CRADA Final Report ANL/NE/C0300701

"Ceramicrete Stabilization of Radioactive-Salt-Containing Liquid Waste and Sludge Water"

This CRADA involved Argonne National Laboratory as the Contractor and overall Project Manager. The CRADA Industrial Participant was CH2M HILL Companies, Ltd of Greenwood Village, CO. The Russian Federation Laboratory Project Subcontractors who did the majority of the work included the following parties:

Vernadsky Institute of Geochemistry and Analytical Chemistry Mayak Site, Laboratory

To improve logistics in contracting in the Russian Federation, the U.S. Civilian Research and Development Foundation (CRDF), not-for-profit organization, put in place the subcontracts. The project number is RCO-10116-MO-03(ANL). Argonne National Laboratory served as the technical manager of this contract under the NIS-IPP program.

The attached RCO-10116-MO-03 (ANL) task reports, 18, 19 and 20 serve as the CRADA Final Report.

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Task 18.1.
Preparation and Testing of actual (hot) samples - bench scale

18.1.1. Mayak Stream 1 solidification (bench scale)

Successful results obtained in Tasks 17.1-17.3 gave grounds to provide synthesis hot (radioactive) Ceramicrete samples according to the advanced technology.

In order to prepare hot samples, real solutions watering to safe treatment level were used. As cesium radiant alkaline supernatant diluted 1000 times was used. As strontium radiant one of technological products was used. As I-129 radiant alkaline regenerative solution of filter gas purification from radiochemistry plant was used.

As a result of three components mixing the solution with specific activity of ^{137}Cs - $1.81 \cdot 10^7$ Bq/L, ^{90}Sr – $1.88 \cdot 10^6$ Bq/L, ^{129}I - $2.81 \cdot 10^6$ Bq/L for preparation surrogate Stream 1 was obtained.

For preparation surrogate Stream 1 34 g NaOH, 33.4 g - $NaNO_3$, 11.5 g - $NaNO_2$, 18 g $Al(NO_3)_3 \cdot 9H_2O$, Na_2SO_4 – 1.27 g, NaCl – 0.59 g, NaF – 0.11 g, K_2CrO_4 – 3.04 g were dissolved in 153 mL of radioactive solution. The acquired solution had volume 190 mL and density 1.31 g/cm^3 . Its composition is given in Table 1.

Table 1

Modified Mayak Stream-1 properties

Components concentration, g/L									^{137}Cs, Bq/L	^{90}Sr, Bq/L	^{129}I, Bq/L
NaOH	Na^+	Al^{3+}	NO_3^-	NO_2^-	SO_4^{2-}	Cl^-	CrO_4^{2-}	TDS			
179.9	175.5	7.2	177.6	40.2	4.5	1.9	9.6	499	$1.46 \cdot 10^7$	$1.51 \cdot 10^6$	$2.26 \cdot 10^6$
TDS – total dissolved solids											

Than, as provided by Ceramicrete advanced technology alkaline solution was neutralized by 25 mL phosphoric acid (ρ=1.69 g/cm^3) up to pH 8. Nitrogen oxide release was observed during the process of neutralization. After it color of the solution changed from primrose to olive caused by reduction of Cr(VI) до Cr(III) and the formation the precipitates of hydroxides $Al(OH)_3$, $Cr(OH)_3$. Next 34 mL of nickel ferrocyanide suspension (ρ=1.17 g/cm^3, consisted of 114.9 g/L nickel ferrocyanide, 6.5 g/L – $Ni(NO_3)_2$, 140.6 g/L – KNO_3), 37.9 g of dry granulated anion exchange resin AV-17 in chloride form (Cl-form)

were introduced into the neutralized solution and it was blended for 60 minutes to fix cesium and iodine.

Than, 21.0 g $Na_2S{\cdot}9H_2O$, dissolved in 50 ml of initially prepared radioactive solution were introduced in obtained mixture stirring up. Its color became black due to precipitation of nickel sulfide. Obtained sludge had pH 10.5. To prevent nickel ferrocyanide from eventual destruction, 4 ml of concentrated nitric acid (12.4 M, density 1.35 g/cm^3) was added in order to stabilize pH at level below 9.

Finally initially prepared radioactive solution was added up to 355 mL. Obtained mixture had density 1.26 g/cm^3 and was used in Ceramicrete synthesis.

Magnesium oxide calcined at 1400 ^{o}C for 4 hours was used for synthesis of the ceramics. Boric acid in quantity 4 % was added to the compound to prolong solidification time. Wollastonite in quantity 15 % was added to the compound to increase compressive strength. The composition is described in Table 2.

Table 2

Composition for Mayak Stream 1 solidification

Composition					
MgO	KH_2PO_4	Stream 1	H_3BO_3	Wollastonite	Total
109.7 g	328.4 g	447.3 g	38.7 g	156.9 g	1081.0 g
10.1 %	30.4 %	41.4 %	3.6 %	14.5 %	100 %

Boric acid and wollastonite were added subsequently with one hour interval continuously stirring up. Than potassium dihydrophosphate was introduced. Mixture was stirred during 2 hours in order to reach the complete dissolution of the introduced components. Further, MgO was added and the obtained mixture was blended 50 minutes and than was poured in the moulds. For next 10 minutes stiffening of the composition occurred.

