

**"PHYSICOCHEMICAL STUDIES OF BASALT-LIKE MATERIALS
INTENDED FOR USE AS RADIOACTIVE WASTE
IMMOBILIZATION MATRICES "**

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This report presents some results obtained in the studies on the immobilization of the most environmentally hazardous actinide fraction of radioactive waste (RW). Immobilization techniques and technology advances may be also applied to the rare earths, cesium and strontium fractions. Our work on improving environmental safety of radioactive waste storage is directed primarily to the use of materials possessing high chemical stability in water and rather simple technology of production. Among others, those materials are represented by basalt-like matrices. Materials used for RW immobilization should meet rather stringent requirements, namely, high radiation and thermal stability, high mechanical strength, and low water solubility rate.

Proposed basalt matrices possess the complex of physicochemical and operating characteristics necessary to meet high requirements imposed on the matrices for long term RW storage. The matrices, having all the above properties, are potentially capable of incorporating and retaining large quantities of different elements contained in radioactive waste, radionuclides included.

For study we have selected samples of acidic and basic silicate and aluminosilicate mountain rocks and minerals, namely, basalts, gabbro, obsidian, and others.

Among the basic rocks there were three samples of basalt and one sample of andesite - basalt from Bashkiriya (Western Ural, Uchaly), samples of methagabbro and pyroxenic porphirite from the Kostomuksha iron ore deposit in Western Karelia.

Acidic volcanic rocks were selected because after embedding large quantities of basic oxides from radioactive waste into the rock its composition would be close to that of the basic ones. The choice of cover rocks from the Kostomuksha deposit (hällflinta and others) was governed by availability, low cost, vast stock, and annual mining capacity thereof. The above rock is recommended as a raw material for glass-making.

Stone cast from the mountain rock (both magmatic and methamorphous) makes one of the promising materials for radioactive waste immobilization. Stone cast is the synthetic aluminosilicate crystalline material obtained from different mountain rocks by means of melting and subsequent crystallization. Stone cast consists of silicate and aluminosilicate minerals, containing primarily oxides of Si, Al, Fe, Ca, Mg, Na, K, and others. In many cases the stone cast composition matches the composition of starting rock minus components volatilized during melting. The stone cast is characterized by low solubility and permeability, physically and chemically stable and resistant to the impact of ionizing radiation. One of the compatibility conditions for a material to be used as the matrix for radionuclide embedding is the absence of large pores and caverns in the cast

which reduce the product strength. Work to identify the connection between composition and porosity of a sample has been performed. Stone cast was obtained from the readily available materials, namely, pyroxenic porphirite, gabbro-diabase, h lleflinta, basalt, and others. In bench scale tests, the blend was melted in a silicon carbide heated furnace, in an oxidizing atmosphere in corundum crucibles of 0.5 L volume at 1350 C. Melts were poured into the heated earth molds, crystallized in the molds for 30 minutes at 900 - 950 C, and cooled during 15 - 17 hours.

Table 1 gives the blend composition and characteristics of some stone cast samples. Chemical composition of some basalt and pyroxenic porphirite samples as well as stone cast compositions are given in Table 2.

Table 1. Blend composition and stone cast characteristics

##	Blend composition, %	Visual appearance	Porosity, %	Water absorption, %
1	Pyroxenic porphirite - 70, gabbro - diabase - 30, chromite - 1 - 1.5 (over 100%)	no bubbles	--	--
2	Pyroxenic porphirite - 70, chromite - 1.5 (over 100%)	no bubbles	0.1	0.08
3	H�lleflinta - 62.5, magnesite - 5.5, marble - 32, chromite - 4 (over 100%)	rare small pores, no bubbles	0.7	0.2

Analysis of the results obtained during determination of the porosity and water absorption (see Table 1) showed that the cast made of pyroxenic porphirite with the additive of chromite (Composition 2) and the cast made of pyroxenic porphirite with the diabase additive (Composition 1) does not contain large pores and bubbles, with the porosity and water absorption of the Composition 2 being close to the detection limit of the methods used. As the amount of pyroxene in the stone cast increases, the porosity and water absorption increase also. This is explained by the material shrinkage due to the difference in density of the original melt (glass) and the pyroxene crystallizing from it.

Besides the basic and acidic volcanic rocks, stone cast samples were also selected as a potential matrix material.

Preliminary studies showed that the stone cast is perfectly suitable for application as a matrix material for incorporating radioactive waste and may be even advantageous, because, unlike the initial rock, it is more homogeneous and gas-free (i.e., volatile compounds are removed in part or completely). Therefore, for further studies we have selected three (3) stone cast compositions based upon pyroxenic porphirite and h lleflinta given in Table 1. The same compositions were selected to study the effect of radiation and heating on the structure and properties of the stone cast used for the matrix material and stone cast container.

