A HISTORY OF VITRIFICATION PROCESS DEVELOPMENT AT SIA RADON INCLUDING COLD CRUCIBLE MELTERS

I.A. Sobolev, S.A. Dmitriev, F.A. Lifanov, A.P. Kobelev, S.V. Stefanovsky
SIA Radon
7th Rostovskii per. 2/14, Moscow 119121 RUSSIA

M.I. Ojovan
University of Sheffield
Sir Robert Hadfield Building, Mappin Street, S1 3JD, Sheffield, UK,

ABSTRACT

This paper describes SIA Radon experience in development and implementation of radioactive waste vitrification technology. Radon is a company involved in the system of Administration of Moscow responsible for management of radioactive waste from non-nuclear applications at Central Russia. Radon has started its activity in a field of waste vitrification process development since the middle of 1970s. The first unit implemented at Radon to vitrify low- and intermediate-level wastes with production of a borosilicate glass was a Joule-heated ceramic melter based plant with waste capacity of up to 10 L/h and glass productivity of up to 10 kg/h. The plant was improved and melter was upgraded step-by-step and semi-industrial-scale melter had waste capacity of up to 50 L/h and glass productivity of up to 35 kg/h. In the middle of 1980s a cold crucible melting process development was started and various cold crucibles for treatment of different liquid and solid wastes were designed. Since 1991 design and construction of a full-scale liquid waste vitrification plant was started. The plant consists of waste preparation, batch preparation and feeding, batch melting, glass annealing units, off-gas, water and energy supply systems. The melting unit is equipped with three cold crucibles with glass productivity each of up to 25 kg/h. Some different vitrification systems for conditioning of liquid and solid wastes (incinerator ash, ion-exchange resins, spent catalysts, etc.) based on cold crucibles and plasma melters were developed and tested. The results are briefly described as well.

INTRODUCTION

Scientific and Industrial Association (SIA) Radon is a state company involved in the system of the Administration of Moscow and responsible for management of radioactive waste from non-nuclear applications at Central Russia. The company deals with collection, transportation, interim storage, conditioning, and final disposal of low and intermediate level wastes (LILW) produced at various institutions, research laboratories, industry, medicine, municipal services, etc. Moreover Radon is responsible for conditioning of spent radiation sources and radioecological monitoring of Moscow and nine surrounding areas. Radon also works in cooperation with Minatom institutions on development and testing of processes for treatment of nuclear power plants (NPP), high level (HLW) and actinide wastes. This paper summarizes SIA Radon experience in development of waste vitrification process and design and implementation of technologies and facilities for its realization. The main attention is paid to the inductive cold

crucible melting (ICCM) and its application to treatment of various types of liquid and solid LILW.

DEVELOPMENT OF JOULE HEATED CERAMIC MELTER BASED PROCESS

Radon is under operation since 1961 and initially technologies of liquid LLW cementation, solid LLW compaction and later ILW bituminization were developed and implemented. Since the middle of 1970s Radon was involved in an activity on development of HLW vitrification process based on borosilicate glass production considered as an alternative to sodium-aluminophosphate glass production at PA "Mayak". A Joule-heated ceramic melter as a basic vitrification unit was chosen. Simultaneously alternatives to bituminization of high-salt ILW were searched and vitrification process was considered as one of the most promising among them. At the end of 1970s a first small-scale ceramic melter for ILW vitrification lined with Bakor-33 (melted baddeleyite-corundum) refractories and heated by molybdenum electrodes has been designed, constructed and tested. High sodium nitrate ILW surrogate was intermixed with calcium borosilicate flux (datolite) and sandstone and vitrified at 1100-1200 ^{0}C. Major process parameters were: ILW capacity – up to 10 L/h, glass productivity – up to 5 kg/h, melting ratio – 3.5 to 6.7 kW h/kg (depending on water content in slurry) [1,2].

In the middle of 1980s a bench-scale ceramic melter with glass productivity up to 15 kg/h was put in operation. To increase glass productivity a semi-liquid feeding (20-25 wt.% water content) was proposed. This plant consisted of waste preparation, batch preparation and feeding units, JHCM, annealing furnace, and off-gas system. Liquid waste was dried in a rotary film evaporator and mixed with glass forming additives (datolite and sandstone). Both screw feeder and peristaltic pump for slurry feeding were tested. JHCM inner dimensions were 800 mm × 400 mm × 600 mm. The bath was divided on melting (0.24 m^2) and pouring (0.04 m^2) zones. Two modifications of melter with different refractory lining were tested. In the first of them bottom, walls contacting with melt, and barrier were manufactured from chromia-alumina-zirconia refractory blocks. Gaps between blocks were sealed with alumina-chromia-phosphate binder. Melter walls over melt level were manufactured from alumina-silica refractory. Melter arch was constructed from high-alumina refractory slabs. The melter was heat-insulated. Melt was poured through tin dioxide tube 24 mm in internal diameter. The melter was energized with two molybdenum electrodes. During the testing refractories used were strongly corroded. Therefore, this melter was dismantled and some of refractories were replaced. The bottom of upgraded melter was manufactured from zirconia-alumina refractory "Bakor-33". Walls contacting with the melt, barrier between melting and pouring zones, and arch were constructed from high-alumina refractory. External cooling of the melter was also applied. "Bakor-33" refractory was resistant to corrosion by borosilicate melt. First tests with actual ILW were performed at this unit [3,4].