Temperature during preparation of the samples has been monitored. The temperature maximum during solidification was about 70 degrees C.

After 4 weeks of curing the samples were extracted from the moulds. Physical parameters of the samples with solidified Stream 1 are given in Table 3.

Table 3

Physical properties of the samples with Mayak Stream 1

Sample #	D, cm	H, cm	Weight, g	ρ, g/cm^3	Sample purpose	Compressive strength, kg/cm^2
1	2.5	5.2	44.08	1.73	for TCLP	90
2	2.5	5.1	43.23	1.73	for PCT	83
3	4.63	11.66	341.69	1.74	for ANS	-
4	4.64	11.08	324.03	1.73		-

18.1.2. Mayak Stream 2 solidification (bench scale)

In order to prepare surrogate Stream 2 the solution $Fe(NO_3)_3$ in HNO_3 14.7 mL in volume was taken, than it was neutralized by 7 mL NaOH (600 g/L) and radioactive product containing alpha-emitting nuclides (AENP) was added up to 50 mL. As a result radioactive Fe(III) hydroxide sludge with density 1.135 g/cm^3 was obtained.

The following salts were dissolved in 16.7 mL AENP - $Sr(NO_3)_2$ – 9.47 g, K_2CrO_4 – 0.3 g, $Ni(NO_3)_2 \cdot 6H_2O$ – 2.3 g and combined with the Fe(III) hydroxide sludge. Further 61.3 mL nickel ferrocyanide suspension (nickel ferrocyanide – 115 g/L, $Ni(NO_3)_2$ – 6.5 g/L, KNO_3 – 140.6 g/L, ρ=1.17 g/cm^3) was added to the obtained sludge. As a result the volume of received radioactive sludge achieved 128 mL.

Than 15.06 g $Na_2S \cdot 9H_2O$ previously dissolved in 30 mL AENP was introduced into the sludge, whose color became black due to precipitation of nickel sulfide. Further pH was corrected to 10 by introducing 10.2 mL NaOH (600 g/L). At last AENP was added up to 250 mL. The sludge with density 1.10 g/cm^3 and specific alpha-activity $1.29 \cdot 10^5$ Bq/L was used in Ceramicrete synthesis. Its chemical content is presented in Table 4.

Table 4

Modified Mayak Stream-2 properties

Components concentration, g/L										Σα, Bq/L
Na^+	Sr^{2+}	K^+	Ni^{2+}	Cr^{3+}	$Fe(OH)_3$	SO_4^{2-}	NO_3^-	NFC	TDS	
24.0	15.7	13.6	2.36	0.25	19.7	24.2	82.6	28.2	210.7	$1.29 \cdot 10^5$
NFC - nickel ferrocyanide, g/L; TDS – total dissolved solids, g/L; ρ – solution density, g/cm^3; Σα – total activity of α-emitting nuclides, Bq/L										

Magnesium oxide calcined at 1400 ^oC for 4 hours was used for synthesis of the ceramics. Boric acid in quantity 2.5 % was added to the compound to prolong solidification time. Wollastonite in quantity 15 % was added in order to increase compressive strength. The composition is described in Table 5.

Boric acid and wollastonite was added subsequently with one hour interval continuously stirring up. Than potassium dihydrophosphate was introduced. The solution was stirred during 2 hour in order to reach the complete dissolution of the introduced components. After it, MgO was added and the obtained mixture was blended 30 minutes and than was poured in the moulds. For next 20 minutes stiffening of the composition

occurred. Temperature during preparation of the samples has been monitored, the temperature maximum during solidification was about 65 degrees C.

Table 5

Composition for Mayak Stream 2 solidification

Composition					
MgO	KH_2PO_4	Stream 2	H_3BO_3	Wollastonite	Total
110.8 g	333.4 g	275.0 g	21.5 g	128.8 g	869.5 g
12.8 %	38.3 %	31.6 %	2.5 %	14.8 %	100 %

After 4 weeks of curing the samples were extracted from the moulds. An exterior of the samples with solidified Mayak Stream 1&2 are shown in Fig. 1 and its physical parameters are given in Table 6.

Table 6

Physical properties of the samples with Stream 2

Sample №	D, cm	H, cm	Weight, g	ρ, g/cm^3	Sample purpose	Compressive strength, kg/cm^2
1	2.5	5.1	45.04	1.80	for TCLP	97
2	2.5	5.2	45.67	1.79	for PCT	102
3	4.61	9.14	274.53	1.80	for ANS	-
4	4.61	11.10	335.18	1.81		-

Chemical resistance of Ceramicrete has been assessed in concordance with three test procedures: ANS, TCLP and PCT. Leaching of radionuclides Cs, Sr, I and Na, NO_3, SO_4, Cr, Ni, Sr, K, Mg, PO_4 were tested according to ANS 16.1, TCLP procedure was used for Ni, Cr and Sr, and PCT procedure was used for Mg, K, P and Na.

For test operation according to ANS 16.1 Ceramicrete samples were hooked on a loop of copper wire (Fig. 2).

