

HIGH LEVEL LIQUID WASTE SOLIDIFICATION USING A "COLD" CRUCIBLE INDUCTION MELTER

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ABSTRACT

At the present time the primary problem in a closed nuclear fuel cycle is the management of high level liquid waste (HLLW) generated by the recovery of uranium and plutonium from the spent nuclear fuel. Long-term storage of the HLLW, even in special storage facilities, poses a real threat of ecological accidents. This problem can be solved by incorporating the radioactive waste into solid fixed forms that minimize the potential for biosphere pollution by long-lived radionuclides and ensure ecologically acceptable safe storage, transportation, and disposal. In the present report, the advantages of a two-stage HLLW solidification process using a "cold" crucible induction melter (CCIM) are considered in comparison with a one-stage vitrification process in a ceramic melter. This paper describes the features of a process and equipment for two-stage HLLW solidification technology using a "cold" crucible induction melter (CCIM) and its advantages compared to a one-stage ceramic melter. A two-stage pilot facility and the technical characteristics of the equipment are described using a once-through evaporated and induction cold-crucible melter currently operational at the IA "Mayak" facility in Ozersk, Russia. The results of pilot-plant tests with simulated HLLW to produce a phosphate glass are described. Features of the new mineral-like waste form matrices synthesized by the CCIM method are also described. Subject to further development, the CCIM technology is planned to be used to solidify all accumulated HLLW at Mayak – first to produce borosilicate glass waste forms then mineral-like waste forms.

INTRODUCTION

The process for HLLW solidification should accept different radioactive and toxic reprocessing waste feeds, operate under remote and safe controls, convert all radionuclides into an acceptable solid form, and purify off gases to achieve acceptable atmospheric emission concentrations.

The main source of HLLW is the aqueous waste solutions remaining after extraction of U and Pu during reprocessing of spent nuclear fuel from nuclear reactors. Improvements in existing reprocessing technologies and development of new ones considerably broaden the spectrum of HLLW requiring solidification. Currently, HLLW fractionation technology is under development to separate out, for example, Cs, Sr, lanthanides, and actinides. All of these fractions will require to be immobilized in suitable waste forms. (1,2). Table 1 gives compositions of candidate HLLW fractions produced by nuclear fuel reprocessing.

Table 1. Chemical composition of six candidate HLLW fractions (g/L)

Oxide	#1	#2	#3	#4	#5	#6
Al ₂ O ₃		41.9	18.9	19.0		
Na ₂ O	5.0	3.1	54.0	67.4		
CS ₂ O	5.3		0.5		9.2	
K ₂ O	3.7					
NiO	0.2	0.1	7.6	6.3		
CaO	0.3		5.6			
Fe ₂ O ₃	1.3	1.2	14.3	7.0		
Cr ₂ O ₃	0.3	0.3	3.0	3.0		
MnO ₂	0.5		3.2			
SrO	2.1		0.4		4.5	
BaO	22				4.8	
ZrO ₂	6.8					8.5
MoO ₃	4.5					
RuO ₂	4.0					
Rh ₂ O ₃	1.7					
PdO	1.7					
REE _{ox}	16.7	0.2				30.3
PbO					1.1	

EXPERIMENTS AND DISCUSSION

HLLW is commonly solidified by incorporating into phosphate- or borosilicate-glass-like compositions that can be produced by melting at 900 to 1200 °C – such as in Joule-heated ceramic melters (EP-500, Ozersk, Russia and Pamela, Belgium and Germany) or in inductive melters (La Hague, France and Sellafield, Great Britain) (1-6). A more advanced technology is under investigation that uses two-stage HLLW solidification, including a CCIM, which allows new types of solid waste form materials to be produced. The CCIM's advantages compared with the commonly used glass forming processes are:

- No direct contact between melter material and melt due to the formation of a protective layer of solidified melt on the cooled crucible walls,
- Small dimensions of the CCIM relative to a ceramic melter, and
- Possibility of remote disassembly and removal.

The CCIM technology allows synthesis at temperatures up to 2500 °C of different final waste form materials having a wide range of compositions, including toxic wastes containing heavy metals. Additionally, the experiments reported here proved that melting in a CCIM can be used to incorporate Fe, Cr, Ni, and Rare-Earth elements (REE) into phosphate and borosilicate glass at considerably higher concentrations in the waste than their solubility in melts of these glass matrices.

The melting process in a CCIM is based on Joule heating by electrode-less induction of a high frequency electromagnetic field of the electrical conducting molten glass, in which the induced electromagnetic field energy is converted to thermal energy, using.