Correct approach to the study of basalts and other mountain rocks for application as a matrix for incorporating radionuclides necessarily assumes determination of certain physicochemical properties and, above all, the melting point and weight loss during thermal heating. Those properties were studied within the temperature range of 20 - 1450°C. For study we took the basalt samples and some other mountain rocks, namely, obsidian, diabase, gabbro, pyroxenic porphirite, and stone cast. X-ray diffraction studies and chemical analysis of the rock samples proved that both by the mineralogical and chemical composition those rocks belong to the corresponding mountain rocks.

Results of the derivatographic studies are presented in Table 3 and in Figures 1 - 2 describing rock sample and cast stone behavior under heating to 1450°C.

Character and its intensity of the process occurring in the heated material is governed by the material composition, temperature, etc. During the warm up at 400 - 500°C the following processes basically occur in the blend: removal of hydroxyl water, cracking of conglomerates and mineral grains, burn up of the organic matter, and removal of volatile components, which is accompanied by the weight loss. No substantial change in the chemical and mineralogical composition of the blend is observed. As the temperature increases to 1000 - 1100°C, processes in the materials occur as follows: removal of the chemically bound water, polymorphous transformations in some mineral phases, dissociation of sulfides and carbonates, volatilization of fluorine compounds, oxidation of Fe^{2+} to Fe^{3+} , softening and fusion of glass phase and low melting minerals, which are accompanied both by the weight loss and weight gain of the phase. Heating to 1300°C and higher leads to the complete melting of the solid phase and melt formation due to the interaction and dissolving of high-melting minerals in the melt, melt homogenization and degassing processes. Melting point range of the mountain rocks and stone cast depends primarily on the chemical and mineralogical composition.

Although the oxides of element constituents are high-melting themselves (for example, SiO_2 - 1713 °C, Al_2O_3 - 2050°C, CaO - 2570°C, MgO - 2800°C) the minerals consisting of them are considerably lower melting, especially monoclinic pyroxenic and feldspar minerals as well as ferrous varieties of olivine.

Increased content of basic plagioclase and diamond shaped pyroxenes raises the melting point of the rock.

Materials with high content of SiO_2 and Al_2O_3 are more high-melting (obsidian, flint). As the alkali element and iron oxide content increases, both the content of iron and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio playing its own part, the melting point decreases.

To get good fluidity of the melt it must be heated above the melting point. From the above standpoint, rocks with the high content of silica (obsidian, flint) may be considered promising for the matrices if only special equipment is used, for example, a cold crucible. Basalt, porphirite, and gabbro are much more promising. Application of stone cast for the matrix is supposed to be the most effective as the material melted earlier is more homogeneous, less viscous, gas-free, and shows no weight loss on account of volatile components which is important in the radiochemical industry. Evidently, the rock and stone cast melts should meet certain requirements, namely, possess high chemical and

physical homogeneity, optimum casting, crystallization and technological properties to be studied in further research.

Viscosity of a number of basalt sample melts has been studied. It was shown that the viscosity - temperature curves correspond to the reference data. Data are presented in Tables 4 - 5 and in Figure 3

Table 2. Chemical composition of mountain rock and stone mold, % by weight

Material under study	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	Cr ₂ O ₃
1. Hällefliinta Na, Kostomuksha, Karelia	67,89- 71,89	0,03- 0,14	15,30- 18,91	0,02- 1,92	0,11- 2,70	0,01- 0,17	0,28- 1,30	0,74- 2,70	4,25- 6,87	0,37- 3,06	
Average of 50 analyses	69,98	0,08	17,28	0,44	0,80	0,02	0,70	1,84	5,64	1,35	
2. Stone cast	44- 49	-	12- 19	2- 6	7- 12	-	6- 10	9- 16	2- 5		
3. Major types of basalt and diabase based stone cast	46- 49	-	12- 15	2,5- 8,5	5,4- 11,7	-	4,8- 11	10- 16	1,5- 3,5		
4. Stone cast by Kondopozhskii factory	46,90- 55,68	0,08- 2,16	6,06- 13,40	1,37- 7,95	0,29- 7,33	0,04- 0,22	6,85- 11,61	7,99- 21,26	0,50- 4,78	0,49- 2,64	
5. Basalt #3, Uchaly, Bashkiriya	48,71	0,85	16,57	13,40		0,20	5,84	6,90	3,75	0,43	0,02
6. Pyroxenic porphirite, Karelia	49,58	1,76	13,06	14,13		0,26	7,76	11,15	1,97	0,63	0,05
7. Stone cast (Composition ¹¹)	50,50	2,16	12,52	7,95	7,36	0,22	6,85	7,99	2,73	0,86	0,58
8. Stone cast (Composition ¹²) sample ¹⁰	50,81	1,76	13,31	12,32		0,22	7,91	9,48	2,23	0,89	0,56
9. Stone cast (Composition ¹³)	48,95	0,11	13,46	2,50		0,59	8,98	17,23	4,42	0,71	0,84

