

VITRIFICATION OF LOW AND INTERMEDIATE LEVEL WASTE: TECHNOLOGY AND GLASS PERFORMANCE

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ABSTRACT

Vitrification currently is being used successfully to immobilise high-level radioactive waste (HLW) from spent nuclear fuel reprocessing. Development of vitrification technologies for low and intermediate level radioactive waste (LILW) is becoming increasingly important and large programmes are initiated in a number of countries including Russia. Moscow SIA "Radon" has immobilised LILW operational waste from nuclear power plants (NPP) and institutional radioactive waste in borosilicate glass matrices since the 1970s. The current cold crucible high frequency induction melters (CCM) are used to vitrify liquid radioactive wastes collected from facilities in the central European part of Russia. Borosilicate glasses and glass composite materials immobilising LILW demonstrate reliable retention of radionuclides as confirmed by extended long-term tests in field conditions.

INTRODUCTION

Vitrification provides the maximum volume reduction of waste which, taking into account the large volumes of low and intermediate level radioactive waste (LILW), may result in significant reduction of transport and disposal costs. Development of vitrification technologies for LILW by the beginning of the 1970s provided waste forms with excellent resistance to corrosion and the possibility of developing simple engineered barrier systems [1-8]. The simplest disposal option for vitrified LILW is to locate the waste packages directly into earthen trenches as long as the host rock has the necessary sorption and confinement properties.

Vitrification of low-level radioactive waste is becoming currently increasingly important and large programmes are set up currently in a number of countries [1, 9-11]. Moscow SIA "Radon" began experimental vitrification of radioactive waste in the early 1970s [2-5]. The focus of this activity has been low-level operational waste from nuclear power stations and institutional radioactive waste that had previously been cemented or bituminised. Borosilicate glass was selected as a matrix to incorporate waste contaminants. Initially, single-stage slurry-fed Joule heated ceramic melters (JHCM) were used later replaced by cold crucible high frequency induction melters (CCM).

JOULE HEATED CERAMIC MELTER TECHNOLOGY

Figure 1 shows a schematic diagram of a single-stage slurry-fed JHCM from the pilot LILW vitrification plant EPOS [2]. The electrical power supply of this melter was 150 kW, with operational temperature in the melter of 1150 - 1250°C. The specific glass rate was from 40 to 50 kg/m²h at a melting ratio of 3.2 – 3.4 kWh/kg. The capacity of vitrification plant has been 50 kg of glass per hour for a reference liquid radioactive waste with total salt content about 200 g/l [2-5].