The CCIM consists of water-cooled tube sections assembled on a common header. The crucible is surrounded by a water-cooled inductor connected to a high-frequency generator (Fig. 1).

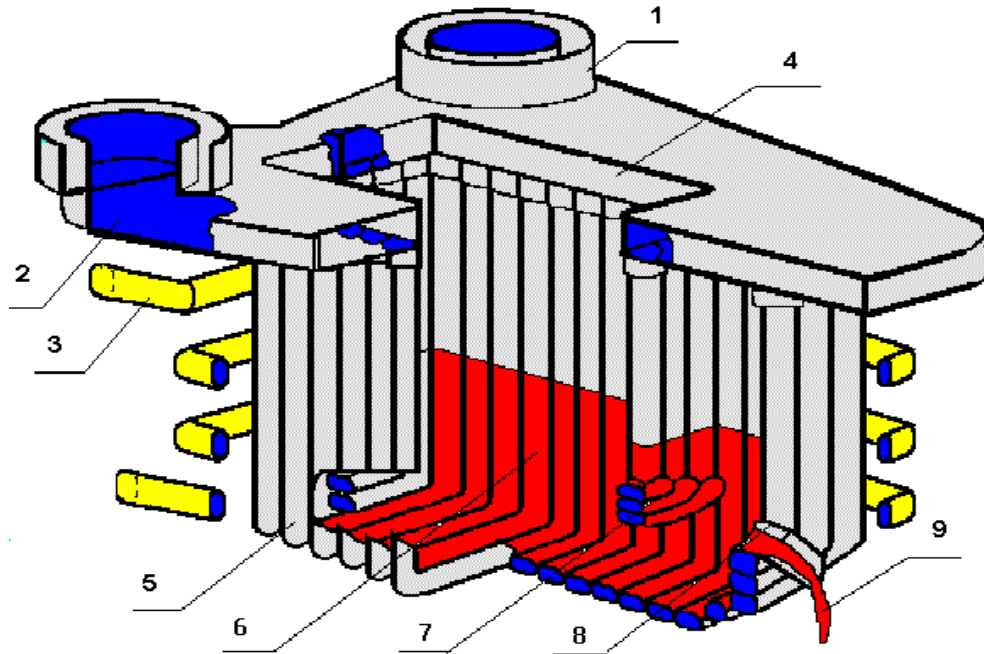


Fig. 1. CCIM

1-Connector; 2-Cooling water pipe section; 3-Inductor; 4-Melter feed inlet; 5-Crucible pipe section; 6-Glass melt; 7-Partition; 8-Outlet for melted glass; 9-Melted glass stream.

Special tests using simulated HLLW are being performed at a two-stage pilot facility installed at the solidification department of the IA Mayak facility in Ozersk, Russia. The system throughput is up to 100 dm³/h HLLW (Fig. 2, Table 2). This HLLW solidification includes the following basic steps:

- Selection of the composition of an HLLW and orthophosphoric acid flux mixture that will produce the required phosphate glass composition and preparation of this mixture
- Concentration of the simulated HLLW/flux mixture in a once-through evaporator
- Production of a glass melt from the concentrated salt mixture in the CCIM
- Canister filling with the molten glass
- Overpacking the canisters
- Filtration of the off gases.

The HLLW/flux solution is continuously fed to the once-through evaporator at a flow rate of 35 to 100 dm³/h. The evaporator consists of a vertical device housed in a steam jacket. Countercurrent flow of the HLLW/flux solution and heating vapor is maintained. The internal shell of the steam jacket separator provides a stationary area in which the vapor phase and concentrated salt melter feed material separate.

Heating, partial reaction of the nitrates with orthophosphoric acid, evaporation with nitric/nitrous acid removal, and drying take place sequentially in the countercurrent flow evaporator (CFE) depending on the product desired. After separation of the vapor phase from the salt melt feed material, the latter is gravity fed to the CCIM at a rate of 20 to 24 kg/h. The vapor phase is directed into the first stage of the gas filtration system.

Further dewatering and denitration of the salt melt feed material, together with melting, take place in the CCIM at 1100 to 1200 °C to produce the phosphate glass (up to 18 kg/h).