In 1987 a pilot plant based on large-scale ceramic melter was designed and constructed (Fig. 1). New large-scale melter was manufactured from the same refractories as the preceding one. But melter dimensions were increased. Melting and pouring zones measure 1500 mm × 400 mm and 600 mm × 200 mm, respectively. Water-cooled barrier between them was manufactured from heat-resistant steel pipe and cooled with water. Melt pouring was carried out from the level of 150 mm through vertical hole drilled in a tin dioxide block. This plant was equipped with off-gas

system consisted of wet scrubber, heat-exchanger, condensate collector, drop collector, and HEPA filter.

Experiments on vitrification of institutional and Nuclear Power Plants wastes were successfully performed at that plant. Melting ratio ranged between 2.9 kW h/kg and 3.2 kW h/kg. Waste capacity and glass productivity achieved were 50 L/h and 35 kg/h, respectively.
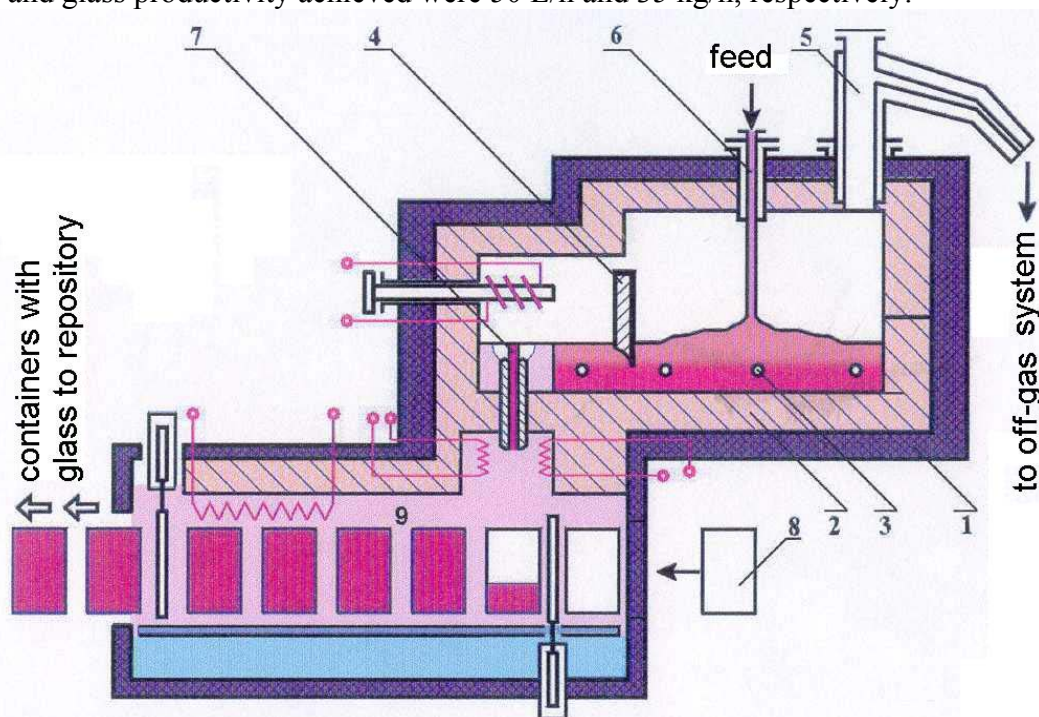

Fig. 1 The Radon JHCM Design.

1 – Heat insulation, 2 – Refractory lining, 3 – Mo electrodes, 4 – Barrier between melting and pouring zones, 5 – Off-gas pipe, 6 – Batch feeding port, 7 – Pouring unit, 8 – Containers, 9 – Annealing furnace.

Specific glass productivity was 50-50 kg/(h m^2). Cesium loss ranged between 2.5 % and ~7 % depending on batch composition and moisture [5,6].

Nevertheless numerous disadvantages of the JHCM such as high refractories and electrodes corrosion rate, low specific productivity, large overall dimensions and weight forced to search new solutions free from above-listed problems. Various types of melters such as ceramic pot, "hot crucible", metal pot with submerged metal electrodes, plasma melter and "cold crucible" were tested to find more reliable, low dimensional, high-temperature melter with longer lifetime. The most attention was paid to a cold crucible melter successfully applied before to produce high-temperature glasses and ceramics [7].

DEVELOPMENT OF COLD CRUCIBLE MELTING PROCESS

The cold crucible is preferable over JHCM due to absence of refractories and electrodes, no contact of metal walls with high temperature melt, and the presence of an active hydrodynamic regime. The "cold crucible" is a vessel formed by metal tubes with good heat conductivity and placed within the copper inductor. Tubes from the inside are water-cooled. Thus, even during melting, tubes remain cold and the protective layer (so-called "skull") forms between melt and tubes. The "cold crucible" is preferable over JHCM due to no refractories and electrodes, no contact of metal walls with high temperature melt, and active hydrodynamic regime. The "cold crucible" has high specific capacity and small overall dimensions and weight. The principle of the cold crucible "skull" melting is based on heating of conductive melt in high-frequency electromagnetic field, which is created by generator operated at frequencies of 10^5-10^6 Hz (allowed frequencies are 0.44, 1.76, 5.28 MHz). Electromagnetic field from inductor penetrates through the gaps between the pipes forming the "cold crucible". Due to vigorous mixing by Foucault currents, melt is homogeneous and melt productivity is very high.

