications have been performed on the equipment of the VICHR facility, particularly on these parts: melting crucible, off-gas cleaning, processing of secondary waste generated in the off-gas cleaning process, sealing of the melting crucible and vitrification furnace and adjustment of the ventilation system.

Due to the different chemical composition of chrompik III compared to chrompik I the time-temperature regime of releasing gaseous products which are formed during the reaction by surrogate salts of chrompik III with a glass frit was examined in a laboratory. It was important to optimize the temperature regime during the evaporation of the water in the melting crucible and also during the reactions of the salt of chrompik III with the glass up to the maximum melting point of 1050 °C. To investigate the possibility of ^{137}Cs releasing reduction from the mixture of chrompik III salt and glass during melting, an experimental laboratory program using additives into the glass-based alumina-silicate was also prepared.

After completion of laboratory research and after the tests of modified parts of VICHR facility, the trial s were performed with inactive surrogate solution of chrompik III and also trials with active surrogate solution of chrompik III.

2 VICHR Technology Description

2.1 Development of vitrification technology in former Czechoslovakia

Research and development of technology for chrompik vitrification was carried out in the 80's and early 90's by NRI Řež (1). The technology was tested on the laboratory and industrial scale on the NRI Řež facilities for vitrification and later also in the NPP A1. The solution of the vitrification technology of the chrompik was adopted according to the French AVM vitrification facility. At the time only the approximate composition of the waste was known.

To deal with chrompik vitrification, partial problems such as had to be solved (2):

- Chemical process of vitrification, high-temperature reduction of CrO_4^{2-} to Cr_2O_3 oxide during melting of salts with glass,
- composition of borosilicate glass frit, which would support the reduction mentioned above, creates a bond with Cr_2O_3 and K_2O and ensures low leachability of radionuclides from the glass product,
- development of remotely controlled equipment for vitrification facility,
- corrosion of the melting crucible and its durability for the tested glass type and surrogate solution,
- verification of emergency state management in the vitrification furnace.

2.2 Chemism of chrompik vitrification

The chemism of chrompik I vitrification was designed so that during the melting of glass frit with dried Cr (VI) salts, there were reduced to Cr (III), compounds, Cr in this form is soluble in the glass frit, respectively together with K it will be incorporated into the glass matrix. The Cr (VI) and Cr (III) content in the glass melt is affected by: the composition of the glass frit, the effective O_2 partial pressure in the furnace´s atmosphere, melting temperature and interaction of other polyvalent elements. Redox chemistry of the melting also affects the volatility of Cs compounds, foaming of the melting, corrosion of the crucible walls (3).

Cr (VI) reduction was initially solved by the addition of a reducing agent, formic acid, which, however, caused undesired hydrogen release. The reduction of the chromate anion to chromium cations in the melt can be described by the following equation: $4\ CrO_4^{2-} \rightarrow 4\ Cr^{3+} + 10\ O^{2-} + 3\ O_2$.

The equation shows that the concentration ratio of CrO_4^{2-}/Cr^{3+} depends on the concentration of free O^{2-} in the melting, i.e. from the depolymerization of silicate and borate matrix. With increased acidity and temperature of the melting, the concentration of Cr^{3+} increases.

Using a sufficiently acidic glass frit, there was no yellow surface layer of soluble chromates, even in the case of vitrification at normal atmospheric oxygen pressure. This eliminated the need for formic acid addition and excessive hydrogen evolution in experimental melts. Melt / glass acidity has been shown to be a driving factor in the chrompik vitrification process in terms of chromium valence.

For development of chrompik vitrification several types of chrompik surrogate solution and glass were used, their composition is listed in Table 1 and Table 2 respectively.

Table 1 Composition of chrompik surrogate solution used for chrompik vitrification development

component	K_2CrO_4	Cr_2O_3	K_2CO_3	MgO	KCl	$FeCl_3$	sum
surrogate solution	g/L						
A14	3.80	8.70	15.83	3.27	-	-	31.61
CH2	15.13	-	0.58	0.74	0.34	0.02	16.81
PAC	18.00	-	26.15	0.85	-	-	45.00

Table 2 Composition of glass for used for chrompik vitrification development

	SiO_2	TiO_2	Al_2O_3	B_2O_3	Na_2O	Li_2O	Fe_2O_3	K_2O	CaO	MgO	ZnO	SrO	sum
	wt %												
USA	41.1	-	4.0	12.5	4.7	-	-	4.3	2.2	1.9	25.1	1.6	97.3
B270	50.3	15.3	1.7	12.9	11.3	3.5		0.5	3.8	0.2	-	-	99.5
LKU	57.0	5.5	5.3	14.8	8.5	3.5	4.5	-	-	-	-	-	99.0

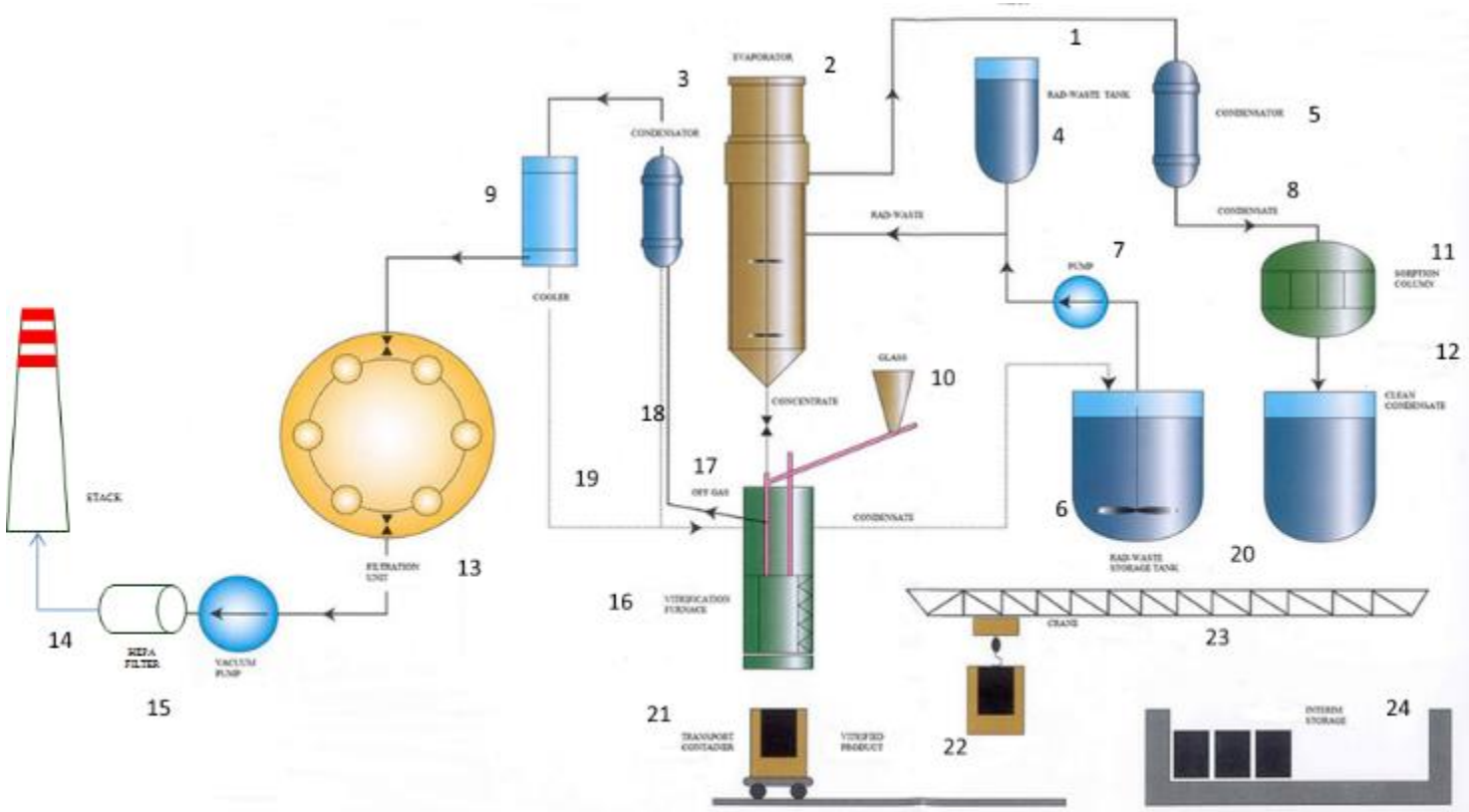
Laboratory tests and trials on the EXTÁZA (NRI Řež), NEVILI (NPP A1 - Jaslovské Bohunice) facilities showed that the LKU glass can fixed 8.75 wt % of chromate, while the reaction with the LKU glass causes the reduction of Cr (VI) and Cr (III), and the vitrification product is not yellowy coloured.

2.3 Description of the VICHR facility and the vitrification process of chrompik I

The original chrompik was a 1-3 % solution of $K_2Cr_2O_7$ (with added 0.5 % KF) or a 1-3 % solution of K_2CrO_4. The solution was called chrompik I, it had a ^{137}Cs activity of approximately 10^9 Bq/dm^3, pH of the chrompik I solution at the time of vitrification was 7-7.5, K content was app. 6.2-9.7 g/ dm^3 and the content of Cr was 2.5-4.0 g/ dm^3.

