CCIM Technology for Treatment of LILW and HLW - 10209

Vladimir V. Lebedev, Dmitriy Y. Suntsov, Sergey Y. Shvetsov, Sergey V. Stefanovsky, Alexander P. Kobelev, Fedor A. Lifanov, Sergey A. Dmitriev
SIA RADON, 7th Rostovskii lane 2/14, Moscow 119121 Russia

ABSTRACT

Cold Crucible Inductive Melting (CCIM) technology is developed and applied at SIA Radon for vitrification of low- and intermediate-level radioactive wastes (LILW). During last eight years SIA Radon researchers were dealing with application of CCIM for vitrification of high level wastes (HLW). HLW surrogates of Savannah River Site (SRS), USA, and Production Association (PA) “Mayak”, Russia, were vitrified and products were examined in details. CCIM operational conditions and process variables (feed rate, melt rate, melting ratio, etc.) were determined. Feasibility of vitrification of HLW with high aluminum and iron contents has been proven. Various types of pumps to feed slurries into the crucible were tested. Maximum waste loading in glass keeping its high chemical durability was determined. The heat balance in the system “high frequency generator - crucible” was summarized and effective power spent for batch melting and melt homogenization was measured.

Since 2007 design and construction works on cold crucible for HLW treatment were carried out. Previous experience in cold crucible design and operation experience during vitrification of actual LILW and HLW surrogates were applied. Principles of operation and control of the inductive melter were formulated. Automated control system has been designed and a set of the equipment required has been completed. The new cold crucible with the automated control system and auxiliary equipment is recommended for implementation at PA “Mayak” for study of HLW vitrification process of both spent nuclear fuel (SNF) reprocessing and old (“historical”) tanks with variable chemical composition.

INTRODUCTION

Vitrification is generally accepted as the most preferable method of HLW treatment. This method allows to provide high waste volume reduction factor and to produce chemically durable, radiation resistant and mechanically strong waste form. Random glass network being capable to accommodating of ions with variable charges and radii seems to be the most appropriate material for immobilization of radionuclides of fission and corrosion products as well as process contaminants (chemicals) [1]. An inductive heating has some advantages over other methods of heating due to contactless energy supply. Unlike a melting at middle frequencies (10^3-10^4 Hz) when metallic crucible wall is heated and heat-transfer takes place from heated wall to melt, at high-frequency (10^5-10^7 Hz) direct heating of conductive material through radio-transparent crucible wall occurs. Cold crucible melter is a vessel of copper or stainless steel pipes or sections where high-frequency electromagnetic field penetrates through the gaps between the pipes or sections heating the melt inside. Pipes or sections are water-cooled inside and as a result an intermediate layer (“skull”) is formed between liquid melt and inner surface of the cold crucible forming pipes or sections protecting them from the melt [2]. So, the CCIM is one of the most promising methods of melting/vitrification.

THE RADON FULL-SCALE VITRIFICATION FACILITY

CCIM technology was being developed at SIA Radon for more than twenty years and currently a full-scale LILW vitrification facility is under operation. In accordance with the governmental license SIA Radon processes LILW from non-nuclear applications and performs experimental works on vitrification of Nuclear Power Plant wastes and contractual works on development and testing of HLW vitrification using HLW surrogates. The full-scale facility is energized from 1.76 MHz/160 kW generators and produces alkali borosilicate glass with ~30-35 wt.% waste loading. Temperature of glass melt ranges between 1150 and 1250 ºC, electric resistivity of molten glass may be within the range of 0.02 to 0.1 Ω×m (normally 0.03-0.06 Ω×m). In total for all the period of active operation (since 1999) about 25 metric tons of glass were obtained. The facility is equipped with automated control system of the CCIM process. The current scheme of the Radon full-scale LILW vitrification plant is shown on Fig. 1 and the main technical characteristics of the plant are listed in Table I.