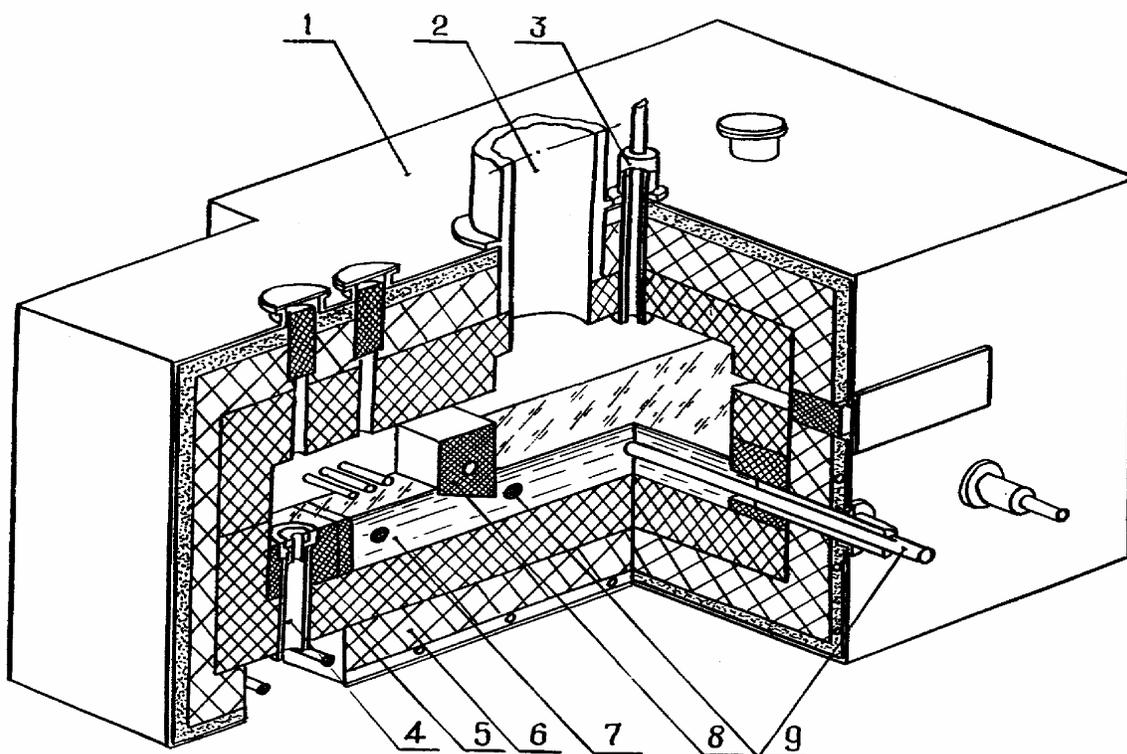


Fig. 1 Joule heated ceramic melter for LILW vitrification.

1-casing, 2-off gas outlet, 3-inlet tube, 4-pouring outlet, 5-ceramic vessel, 6-heat insulation, 7-glass melt, 8-baffle plate, 9-electrodes.

Liquid and solid low-level wastes have been vitrified from various sources including the Moscow wastewater purification plant, NPP and other minor producers. Wastes with specific activity up to 37 MBq/l and among them wastes from NPP using water-water (WWER) and channel type (RBMC) reactors have been vitrified [2-5]. The volume reduction factor in the process of vitrification has been from 4.2 to 4.5. Losses (carryover) of radioactive Cs from the melter in the process of vitrification have been below 3.5 %. The total amount of glass produced by the ceramic melter constituted more than 10 tonnes. This glass has been disposed at the experimental site for observation and safety evaluation.

COLD CRUCIBLE MELTER TECHNOLOGY

From 1999/2000 Moscow SIA “Radon” has operated a vitrification plant based on CCM to vitrify liquid radioactive wastes collected from facilities in the central European part of Russia [1, 6]. 20 – 25 kg/h capacity is suitable for vitrification of operational radioactive waste arising at a typical 1GW NPP [1] and the vitrification plant has three operating CCM. The total LILW vitrification plant capacity is therefore up to 80 kg/h of glass. In 2001 the vitrification plant processed 254.3 m³ of liquid LILW producing 2900 kg of glass. Some 30-tonnes of waste glass was synthesized by the middle of 2001 and disposed of at the site. Currently, the Moscow SIA “Radon” vitrification plant is considered as typical for erecting waste processing plants at Russian NPP to vitrify operational radioactive waste.

The vitrification technology comprises several stages, starting with evaporation of excess water from liquid radioactive waste (Fig. 2).