The scheme of the VICHR facility is illustrated in Figure 1, the model of the vitrification furnace is in Figure 2 and the crucible is shown in Figure 3.

Figure 1 Simplified scheme of VICHR processing plant



1 – steam from evaporator
2 – evaporator
3 – condenser II
4 – dosing tank
5 – condenser I
6 – RAW
7 – dosing pump
8 – condensate I
9 – cooler
10 – glass feeder
11 – sorption column
12 – purified condensate I
13 – off - gas filtration column
14 – stack
15 – vacuum pump
16 – vitrification furnace
17 – off gases
18 – condensate II
19 – condensate
20 – tank with active condensate I after purification
21 – transport container
22 – vitrification product
23 –crane
24 – temporary storage

Figure 2 Model of the vitrification furnace, vitrification furnace with temperature sensors

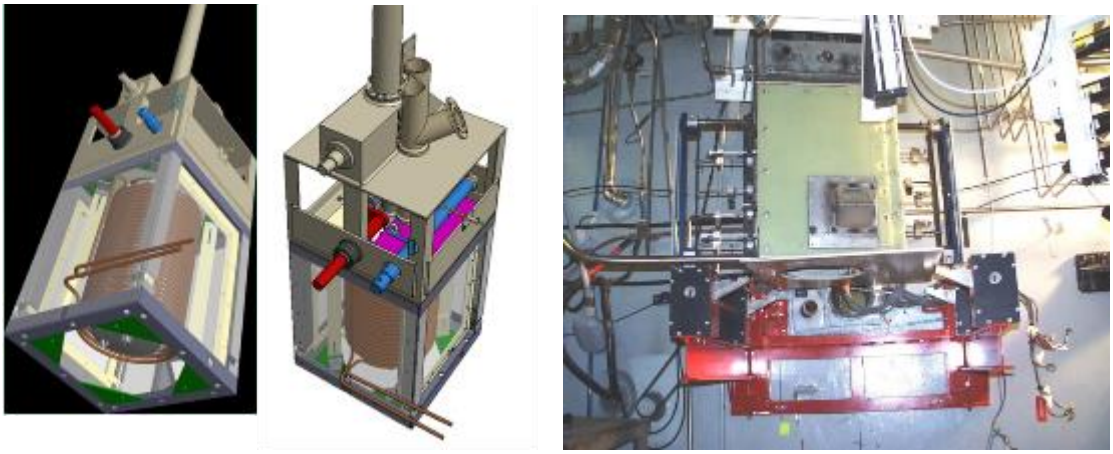
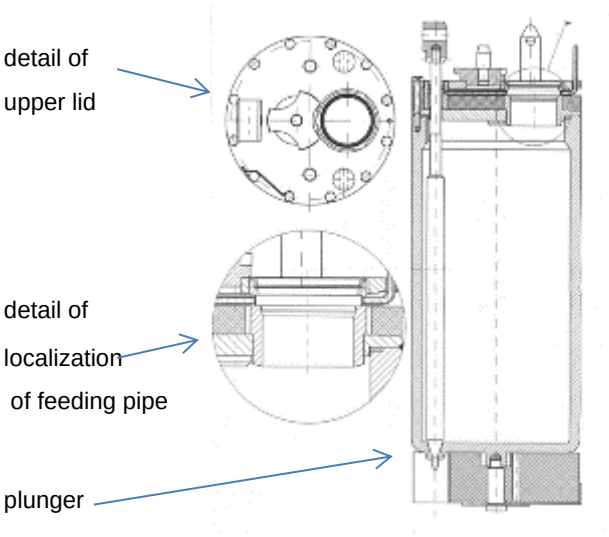


Figure 3 Scheme of melting crucible



The vitrification technology was designed as a batch and discontinuous technology, 50 dm^3 of chrompik was concentrated in an evaporator to a volume of 3-5 dm^3. The evaporator had a volume of about 100 dm^3, the evaporator was heated by steam. Vapor from the evaporator condenses in condenser I. The condensate was purified on filters filled with an inorganic sorbent.

From evaporator was chrompik then discharged into a crucible on the layer of glass frit with weight of 7.5 kg. The crucible was heated up and residual water was evaporated. Vapor from drying of salts in the crucible condensed in condenser II. When the residual water was evaporated and salts were dried, the temperature in the crucible was increased and the glass frit was remelted with the salts. The maximum temperature in the crucible was given by high-temperature structural characteristic of the crucible material and it must not exceed 1050°C. The vitrified product was discharged into steel containers from the crucible by opening of a plunger after remelting. Drying and melting process in the crucible, takes 3.5- 4 hours. Vapor from drying of salts in the crucible condenses in condenser II. The

off-gas from vitrification crucible was purified by a sorbent in the filtration column and HEPA filters and after the activity control was discharged into the stack. Vitrification furnace (Fig.2) consists from a frame, inductor, crucible and a temperature measurement system. Crucible: height 450 mm, diameter 250 mm, wall thickness 15 mm, made from alloy F (content of Cr 49.5-52 %, Fe max 2.5 % and Ni 23 %), its maximum temperature was 1150 °C, the outlet opening was closable by a remotely controlled plunger. The lifetime of the one melting crucible is 40- 60 melts, the crucible was replaceable from the vitrification furnace by remote manipulators. The inductor coil was made from a copper pipe, coil diameter was 324 mm and its height was 490 mm, it was cooled by water, has a maximum voltage of 180 V and its maximum frequency was 3.2 kHz. Temperature measurement of the crucible was ensured by thermocouples and pyrometers.

2.4 Processing of chrompik I - experience from operation

Between 1996- 2001 chrompik I with activity of ^{137}Cs of up to $1.2.10^9$ Bq/dm^3 was treated on the VICHR facility (4).

VICHR facility was operated about 4000 hours to process chrompik I. All chrompik I with volume of 18.5 m^3 was vitrified to the glass matrix. 211 pieces of the glass products with total volume of 1.53 m^3 were produced. The cartridges with the glass product CHR I are stored in the interim storage facility (room number 702) in the main reactor building of NPP A1.

Total period of chrompik I processing includes facility preparation for the operation cycles, product and equipment´s cool down process, including required outages of the VICHR facility from the other reasons, presents 5 years:

- ✓ ***18.5 m^3 of chrompik I (0.3-1.2 GBq/L ^{137}Cs) were treated into the glass matrix successfully,***
- ✓ ***average content K 6.17 g/L, Cr 2.47 g/L in chrompik I, pH 7-7.5***
- ✓ ***loading of K_2O and Cr_2O_3 from chrompik I 3-10 wt % in glass***

In Figure 4 and Figure 5 are shown main operational parameters from Chrompik I treatment at the vitrification facility- activity of ^{137}Cs/ content of chrompik I and distribution of ^{137}Cs in glass cartridge prepared from Chrompik I. The typical process of crucible heating, residual water evaporation and remelting of dried chrompik salt with glass is shown in Figure 6.