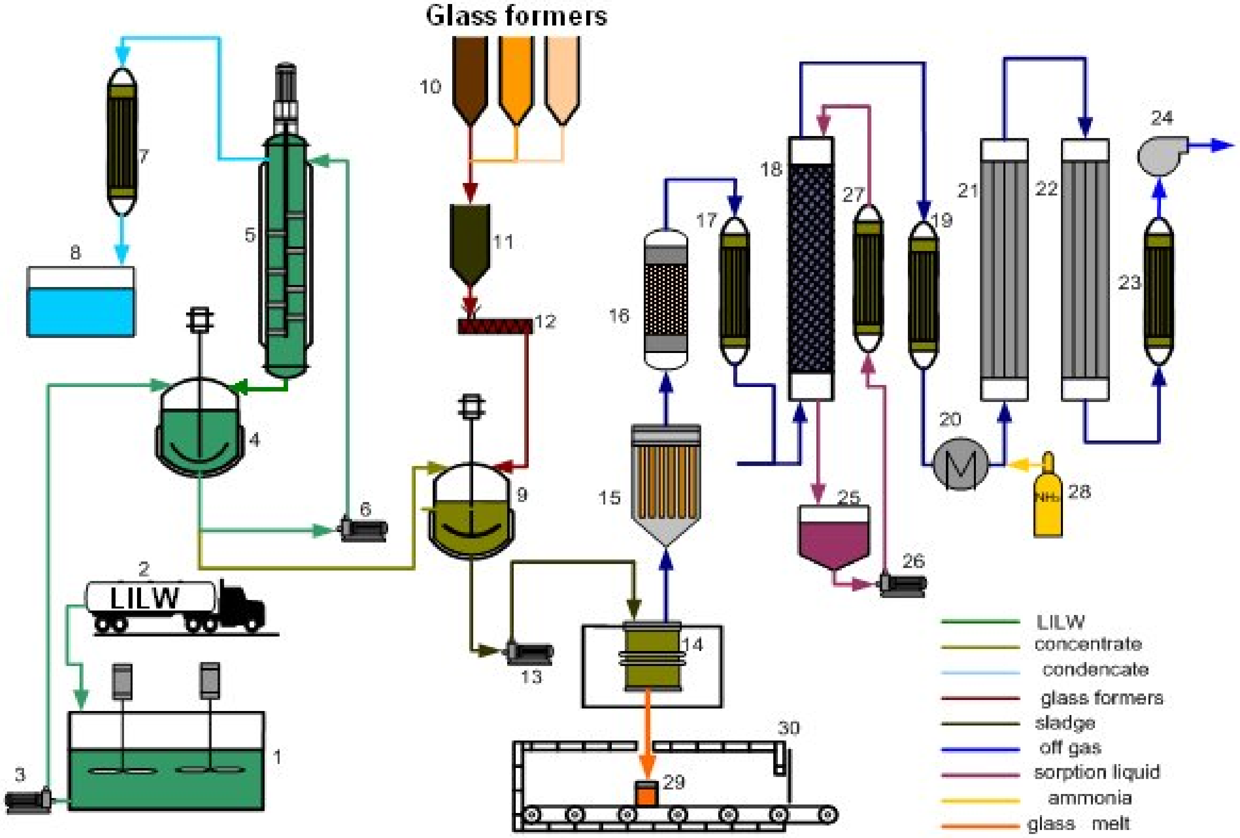


Fig.1. LILW vitrification plant.

1 – LILW interim storage tank; 2 – LILW transportation vehicle; 3 – pump; 4 – concentrate collector; 5 – rotary film evaporator; 6, 13, 26 – pumps; 7 – condenser; 8 – condensate collector; 9 – batch (feed) mixer; 10 – glass formers bins; 11 – glass formers mixture bin; 12 – screw feeder; 14 – cold crucible; 15 – bag filter; 16 – HEPA filter; 17, 19, 23, 27 – heat exchangers; 18 – scrubber; 20 – heater; 21 – catalytic reactor for reduction of nitrogen oxides; 22 – catalytic reactor for oxidation of ammonia; 24 – fan; 25– sorbent bin; 26. - Pump; 28 – ammonia balloon; 29 – glass canister; 30 – annealing furnace.

Treatment of LILW is two-phase process. Liquid waste is concentrated to salt content of ~1000 g/L. The concentrate is intermixed with glass formers preparing a paste with a water content of 22-25 wt.%. This paste is fed into the cold crucible. Molten glass is periodically poured into 20 L canisters. The glass blocks obtained are annealed in the annealing furnace to remove thermal stresses in the blocks. The mix of gases, steam and aerosol formed during melting is cleaned step by step in the off gas system.

Table I. Major Technical Characteristics of the LILW Vitrification Plant.