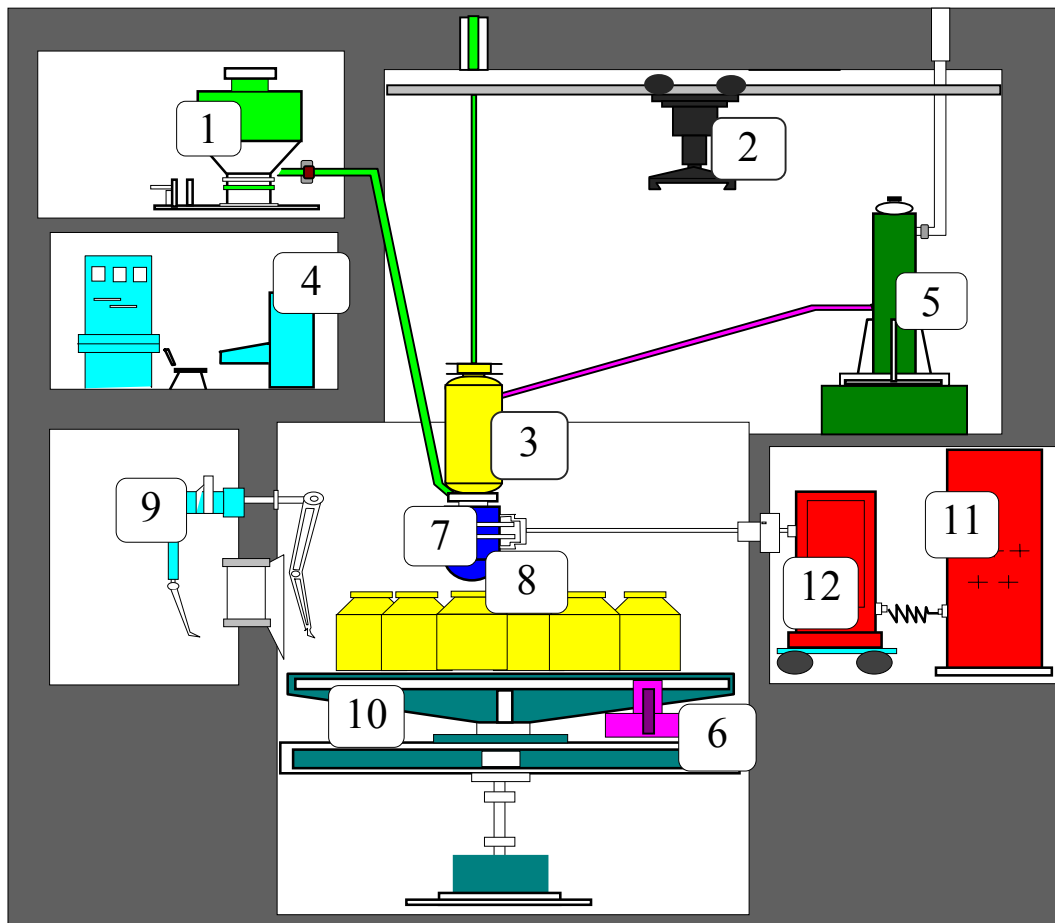


Fig. 2 Two-stage CCIM process installation. 1-Feed cell; 2-Crane; 3-Countercurrent flow evaporator; 4-Control room; 5-Barbotage-cooler; 6-Weighing device; 7-Inductor; 8-Cold crucible; 9- Remote manipulator; 10-Rotating table transporter; 11-High-frequency generator; 12-Condenser battery.

Table 2. Technical features of the CFE–CCIM two-stage vitrification facility equipment

COUNTERCURRENT FLOW EVAPORATOR:

Volumetric throughput of original simulated HLLW, dm ³ /h	up to 100
Vapor flow rate, kg/h	120
Vapor temperature at evaporator inlet, °C	150
Operating vapor pressure at evaporator inlet, MPa	0.4-0.5
Dimensions, m (diameter/height)	0.55/1.2

COLD CRUCIBLE:

Crucible structure	two sections, water-cooled
Tank rated capacity, dm ³	22.6
Melt surface area, dm ² (welding area/producing area)	6.7/1.8
Temperature of glass during container filling, °C	1200
Maximum working temperature, °C	1500
Mass production rate (glass), kg/h	up to 18
HF-generator power rating (ac), kW	160
Operating frequency, MHz	1.76

To attain operating conditions, the CCIM must initially contain conducting material to be heated by the electric induction current to form an initial amount of molten glass in the crucible. This initial heating can be performed using either added conducting materials and glass frit, or a conducting glass compound already solidified on the crucible walls. The routine operating mode of the CCIM is characterized by continuous discharge of the glass melt from the crucible into containers. The melt flow is interrupted only during container changeout. Melted glass from the crucible fills the 200 dm³ capacity containers installed on the rotating conveyer. Container filling is controlled by a weighing system. After cooling of the glass, the filled containers are overpacked in special containers that are seal welded. After pressurization leak tests, these overpack containers are sent to storage. A gas filtration system with a 10⁸ - 10⁹ decontamination factor for radionuclides is used to treat the CFE-CCIM facility offgases.