Figure 4 Treatment of Chrompik I

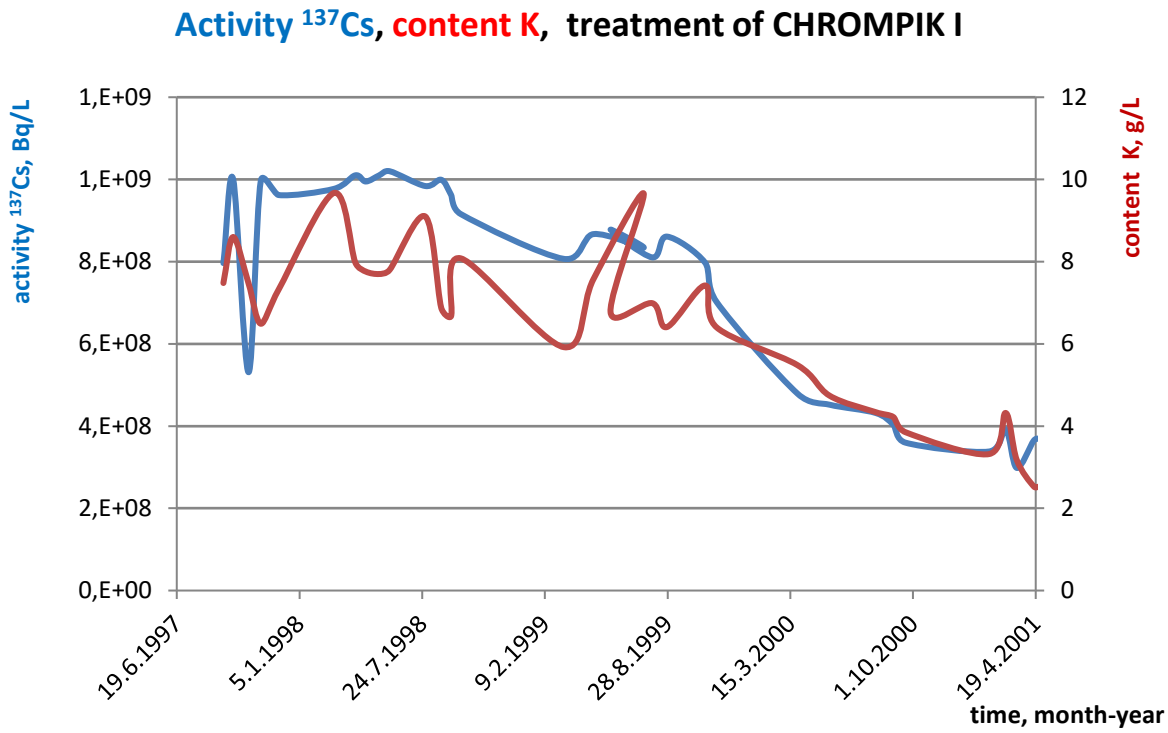


Figure 5 Distribution of ^{137}Cs in glass cartridge prepared from Chrompik I

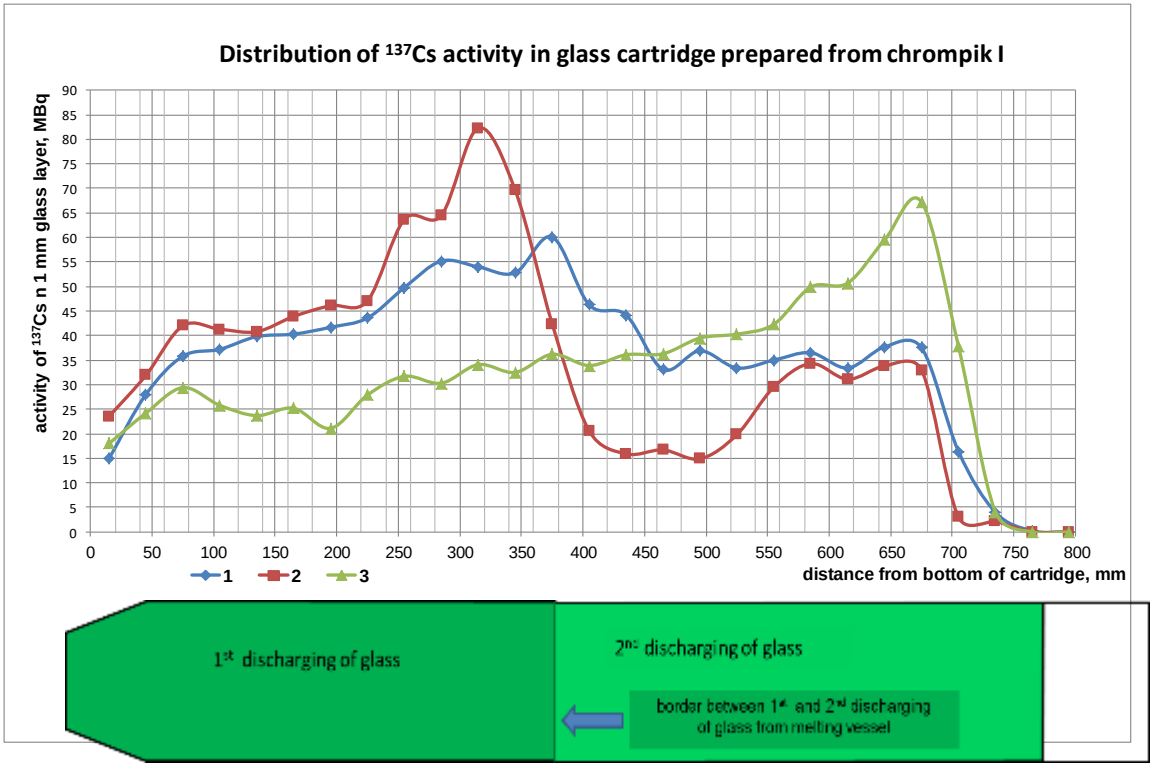
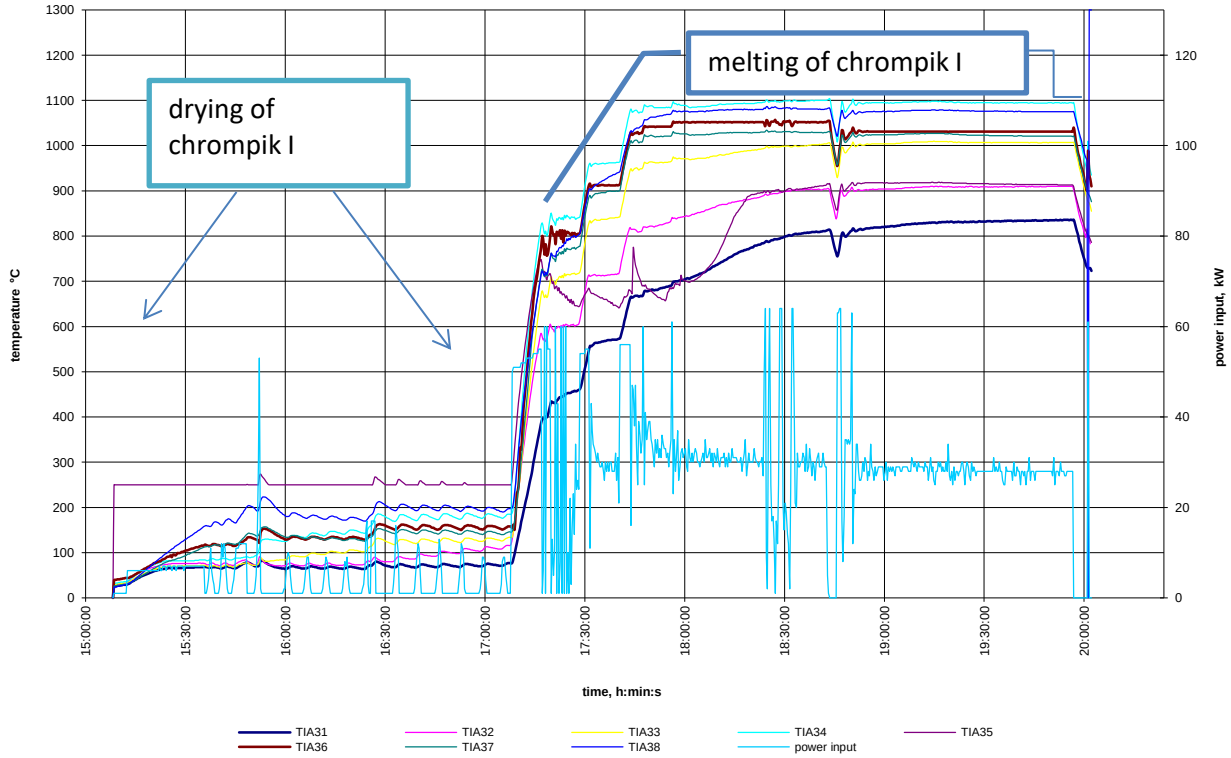


Figure 6 Treatment of chrompik I Time-temperature diagram of chrompik I drying and melting in crucible



The operation of vitrification facility with chrompik I can be characterized as follows:

- There were no events with impact to environment in the technological system. There were no leakages of chrompik I from the equipment to the non serviced or semi-serviced areas.
- Event of solidification of the glass melt in a part of feeding pipe leading to the melting crucible can be considered for the most significant event which occurred.
- Other operational events can be classified as failures connected with loss of equipment functionality, and those failure were as follows:
  - repeated failures of glass frit feeding equipment,
  - mechanical failure of melting crucible holder,
  - untightness of connection in cooling demineralized water pipeline to the vitrification furnace inductor,
  - untightness of glass frit feeding,
  - untightness of whole system of purification of gases exhausted from the melting crucible.

These failures led to modifications to the VICHR facility prior to chrompik III processing.

2.5 Improvement of the VICHR facility and preparation for Chrompik III treatment

Because the specific activity of ^{137}Cs in chrompik III compared to chrompik I is two orders higher and the chemical composition of chrompik III differs from chrompik I composition, it was necessary to make some improvements of the VICHR facility and also modify the thermal process of vitrification.

Some technological modifications have been performed on the VICHR facility, particularly on these parts to avoid some difficulties (to prevent releases of radioactive aerosols from melting crucible into room No 714, to eliminate difficulties at replacement of used melting crucible, improvement of radiation measurements etc.): sealing of the glass frit feeder, melting crucible off-gas cleaning, processing of secondary waste generated in the off-gas cleaning process, sealing of the melting crucible and vitrification furnace and adjustment of the ventilation system.