Since the middle of 1980s a cold crucible melting (CCM) process was being developed and cold crucibles with variable dimensions and geometry and experimental facilities were being designed and constructed. Three types of crucibles for continuous and semi-continuous modes of operation were designed. First of them was analog of the JHCM. It was a vessel of elliptic form with barrier dividing melting and homogenizing (pouring) zones and preventing an ingress of feed into the pouring zone. Melt is poured from the melt level. This crucible was preferably designed for liquid waste vitrification.

The second type of the "cold crucible" was the vessel of round or elliptic form equipped with pouring unit. The feed may be performed periodically or continuously. The melt level in the crucible rises until specified value. Then, melt is discharged until pouring level. Such crucible was originally designed for incinerator ash vitrification, but it may be used for liquid waste vitrification as well.

The third type of the "cold crucible" is crucible equipped with agitator. This crucible was designed for production of glass composites and high viscous melts [8].

First experiments were performed with small-scale copper cold crucibles (1 to 3 L) energized from 20 kW high frequency (HF) generator operated at 5.28 MHz. The next step was a small-scale plant equipped with 60 kW HF generator operated at 1.76 MHz [4]. Most of lab- and bench-scale tests including development and testing of waste forms were performed and is performed now at this plant.

Numerous experiments were also carried out with 160 kW HF generator operated at 1.76 MHz designed by Institute of High Frequency Currents (St-Petersburg) [9]. This unit was used for development, optimization, and testing of cold crucibles designed for industrial-scale liquid and solid LILW vitrification plants. In particular, industrial-scale "cold crucible" with measures 590 mm in length, 300 mm in width, 655 mm in height and 10.18 dm^2 in melt surface area has been designed (Fig. 2).

Various glass, glass-crystalline, ceramic, and glass-composite materials containing insoluble components distributed in a glass matrix were produced at lab- and bench-scale units. These early works were performed in cooperation with Bochvar Institute of Inorganic Materials (Moscow) and Institute of Electric Engineering (St-Petersburg). Numerous materials containing simulated ILW and HLW and actual ILW such as borosilicate glass, high fusible aluminosilicate and aluminosilico-phosphate glasses and glass-crystalline materials, melted incinerator ash, melted contaminated soils, various Synroc formulations which cannot be obtained in the JHCM were successfully produced in the CCM and examined in details. First CCM samples of melted Synroc-A, B, and C formulations were obtained in early 1991 [10]. The cold crucibles for various applications, including spent ion-exchange resin incineration, inorganic ion-exchangers melting were also designed and tested. Some of these works were performed in cooperation with SGN Company, France [11].

Successful CCM tests on vitrification of ILW surrogate allowed to starting design of a full-scale vitrification plant. Its construction has been started since 1990 and completed in 1997. The plant was put in inactive operation in 1998 and vitrification of actual ILW was started since the beginning of 1999. The plant consists of waste preparation, batch preparation, vitrification, off-gas, process control, and supply systems. Liquid ILW is concentrated in a rotary film evaporator to salt content of ~1000 kg/m^3 and intermixed with glass-forming additives (datolite, bentonite and silica) producing slurry with 20-25 wt.% water content. Slurry is fed by peristaltic pumps into the cold crucibles (3 items) melted and molten glass is poured into 10 L containers following by annealing in a tunnel furnace (pouring into 200 L drums was also tested). Process temperature is 1150-1200 ^{0}C, total glass productivity (for 3 crucibles) is up to 80 kg/h at 30-35 wt.% of waste oxides loading. Resulting glass composition (in wt.%) is 15-20 Na_2O, 13-17 CaO, 2-5 MgO, 4-6 Al_2O_3, 4-6 B_2O_3, 2-5 Fe_2O_3, 45-50 SiO_2, 2-4 the others (including radioactive isotopes of Cs, Sr and corrosion products). Cs and Sr leach rates (IAEA test) are 10^{-6}-10^{-7} $g/(m^2$ day), electric resistivity – 0.03-0.05 Ohm m, melt viscosity – 4-5 Pa s. Off-gas system consists of sleeve filters, HEPA filters, NO_x absorbing columns, and catalytic reactor for residual NO_x decomposition. Process flow sheet is shown on Fig. 3 [9,12,13].
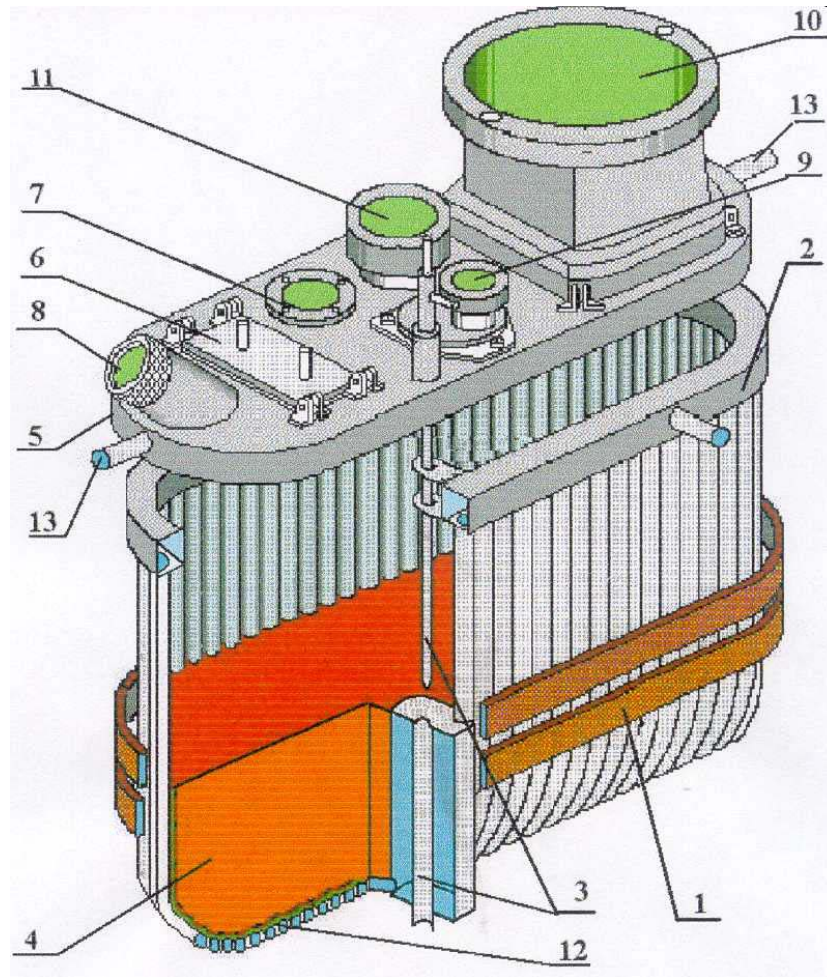
Fig. 2 Design of the CCM for liquid waste vitrification