Parameters	Values
Liquid LILW capacity, m^3/h	≤ 0,3 (at salt concentration of 200kg/m^3)
Glass productivity (single crucible), kg/hr	≤ 25
Specific glass productivity (single crucible), kg/(m^2×d)	4380
Glass productivity (three crucibles)	≤ 75
Melting ratio, kW×hr/kg	4-6
Glass block weight, kg	50
LILW volume activity, Bq/L	$\leq 3.7\times10^6$
Glass specific activity, Bq/kg	$\leq 6.3\times10^8$
Installed electric capacity, kW	1500
Cooling water flow rate, m^3/h	60
Overall dimensions, m	9×12×24

COLD CRUCIBLE DESIGNING

SIA Radon experts have more than twenty years' experience in designing and management of the cold crucibles. This experience allows looking for the ways of expanding of application area for CCIM technology. The process of designing may be divided into the following parts:

- formulation of main technical requirements and formalization of these requirements in the requirements list; usually in SIA Radon two kinds of tasks are solved: designing the crucible for treatment of the given material and working out of requirements to power and auxiliary equipment (cooling system, high frequency generator, off-gas system, etc.) or design of crucible for existing facility; sometimes solution of both tasks is required;
- preliminary lab-scale experiments with initial material to determine chemical composition (if it's unknown), its ability to thermal destruction and melting, parameters of treatment; adjustment of initial composition for gaining of required work material features (if necessary);
- determination of melter diameter optimal for treatment of target material with the given generator (notably with the given characteristics of the electromagnetic field);
- hydraulic calculation of the melter as water-cooled equipment to achieve the optimal cooling regime; cooling regime is the key factor providing for technologically acceptable melter lifetime;
- working-out the requirements for the automated control of the cooling system and auxiliary equipment, selection of elements for the control system, formulating of the principle of water cooling system control and algorithms of operation for auxiliary equipment;
- construction, adjusting and testing of the melter designed, refinement of technological regime, tuning of control facility, preparing of the melter to the treatment of RW

EVOLUTION OF THE CCIM TECHNOLOGY TOWARDS HLW TREATMENT

HLW treatment is one of the most important areas of CCIM application. Currently SIA Radon participates in activity to adapt the CCIM to HLW vitrification. Significant efforts were applied to feasibility study of cold crucible vitrification of HLW surrogates. Chemical compositions of these surrogates were specified by Savannah River National Laboratory (SRNL) and PA "Mayak" (Table II). Both bench- and industrial-scale cold crucible vitrification tests of SRS high-Fe and high-Fe/Al wastes have been successfully performed. Glass frits (Table II) commercially available in USA were used as the glass formers. Optimal proportions between the HLW salts and frits in the batches fed into the crucible were determined, technological regimes of the process were worked out, and major process variables such as waste capacity, slurry feed rate, glass productivity, melting ratio were measured during the tests. Then the heat balance was amounted and process efficiency was determined. The results of CCIM tests with SRS waste surrogates are described in details in our previous papers [3-6]. Maximum waste loading in both SB2 and SB4 waste glasses not resulting in decreasing of chemical durability was determined to be 55-60 wt.% (Table II). The only crystalline phases occurred in amount of ~10-15 vol.% of total bulk in all the glassy products was spinel corresponding in chemical composition to magnetite/trevorite solid solution and generalized formula $(Fe,Ni,Mn,Mg)^{2+}(Fe,Cr,Al)^{3+}O_4$ (traces of Cu^{2+} and Zn^{2+} were also present).

Table II. Chemical compositions of waste surrogates, frits and SRS and PA "Mayak" waste glasses.

Oxides	SRS								PA "Mayak"	
	SB2 HLW surrogate	Frit 320	Glass (50% WL)[a]	Glass (60% WL)[a]	SB4 HLW surrogate	Frit 503-R4	Glass (50% WL)[a]	Glass (60% WL)[a]	HLW surrogate	Glass (30 wt.% WL)[a]
Li_2O	-	8.00	4.00	3.20	-	8.00	4.00	3.20	-	-
B_2O_3	-	8.00	4.00	3.20	-	16.00	8.00	6.40	-	20.04
F	0.01	-	0.005	0.01	-	-	-	-	-	-
Na_2O	12.08	12.00	12.04	12.05	18.71	-	9.35	11.22	25.41	19.52
MgO	0.24	-	0.12	0.14	2.77	-	1.39	1.66	0.89	0.27
Al_2O_3	16.83	-	8.415	10.10	25.49	-	12.75	15.29	37.36	11.21
SiO_2	1.98	72.00	36.99	30.00	2.71	76.00	39.36	32.03	-	38.06
P_2O_5	0.14	-	0.07	0.08	-	-	-	-	-	-
SO_3	0.83	-	0.41	0.50	0.87	-	0.43	0.52	5.31	1.59
Cl	1.51	-	0.75	0.90	-	-	-	-	-	-
K_2O	0.09	-	0.045	0.05	0.07	-	0.03	0.04	12.54	3.76
CaO	3.76	-	1.88	2.25	2.77	-	1.38	1.66	5.29	1.59
TiO_2	-	-	-	-	0.04	-	0.02	0.02		-
Cr_2O_3	0.37	-	0.185	0.22	0.20	-	0.10	0.12	1.62	0.49
MnO	3.89	-	1.945	2.33	5.78	-	2.89	3.47	0.57	0.17
Fe_2O_3	42.24	-	21.12	25.36	28.99	-	14.49	17.39	7.61	2.28
NiO	2.17	-	1.085	1.30	1.66	-	0.83	1.00	3.40	1.02
CuO	0.20	-	0.10	0.12	0.05	-	0.03	0.03	-	-
ZnO	0.39	-	0.195	0.23	0.05	-	0.02	0.03	-	-
SrO	0.10	-	0.05	0.06	-	-	-	-	-	-
ZrO_2	0.79	-	0.395	0.47	0.09	-	0.05	0.05	-	-
I	0.04	-	0.02	0.03	-	-	-	-	-	-
BaO	0.27	-	0.135	0.16	0.07	-	0.03	0.04	-	-
PbO	0.32	-	0.16	0.19	0.38	-	0.19	0.23	-	-
U_3O_8[b]	11.75	-	5.875	7.05	9.03	-	4.52	5.42	-	-
Ce_2O_3	-	-	-	-	0.21	-	0.11	0.13	--	-
La_2O_3	-	-	-	-	0.03	-	0.02	0.02	-	-
ThO_2[b]	-	-	-	-	0.02	-	0.02	0.02	-	-
Total	100	100		100	100	100	100	100	100	100