Table 3. Rock sample behavior under heating and cooling

smp l. No	Material under study	Thermal effects and temperature ranges corresponding to the processes of weight change							Thermal effects with no weight loss			Weight loss at T=1250 °C, t=1hr(*), %
		T range, °C	$\Delta G/G$, %	T range, °C	$\Delta G/G$, %	T range, °C	$\Delta G/G$, %	Total weigh t loss %	T of phase transition, °C	Peaks on the heating curve, °C	Peaks on the cooling curve, °C	
1	Basalt, Uchaly Bashkiriya	100-215	-0,6	310-710 380-505	-4,5 -2			-5,1	480 endoth	1090, 1215 1235		-3,8
2	Basalt, Uchaly, Bashkiriya			350-440	-2,3	530- 715	-6,5	-8,8	85	1095- 1155		-4,0
3	Andesite-basalt, Uchaly, Bashkiriya.	220-250	-1,2	350-440	-3,6			-4,8	-	1120		-2,3
4	Obsidian, Bashkiriya	150-340	+0,2			890- 1400	+0,67	+0,87		not melted		-2,1
5	Stone cast	70-220	-0,2	650-825	+0,3	915- 1060	+0,3	+0,4		1060	1065	+0,7
6	Diabase West. Karelia	80-200	-0,3	380-870 470-585	-4,9 -2,1			-5,2		1185	1180	
7	Pyroxenic porphirite West. Karelia			400-500	-4	800- 900	-1,5	-5,5	-	1140		

Note: minus (-) sign denotes weight loss, plus (+) sign denotes weight gain

Column (*) gives weight loss in the course of holding 3 g substance samples for 1 hour at 800, 900, 1000, 1100, 1200, and 1250 °C.

Those values in total correspond to the total weight loss of 200 - 400 mg aliquot weights (about 10 times less) in derivatographic investigation.

Table 4. Viscosity of some rocks and minerals

Substance	t, °C	η , Pa·s
Minerals		
Diopside	1400	3.8×10^0
Anortit	1400	3.8×10
Albit	1400	4×10^4
Orthoclase	1400	1×10^8
Rocks		
Diabase	1400	$6 \times 10 - 9 \times 10$
Basalt	1400	5.5×10
Nephelinitic basalt	1400	8×10
Olivinitic basalt	1400	$1.2 \times 10^2 - 1.36 \times 10^2$
Andesite basalt	1400	1.38×10^2
Mount Vesuvius lava	1400	2.5×10^2
Andesite	1400	1.17×10^3
Obsidian	1400	1.7×10^5
Results obtained		
Basalt (sample #1 Tab.3)	1400	1.5×10^2
Stone cast (sample #5 Tab.3)	1400	4.05×10
Basalt (sample #2 Tab.3)	1400	5.0×10

Viscosity of basalt and diabase melts at $T = 1200 - 1400^\circ\text{C}$ is practically a match and is substantially lower than that for andesite and volcanic glass. Viscosity of obsidian at $T = 1400^\circ\text{C}$ is 3 - 4 orders of magnitude higher, and hence, the melt fluidity is lower which would cause major technological complications. Higher melt viscosity for acidic volcanic rocks (especially obsidian) also puts them at a disadvantage as compared to the basic ones (basalt) with regard to the matrix material.

Thus, basalt, porphirites, and stone cast should be preferred for the matrix material.

Chemical resistance of the initial mountain rocks and cast stone to water has been investigated. Leach rate was determined by the electroconductivity of bidistilled water (Kolraush's method) and radiochemical analysis after the sample was held in it for the certain period of time at the temperature of 20°C . The results are presented in Table 6.

Table 5. Results of basalt melt viscosity measurements

	Composition #1 Tab.3		Composition #3 Tab.3		Stone cast Composition #5 Tab.3	
Temperature, °C	Viscosity Puas	decimal viscosity logarithm	Viscosity Puas	decimal viscosity logarithm	Viscosity Puas	decimal viscosity logarithm
980			181000	5.26		
1000			83000	4.92		
1020			43600	4.64	76000	4.88
1040	57500	4.76	29400	4.42	16400	4.21
1060	19200	4.28	15000	4.17	11000	4.04
1080	8700	3.94	10700	4.03	5360	3.73
1100	4360	3.64	7300	3.84	3000	3.47
1120	3160	3.5	4560	3.66	2080	3.32
1140	2180	3.34	2880	3.46	1460	3.16
1160	1450	3.16	2000	3.3	870	2.94
1180	980	2.99	1520	3.18	565	2.75
1200	660	2.83	1090	3.04	400	2.6
1220	510	2.71	795	2.9	304	2.48
1240	380	2.58	575	2.76	234	2.37
1260	270	2.43	435	2.64	190	2.28
1280	218	2.34	362	2.56	145	2.16
1300	177	2.25	262	2.42	119	2.07
1320	136	2.14	200	2.3	87	1.94
1340	109	2.04	150	2.17	78	1.89
1360	79.5	1.9	124	2.09	61.5	1.79
1380	63	1.8	100	2	48.5	1.69
1400	50	1.7	84	1.92	40.5	1.61
1420	40	1.6	63	1.8	33.8	1.53
1440	33	1.52	50	1.7	30	1.48
1460					26.2	1.42
1480						