1 – Inductor, 2 – Water collector, 3 – Pouring unit, 4 – Melt, 5 – Cover, 6 – Starting material feeding port, 7, 9 – technological ports, 8 – Monitoring window, 10 – Off-gas pipe, 11 – Slurry feeding port, 12 – Cold crucible forming pipes with skull, 13 – Cooling water inlet and outlet.
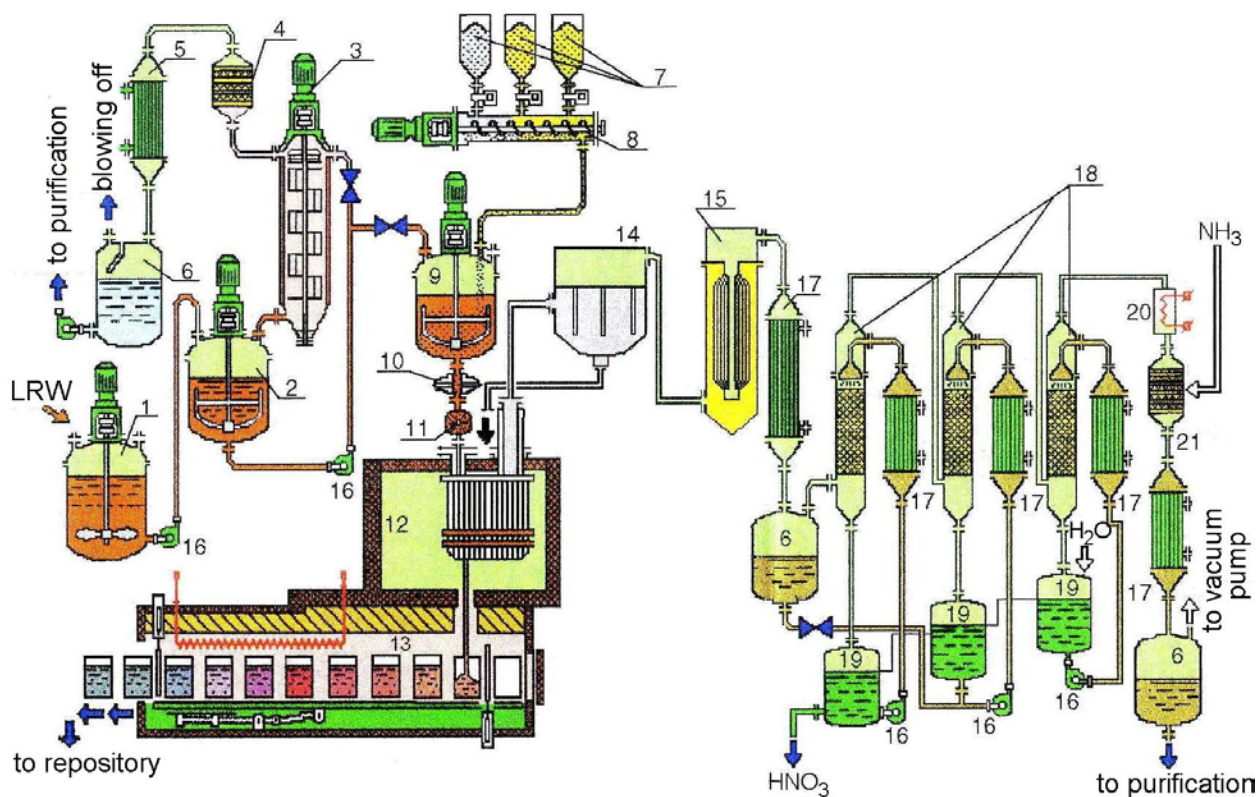
Fig. 3 Liquid ILW vitrification process flowsheet.