Figure 1 - Ceramicrete samples with solidified Mayak Streams 1&2

Figure 2 - Attachment of test specimen

18.1.3. Hazardous contaminants leaching study using TCLP test

Hazardous contaminants fixation in Ceramicrete has been assessed according to TCLP test procedure. Ceramicrete samples with 1′ diameter were used. TCLP test conditions are presented in Table 7. TCLP test results for Ceramicrete samples with Stream 1&d 2 are presented in Table 8.

Table 7

Summary of TCLP Test conditions

Liquid/Solid ratio, g/g	Leachant	Extraction time, hours	Sample mass, g	Particle size, mm	Test Vessel	Filter type
20	Extraction fluid #1	20	5	3-8	TFE-fluorocarbon	0.7 μm glass fiber

Table 8

TCLP Test Results for Hot Ceramicrete Samples with waste Stream 1&2 (element content in mg/L)

Waste type	Initial weigh, g	Final weigh, g	Loss of weight, %	Leachate pH	Components concentration, mg/L		
					Cr (0.85*)	Ni (1.0*)	Sr
Leachant	-	-	-	4.9	**< 0.01**	**< 0.01**	-
Stream 1	5.00	4.29	14.2	6.45	0.08	-	-
	5.00	4.36	12.8	6.25	0.06	-	-
Average	5.00	4.33	**13.5**	6.35	**0.07**	-	-
Stream 2	5.00	4.66	6.8	7.20	0.08	0.71	9.1
	5.00	4.68	6.4	7.30	0.08	0.62	8.7
Average	5.00	4.67	**6.6**	7.25	**0.08**	**0.67**	**8.9**
* - UTS limits for these elements are shown in brackets							

TCLP test shows that Ceramicrete samples with solidified Mayak Stream 1&2 leach Ni, Cr into leachate in concentrations considerably below the UTS limits.

18.1.4. Matrix constituents, Na^+ and NO_3^- leaching study using PCT test

PCT test has been carried out with 1′ diameter Ceramicrete samples synthesized using surrogate wastes. Ceramicrete samples were kept in moulds during 4 weeks. Then these samples were extracted, their physical parameters were determined, and they were prepared for PCT leaching tests.

PCT Test conditions are presented in Table 9. PCT test results for different Ceramicrete samples are presented in Table 10. Two samples were used in parallel for the tests.

Table 9

Summary of PCT Test conditions

Liquid/ Solid ratio, g/g	Leachant	Test temperature, ^{0}C	Extraction time, days	Sample mass, g	Particle size, μm	Test Vessel	Filter type
10	Distilled water	90	7	4	74-149	TFE-fluoro-carbon	0.7 μm glass fiber

As shown in the Table 10, reference Ceramicrete samples lost 35-47 % of their weight. Salt constituent of the wastes is not fixed chemically in the Ceramicrete matrix, therefore it should have been expected that soluble components of the wastes would completely transfer from powder samples into leachate. However, even in this case the loss of weight should not be such great as far as salt component make up about 15 % of the sample weight for Stream 1 and about 4 % for Stream 2. Thus, the considerable loss of weight is probably caused by leaching of structural components of the matrix. There are two reasons that may cause it. In our opinion, the main reason is a destruction of the original crystal structure of the sample under thermal effect. Thermographic analysis showed that Ceramicrete looses 22-25 % of weight in the range of temperatures from 70 to 90 ^{o}C. Apparently, it is connected with elimination of crystal water from the matrix and changes in original crystal structure of the material and its properties. Another reason is a mechanical destruction of the crystal structure that is forming around particles of unreacted magnesium oxide. As a result of the destruction of Ceramicrete crystals unreacted initial components are transferred into leaching medium.

Table 10

PCT Test Results for Ceramicrete Samples with Mayak Stream 1&2

Waste type	Initial weight, g	Final weight, g	Loss of weight, %	Leachate pH	Components concentration, mg/L				
					Na	NO_3	K	Mg	PO_4
Stream 1	4.00	2.57	35.75	9.80	1934	3500	5796	8.0	5200
	4.00	2.59	35.25	9.80	1977	4000	6397	9.0	5900
Average	4.00	2.58	**35.50**	9.80	**1956**	**3750**	**6097**	**8.5**	**5350**
Stream 2	4.00	2.10	47.50	9.30	315	1900	7250	3.0	8700
	4.00	2.14	46.50	9.50	320	1800	7520	2.9	8300
Average	4.00	2.12	**47.0**	9.40	**317**	**1850**	**7385**	**3.0**	**8500**

PCT test data were used for leaching rate calculation of structure-forming constituents of the ceramics matrix (K, Mg, PO_4) and major salt components ($NaNO_3$). Results of the leaching rate calculation are obtained for the surface of powder material 12.2 m^2/g (Stream 1) and 17.5 m^2/g (Stream 2). Data for different Ceramicrete samples are presented in Table 10-1.