[a] WL – waste loading;

[b] were not introduced in full-scale cold crucible tests.

The data for the full-scale tests using a 418 mm inner diameter cold crucible are summarized in Table III.

Table III. Major Process Variables at Vitrification of SRS SB2 (high-Fe) and SB4 (high-Fe/Al) Waste Surrogates in the 418 mm Inner Diameter Cold Crucible.

Parameters		SB2			SB4		Mayak waste glass
Glass forming additive (frit)		SS-320	CS-320	Average (total)	CS-503	SS-503	
Test duration, hr:min		13:08	18:44	(31:52)	29:40	32:50	36:00[6]
Average generator's vibration power, kW		143	150	147	121.6	134.1	~145
Water content in slurry, wt.%		~45	~60	~55	27−28	50−52	29
Mass of slurry vitrified, kg		465	751	(1216)	745.8	1307.9	~1200
Mass of glassy product produced, kg		213	205	(418)	414.3	458.6	~600
Average melt surface temperature, °C		1160	1160	1160	1300	1300	1150
Average slurry feeding rate, kg/hr		36	40	38	25.1	39.8	~50
Average melt production rate, kg/hr		16	11	13.5	14	14	~20
Melting ratio, kW·hr/kg	Slurry processing	4.0	3.8	3,9	4,8	3,4	2.9
	Melt production	8.8	13.8	11.3	8.7	9.6	7.25
Heat losses (spent power), kW	Vitrification	27	25	26	36	34	35
	HF generator's cooling	27	24	25,5	38	37	37
	Cold crucible cooling	43	48	45,5	22	25	25
	Off-gas	3	3	3	4	4	3
Specific glass productivity, kg/(m^2·day)		2830	1910	2370	~2450	~2450	3504
Volatile losses, wt.%	Li_2O	-	-	-	8[1]		-
	Na_2O	3	7	5	7[1]/3.5[2]/8[3]		-
	Cs_2O	-	-	-	60[1]/56[2]/48[3]		-
	B_2O_3	9	17	13	4,5[1]/12[4]/10[5]		-
	SiO_2	-	-	-	0.1[1]		-
	CaO	-	-	-	2[1]/0.5[2]		-
	MnO	-	-	-	3[1]/7[2]/5[3]		-
	Fe_2O_3	-	-	-	2[1]/5[2]/3[3]		-

[1] from off-gas measurements;

[2-5] by difference between oxide contents in feed and glass using: XRF[2], EDX[3]; potentiometric titration[4]; mass-spectrometry[5].

[6] including time spent for process start-up and achieving of steady-state conditions.

SS-320 – slurry from sludge prepared by SRNL procedure and Frit 320; CS-320 – slurry from mixture of chemicals and Frit 320; CS-503 – slurry from chemicals and Frit 503-R4; SS-503 – slurry from sludge prepared by SRNL procedure and Frit 503-R4.

The CCIM process demonstrated rather high effectiveness even at high water content in the slurry (up to 60 wt.%). The efficiency (power spent for batch melting and melt homogenization) achieved 36% at specific glass productivity of up to 2400-2800 kg/(m^2·day). At that, volatile losses of constituents, except Cs) were rather low (Table III). The most important result is that up to 55-60 w.% waste loading in glass may be achieved without decrease of chemical durability beyond the limits established by the US EPA [7] whereas maximum waste loading in glass produced at DWPF is 38 wt.% [8].