1 – Interim storage tank, 2 – Concentrate collector, 3 – Rotary film eveporator, 4, 15 – HEPA-filters, 5, 17, 21 – Heat-exchangers, 6, 19 – Reservoirs, 7 – Glass forming additives hoppers, 8 – Screw feeder, 9 – Batch mixer, 10 – Mechanical activator, 11 – Peristaltic pump, 12 – Cold crucible, 13 – Annealing furnace, 14 – Sleeve (coarse) filter, 16 – Pumps, 18 – Absorption columns, 20 – Heater.

Process parameters are: liquid waste capacity – up to 200 L/h, single melter glass productivity – up to 25-30 kg/h, maximum glass productivity (3 crucibles) – up to 80 kg/h, off gas purification efficiency – up to 99.9%, NO_x purification efficiency – up to 99.5%, energy expenses – 5-7 kW h/kg.

Simultaneously alternative vitrification routes such as cyclone vitrification, plasma melting, solidification with powder metal fuel (similar to self-sustaining synthesis process) were developed and tested. Plasma melting/vitrification may be designed in continuous (flow) and periodical (batch) versions. Flow process was developed as an alternative to vitrification in ceramic melters. There was an attempt to develop small-sized high productive melter to replace large JHCM. Such a system based on a flow plasmachemical reactor was designed by specialists of Radon Institute and Institute of Heat and Mass Transfer (Minsk, Belarus) [14]. However, it has been found that residence time in the plasma reactor was insufficient to complete glass formation and homogenization and an additional homogenization unit under plasma reactor should be installed. In this case plasma flow reactor was suggested to be used as a high efficient denitration and calcination unit to be combined with the bulk melter. The system consisted of the

plasma reactor and the JHCM was constructed in 1983. Then, the cold crucible was substituted for the ceramic melter. Glass productivity of the combined system was calculated to range between 70 and 100 kg/h at 400-500 kW of overall power. An availability of a batch pre-treatment (granulation, fritting in the off-gas flow) is also under consideration. Possible application of high-frequency inductive plasmatrones is being also discussed.

Recently a combined shaft furnace – cold crucible melting/vitrification system was proposed (Fig. 4). This system is supposed to be efficient for treatment of solid radioactive and mixed wastes. Solid waste packages are fed into the shaft which may be additionally heated by plasmatrones and move to the bottom part passing steps of heating, drying, decomposition, mineral formation, and melting of inorganic residue in the cold crucible. Currently operating bench-scale unit has solid waste capacity of up to 5 kg/h at vibrating power of HF generator of 60 kW but waste capacity may be substantially increased by applying of plasma heating.

The batch plasma melting/vitrification process is effective for conditioning of small amounts of high-fusible wastes. A unit with swinging bottom heated by two arc plasmatrones with solid waste capacity of up to 25-30 kg/h has been designed and constructed [15].

A powdered metal fuel (PMF) solidification process seems to be promising for treatment of various LLW such as contaminated soils, silts, and spent inorganic ion-exchangers [13,16-18]. The process is based on application of thermochemical exothermic redox reactions in the mixture of PMF and radioactive waste with high heat release, to achieve high temperatures in reaction zone and melting of the mixture producing glass-like material without external energy source. Powdered metal fuel (PMF) is selected especially for the specified waste composition. The PMF is composed of metal or intermetallic powders, stabilizers, surfactants and other constituents. The process of batch vitrification of small portions of inorganic radioactive wastes such as incinerator ashes, contaminated soils, inorganic sorbents is performed in metallic containers having double walls with filling with refractory material between them. The technology provides for intermixing of waste with PMF, charge of this batch in the crucible, initiating, and thermochemical process conduction. The final product in blocks with weight of up to 50 kg is composed of PMF and waste oxides and has glassy structure, quite high density and low porosity.

DEVELOPMENT OF INTERMEDIATE-LEVEL WASTE FORMS

Vitrification of low- and intermediate-level radioactive wastes (LILW) was proposed in SIA "Radon" in the middle of 1970's [1,2]. First step of work included the development and testing of borosilicate glasses for immobilization of liquid waste containing mainly sodium nitrate. Various boron-containing minerals as well as sandstone were tested as glass-forming additives. Datolite $CaBSiO_4(OH)$ seemed to be the most suitable fluxing agent. Partial systems Na_2O (LILW oxides) - $2CaO \cdot B_2O_3$ - SiO_2 were studied and glass formation regions, melt viscosity and resistivity, leach rate of sodium (and ^{137}Cs for actual waste), density, radiation stability, and compressive strength were measured. Suitable glass composition areas were established [4]. The most important properties of these glasses are given in Table I.