Table 6. Leach rate of the studied material in bidistilled water, $\text{g/cm}^2/\text{day} \times 10^{-7}$, at $T = 20^\circ\text{C}$

smpl. ##	Material under study	Days			
		1-7	8-14	15-21	22-28
1	Basalt, Uchaly Bashkiriya	1,4	1,5	1,6	1,4
2	Basalt, Uchaly Bashkiriya	1,5	0,8	0,8	0,5
3	Basalt, Uchaly Bashkiriya	1,9	1,5	1,3	1,4
4	Andesite basalt, Uchaly, Bashkiriya	1,5	0,5	0,5	0,4
5	Obsidian Bashkiriya	0,7	0,25	0,2	>0,1
6	Flint Moscow region	1,1	0,7	0,7	0,5
7	Methagabbro Western Karelia	0,8	0,7	0,5	-
8	Stone cast	0,25	0,25	0,1	-

Leach rate in water measured $0.1 - 1.4 \cdot 10^{-7} \text{ g/cm}^2/\text{day}$ ($t = 20 - 28$ days). Obsidian distinguishes itself by the low leach rate of about $0.1 \cdot 10^{-7} \text{ g/cm}^2/\text{day}$. Chemical stability of the stone cast of $0.1 \cdot 10^{-7} \text{ g/cm}^2/\text{day}$ at average is one order of magnitude higher than for the initial mountain rocks.

The stone cast has certain advantages over the initial rocks. Therefore, studies of the effect of different additives to the mountain rocks and stone melt on their melting point, viscosity, and leach rate have been accomplished. The following compounds were studied for the additives: PbO , NaF , B_2O_3 , Fe_2O_3 , NaPO_3 , CaO , Na_2O (Na_2CO_3), and CeO_2 in the amount of 5 and 10% by weight over 100%. A thoroughly stirred blend was held in alundum crucibles at $T = 1100, 1150, 1200$, and 1250°C and the sample behavior in the course of heating, sample condition after the holding period according to the developed criteria, weight change, and efficiency of the additive were evaluated.

Data obtained allowed evaluation of the efficiency of the tested additives on the melting point of the initial material, its viscosity, etc.

Added PbO both in 5 and 10% by weight either does not produce any change or worsens the properties for all four compositions, i.e. ineffective.

Added NaF is not effective for basalt, and to some extent shows the effect on obsidian, methagabbro, and stone cast, especially in the amount of 10%, lowering the melting point, and viscosity. The possibility of evolving SiF_4 in the reaction with silicates may be considered as a disadvantage.

Added Fe_2O_3 gives some effect, lowering the melt viscosity and melting point of the blend, especially for obsidian and methagabbro. It produces no change for basalt and stone cast, i.e. was not efficient.

Added B_2O_3 is the most effective for all compositions as it lowers the melting point and melt viscosity.

Added NaPO_3 is ineffective, and gives practically no change in melt properties.

Added CaO is ineffective, either worsens or makes no difference in properties of three melts. Stone cast melt incorporates up to 10% of CaO without a negative effect on the properties.

Added Na_2O introduced into the blend as Na_2CO_3 is effective, to some extent improves the properties of basalt, methagabbro, and stone cast in the amount of $\geq 10\%$, slightly improves the melting of obsidian.

Added CeO_2 is ineffective, slightly improves the melting and sintering of obsidian, worsens properties of the other compositions, does not incorporate in the melt composition ($< 5\%$), exists as a separate crystalline phase in the melt and on its surface.

Therefore, for further studies we selected the B_2O_3 additive as the most effective of all the additives investigated. To some extent the Fe_2O_3 and Na_2O additives are also effective.

For the matrix, stone cast was selected (based on porphirite with 1.5% chromite additive) with 10 and 15% B_2O_3 additive by weight which, according to the data shown above, possesses the optimum properties.

The following components were studied for incorporation into the matrix: Cs_2O , SrO , CeO_2 , and oxides of actinides U_3O_8 , ThO_2 , and PuO_2 . Maximum loading for element oxides in the melts made at 1250°C and holding time of 1 hour (until the crystalline phase started to settle) was determined by means of evaluating the melt condition after melting and cooling. Leach rate in bidistilled water was also determined.

Since ThO_2 at $T = 1250^\circ\text{C}$ did not incorporate into the melt composition, the melting was repeated at $T = 1350^\circ\text{C}$. The results are shown in Table 7. A possible principle scheme for α -active radwaste immobilization in a Basalt-like matrix is shown in Fig. 4.