Table 10-1

PCT Test Results for Ceramicrete Samples

Waste type	Leaching rate, $g/(cm^2 \cdot day)$				
	Na	NO_3	K	Mg	PO_4
Stream 1	$2{,}9 \cdot 10^{-6}$	$4{,}6 \cdot 10^{-6}$	$3{,}3 \cdot 10^{-6}$	$7{,}0 \cdot 10^{-9}$	$1{,}1 \cdot 10^{-6}$
	$2{,}7 \cdot 10^{-6}$	$4{,}8 \cdot 10^{-6}$	$3{,}4 \cdot 10^{-6}$	$7{,}1 \cdot 10^{-9}$	$1{,}1 \cdot 10^{-6}$
Average	$\mathbf{2{,}8 \cdot 10^{-6}}$	$\mathbf{4{,}7 \cdot 10^{-6}}$	$\mathbf{3{,}4 \cdot 10^{-6}}$	$\mathbf{7{,}0 \cdot 10^{-9}}$	$\mathbf{1{,}1 \cdot 10^{-6}}$
Stream 2	$1{,}2 \cdot 10^{-6}$	$2{,}1 \cdot 10^{-6}$	$2{,}2 \cdot 10^{-6}$	$1{,}4 \cdot 10^{-9}$	$1{,}1 \cdot 10^{-6}$
	$1{,}2 \cdot 10^{-6}$	$2{,}0 \cdot 10^{-6}$	$2{,}2 \cdot 10^{-6}$	$1{,}3 \cdot 10^{-9}$	$1{,}0 \cdot 10^{-6}$
Average	$\mathbf{1{,}2 \cdot 10^{-6}}$	$\mathbf{2{,}0 \cdot 10^{-6}}$	$\mathbf{2{,}2 \cdot 10^{-6}}$	$\mathbf{1{,}3 \cdot 10^{-9}}$	$\mathbf{1{,}0 \cdot 10^{-6}}$

18.1.5. Contaminants leaching study using ANS 16.1 test

18.1.5.1. Matrix with solidified Mayak Stream 1

In accordance with ANS 16.1 chemical resistance of Ceramicrete samples leaching was studied at 20°C. Twice-distilled water was used as leaching agent. Sampling of the leaching medium was performed in 2 hours, 7 hours, 1 day, 2 days, 3 days, 4 days, 5 days, 19 days, 47 days and 90 days. A volume of the contact solution (leaching medium) was calculated for each sample taking into account its surface area in according to requirements of the procedure to ensure solid surface/liquid volume ratio equal 1:10. Contents of waste components ^{137}Cs, ^{90}Sr, ^{129}I, Na, Cr, NO_3, SO_4 as well as matrix elements K, Mg, PO_4 were determined in the leaching medium. Concentrations of the chemical components in the leaching medium were determined by the method of liquid chromatography. On determining quantity of each component leached from matrices for test time its initial content in the leaching medium was taken into account.

Analysis of leaching curves (Fig. 3) have shown that waste macro-components (sodium, nitrates) are leached in considerable degree. For sodium and sulfates the results get close to the results obtained in previous investigations: 41 % and 15 %, respectively. Nitrates are leached completely up to 100 %.

Strength of chromium fixation with Ceramicrete was two orders of magnitude higher than sodium fixation strength. Concentrations of chromium in leachate samples were $\leq$ 0.01 mg/L. In cases when concentration was < 0.01 mg/L the value of 0.01 mg/L was taken for calculations. Chromium cumulative fraction leached is stabilized on levels 0.65 % (Fig.4).

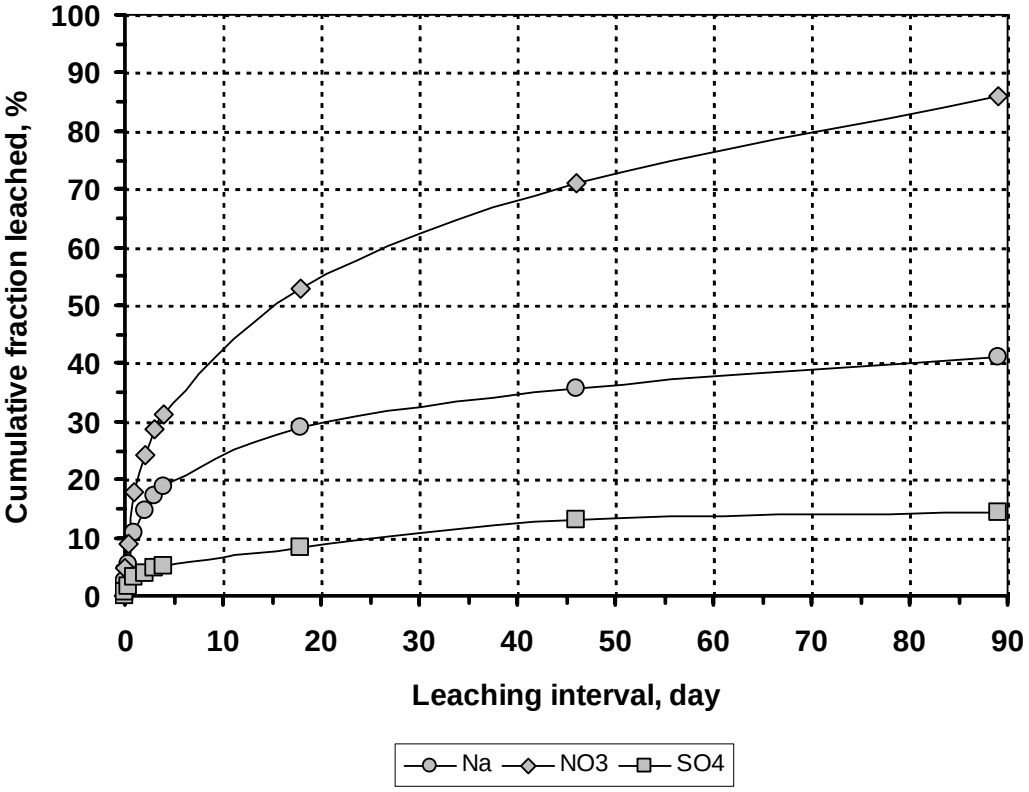


Figure 3 - Waste components cumulative fraction leached as a function of leaching interval