Loam and bentonite clays as glass forming additives were also used. Up to 50% of either loam clay or bentonite in the batch was substituted for sandstone. This substitution increases chemical durability of glass and, moreover, such batch containing 20-25 wt% of water forms stable homogeneous paste being able to be maintained for a long time without segregation and transported in pipes for a long distance [4].
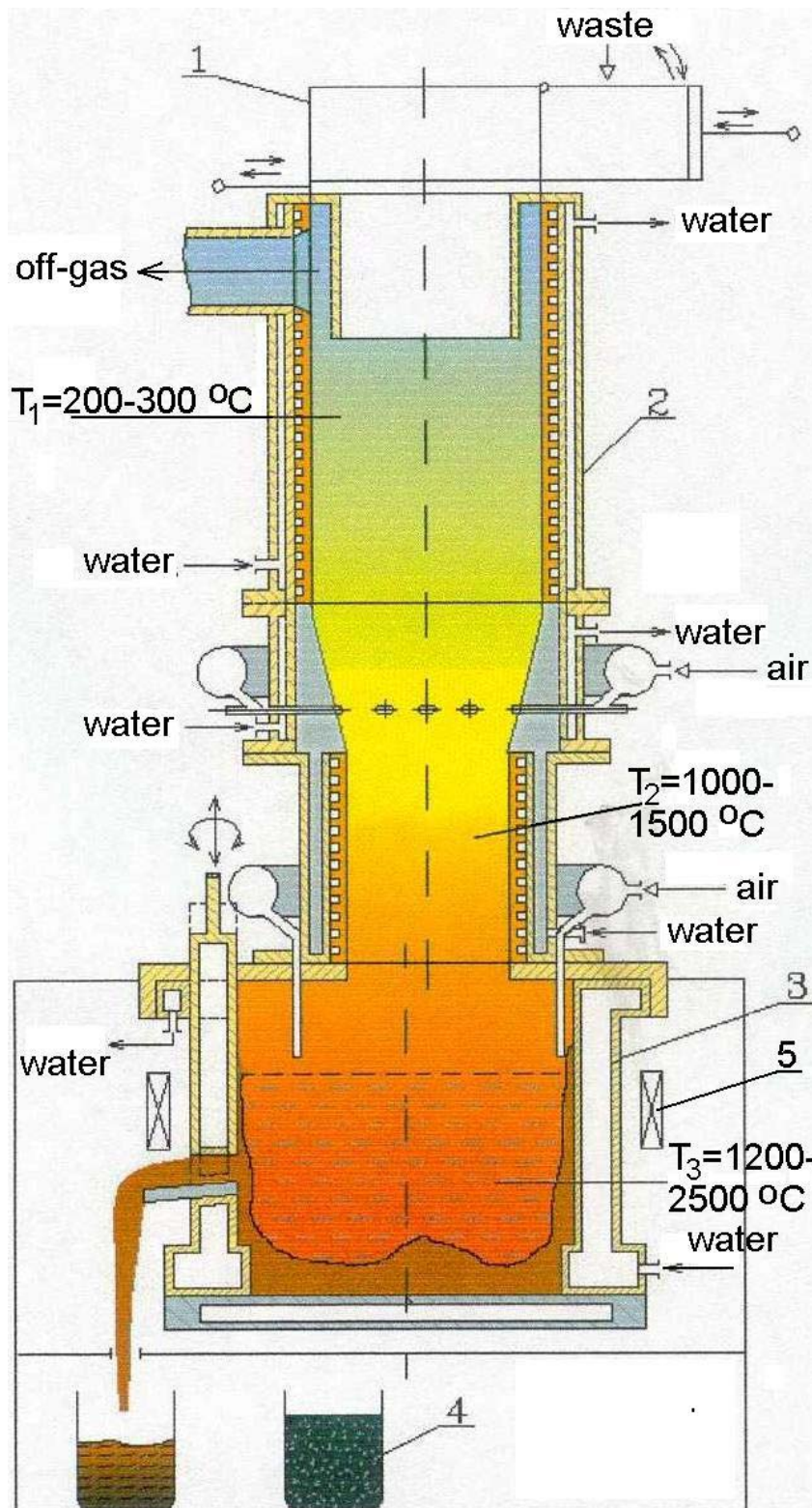
Fig. 4 The combined shaft furnace – cold crucible unit