From the data obtained, one may conclude the following:

1. The basalt-like #10 stone cast based matrix (melted blend of porphirite + 1.5% chromite $\text{Fe}^{+2}\text{CrO}_4$) with the additive of 10 - 20% B_2O_3 by weight is capable of incorporating sufficiently large quantities of radioactive element oxides for all the major radionuclides encountered in high-level waste (HLW) arising from spent nuclear fuel reprocessing. It should be mentioned that the matrix in question is capable of incorporating about 20% wt. of PuO_2 .

2. Melting temperature of $T = 1250^\circ\text{C}$ is perfectly acceptable for the technology. Melting results in the sufficiently fluid melt which may be poured into containers. After cooling it makes a homogeneous glass-like or glass-crystalline material possessing sufficiently high chemical resistance to leaching in water at the level of $n \cdot 10^{-7}$ - $n \cdot 10^{-8}$ g/cm²/day at 20°C . Incorporated quantities of radionuclide oxides and chemical stability

of the melt are high enough, not inferior and in some cases superior to the well known glass systems currently used for HLW immobilization. 3. Work on the study of physicochemical properties and technological parameters of the system in question will be continued.

Table 7. Incorporation of element oxides into the basalt - like stone cast based matrix at T = 1250°C and the leach rate from melts into bidistilled water

No. of run	Blend composition, % by weight		Element	Melt condition	Leach rate
	Stone cast sample #5 Tab.3	B ₂ O ₃	oxide	after cooling	g/cm ² /day x10 ⁻⁷
			CeO₂		
1	83.4	8.3	8.3	GLASS-LIKE MELT	2
2	80	8	12	GLASS-LIKE MELT	4
3	76.9	7.7	15.4	GLASS-LIKE MELT	0.7
4	80	12	8	GLASS-LIKE MELT	4
5	77	11.5	11.5	GLASS-LIKE MELT	2
6	74.1	11.1	14.8	GLASS-LIKE MELT	1.5
7	74.1	7.4	18.5	GLASS + CRYSTALLINE PHASE	
8	71.4	7.2	21.4	GLASS + CRYSTALLINE PHASE	-
9	71.4	10.7	17.9	GLASS + CRYSTALLINE PHASE	-
10	69.0	10.3	20.7	GLASS + CRYSTALLINE PHASE	-
			U₃O₈		
11	75.2	7.5	17.3	GLASS	0.5
12	71.4	7.2	21.4	GLASS	2
13	72.4	10.9	16.7	GLASS	1
14	69.0	10.3	20.7	GLASS	2
			ThO₂ 1350°C.		
15	75.2	7.5	17.3	GLASS-LIKE MELT	<0.5
16	71.4	7.2	21.4	GLASS-LIKE MELT	<0.5
17	72.4	10.9	16.7	GLASS-LIKE MELT	<0.5
18	69.0	10.3	20.7	GLASS-LIKE MELT	<0.5
			SrO		
19	76.9	7.7	15.4	GLASS	2
20	71.4	7.2	21.4	GLASS	5
21	66.7	6.7	26.2	GLASS	10
22	74.1	11.1	14.8	GLASS	2
23	69.0	10.3	20.7	GLASS	4
24	64.5	9.7	25.8	GLASS	10
			Cs₂O		
25	76.9	7.7	15.4	GLASS	<0.5
26	71.4	7.2	21.4	GLASS + CRYSTALLINE PHASE	-
27	66.7	6.7	26.7	GLASS + CRYSTALLINE	-

				PHASE	
28	74.1	11.1	14.8	GLASS	<0.5
29	69.0	10.3	20.7	GLASS + CRYSTALLINE PHASE	-
30	64.5	9.7	25.8	GLASS + CRYSTALLINE PHASE	-
			PuO₂		
31	74.1	7.4	18.5	GLASS	0.3
32	71.4	10.7	17.9	GLASS	0.2