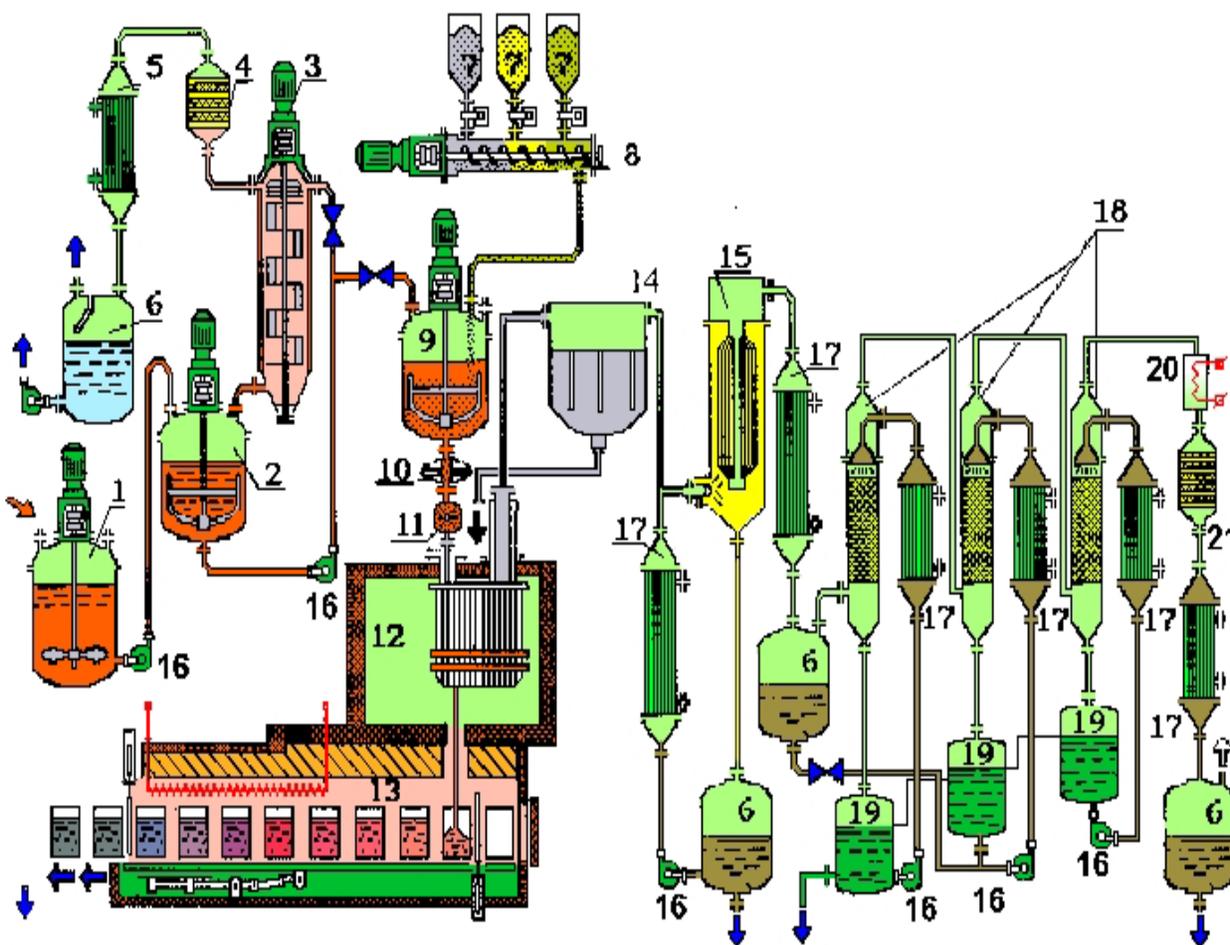


Fig. 2. Schematic of the Moscow SIA “Radon” LILW vitrification plant (USA Patent 6058741). 1-storage tank, 2-concentrator tank, 3-rotary evaporator, 4-filter, 5-heat exchanger, 6-collecting tank, 7-bins with glass-forming additives, 8-screw feeder, 9-mixer, 10-grinder, 11-feeder, 12-cold crucible melter, 13-annealing tunnel furnace, 14-coarse filter, 15-fine filter, 16-pump, 17-heat exchanger, 18-absorbing column, 19-acid collecting tank, 20-heater, 21-chemical reactor.

Concentrates with about 1000 g/l are obtained which then are intermixed with glass forming additives to form a paste-like batch. The paste contains both waste salts and glass-forming additives. Loam, datolite, bentonite, and silica are used as glass forming additives. Clay minerals stabilize the paste for extended periods of time sufficient for temporary storage and transportation through pipes to the processing area since the batch paste can be pumped without any settlement of salts. The batch paste is pumped directly into the CCM where both calcining and melting processes are carried out. The single stage vitrification process used in this immobilisation scheme diminishes radionuclide carryover and enhances efficiency.

The CCM has a modular assembly allowing easier maintenance. The CCM dimensions are (in mm) 250 x 800 x 700 with a filled weight of 130 kg. The crucible is located inside a copper induction coil (Fig. 3).

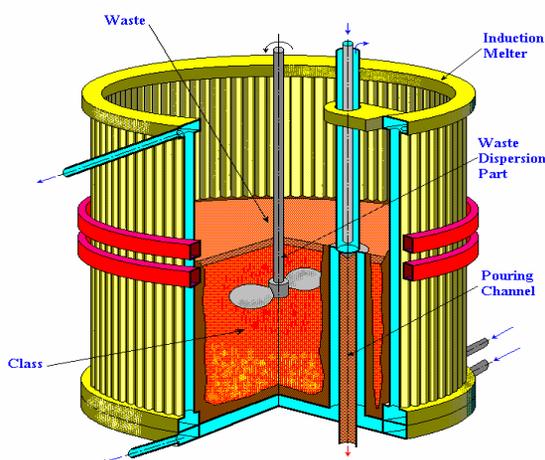


Fig. 3. Schematic of the Moscow SIA “Radon” cold crucible melter.