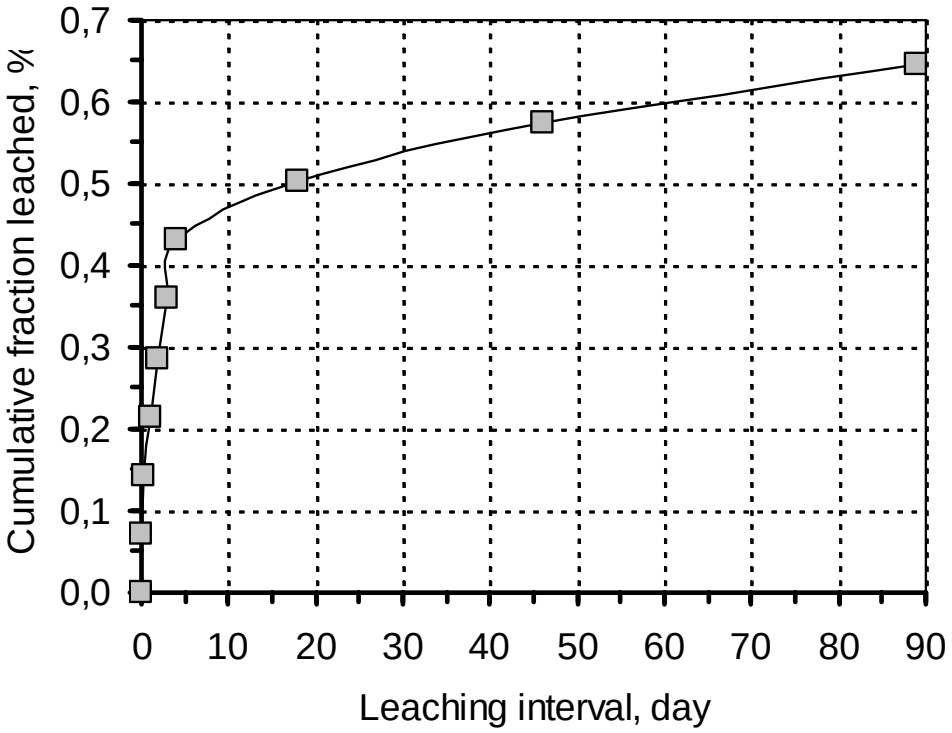


Figure 4 - Cr cumulative fraction leached as a function of leaching interval

Concentration measurements structure-forming constituents of the ceramics matrix (K^+, Mg^{2+}, PO_4^{3-}) in leaching medium have shown that contents of phosphates, potassium and magnesium changed within the ranges of 300-900 mg/L, 300-1200 mg/L, and 6-14 mg/L, respectively. Based on the data obtained cumulative fractions leached of the structure-forming constituents of Ceramicrete were determined. Results of the calculations are presented graphically in Fig. 5. Potassium cumulative fraction leached is about 32 %, phosphate cumulative fraction leached is about 9 %, and magnesium cumulative fraction leached is about 0.6 %.