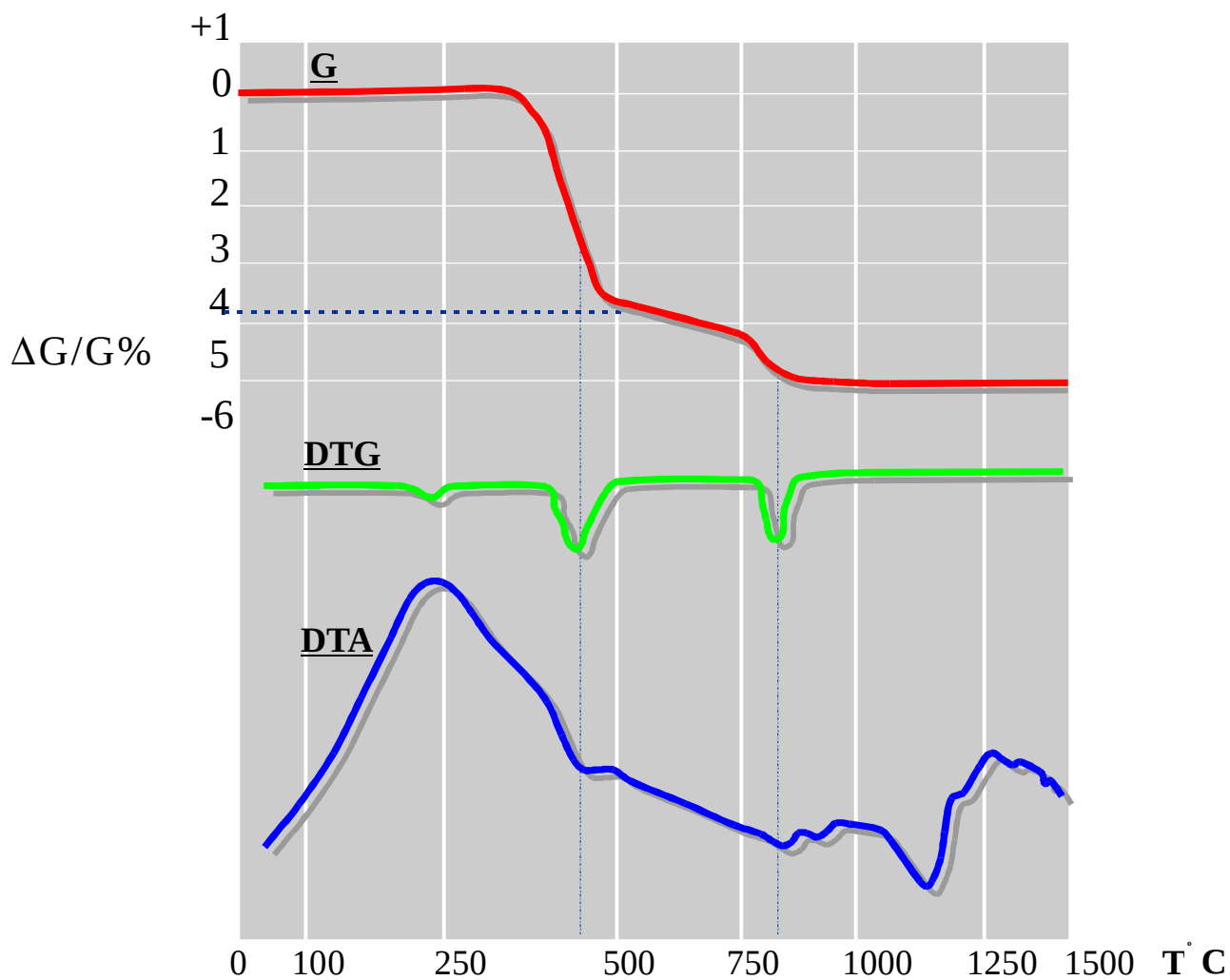


Fig. 1. Pyroxenic porphirite sample behavior under heating.