1 – Loading unit, 2 – Shaft, 3 – Cold crucible, 4 – Containers,
5 – Inductor

Table I Properties of liquid LILW glasses

Properties		Datolite-based borosilicate glasses, containing high sodium LILW	Borosilicate glasses, containing WWER waste	Loam-based alumino-silicate glasses, containing high sodium LILW	Sulfate-containing vanadia-doped borosilicate glasses	Sulfate-containing lead-doped borosilicate glasses	Glass composites
Waste oxide content, wt.%		30-35	35-45	30-45	15-25	10-20	15-30
Viscosity, Pa s, at 1200 ^{0}C		3.5-5.0	2.5-4.5	3.5-6.5	2.5-4.5	2.0-3.5	3.0-6.0*
Resistivity, Ω m, at 1200 ^{0}C		0.03-0.05	0.02-0.04	0.04-0.06	0.015-0.035	0.015-0.025	0.03-0.05*
Density, g/cm^3		2.5-2.7	2.4-2.6	2.5-2.6	2.5-2.6	2.8-3.5	2.4-2.7
Compressive strength, MPa		80-100	70-85	70-90	80-100	80-100	50-70
Leach rate, g/(cm² day), (28-day IAEA test)	^{137}Cs	10^{-5}-10^{-6}	~10^{-5}	~10^{-5}	~10^{-4}-10^{-5}	~10^{-5}	10^{-4}-10^{-5}
	^{90}Sr	10^{-6}-10^{-7}	~10^{-6}	~10^{-7}	10^{-6}-10^{-7}	10^{-6}-10^{-7}	10^{-6}-10^{-7}
	Cr, Mn, Fe, Co, Ni	~10^{-7}-10^{-8}	~10^{-7}	~10^{-7}-10^{-8}	~10^{-7}-10^{-8}	~10^{-7}	10^{-7}-10^{-8}
	REE, An	~10^{-8}	~10^{-8}	~10^{-8}	~10^{-8}	~10^{-8}	~10^{-8}
	Na	10^{-5}-10^{-6}	~10^{-5}	~10^{-5}	~10^{-4}-10^{-5}	~10^{-5}	10^{-4}-10^{-5}
	B	<10^{-8}	<10^{-8}	-	10^{-6}-10^{-7}	~10^{-8}	≤10^{-8}
	SO$_4$$^{2-}$	~10^{-6} (if present)	-	10^{-5}-10^{-6} (if present)	~10^{-5}	~10^{-5}	10^{-4}-10^{-5}

* for vitreous phase

Sodium nitrate is the major component of both institutional liquid LILW and Nuclear Power Plant (NPP) operational wastes from RBMK reactor. NPP waste from WWER reactor contains boron and the major components of this waste are sodium nitrate and sodium tetrahydroxyl borate NaB(OH)$_4$. To vitrify WWER waste there is no necessity to add boron-containing additives to waste. Silica, loam or bentonite clay or their mixtures are suitable as glass forming additives [4-6,8,9]. Respectively, WWER waste glasses relate to systems Na$_2$O-(Al$_2$O$_3$)- B$_2$O$_3$-SiO$_2$. Glass formation regions in these systems are well-known. Some of glass properties are given in Table I.

Aluminosilicate-based boron free glasses for immobilization of institutional and RBMK wastes were also designed. They are produced from waste, sandstone and loam clay (or bentonite) and relate to Na$_2$O-(CaO)-Al$_2$O$_3$-SiO$_2$ system.

As seen from Table I, both institutional and NPP waste glasses have a good chemical durability, mechanical strength and radiation stability.

However, some liquid waste streams contain essential content of sulfate and chloride ions. Because of very low sulfate and chloride solubility in silicate and borosilicate melts, waste oxide

content is limited by 5-10 wt% and LILW vitrification becomes inefficient. Solubility limit for each sulfate and chloride ions was estimated to be 1%. Excess is segregated as a separate phase floating on the melt surface due to immiscibility of silicate and sulfate (chloride) melts. The same phenomenon occurs at molybdate- and chromate-containing waste vitrification, where separate phase is colored and named "yellow phase" [19]. To increase the waste oxide content in glass two ways are possible: 1) addition of components increasing sulfate and chloride solubility, such as lead or vanadium oxides; 2) vigorous melt agitation following by fast cooling down to upper annealing temperature to fix dispersed sulfate-chloride phase into the host borosilicate glass. Sulfate-chloride-containing glasses have slightly lower chemical durability compared to sulfate-chloride free aluminosilicate and borosilicate glasses (Table II), but it is sufficiently high to apply these glasses for waste immobilization.

Table II Properties of solid LILW glasses and glass-ceramics (containing incinerator ash)

Properties	Fluxing agent				
	$Na_2O\ 2B_2O_3$	$Na_2O\ nSiO_2$	TiO_2 and other Synroc oxides (CaO, BaO, Al_2O_3, ZrO_2)	Borosilicate frit	Dolomite: Loam clay (Bentonite) = 2:1
Waste oxide content, wt.%	80-95	40-80	30-80	50-80	70-85
Viscosity, Pa s, at 1300 ^{0}C	3.0-6.0	4.0-9.5	4.0-8.5	4.0-8.0	6.0->10
Resistivity, Ω m, at 1300 ^{0}C	0.025-0.050	0.03-0.13	0.05-0.10	0.035-0.075	0.04-0.10
Density, g/cm^3	2.5-2.7	2.5-2.7	3.0-4.0	2.5-2.7	2.6-2.8
Compressive strength, MPa	500-800	70-90	80-130	75-90	80-100
Leach rate, g/(cm²day) (28-day IAEA test) ^{137}Cs	$\sim 10^{-5}$	10^{-6}-10^{-7}	10^{-6}-10^{-7}	10^{-6}-10^{-7}	10^{-7}-10^{-8}
^{90}Sr	$\sim 10^{-6}$	$\sim 10^{-8}$	$\sim 10^{-8}$	10^{-7}-10^{-8}	$\leq 10^{-8}$
Cr, Mn, Fe, Co, Ni	$\leq 10^{-8}$	$\leq 10^{-8}$	$\leq 10^{-8}$	$\leq 10^{-8}$	$\leq 10^{-8}$
REE, An	$\leq 10^{-8}$	$\leq 10^{-8}$	$\leq 10^{-8}$	$\leq 10^{-8}$	$\leq 10^{-8}$
Na	$\sim 10^{-5}$	$\sim 10^{-6}$	$\sim 10^{-6}$	$\sim 10^{-7}$	$\sim 10^{-7}$
B	$\sim 10^{-6}$	-	-	$\leq 10^{-8}$	-