The CCM is assembled from water-cooled stainless steel tubes with cooling water consumption of 1.5 – 6 m³/h. During melting the tubes remain cold and a protective layer of glass batch material forms between the melt glass and tubes, thus insulating the tubes from the melt. The protective layer – skull – plays the role of refractory materials, required in conventional melters. The composition of the skull or *in situ* refractory [18] is determined by the glass batch composition so that the melt glass is always in contact with similar material to itself. The crucible energy supply is a high frequency 1.76 MHz generator with a vibrating power of 160 kW. To start operating the crucible graphite or metal waste chips are added to the first batch. The metal chips used are chosen to produce metal oxides of the same composition as waste constituents. The CCM melt surface area is 0.11 – 0.16 m² and the operation temperature for borosilicate glass melting is 1200 - 1250 °C.

From the melter the glass melt is poured into carbon steel containers with wall thickness of 1.5 – 2.0 mm and volume of 10 - 15 dm³. The glass blocks are then annealed passing slowly through a tunnel furnace, which has a negative temperature gradient (Fig. 2). The glass blocks exit the

plant and are held in a temporary storage area prior to transportation to the storage/disposal area. Table I summarises the CCM operating parameters for vitrification of NPP operational waste.

Table I Composition and properties of glass melts for vitrification of NPP operational wastes and CCM operating parameters.

Parameter/ Waste Arising	RBMC	WVER
Composition, wt. %	16.2Na ₂ O 0.5K ₂ O 15.5CaO 2.5 Al ₂ O ₃ 1.7Fe ₂ O ₃ 7.5B ₂ O ₃ 48.2SiO ₂ 1.1Na ₂ SO ₄ 1.2NaCl 5.7Others	24.0Na ₂ O 1.9K ₂ O 6.2CaO 4.3Al ₂ O ₃ 1.8Fe ₂ O ₃ 9.0B ₂ O ₃ 46.8SiO ₂ 0.8Na ₂ SO ₄ 0.9NaCl 4.3Others
Specific radioactivity of glass wasteform, Bq/kg	3.7 - 7.0 10 ⁶	2.7 10 ⁶
Melting temperature, °C	1150 ± 25	1130 ± 20
Viscosity (Pa s) of glass melt at 1200 °C	3.9	1.6
Specific resistivity (Ohm m) at 1200 °C	0.028	0.027
Specific capacity, kg/m ² h	120-160	140-180
Specific power consumption, kW h/kg	5.0-6.0	4.5-6.0
Carry over of solid fraction (aerosols), wt. %	1.0-1.2	1.0-1.2
Carry over of radionuclides (Cs-137), %	3.0-3.9	3-4

The resulting glasses were X-ray amorphous and replica transmission electron microscopy revealed they were homogeneous without inclusions exceeding 50 nm in size.

The right hand side Fig. 2 represents schematically the off gas purification system which is an integral component of the plant. The overall parameters of this system are summarised in Table II.

Table II Off gas cleaning system operational parameters

Volumetric flow rate, m ³ /h		Up to 100
Off gas temperature, °C	At the inlet	Up to 200
	At the outlet	Less than 50
Radioactive aerosols concentration, Bq/l	At the inlet	Up to 15
	At the outlet	Less than 0.015
Concentration of dust, mg/m ³	At the inlet	Up to 2000
	At the outlet	Less than 0.02
Concentration of NO _x , g/m ³	At the inlet	Up to 70
	At the outlet	Less than 0.01

The off gas purification system employs a series of scrubbers, filters, and chemical reactors (see Fig.2), which efficiently remove entrained particles, volatilised radionuclides, and other chemicals from the off-gas stream.

PRODUCT PERFORMANCE

The main parameters characterising glasses and glass composite materials used for LILW immobilisation are shown in Table III. Glass composite materials are used to immobilise glass-immiscible waste components s sulphates, chlorides, molibdates.