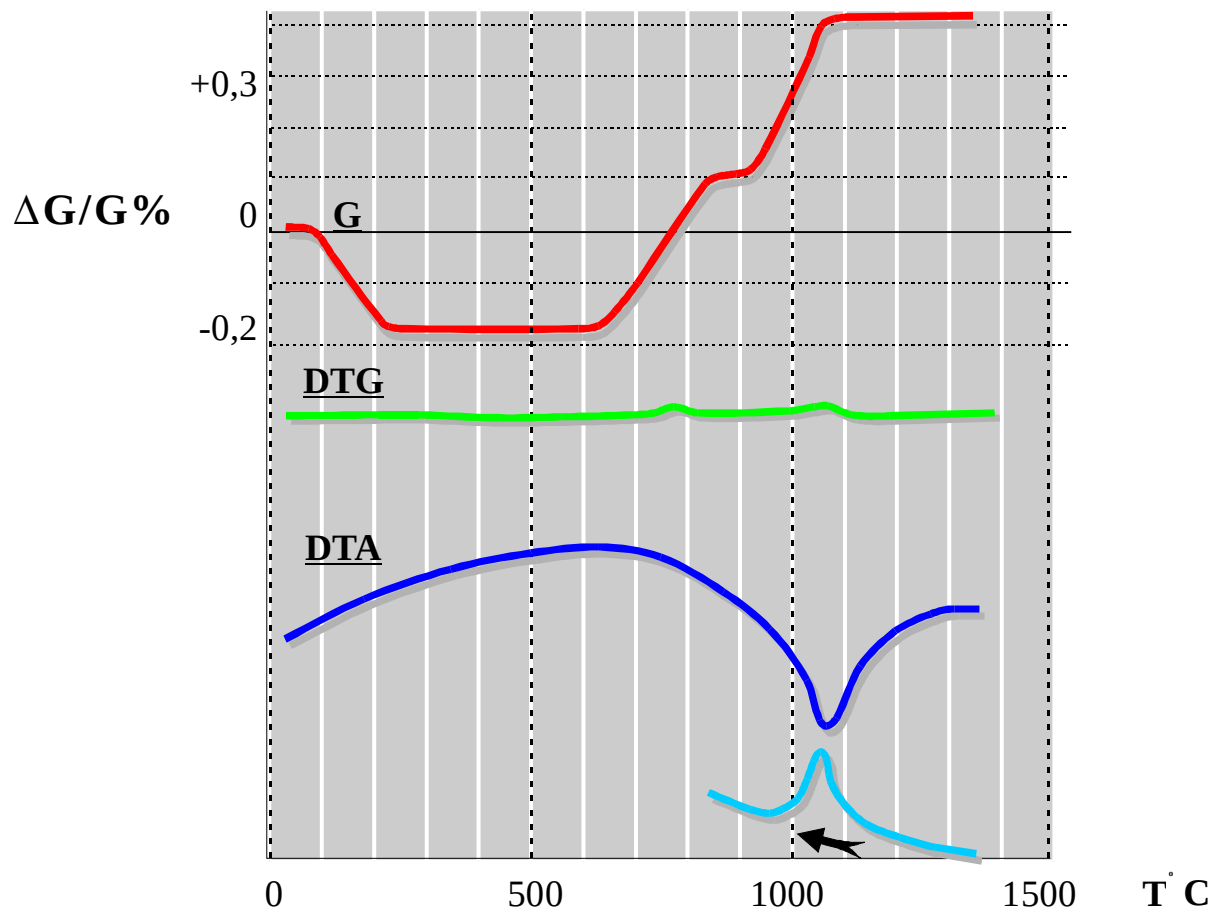


Fig. 2 Stone cast sample behavior under heating.