Main technological upgraded parts of VICHR facility:

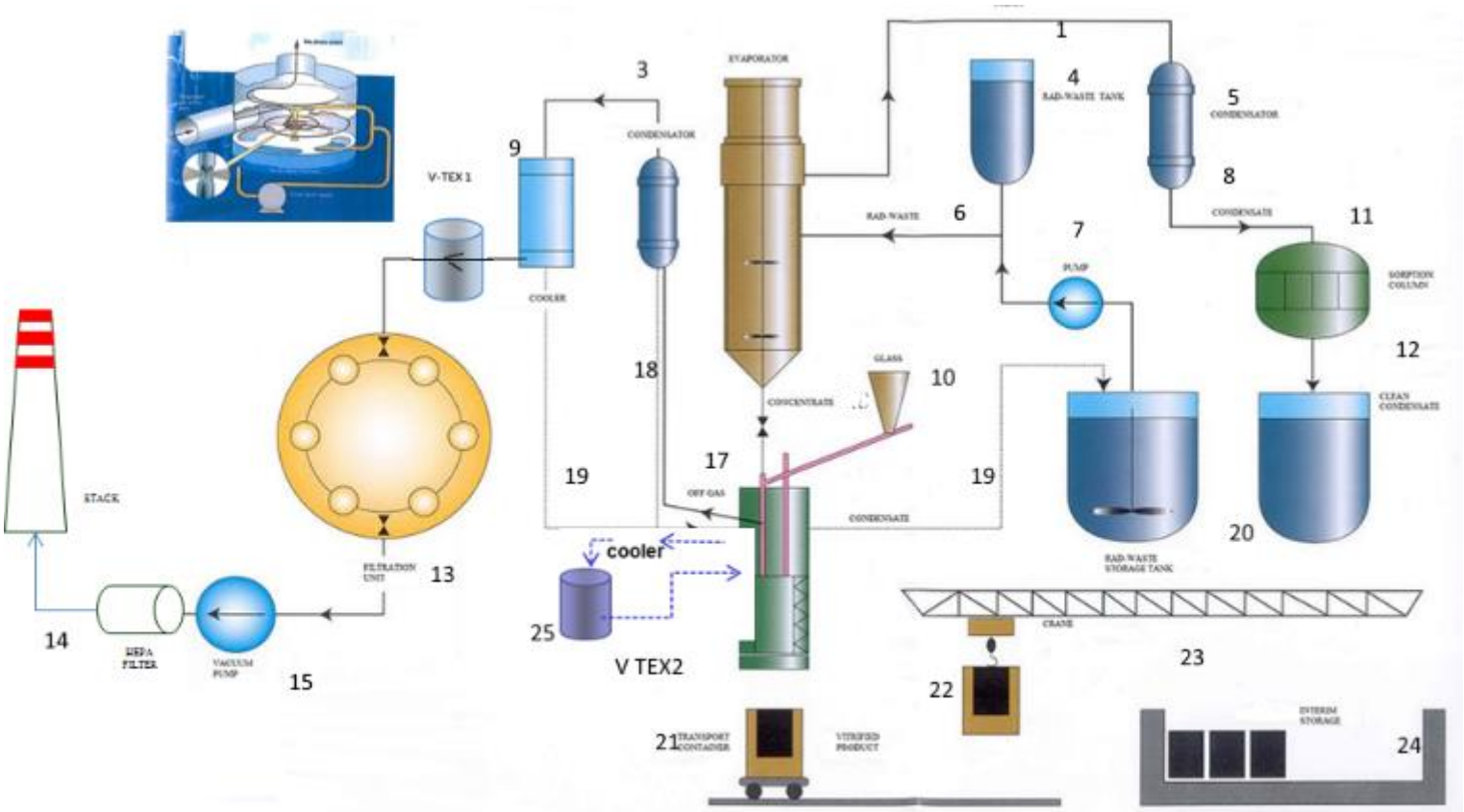
- sorption column and pumps in service tanks for chrompik,
- glass frit feeder,
- vitrification furnace and frequency converter,
- new apparatus- wet scruber V-TEX,
- vacuum station for exhausting off-gas from melting crucible,
- I&C,
- radiation monitoring system (measurement of dose rate and aerosols for technological equipment), containers, trolleys, TV circuit.

The new equipment is shown in Figure 7.

To the off-gas cleaning branch from the crucible a wet V-TEX 100 scrubber from ACCENTUS was placed, the effectiveness of cleaning for particles with a diameter of 3 μm is 99.9%, the water from this equipment constitutes secondary waste, when it reaching an activity app 10^{11} Bq/dm^3 it will be fed back into the operation tanks of chrompik.

The volume of the vitrification furnace above the crucible was sealed and the air pumped out of this volume will be recirculated, cooled and filtered by a new V-TEX 400 scrubber. The model of the vitrification furnace is in Figure 8.

Figure 7 Simplified diagram of modification on the VICHR facility



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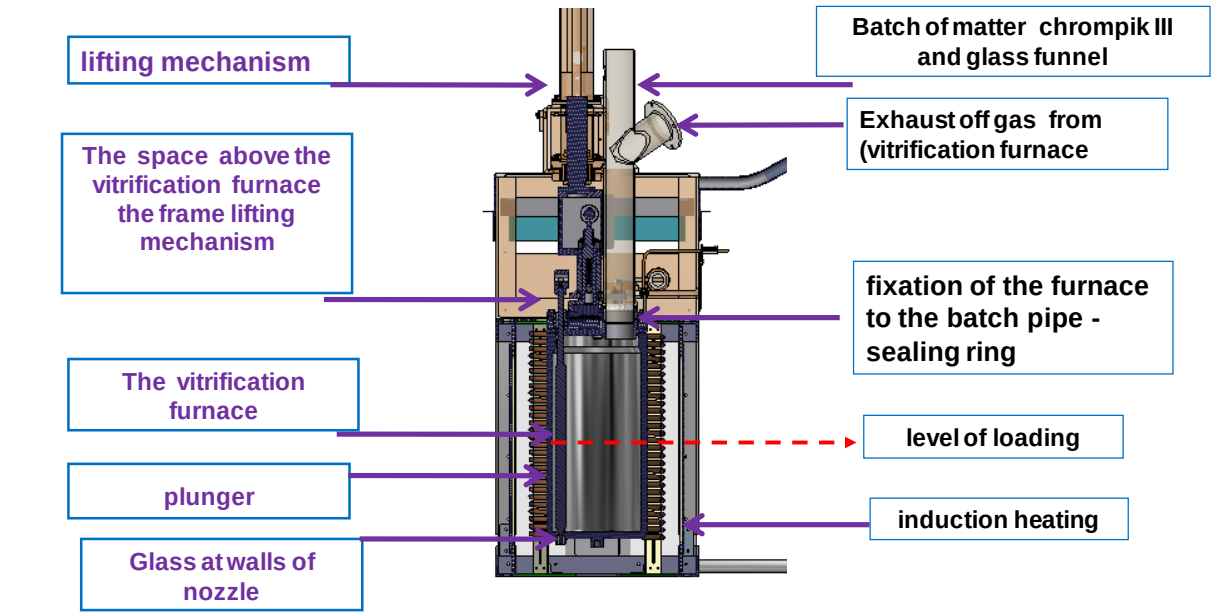
12 – purified condensate I
13 – off - gas filtration column
14 – stack
15 – vacuum pump
16 – vitrification furnace
17 – off gases
18 – condensate II
19 – condensate
20 – tank with active condensate I after purification
21 – transport container
22 – vitrification product
23 –crane
24 – temporary storage
25 – cooler V- TEX2

Figure 8 Model of the vitrification furnace



Chrompik III, Its ^{137}Cs activity is 100 GBq/dm^3, solution's pH is 9.5, it mainly contains K, HCO_3^-, CO_3^{2-} and the Cr content in the soluble form is 1 % from its original amount. Analysis for comparison of the main compounds of chrompik I and III is given in Table 3.

Table 3 Basic analysis of chrompik I performed during treatment in the VICHR facility, chrompik III from sampling of HST tank

	K	Cr	HCO_3^-	CO_3^{2-}	pH	^{137}Cs	alfa nuclides
	g/L	g/L	g/L	g/L	-	Bq/L	Bq/L
chrompik I	9.2-9.7	2.5-4.0	NA	NA	7.0-7.5	$1.2.10^9$	cc 4.10^6
chrompik III	7.6	0.06	7.3	1.8	9.6-10.0	$1.0.10^{11}$	cc 4.10^{6*}

Note: low alpha nuclides in the aqueous phase is a consequence of that alfa radionuclides are precipitated in the sludge at the bottom of the tank

From the comparison of the analyses of chrompik I and III we can clearly conclude that during storage of chrompik III a reduction occurred in the content of chromate anions which were present in the fresh chrompik and thus a significant amount of chromate was reduced into insoluble compounds of Cr(III) settled in sludge phase at the bottom of the HST tank.

Because the chemical composition of chrompik III differs from that of chrompik I, during its vitrification it was not required to principally address the reduction of Cr (IV) to Cr $(III)^{-}$ in quantities that were present in the chrompik III solution the reduction of Cr (VI) to Cr (III) with LKU frit proceeds without difficulties. However, it is necessary to address a new time-temperature mode during the drying of chrompik salts with glass frit and the time-temperature mode during melting because of the release of CO_2, which occurs in the reaction of a glass frit with potassium carbonate.

It was necessary to make some adjustments into to the thermal process of vitrification- to prevent in the crucible the segregation of chrompik salts from the glass frit after drying and the use of additives for absorption of Cs with higher resistance against Cs volatility at process temperatures. It was important to optimize the temperature regime during the evaporation of water and the melting mode up to the maximum melting temperature of 1050 °C. To investigate the possibility of ^{137}Cs volatility and release reduction from the mixture of chrompik III salt and glass during melting, an experimental laboratory program using additives into the glass-based alumina-silicate was prepared.

The time-temperature regime of releasing gaseous products which were formed during the reaction by surrogate salts of chrompik III with a glass frit was examined in a laboratory. Based on the experimentally measured thermogravimetric data from the laboratory tests with LKU glass frit melting and chrompik III surrogate solution was proposed the rate of development of gases as a function of time and temperature, and a new time - temperature function was proposed for concentration of dried chrompik III and for melting of chrompik III salts with glass frit.