Table III Properties of vitreous waste forms for LILW

Waste Properties		form/	RBMK borosilicate	waste glass	WVER borosilicate	waste glass	Glass material	composite
Waste wt. %	oxide loading,		30-35		35-45		30-35 + up to 15% of yellow phase	
Viscosity, at 1200 °C	Pa	s	3.5-5.0		2.5-4.5		3.0-6.0	
Resistivity, at 1200 °C	Ohm	m	0.03-0.05		0.02-0.04		0.03-0.05	
Density, g/cm ³			2.5-2.7		2.4-2.6		2.4-2.7	
Compressive strength, MPa			80-100		70-85		50-70	
Leach rate, g/cm ² d after 28-th day of leaching for given nuclide	¹³⁷ Cs		10 ⁻⁵ – 10 ⁻⁶		~10 ⁻⁵		~10 ⁻⁵	
	⁹⁰ Sr		10 ⁻⁶ – 10 ⁻⁷		~10 ⁻⁶		10 ⁻⁶ – 10 ⁻⁷	
	Cr, Mn, Fr, Co, Ni		~10 ⁻⁷ – 10 ⁻⁸		~10 ⁻⁷		~10 ⁻⁷ - 10 ⁻⁸	
	REE, Actinides		~10 ⁻⁸		~10 ⁻⁸		~10 ⁻⁸	
	Na		10 ⁻⁵ – 10 ⁻⁶		~10 ⁻⁵		10 ⁻⁴ - 10 ⁻⁵	
	B		<10 ⁻⁸		<10 ⁻⁸		<10 ⁻⁸	
	SO ₄ ²⁻		~10 ⁻⁶ at content less than 1%		-		10 ⁻⁴ - 10 ⁻⁵ at content up to 15%	

Long-term tests of vitrified LILW have been carried out in a shallow ground experimental repository since 1987 [8]. These show a reasonable low and diminishing radionuclide leach rate summarised in Table IV [8, 12].

Table IV Annual Means for Normalized Leach Rates of Radionuclides (*R*) and Leached Inventory Fractions (*F*) for Exposure Durations of 1 Year and 14 Years

Waste glass	Leach rate <i>R</i> , g/cm ² day,		Leached inventory fractions <i>f</i> , %	
	For 1 st year	Over 14 years	For 1 st yr.	Total for 14 years
K-26	1.3·10 ⁻⁶	5.8·10 ⁻⁷	4 10 ⁻⁴	1.36·10 ⁻³
Bs-10	3.0·10 ⁻⁶	9.9·10 ⁻⁷	2 10 ⁻³	7.75 10 ⁻³

It is important to understand the potential changes in the leaching of radionuclides from the immobilising glass. Kinetics of glass alteration and leaching of radionuclides are governed by complex processes that depend on parameters of the glass, manufacturing technology, physical state and aqueous medium [13]. The initial stage of glass corrosion is controlled by incongruent ion exchange/interdiffusion, which is followed by congruent dissolution of glass. There is a certain time τ , which separates these basic mechanisms in such a way that for times $t \ll \tau$ the glass corrodes through ion exchange/interdiffusion, whereas for $t \gg \tau$ the glass corrodes through dissolution [13-15]. The characteristic time τ , which separates the two basic mechanisms of corrosion, is given by the universal equation:

$$\tau \cong \tau_0 \exp(2E_a/RT), \quad (\text{Eq. 1})$$

where τ_0 depends on the diffusion parameters of glass, E_a is the apparent activation energy of glass dissolution, R is the gas constant, and T is absolute temperature. For nuclear waste borosilicate glasses E_a is 70–90 kJ/mol [16]. Hence the transition from one mechanism of corrosion to another may take from several months to many thousands years, demonstrating that nuclear waste glasses may corrode both via ion exchange/interdiffusion and dissolution depending on the temperature of the disposal environment.

Figure 4 compares corrosion behaviour of vitrified HLW ($E_a=75\text{kJ/mol}$) and LILW ($E_a=68\text{kJ/mol}$). Heat is generated in HLW from radionuclide decay which therefore has a higher initial disposal temperature. In addition the disposal environment for HLW can also have a higher temperature. Hence leaching of vitrified HLW at high temperatures rapidly passes to the region where dissolution of the glass occurs.

In contrast to this LILW vitrified wastes are characterised by an extended period of ion-selective leaching, which is controlled by interdiffusion and ion exchange processes [13, 15, 17]. This period extends to many hundreds of years hence practically determining the behaviour of these glasses during the required period of disposal. The relatively low temperatures of the disposal environment cause extended incongruent leaching of vitrified LILW. For all of this period the leaching rate of radionuclides is expected to diminish slowly as seen from long-term tests of vitrified LILW in natural conditions [8, 12, 15].