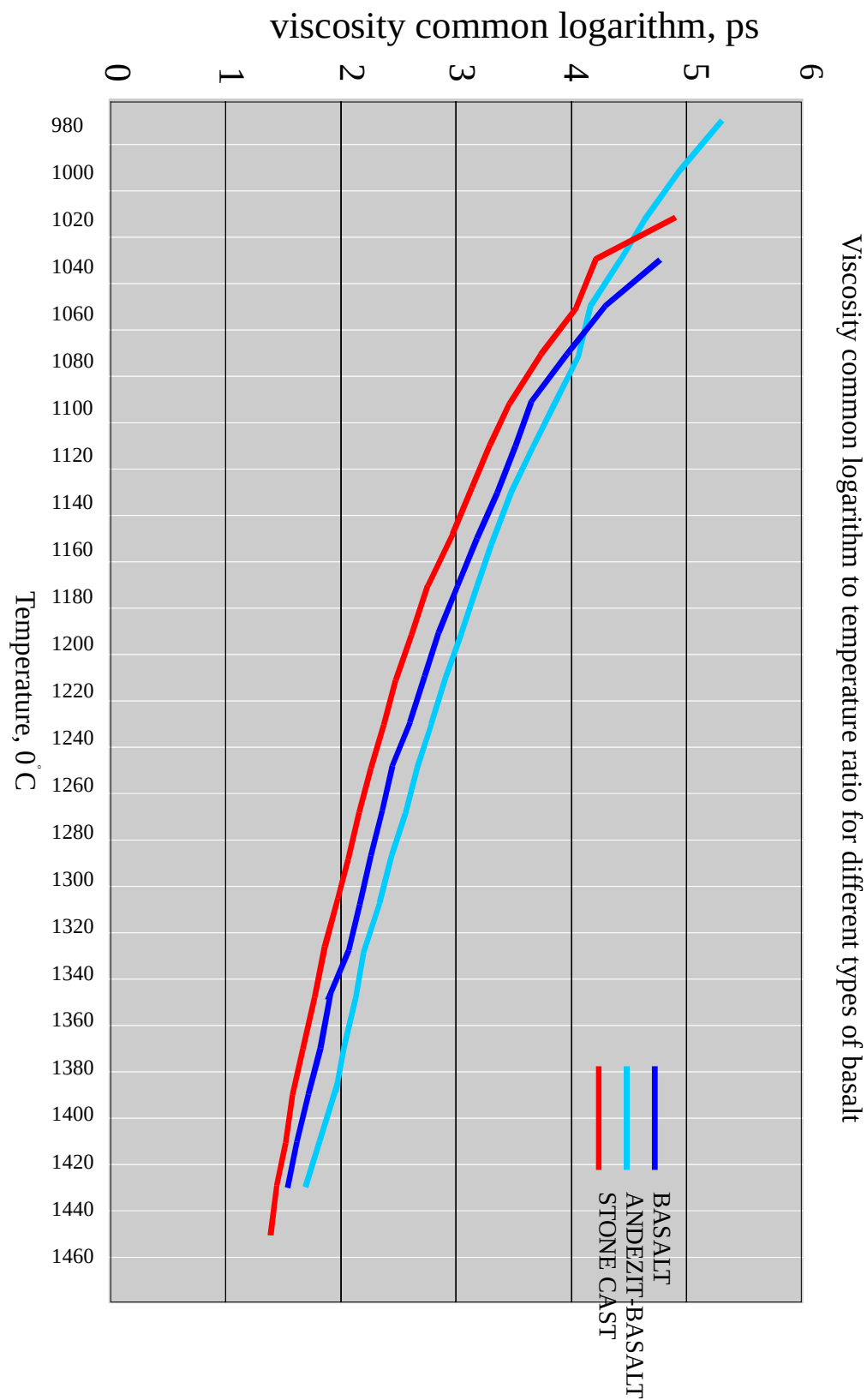


Fig. 3

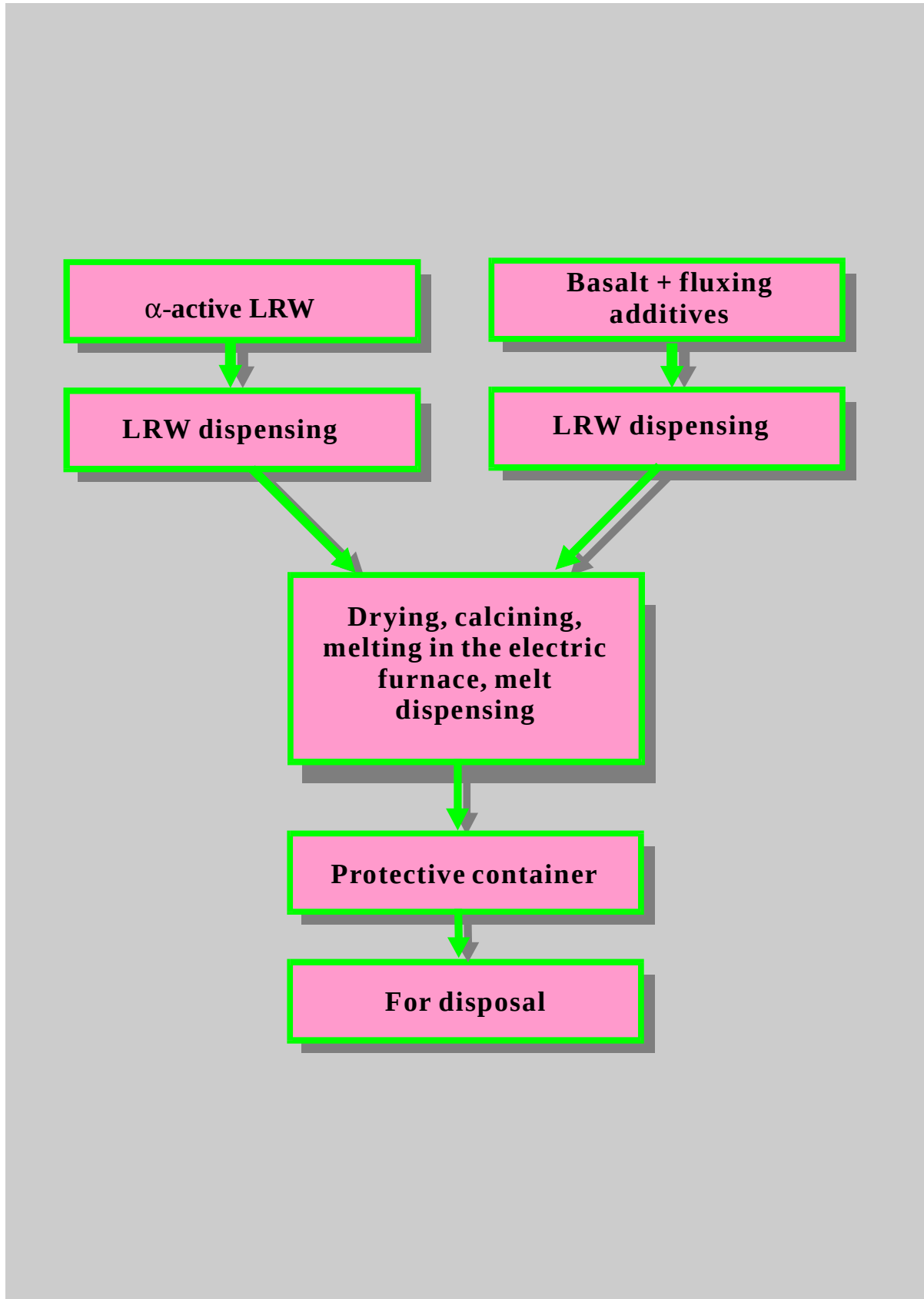


Fig.4. Proposed flowsheet of Immobilization of α -active Liquid Radwaste in Basalt Matrix.

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