The temperature regime mode for chrompik III treatment was proposed as follows:

- Temperature mode of drying - evaporation of water up to 95°C with a heating rate of 10°C/min, at temperature 120- 130°C within 2-3 hours the rest part of water from concentrated chrompik is evaporated,
- 10°C/ min heating rate, after reaching a temperature of 650° , a holding time of 2 hours
- 10°C/ min heating rate, after reaching a temperature of 800°C, hold time 2 hours
- 10°C/ min heating rate, after reaching a temperature of 990°C, a holding time of 1 hour. 30 min..

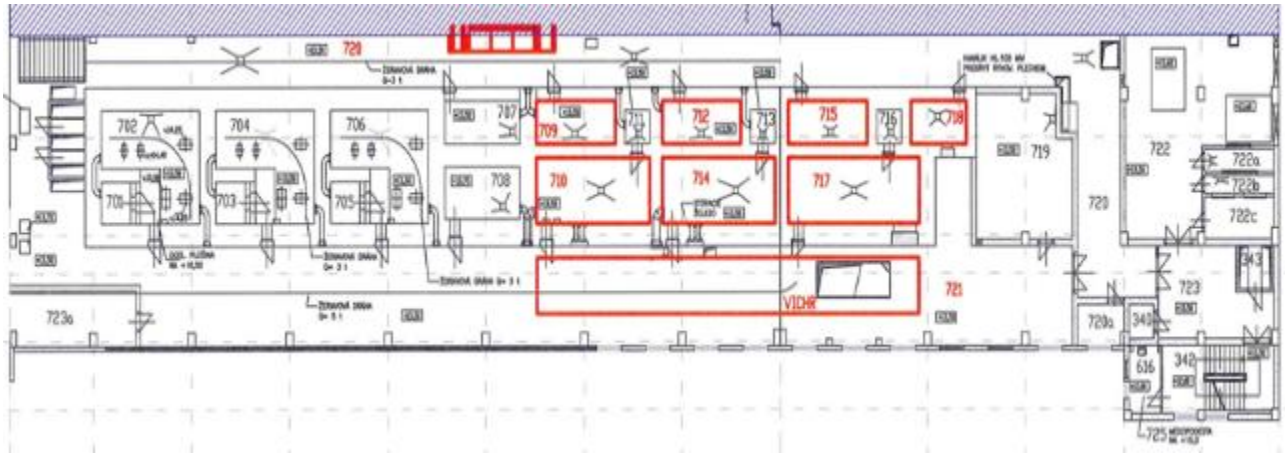
After the reconstruction VICHR facility provides the technology of processing chrompik III with activity 1.10^{11} Bq/dm^3 into the glass matrix of required quality.

2.6 Chrompik III treatment

Vitrification facility is situated in MRB of NPP A1 on the floor (+13.5) m in individual rooms Room No. 710- Room No. 721. During operation, it is not possible to access the technological equipment (tanks, evaporator, vitrification furnace) located in the room No. 714 and 717. Only after decontamination of the equipment, access to these rooms is possible. In

Figure 9 9 is shown layout of vitrification facility on +13.5 floor.

Figure 9 VICHR Layout



Due to the high specific activity of treated chrompik, all manipulations of the chrompik and the glass products are carried out remotely. The devices are located in rooms with a sufficient thickness of concrete walls, vitrified waste is transported in steel shielding containers.

VICHR equipment including the following operating files are used for processing of chrompik III:

I. Transport of chrompik
II. Vitrification furnance
III. Transport equipment
IV. Instrumentation and control system
V. I&C, Electro
VI. Radiation monitoring (RM)
VII. Closed circuit TV (CCTV)
VIII. Technological platforms

The equipment of the VICHR facility provide: storage of the chrompik in operation tanks, transfer of chrompik to the evaporator, concentration in the evaporator, drying of the concentrated concentrate mixed with glass frit and additives, melting the mixture into a homogeneous glass at a temperature of approximately 1000°C, pouring the vitrified glass into a steel cartridge, transport of glass cartridge in shielding containers from the VICHR facility to a storage located in the reactor hall. The operation of the VICHR facility is batched, 50 dm^3 of chrompik is processed in one batch by the technological steps described below. Two batches of glass products are filled to one cartridge.

Chrompik III is pumped from HST tank into the operation tanks. After homogenizing process it is transported into the measuring tank of chrompik in volume 50 dm^3 (volume of one batch) by the pumps. The measuring tank of chrompik serves for exact feeding of chrompik into evaporation. Measured volume of chrompik is discharged into the evaporator. Chrompik is thickened to volume of app 3,6- 5 dm^3 at maximum temperature 140 ^{0}C. Here is achieved 10 multiple reduction of volume. Melting crucible is filled with amount of glass frit and additives (total weight of glass and additives 7.5 kg) with required granulometric proportion through the feeder.. Thickened chrompik pours on the glass frit and additives. Process of vitrification is controlled by heating of the inductive furnace and other related systems. For safety reasons there is permanently maintained negative pressure 100 – 200 Pa in the melting crucible.

At the beginning of the process in the melting crucible at temperature 120-130°C within 2-3 hours the residual water from thickened chrompik is evaporated. After drying the temperature in the melting crucible is gradually increased up 990 - 1020 °C with holding time app. 2 hours. (Maximum temperature for ALLOY F , which the melting crucible is made of, is limited to 1100 °C). Temperature holding time to 990-1020°C is necessary for achieving such viscosity of melting, which ensures continuous discharge of glass product into the patron and safety manipulation with plunger for the assurance of back failure-free closing of the melting crucible).

Glass product is discharged through the bottom opening of the crucible into the steel patron inserted into the shield container. Volume of glass product from one rank (melting) is app 7.27 dm^3. Two batches are placed into one cartridge. The cartridge is then placed into hermetic penal and stored in the storage.

The condensate I - secondary waste - condensate from the evaporation process- is purified on sorption columns. Off-gas from the vitrification furnace passes through the condenser II where vapours from process of evaporation residual water from thickened chrompik are condensate. Then off-gas passes the separator and scrubber V-TEX, the spent aqueous solution from scrubber is returned to operation tanks. The last stage of purification off-gas is on the dry filter. The off-gas from the filter enters to the ventilation system, which is part of the NPP A1 ventilation systems. The off-gas from the ventilation system is filtered and controlled before being discharged into the vent stack.

In Figure 10, Figure 11 and Figure 12 are shown cartridge for vitrified product, melting furnace and melting crucible (5).

Figure 10 Cartridge for vitirifcation product and the transport container for the cartridge

Height 792 mmm, Diameter 115 mm
Wall thickness 1.5 mm
Material stainless steel

Figure 11 View to vitrification furnace, without transport container

The vitrification furnace and medium frequency converter is a medium-frequency induction furnace. Regarding the nature of the processed fluid, it is supplemented with a manipulator to remotely replace the melting crucible and with control equipment for the monitoring system of melting crucible temperature. Melting crucible embedded in the frame comprises of:

- water-cooled tube inductor,
- thermal insulation with a protective cover and complete melting crucible including a lid,
- discharge plunger,
- catch for lift,
- equipment with thermo couples and pyrometers.

Figure 12 Detail of melting crucible, melting crucible before installation into the vitrification furnace

The radiation monitoring system of the VICHR facility is an independent sub-system which is separated from other technological equipment. The radiation monitoring system performs the following functions:

a) monitoring the dose rate (DR) in working areas,
b) monitoring the dose rate (DR) on technological equipment,
c) monitoring the volumetric activity of Ra-aerosols in working areas,
d) monitoring the activity of aerosols in technological circuits,
e) monitoring of the radiation situation.

The trials at the vitrification facility VICHR started with activity of Chrompik III surrogate solution of 10^7 Bq.dm^{-3} in March 2016. In 2017 started the treatment of real Chrompik III with an activity 10^{11} Bq. dm^{-3}.

3 Waste Feeds

During real CHR III treatment, melting crucible was filled with 5.3 kg LKU glass frit and 2.2 kg additives. In table 4 is given the calculated composition of glass product (glass frit, additives and oxides from CHRIII surrogate solution)

Table 4 Calculated composition of glass product (glass frit, additives and oxides from CHR III surrogate solution)

Wt. %	oxides
51.89	SiO_2
8.54	Al_2O_3
5.48	K_2O
10.24	Na_2O
3.17	Fe_2O_3
3.93	TiO_2
1.37	CaO
0.09	MgO
11.09	B_2O_3
2.38	Li_2O
1.45	PbO
0.13	ZnO
0.12	BaO
0.07	Cr_2O_3

In Figure 13 are shown picture of additives and glass frit used for CHRIII treatment in vitrification process.

Figure 13 Picture of additives and glass frit

4 Trial Information

The demonstration within WP 3.1 waste streams suitable for treatment through the vitrification process-chrompik was executed in the full operation of the vitrification facility (VICHR) and same experiments were conducted in VUJE´s laboratories.

The treatment of the chrompik III started after the reconstruction of the VICHR facility in the year 2016. An important goal for chrompik III technological process of vitrification was to find and optimize the chemical composition of the glass frit- additives mixture with the addition of thickened chrompik III in order to suppress ^{137}Cs evaporation throughout the heat treatment process.