Since 2007 SIA Radon is involved in developing of CCIM technology for the treatment of current and accumulated (“historical”) HLW at PA “Mayak” (Russian Federation). Implementation of two-stage process consisting of liquid waste concentrating and cold crucible vitrification of slurry prepared from concentrate and glass forming additives (frit) is under consideration now. PA “Mayak” HLW surrogate (averaged composition) was concentrated in a rotary film evaporator to a salt concentration of ~700 kg/m^3, the concentrate was intermixed with a borax and a sandstone as glass-formers, and the paste obtained was vitrified in the industrial-scale 418 mm inner diameter cold crucible at the Radon full-scale vitrification plant (Fig. 1) with production of alkali borosilicate glass with ~30 wt.% waste loading. Higher waste loading is mainly restricted by sulfates/chlorides content in waste.

The glass containing ~30 wt.% Mayak waste surrogate requires lower melting temperature (~1150 °C), has lower viscosity at this temperature, and “longer” (Fig. 2) than the SRS waste glasses and this results in higher slurry feeding, glass production rates and specific glass productivity as well as lower melting ratio (Table III). Major process variables given in Table III demonstrate high rate of the CCIM vitrification process, high specific glass productivity [~3500 kg/(m^2×day)] and rather low glass production melting ratio (~7.25 kW×hr/kg).

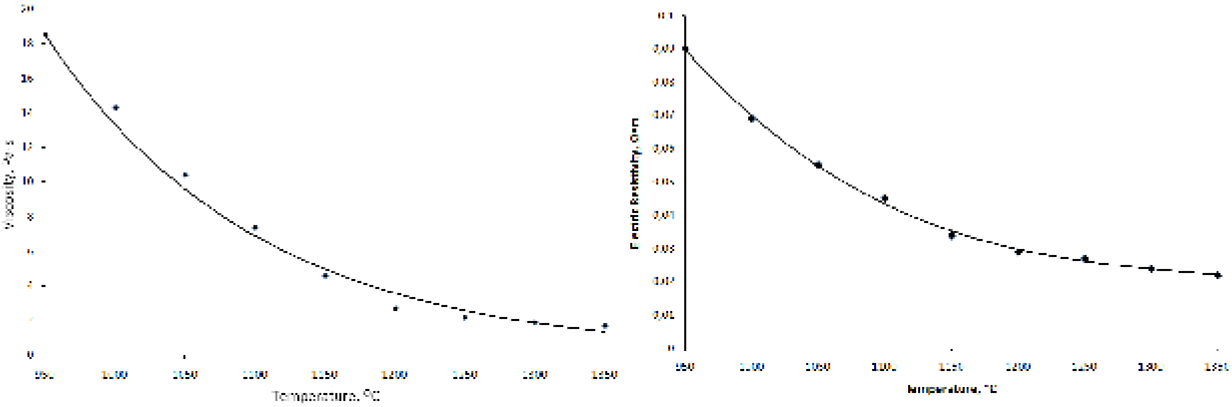
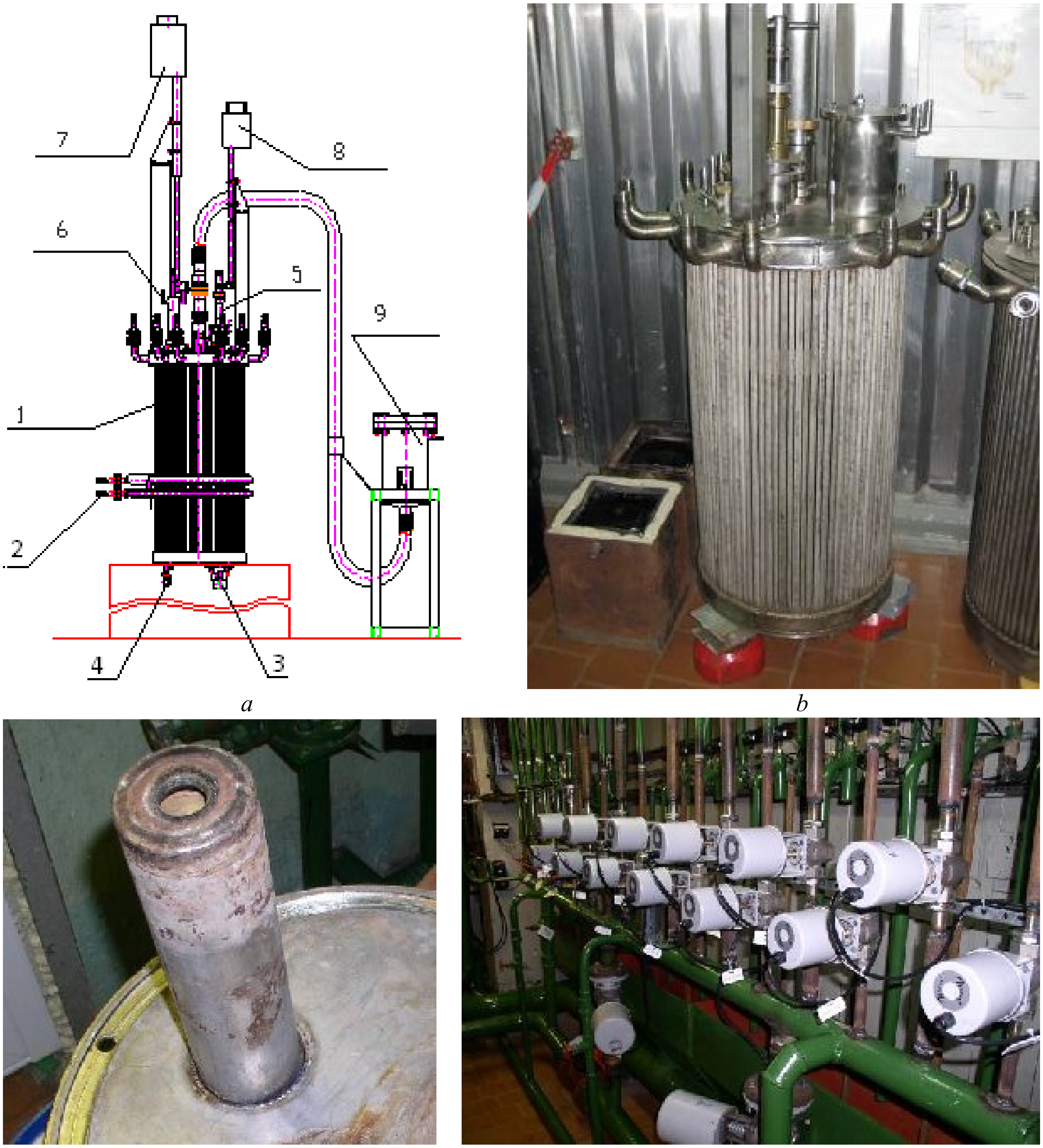