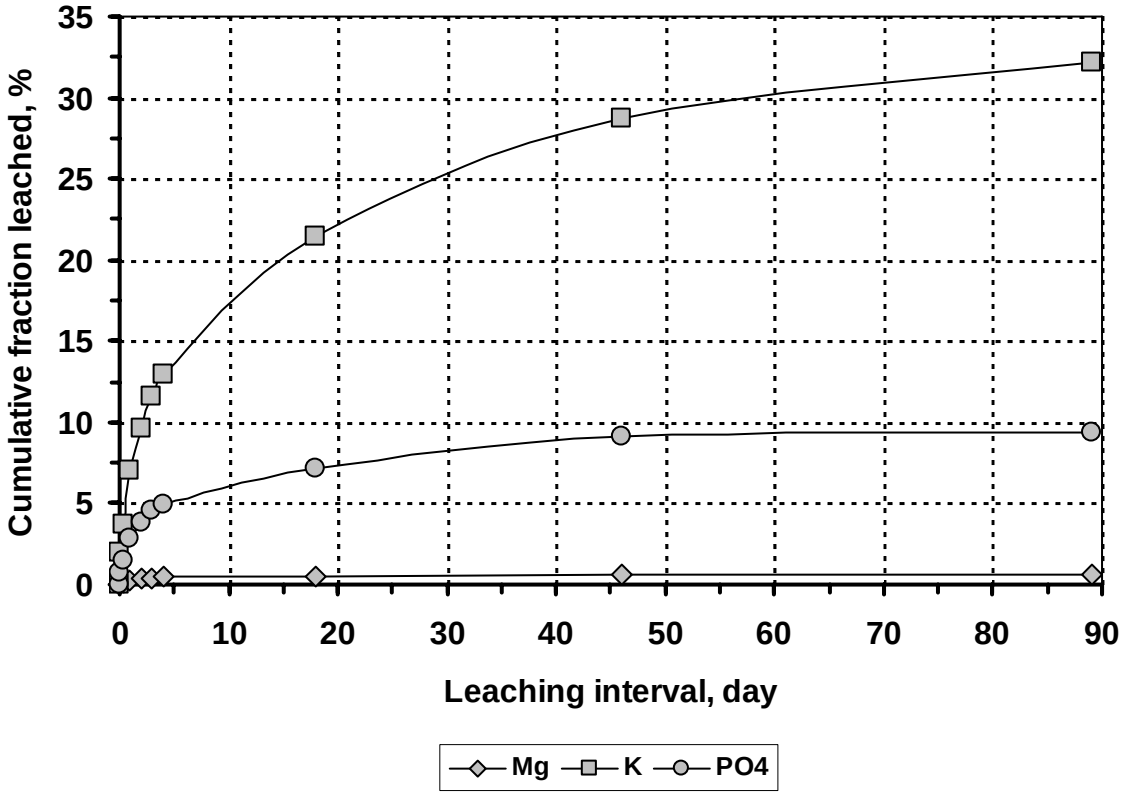


Figure 5 – Matrix components cumulative fraction leached as a function of leaching interval

Activity measurements of leaching medium have shown that the application of nickel ferrocyanide to fix cesium turned out effective. Cesium cumulative fraction leached was only 0.08 %. ^{90}Sr also fix in matrix strongly and its cumulative fraction leached was 0.67 % (Fig. 6). For ^{129}I this value is considerably higher, namely 28.7 % (Fig. 7). Based on radionuclides leaching data Leachability Indexes were calculated (Fig. 8).

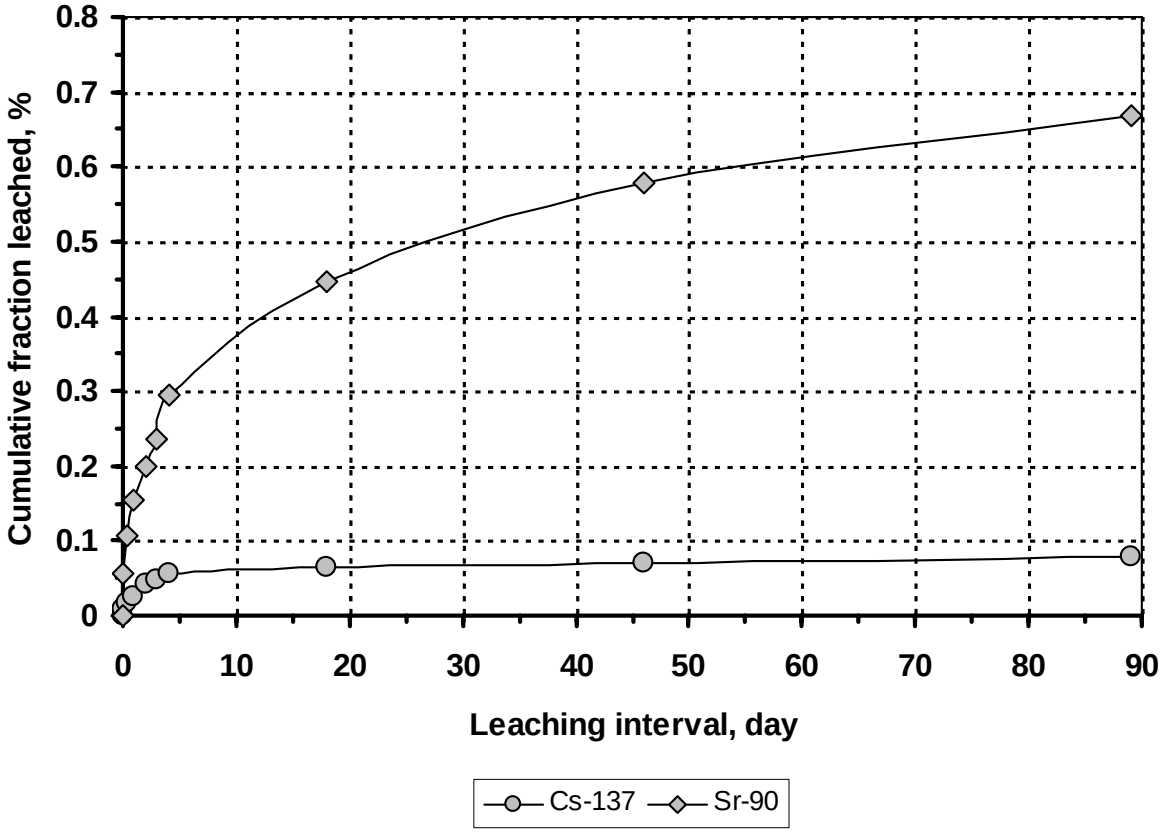


Figure 6 - ^{137}Cs and ^{90}Sr cumulative fraction leached as a function of leaching interval