4.1 Preparation of glass samples on vitrification facility

Processing the chrompik III by original standard procedure at VICHR plant is carried by the following sequence of the operations:

1. pumping the chrompik solution to the operation tank,
2. displacement of the cartridge in open transport container under vitrification furnace,
3. pumping one batch (50 dm^3) from the operation tank to the measuring tank,
4. discharging chrompik III from the measuring tank to evaporator,
5. thickening of chrompik III in the evaporator up to required volume of about 3,5-5 $dm^{3,}$
6. feeding 5.3 kg of glass frit and 2.2 kg of additives to the melting crucible of the vitrification furnace, for testing of effect of additives some batches were performed without adding of additives, so only 7.5 kg of glass frit was feeded,
7. discharging the thickened CHR III solution from the evaporator to the melting crucible,
8. evaporating of residual water and drying of the mixture of the thickened CHRIII, additives and glass frit in the melting crucible,
9. melting of the mixture in the melting crucible,
10. discharging of melt into cartridge,
11. cooling down the product in the container,
12. closing the product in the container by a cap,
13. transportation of the container,
14. placement of the cartridge into hermetic penal,
15. discharging the condensate I from through sorption columns into collecting tank

Following temperature regime was proposed drying and melting in crucible during chrompik III treatment (5):

1. Temperature mode of drying - evaporation of residual water and interaction of ^{137}Cs with additives - geopolymer reaction. Drying temperature - evaporation of water up to 95°C with a heating rate of 10°C/min. (Condensation water keeps the temperature of condenser II at a certain value when evaporation is complete, temperature changes - comes up, which will be the signal to terminate the evaporation mode and start another temperature mode)
2. Temperature regime of Chrompik III salts interaction (after evaporation of residual water and thermal decomposition of crystalline hydrates formed during evaporation of water phase) with additives and glass frit. Heating rate 10°C/min. After reaching a temperature of 650°C, holding time 2h. Dehydroxylation - release of H_2O due to decomposition of crystalline hydrates and gradual

thermal transformation of geopolymer. At this stage, as a result of the interaction of the salts with the glass frit and the additives, the onset of CO_2 release can be observed.

3. Temperature regime of CO_2 release. Heating rate 10°C/ min. After reaching a temperature of 800°C holding time 2h. In this mode, process No. 2 is completed, with a vigorous release of CO_2.
4. Temperature regime of melting (degassing of the melt, CO_2 release). Heating rate 10°C/ min. After reaching a temperature of 1020°C, a time of 1 hour. 30 min.
5. After the above temperature regime steps have elapsed, the melting process is complete and the melt can be drained from the melting crucible.

Operational process parameters such as process evolution versus time, power input and temperature of melting are evaluated for each batch, also material balance across the vitrification process were evaluated. In Figure 14 and Figure 16 are shown operational process parameters during processing of chrompik III on vitrification facility for drying and melting. In Figure 16 is shown evalutation of material balance across the vitrification process and glass product discharge rate.

Figure 14 Operational process parameters: Time-temperature diagram of the crucible during evaporation residual water from thickened chrompik III and drying of mixture in crucible

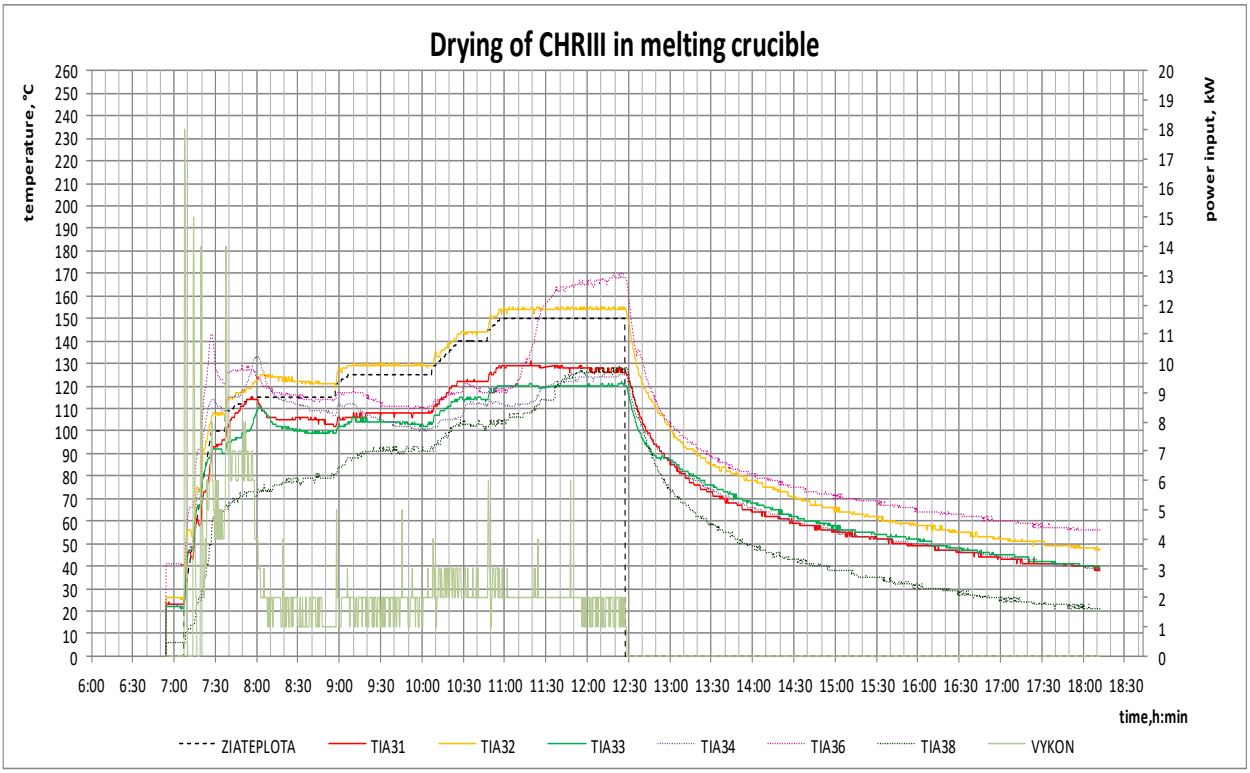


Figure 15 Operational process parameters: Time-temperature diagram of the crucible during melting of the mixture in the melting crucible

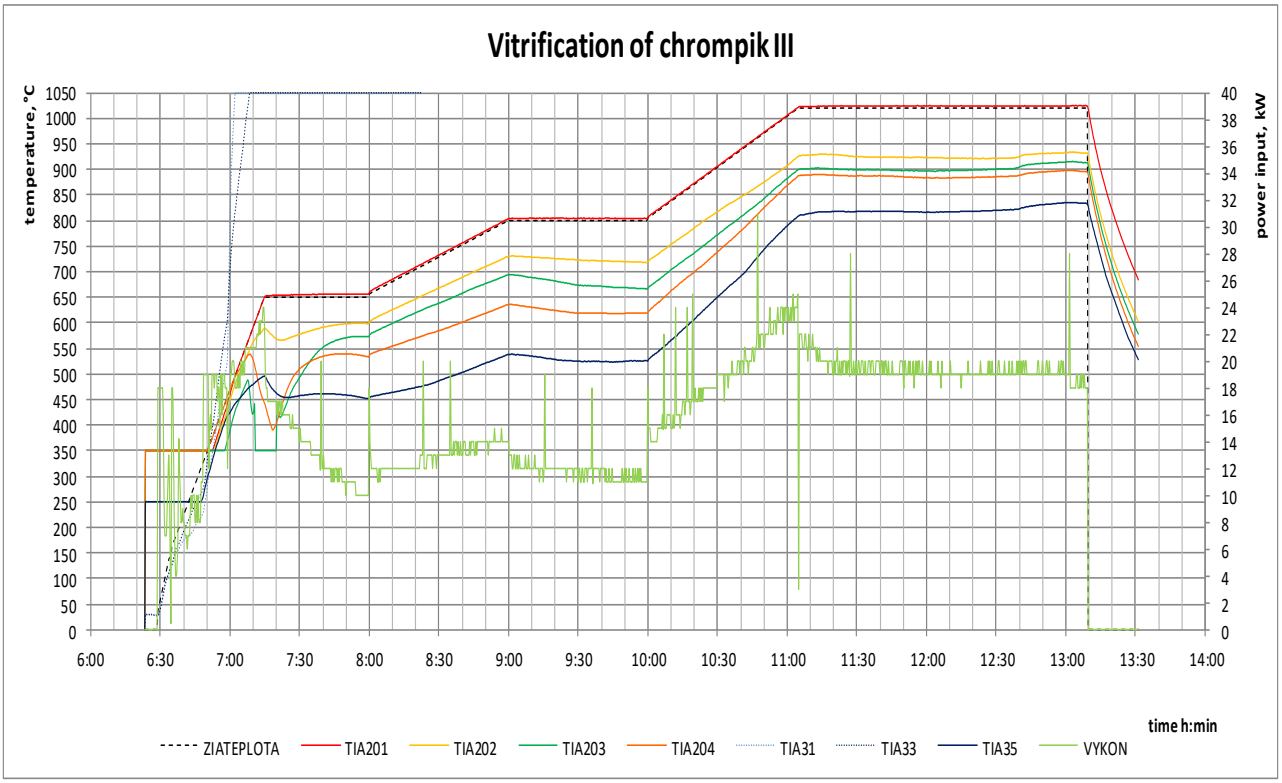
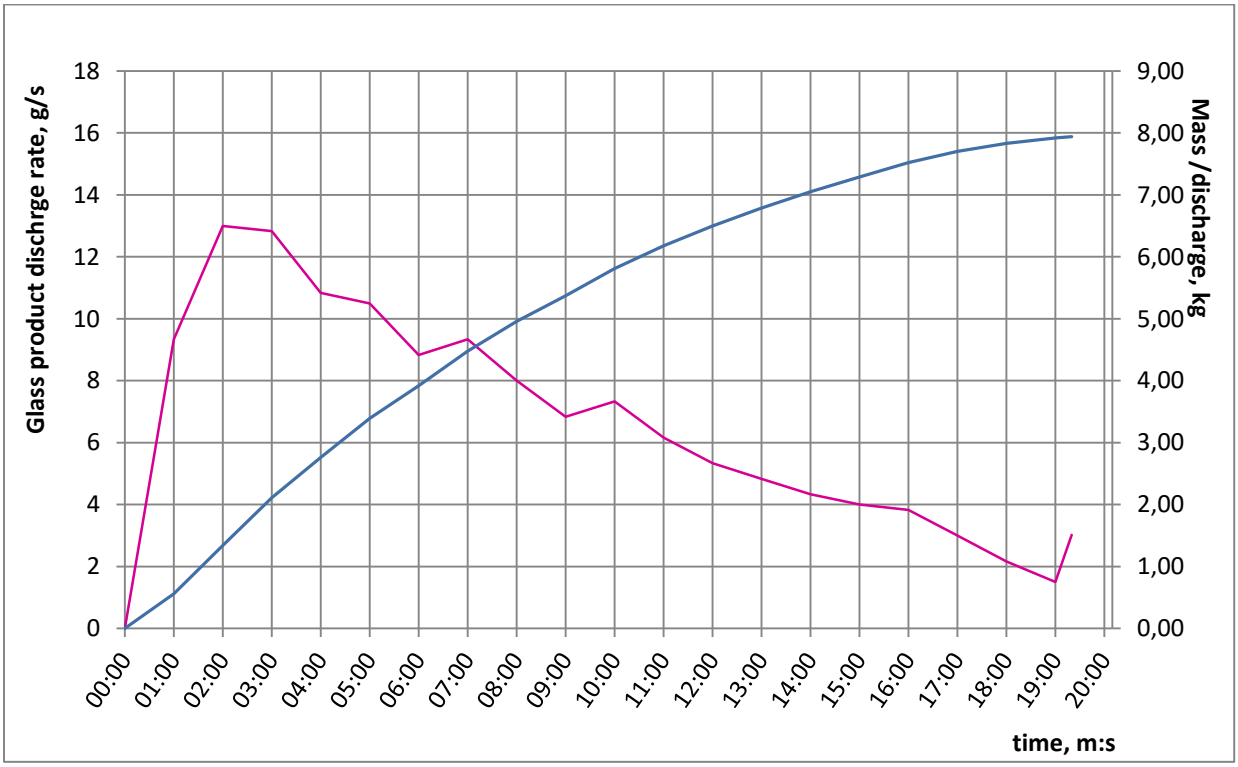