Fig. 2. Viscosity vs temperature (a) and electric resistivity vs temperature (b) dependences for the PA “Mayak” waste glass (see Table II).

Thus, the feasibility of two-stage concentrating/vitrification technology for PA “Mayak” HLW using the same equipment as the one of the SIA Radon vitrification plant has been confirmed.

Except experimental work SIA Radon engineers have designed, manufactured and delivered the trial sample of the cold crucible (Fig. 3*a*,*b*) to PA “Mayak”. This crucible will be installed at the bench-scale unit, equipped with remote operation and automated control systems and tested in inactive variant. Parameters of the cooling regime of the crucible were calculated, the automated control system (ACS) was designed, and its elements were selected and completed by SIA Radon experts. The crucible design includes the most successful and showed good performance structural elements from previous cold crucible designs. Moreover some new elements which are expected to be reliable in operation were designed on the base of current knowledge amassed over the past 20 years of experience in cold crucible design and operation.

For example pouring unit (Fig. 3c) designed at SIA Radon and successfully and reliably operated for more than 2800 hours is applied at the new cold crucible for PA “Mayak”. As seen from Fig. 3c the unit was subject to minor surface corrosion only and still maintains serviceability. Moreover, segmentation of the melter’s body in water-cooled parts was optimized, thus providing for more qualitative and stable cooling regime. At SIA Radon the crucible cooled in such manner has worked for more than 1800 hours without visible damages. The equipment for automated melter cooling control was selected and the contours of automated control for the cooling system (Fig. 3*d*) were designed thus providing for possibility of automatic gathering and offering of data about the heat balance of the melter.



a *b*

c *d*

Fig. 3. The scheme (*a*) and view (*b*) of the cold crucible for the bench-scale unit at PA "Mayak", view of pouring unit after 2500 hrs of operation (*c*), and melter's cooling system (*d*).
1 – wall-forming pipes, 2 – inductor, 3 – pouring unit, 4 – cooling water inlet, 5 – pouring gate, 6 – slurry (paste) feeding gate lift, 7 – staring batch feeder, 8 – pouring gate lift, 9 – starting batch bin.

Currently SIA Radon offers the technical support for construction and adjusting of the bench-scale unit at the PA “Mayak”.