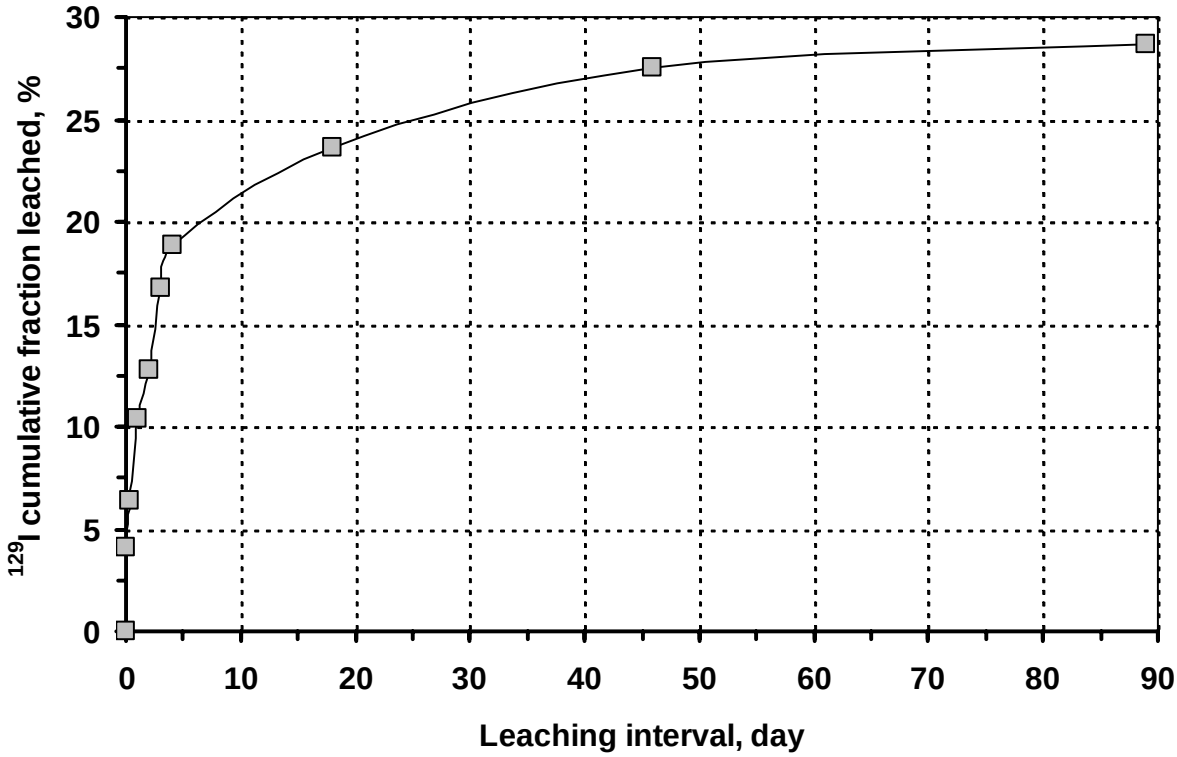


Figure 7 - ^{129}I cumulative fraction leached as a function of leaching interval