Figure 16 Material balance across the process, glass product discharge rate



In Figure 17 and Figure 18 are pictures from vitrified product prepared during trials (with and without additives) on vitrification facility after pouring into cartridge.

Figure 17 Picture of glass product without additives- brown colored

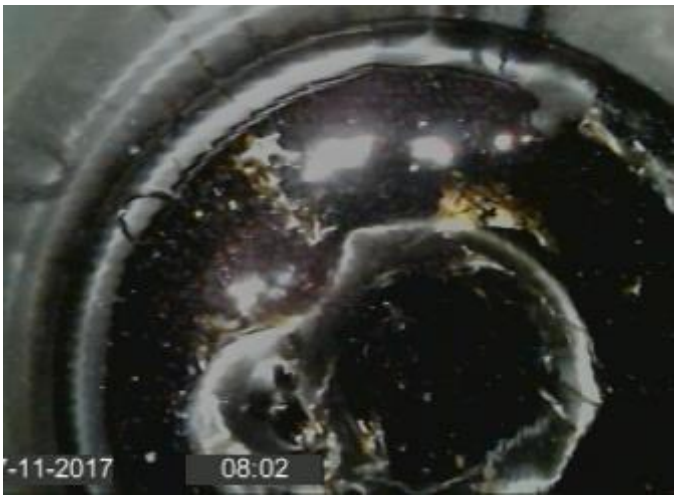


Figure 18 Picture of glass product with additives- light green colored

For a successful vitrification product:

The melting glass during the chrompik III treatment on vitrification facility is before pouring sufficiently molten, the pouring process is smooth and the pouring time for 1 melting batch is 8 to 20 minutes. The vitrified product inside the cartrige has after the cooling a gloss surface. The vitrification product meets the quality requirements, the color of the vitrification product is green (product using additives or brown (product without additives).

In Figure 19 is shown prepared active sample from vitrification trial demonstration.

Figure 19 Prepared active sample from vitrification trial demonstration

4.2 Preparation of glass samples in VUJE´s laboratories

Preparation of inactive glass samples were performed in VUJE´s laboratory.

In Figure 20 are shown samples of real Chrompik III and chrompik III surrogate solution.

Figure 20 Samples of real Chrompik III and chrompik surrogate solution

In the Figure 21 is shown preparation of inactive glass sample in VUJE´s laboratory.

Figure 21 Preparation of inactive glass product samples in VUJE´s laboratory - pouring of glass and melting in the furnace

In Figure 22- Figure 24 are shown prepared samples of inactive glass products with and without additives in VUJE´s laboratory.

Figure 22 Prepared samples of inactive glass product without and with additives

Figure 23 Prepared samples of inactive glass product in VUJE´s laboratory

Figure 24 Prepared samples of inactive glass product

4.3 Effect of additives on the vitrification process

The effect of additives on the vitrification process, decreasing of the volume specific activity of the aerosols (represented mainly by ^{137}Cs) generated by the process and the amount of activity collected in the off gas scrubber were observed and evaluated. The results of the both regimes (with and without additive) were compared (5).

In order to evaluate the effect of additives on ^{137}Cs retention in the melting, a comparison of the additive efficiency on two processes of chrompik III melting was performed. Treatment of CHR III with specific activity 89.9 GBq/dm^3 without additives and melting of chrompik III, with specific activity 73.1 GBq/dm^3 using additives were compared. The parameters were calculated from off gas scrubber (VTEX) records. For chrompik III treatment without the addition of additives, a sample was taken directly from the circulating wash circuit and the wash water activity was determined and the dose rate of the V-TEX

scrubber was calculated. For chrompik III treatment with additives, the dose rate on the V-TEX scrubber was measured directly by a dosimetric probe.

For CHRIII treatment without additives, activity of ^{137}Cs 540 MBq/dm^3 was detected in off gas scrubber, this activity corresponds to the dose rate of 1.5 mGy/h on the V-TEX scrubber. For CHRIII treatment with additives, the dose rate measured on the V-TEX scrubber was 0.275 mGy/h, this dose rate corresponds to activity of 96.5 MBq/dm^3 in the V-TEX scrubber.

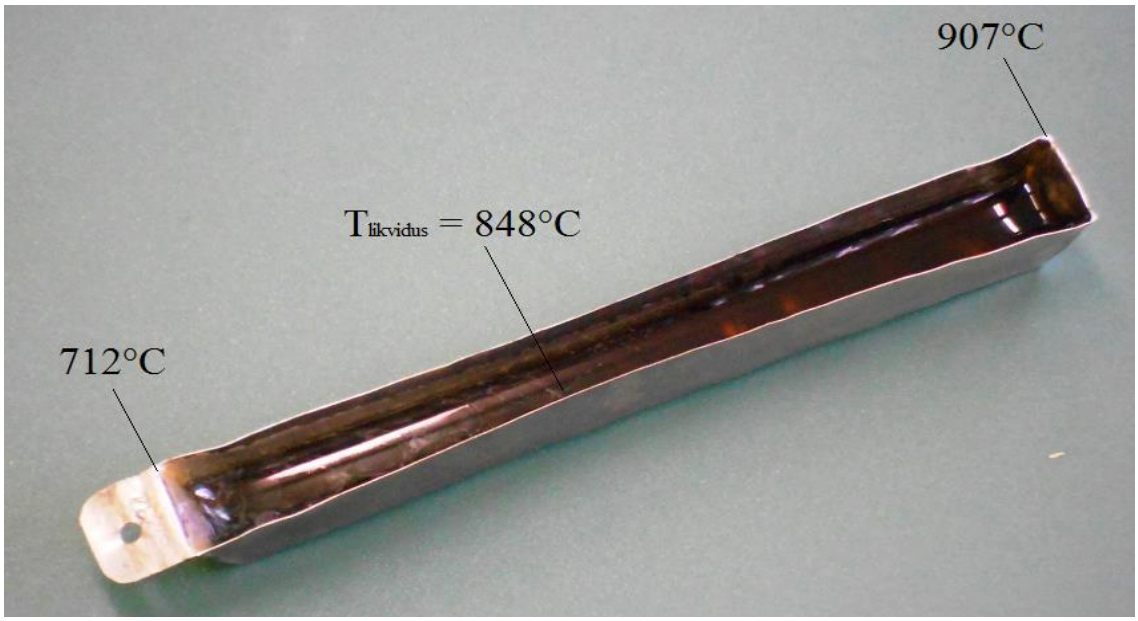
Comparing both regimes (with and without additive) for chromium III treatment, the effect of additives on caesium release has been evaluated. During CHRIII treatment with additives, a lower dose rate was observed in the V-TEX scrubber with the corresponding activity, than it was observed during CHRIII treatment without additives. Mixture with additives retains 5 times more ^{137}Cs.