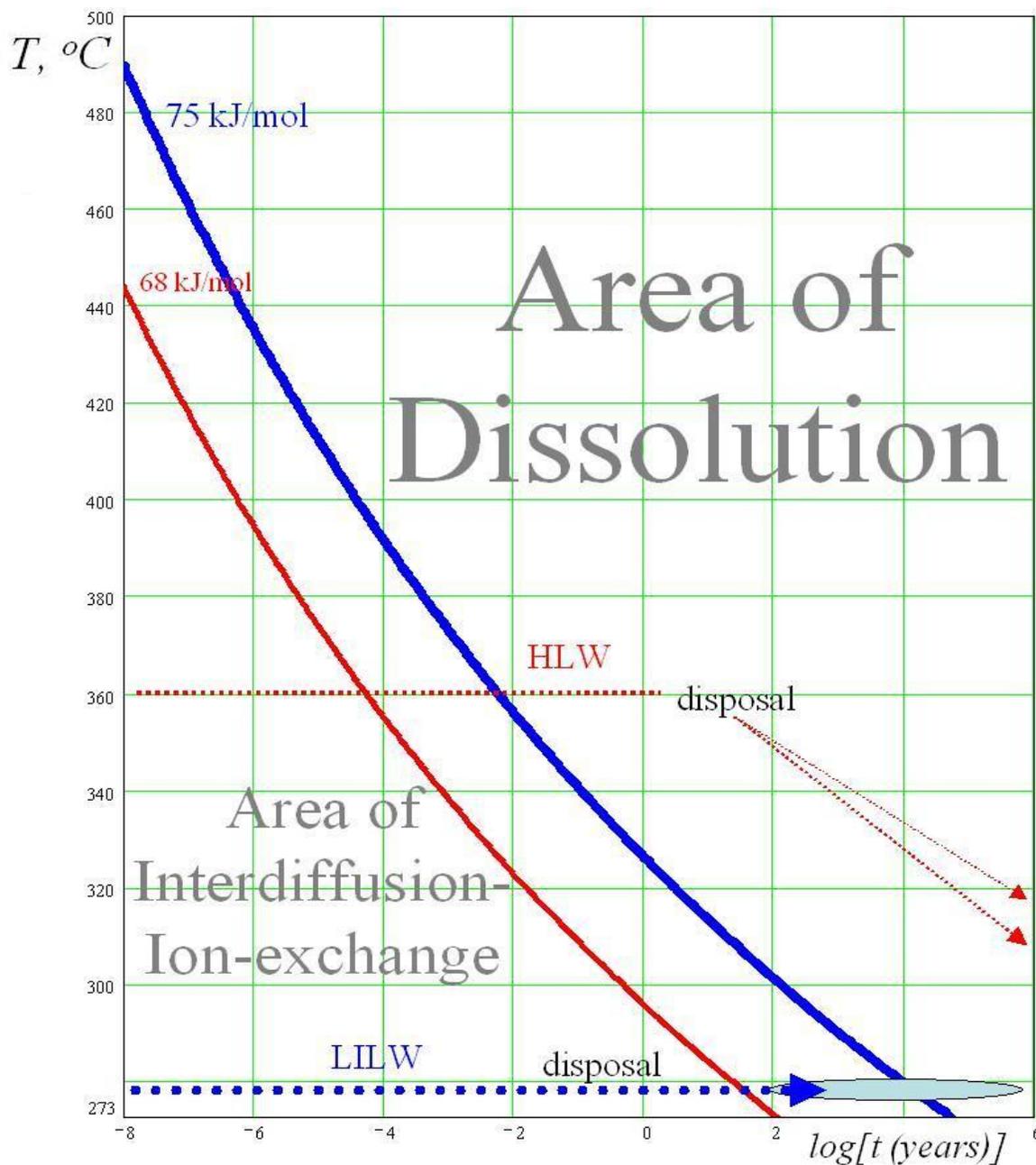


Fig. 4 Corrosion of Nuclear Waste Glasses as Function of Environment Temperature and Time

CONCLUSIONS

Vitrification technology is currently being used to immobilise LILW from NPP and other smaller radioactive wastes sources in Russia. Operational experience and field test experimental data demonstrate the viability and high efficiency of LILW vitrification technology.

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