The test installation for the two-stage HLLW solidification process is a prototype for the industrial units designated for the “second generation” of the IA “Mayak” solidification department operations. To date, pilot-scale tests producing phosphate glass from simulated HLLW with the following final product composition have been the most developed in the CCIM process (Table 3):

Table 3. Specified content of phosphate glass, wt.%

Na ₂ O and other univalent oxides	24.0 ± 2.0
Al ₂ O ₃ and other polyvalent oxides	21.0 ± 3.0
P ₂ O ₅	55.0 ± 5.0
Fission product inclusions	up to 4

During phosphate glass production and while incorporating 3 and 10 wt.% of Fe, Cr, Ni, and REE oxides, a uniform distribution of the these oxides was obtained along the height of the resulting glass block. In the case of 3 wt.% oxides, the glass was homogeneous, while for the

materials containing 10 wt.% oxides a heterogeneous phase was observed to be equally distributed through the entire volume of the glass block. Such uniform oxide distribution in the melt (beyond their chemical solubility) in the phosphate glasses can be explained by the strong mixing caused by the induced current and the magnetic field in the CCIM. The resulting electrodynamic forces can lead (depending on the R-F generator current frequency and crucible structure) to melt circulation with a linear speed of up to 10 to 12 mm/s at the high internal temperatures observed. Thus, application of the CCIM technology allows uniform melts of phosphate glasses with a high content of aggressively corrosive nuclides (Fe, Cr, Ni) and some fission products (including platinides). That results in the opportunity to process HLLW practically without limitation on its composition while significantly increasing the fraction of HLLW components incorporated in the glass.

A major desirable characteristic of solidified HLW with respect to temporary storage and final disposal conditions is chemical stability as determined by low nuclide leaching rates during possible contact with ground water. Leach rates of Cs, Sr, and Zr from phosphate and borosilicate matrices produced in the CCIM have the same value as for glasses obtained by traditional methods.

A significant improvement of the physical-chemical properties of the solidified HLW while simultaneously increasing the content of radionuclides can be achieved by the use of mineral-like materials for the matrix composition. These materials are analogs of natural minerals, which are chosen based on geochemical stability and the capability to incorporate the long-lived HLLW radionuclides into the crystalline cationic structure as stable solid solutions. Application of the CCIM method resulted in the production of matrices with compositions corresponding to different classes of minerals that include piroxen (jadeite, ortite, arfvedsonite, egrin), garnet (andradite, ferrogarnet), titanate (sphene), zirconolite, and boron basalt. Matrix compositions are shown in Table 4.

Table 4. Compositions of matrices synthesized at CCIM

Material	Oxide compound, wt.%											
	Na ₂ O	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	MgO	CaO	TiO ₂	Cs ₂ O	SrO	CeO ₂	ZrO ₂	Gd ₂ O ₃
Jadeite	12.5	20.4	10.0	52.2	-	-	-	5.0	3.0	5.0	-	-
Ortite	-	19.8	17.3	39.0	-	10.9	-	5.0	3.0	5.0	-	-
Arfvedsonite	9.3	2.6	6.0	52.8	16.2			5.0	3.0	5.0	-	-
Sphene	-	-	1.9	28.9	-	23.1	33.1	5.0	3.0	5.0	-	-
Garnet	-	-	36.0	42.5	-	8.5	-	5.0	3.0	5.0	-	-
Zirconolite	-	-	-	-	-	15.5	44.5	-	-	9.5	20.0	10.0

All the materials studied were prepared in the CCIM at 1250 to 1550 °C. The product materials were investigated under the following identical conditions: heat treatment at 650 °C up to 250 hours to simulate annealing as a result of self heating, and exposure to radiation up to 10¹⁰ Rad for estimating irradiation stability. The results demonstrated that mineral-like matrices are more stable in comparison with glasses (7-9). The leach rates of individual elements and the depth of destruction of the matrix were nearly unchanged by heat treatment and irradiation.

CONCLUSION

Laboratory and pilot-scale tests performed in Russia using a two-stage evaporator and CCIM technology confirmed its advantage in comparison with current industrial technologies. The results demonstrated the potential benefits of its use in the future for HLLW solidification to obtain new types of matrices that will be stable after disposal by underground burial. The application of induction melters allows one to synthesize materials (including glass- and mineral-like materials) suitable for solidification of practically all classes of liquid radioactive wastes. The proposed technology uses compact technological equipment more amenable to being moved to the waste disposal location. Production of solidified final waste forms using the CCIM technology could substantially reduce the risk of nuclear accidents during storage of HLLW at radiochemical facility sites and avoid potential catastrophes and ecological effects resulting from such events.

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