The physicochemical properties of glass frit and chemical composition of glass product as a function of temperature over the whole range used during vitrification were also evaluated. The determination of the liquidus temperature was performed to determine the value of the appearance of the last crystal in the melt. From the point of view of the melting used in VICHR technology, this is particularly important in the process of molten glass discharge from the melting crucible and its subsequent cooling in the vitrification cartridge.

The liquidus temperature determination in prepared glass samples

For determination of the liquidus temperature, glass samples were taken according to C 829-81 (Reapproved 2000) Standard Practices for Measurement of Liquidus Temperature of Glass by the Gradient Furnace Method. The measurement results are shown in the following figures.

Figure 25 Glass frit sample after melting by 1400°C and after 24h in furnace



The liquidus temperature of the examined glass frit sample is 848°C.

Figure 26 Glass sample (without additives) after melting by 1400°C and after 24h in furnace

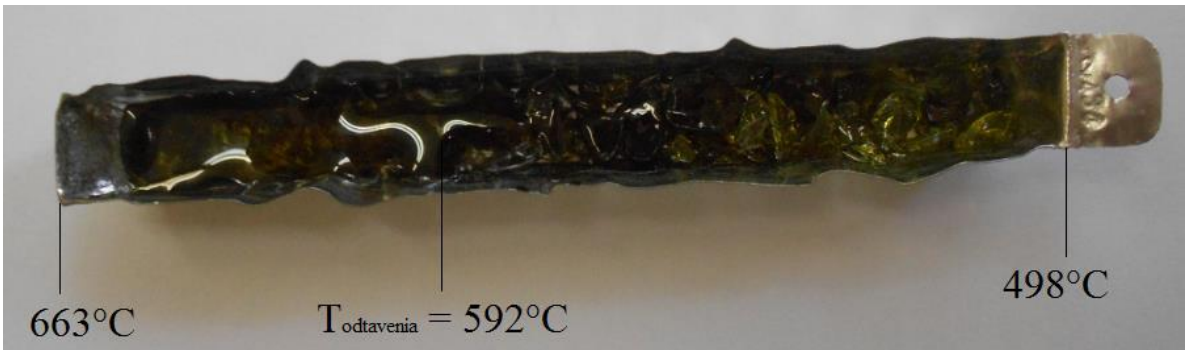
The liquidus temperature of the examined glass sample without additives is 698°C.

Figure 27 Glass sample (with additives) after 24h melting in furnace

The liquidus temperature of the examined glass sample with additives is 762° C.

And setting a suitable temperature for the melting of glass grit was also necessary. This temperature is initial temperature when the free space between the grains begins to close and bind the gases formed and formed in the vitrification process by the chrompik III salt dissolution. This initial temperature is determined optically and represents the temperature at which the melting of the glass grains occurs, i.e., the melting and joining of the grains occurs, i. the formation of the necks between the grains and the molten glass is continuously transformed into a homogeneous melt. When the temperature is increased further, the grains are combined and enclosed in the resulting space by gaseous substances such as, in particular, CO_2 in our case. This is an important indication in vitrification technology because it suggests when we can expect the raising of the glass surface due to the pressure of the CO_2 bubbles. The measurement results are shown in the following figures.

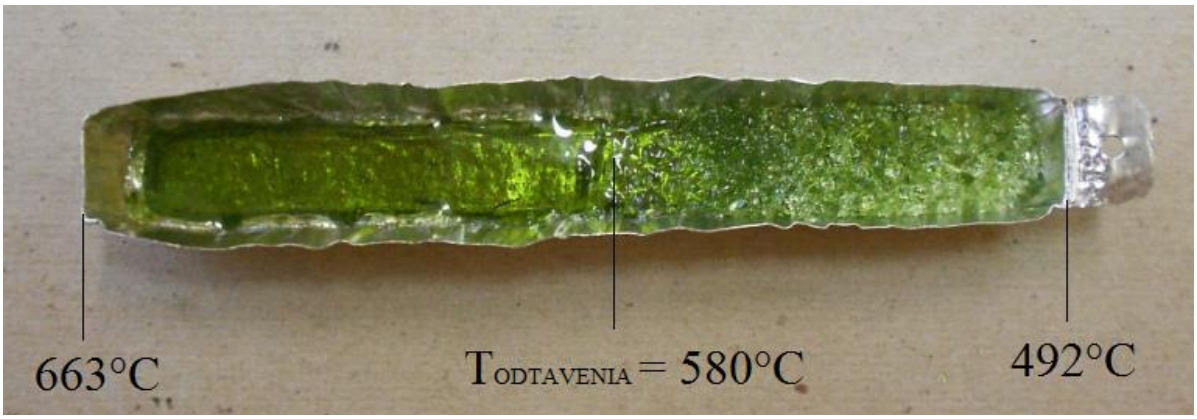
Figure 28 *Initial temperature- where occurrence of grains is observed, of prepared glass sample (without additives) after 24 hours in the furnace.*



Temperature interval 498-663°C

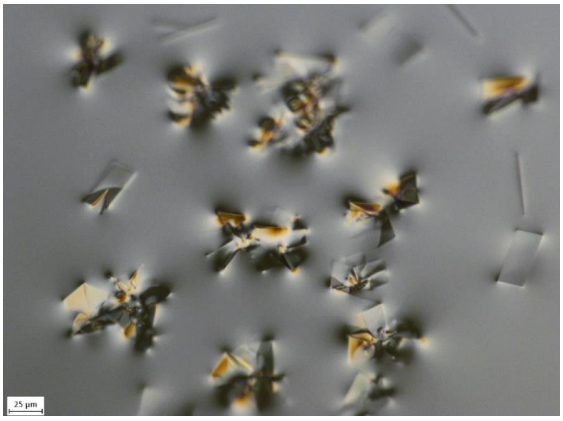
Figure 29 *Microscopic image of the prepared glass product sample (without additives) crystalline phase after 24 hours tempering at a temperature range of 788-607°C*

Figure 30 Initial temperature- where occurrence of grains is observed *of prepared glass product sample (with additives) after 24 hours in the furnace.*



Temperature interval 492-663°C

Figure 31 *Microscopic image of the prepared glass product (with additives) crystalline phase after 24 hours tempering at a temperature range of 787-605°C*



From these liquidus temperature determination results as well as the initial temperature of the additive-containing samples, their positive effect on the liquidus temperature increase (i.e., the higher crystal formation temperature compared to the glass sample without additives,) was seen. It has also been found that the additives reduce the initial temperature- temperature at which the melting of the glass grains occurs, which has a positive effect on the ^{137}Cs retention during the melting because a higher spherical barrier is created due to the formation of a homogeneous melt at a lower temperature for possible ^{137}Cs leakage. Glass necks between the particles of the mixture are formed at a lower temperature.

5 Post Trial Activities

The glass samples produced from chrompik III surrogate solution will be characterized in the framework of the THERAMIN WP4. In this context, the end- product was prepared as a glass monolith- see Figure 32. The leachability tests on Chrompik III non- active surrogate solution and basalt glass samples were estimated.

The characterizations will determine the sample:

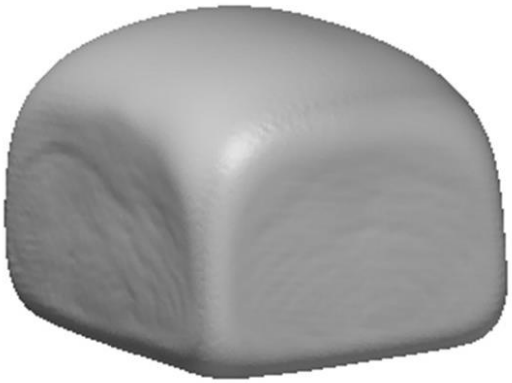
- chemical composition,
- surface of glass monolith,
- amorphous or crystalline nature and the structure of the possible crystals.

The analytical techniques that will be used are:

- scanning electron microscopy associated with X-ray energy dispersive microanalysis,
- SEM/EDX,
- SEM,
- X-ray fluorescence analysis (XRF),
- 3D scanning laser method.

The leachability tests on Chrompik III non- active surrogate solution and basalt glass samples were estimated.

Figure 32 Picture of glass monolith. Surface was determined by 3D scanning laser method



Surface 1257.77 mm^2
Volume 3522.67 mm^3
deviation ± 0.004 mm

In tables below are given results from chemical composition of glass frit, chrompik III and of glass frit and the new chemical composition of vitrified glass after melting with chrompik III and off-gas parameters.

6 Conclusions

Thermal treatment of chrompik III has been successfully demonstrated using the vitrification facility in NPP A1 Jaslovske Bohunice, Slovakia.
After completion of laboratory research and after the trials of modified VICHR facility, the chrompik III treatment on vitrification facility was evaluated. The trials with inactive surrogate solution of chrompik III and trials with real chrompik III were performed. In VUJE´s laboratories inactive glass samples were prepared in the framework of THERAMIN project. The effect of additives on the vitrification process was evaluated.
VICHR facility operation with chrompik III treatment is currently in progress.

7 References

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