Another type of LILW to be vitrified is incinerator ash. Chemical composition of ash formed at Radon incinerator is (wt%) 2-8 Na_2O, 3-9 K_2O, 8-20 CaO, 3-7 MgO, 4-18 Al_2O_3, 3-33 FeO_n, <1-2 MnO, 1-3 Cr_2O_3, 14-38 SiO_2, <1-4 TiO_2, 2-22 P_2O_5, 2-14 ignition loss (organic residue and carbon). Ash contains oxides being jointly able to form glass. However melting point of such glass is very high (>1400 ^{0}C). To decrease the melting point, a flux must be added. A numerous flux additives were tested, for example, sodium silicates $Na_2O\bullet(2\div4)SiO_2$, sodium tetraborate $Na_2O\bullet2B_2O_3$, borosilicate frit (LILW glass breakage with average composition, wt%, 20 Na_2O, 15 CaO, 5 MgO, 4 Al_2O_3, 6 B_2O_3, 5 Fe_2O_3+MnO+Cr_2O_3+TiO_2, 45 SiO_2), mixture of dolomite $CaMg(CO_3)_2$ with loam clay or bentonite (2:1) [20] and TiO_2 and other Synroc additives (CaO, BaO, Al_2O_3, ZrO_2) [21]. All of these fluxes are suitable. The lowest melting temperatures were

in the system with borate flux (1100-1250 ^{0}C). In the systems with borosilicate frit and sodium bisilicate homogeneous melts may be produced at 1250-1350 ^{0}C. Formation of homogeneous products in the systems with sodium tetrasilicate and dolomite-clay mixture requires temperatures as many as 1350 ^{0}C. The products may be partially crystallized. Glass-crystalline materials with Synroc components are melted at 1300-1500 ^{0}C. Solidified products are composed of Synroc (zirconolite, hollandite, rutile) and aluminosilicate (leucite, celsian) or titanosilicate (sphene, fresnoite) phases distributed in matrix glass. Glass-ceramic obtained using Synroc additives is very similar to early Synroc-A formulation. The main properties of ash-containing glasses and glass-crystalline materials are given in Table II.

Leach rates of sodium and cesium from ash-containing materials as a rule are lower than from glasses, containing liquid waste oxides - 10^{-6}-10^{-7} and 10^{-5}-10^{-6} g/(cm^2 day) respectively. Except β-γ-emitters (^{137}Cs, ^{90}Sr, ^{60}Co, ^{144}Ce, etc), ash contains essential amounts of α-emitters (U, Pu, Am). Their leach rates by approximately two orders of magnitude lower than cesium.

It has been recognized that common vitrification of liquid and solid radioactive and toxic wastes is the most expedient. Contaminated soil, spent inorganic ion-exchangers, broken CRT glass and laboratory dishes, and spent filter materials (silica gel, glass fibers, porous glass) were tested as glass forming additives to liquid LILW (Table III) [22]. Joint vitrification of solid and liquid radioactive and hazardous wastes achieves the highest waste volume reduction factor.

Table III Properties of mixed waste vitrification products (in wt%)

Properties		Liquid LILW oxides -30, Contaminated soil (Loam clay)-70	Liquid LILW oxides -30, Broken CRT lead-containing glass - 70	Liquid LILW oxides -30, Spent zeolite -70	Liquid LILW oxides -30, Soil - 30, Laboratory dishes -20, Spent filter materials -20
Waste oxide content, wt.%		100	100	100	100
Viscosity, Pa s, at 1300 ^{0}C		6.1	3.0	3.5	4.3
Resistivity, Ω m, at 1300 ^{0}C		0.047	0.024	0.036	0.040
Density, g/cm^3		2.6	3.5	2.6	2.7
Compressive strength, MPa		75	84	86	83
Leach rate, (28-day IAEA test) g/(cm^{2}day day	^{137}Cs	8 10^{-6}	2 10^{-5}	3 10^{-6}	3 10^{-6}
	^{90}Sr	1 10^{-6}	2 10^{-6}	4 10^{-7}	2 10^{-7}
	Cr, Mn, Fr, Co, Ni	~10^{-7}	~10^{-7}	~10^{-7}	~10^{-7}
	REE, An	~10^{-7}	~10^{-8}	~10^{-8}	~10^{-8}
	Na	1 10^{-5}	3 10^{-5}	6 10^{-6}	5 10^{-6}
	Pb	-	3 10^{-6}	-	-

Glassy slags produced using the PMF are also composed of vitreous and few crystalline phases, mainly silicates and aluminosilicates, but they are compositionally inhomogeneous.

CONCLUSION

For almost 30 years of SIA Radon experience waste vitrification technologies based on JHCM and CCM have been developed and implemented. Radon has passed the way from lab-scale units to industrial-scale facility and the full-scale vitrification plant based on CCM is under operation now processing actual ILW. Development of new technologies is in progress.

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