The tasks of control of the main technological parameters and procedures such as water flow rate in cooled units, slurry (paste) feeding rate into the melter, melter start-up process, collection and processing of the information on process variables were solved. The view of the melter’s symbolic circuit in the screen is shown on Fig. 4.

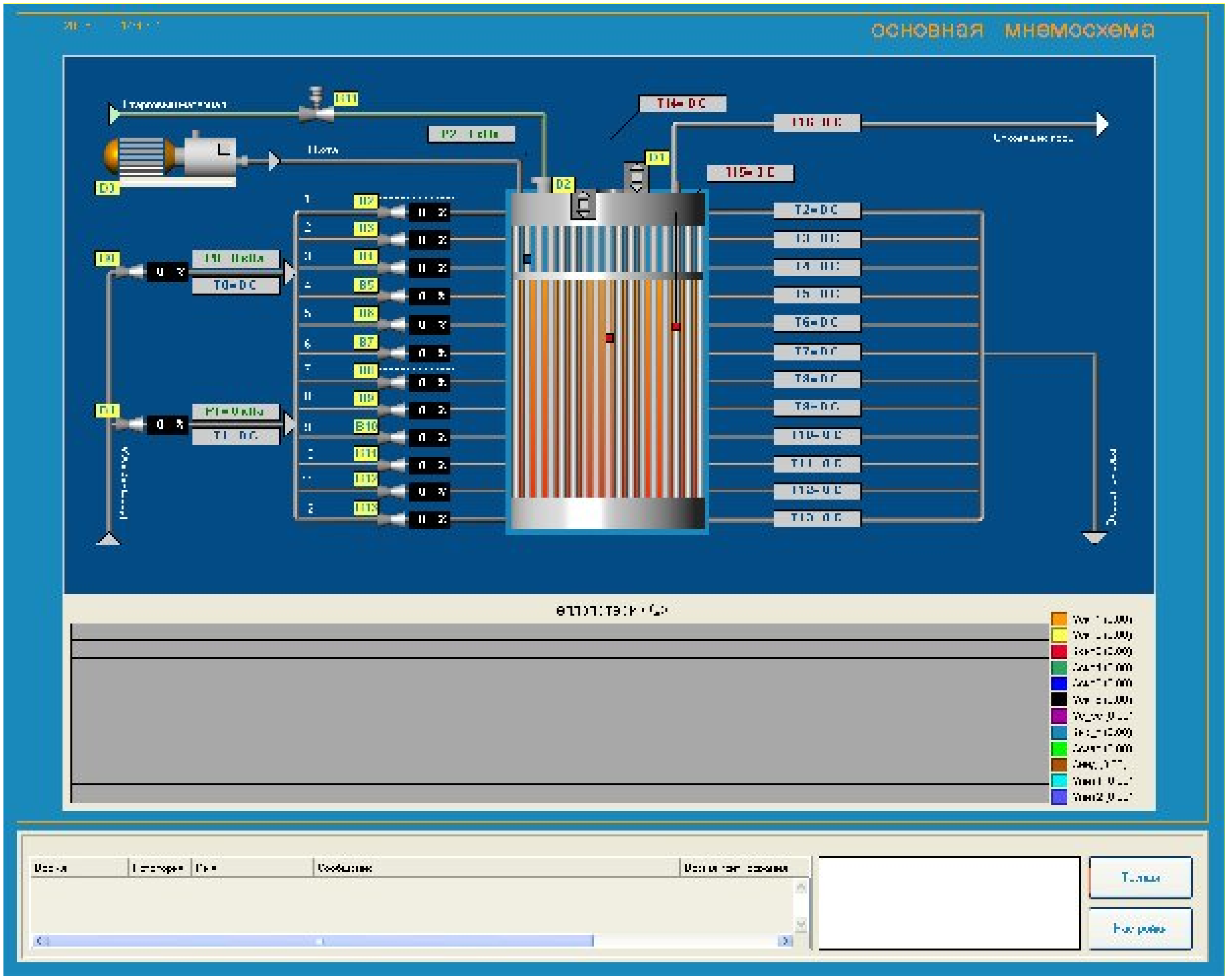


Fig. 4. Melter’s symbolic circuit in the screen.

FURTHER ADAPTATION OF CCIM TECHNOLOGY TO HLW TREATMENT

Within the contract with PA “Mayak” the offers on development of the test plant for HLW treatment with CCIM technology are worked out. In the whole the directions of the works at SIA Radon are as follows:

- to maximize melter’s lifetime to 5000 hours by means of the optimization of the design, control the optimal cooling regime for each element of the melter, to minimization of the amount of moving parts and impacted connections;
- to simplify the melter design to the utmost under conditions of HLW treatment and to facilitate dismantling and disposal of the melter in the case of failure;

- to search the most heat and corrosion resistant construction materials;
- to ensure remote (ideally fully automatic too) control of melter start-up, slurry (paste) feeding, and melt pouring;
- to adjust the algorithms of the process control to provide for their adequacy to real characteristics of the process, applying the data gained during the work of the bench-scale facility;

In spite of absence of practical experience in design of equipment for HLW treatment, SIA Radon experts on the basis of their experience in LILW treatment and the results of their own collection and processing of the operational data are capable to bring substantial contribution to development of the CCIM technology for HLW treatment and to the design, construction and operation of the cold crucible based facility.

CONCLUSION

The cold crucible based full-scale LILW vitrification plant is under operation at SIA Radon now. Total liquid waste capacity and glass productivity are ~100 L/hr and ~75 kg/hr, respectively (three streams), at a single crucible glass productivity is up to 25 kg/hr. Both the full-scale and the bench-scale facilities were used for demonstration tests on vitrification of SRS and PA “Mayak” HLW surrogates. At vitrification of SRS high-Fe and high-Fe/Al waste surrogates maximum waste loading achieved was 55-60 wt.% whereas waste loading in DWPF glass is limited by 38 wt.%. Waste loading in the “Mayak” glass was ~30 wt.% and is restricted by elevated sulfate and chloride content in waste and glass. Specific glass productivity of up to 3000-3500 kg/(m^2·day) was achieved.

Successful demonstration of SRS and PA “Mayak” waste vitrification allowed recommending the CCIM technology for implementation at HLW vitrification facilities. On the basis of the Radon experience in design, manufacturing, and operation of cold crucibles a new cold crucible for the bench-scale vitrification plant at PA “Mayak” has been designed, manufactured, tested, and delivered to PA “Mayak”. The crucible is equipped with improved pouring unit, upgraded cooling system and automated process control system.

REFERENCES

1. W. LUTZE, “Radioactive Waste Forms for the Future,” eds. W. Lutze and R.C. Ewing, Elsevier Science Publishers, B.V. (1988) 1-159.
2. S.A. DMITRIEV and S.V. STEFANOVSKY, “Management of Radioactive Waste,” Publishing Center at Mendeleev University of Chemical Technology (2000).
3. A.P. KOBELEV, S.V. STEFANOVSKY, O.A. KNYAZEV, T.N. LASHCHENOVA, A.G. PTASHKIN, M.A. POLKANOV, E.W. HOLTZSCHEITER, and J.C. MARRA, “Results of a 50% Waste Loading Vitrification Test Using the Cold Crucible Melter for Savannah River Site,” Proc. Int. Conf. Waste Management ’06, February 26 – March 2, 2006, Tucson, AZ (2006) CD-ROM. Paper # 6127.
4. S.V. STEFANOVSKY and J.C. MARRA, “The Effect of Waste Loading on the Structure and Leach Resistance of Borosilicate Glass for Savannah River Site SB2 Waste Immobilization,” Proc. Int. Conf. Waste Management ’07, February 25 – March 1, 2007, Tucson, AZ (2007) CD-ROM, Paper #7132.
5. S.V. STEFANOVSKY, A.P. KOBELEV, V.V. LEBEDEV, M.A. POLKANOV, A.G. PTASHKIN, O.A. KNYAZEV, and J.C. MARRA, “Vitrification of Savannah River Site SB4 Waste Surrogate in the Radon Bench-Scale Cold Crucible Unit,” Proc. Int. Conf. Waste Management 2008, February 24 -28, 2008, Phoenix, AZ (2008) Paper # 8035.
6. S.V. STEFANOVSKY, A.P. KOBELEV, V.V. LEBEDEV, M.A. POLKANOV, A.G. PTASHKIN, O.A. KNYAZEV, and J.C. MARRA, “Cold Crucible Vitrification of SRS SB4 Waste at High Waste

Loadings," Proc. ICEM '09 /DECOM '09: 12th International Conference on Environmental Remediation and Radioactive Waste Management, October 11-15, 2009, Liverpool, UK (2009) Abstract, p. 122-123. CD-ROM. Paper #16197.

7. C.M. JANTZEN, N.E. BIBLER, D.C. BEAM, C.L. CROWFORD, and M.A. PICKETT, "Characterization of the DWPF Environmental Assessment Glass SRM," WSRC-TR-92—346 REV. 3, Savannah River, GA (1993).
8. C.C. HERMAN, "Summary of Results for Expanded Macrobatch 3 Variability Study," WSRC-TR-2001-00511 (2001).