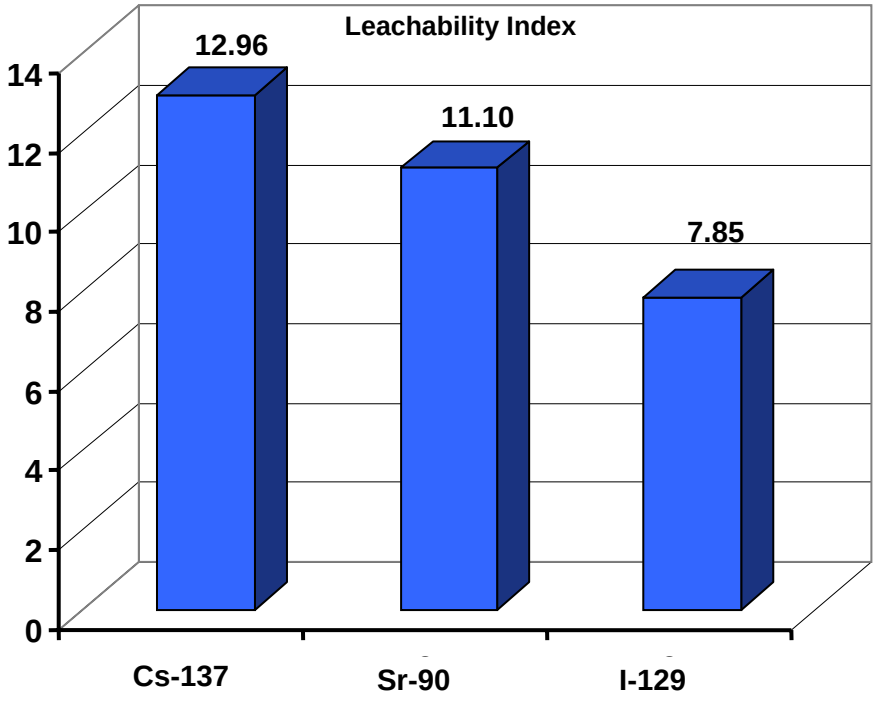


Figure 8 – Radionuclides Leachability Indexes according to ANS 16.1

18.1.5.2. Matrix with solidified Mayak Stream 2

In accordance with ANS 16.1 chemical resistance of Ceramicrete samples leaching was studied at 20°C. Twice-distilled water was used as leaching agent. Sampling of the leaching medium was performed in 2 hours, 7 hours, 1 day, 2 days, 3 days, 4 days, 5 days, 19 days, 47 days and 90 days. A volume of the contact solution (leaching medium) was calculated for each sample taking into account its surface area in according to requirements of the procedure to ensure solid surface/liquid volume ratio equal 1:10. Contents of waste components ^{137}Cs, ^{90}Sr, ^{129}I, Na, Cr, NO_3, SO_4 as well as matrix elements K, Mg, PO_4 were determined in the leaching medium. Concentrations of the chemical components in the leaching medium were determined by the method of liquid chromatography. On determining quantity of each component leached from matrices for test time its initial content in the leaching medium was taken into account.

Analysis of leaching curves (Fig. 9) have shown that waste macro-components (sodium, nitrates) are leached completely. Strength of chromium, nickel and strontium fixation with Ceramicrete was much better than for sodium (Fig. 10). Concentrations of chromium and nickel in leachate were ≤ 0.01 mg/L (in this case the value of 0.01 mg/L was

taken for calculations). Cumulative fraction leached have been calculated based on these conservative assessments. Chromium, nickel and strontium cumulative fraction leached are reached 6.9 % 0.7 % and 1.8 %, respectively.

Leaching of Ceramicrete structure-forming constituents (K^+, Mg^{2+}, PO_4^{3-}) were the same as for Stream 1 (Fig. 11). Potassium cumulative fraction leached is about 30 %, phosphate cumulative fraction leached is about 11 %, and magnesium cumulative fraction leached is about 0.7 %. Radiometric measurements of leaching medium have shown that activity changed from 0.3 to 1 Bq/L.

Based on the radiometric measurements of the leaching medium cumulative fraction leached of α-emitting nuclides were calculated. During leaching test (90 days) 0.08 % of total alpha-activity of the samples passed into leaching medium and Leachability Index of alpha-emitting nuclides was 12.9. The tests have shown that for the first 4 days more than 50 % of α-activity passed into the leaching medium and then leaching rate decreased sharply. The results of these calculations are presented in Fig. 12. The data obtained permit to state that Ceramicrete fixes α-emitting nuclides rather strongly.

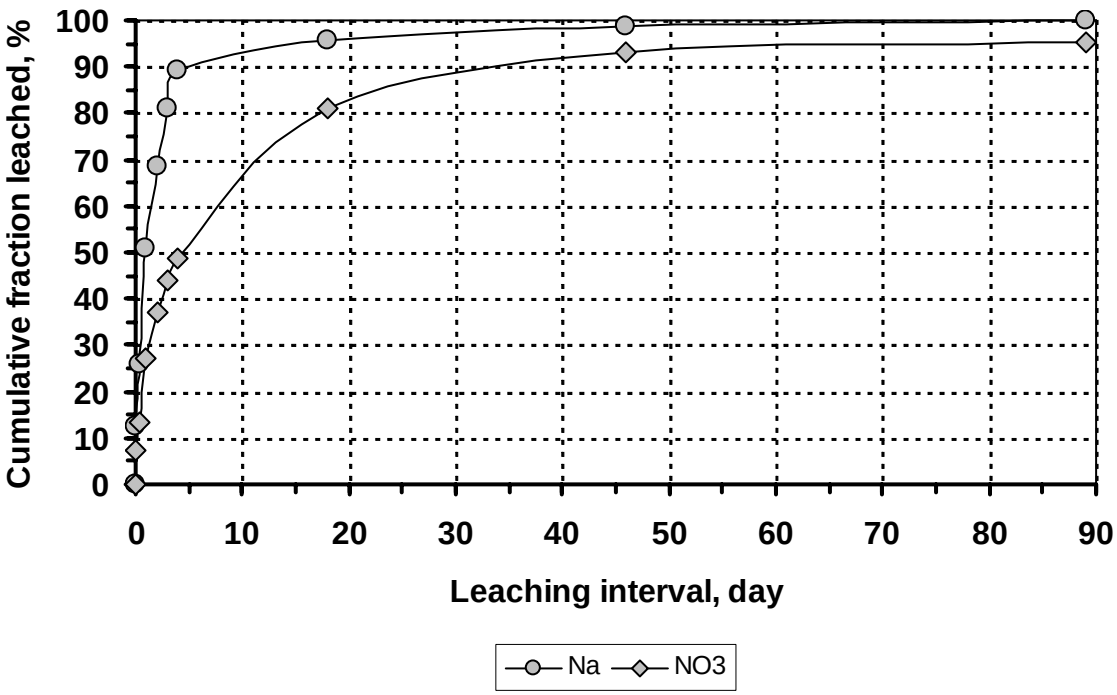


Figure 9 - Waste components cumulative fraction leached as a function of leaching interval

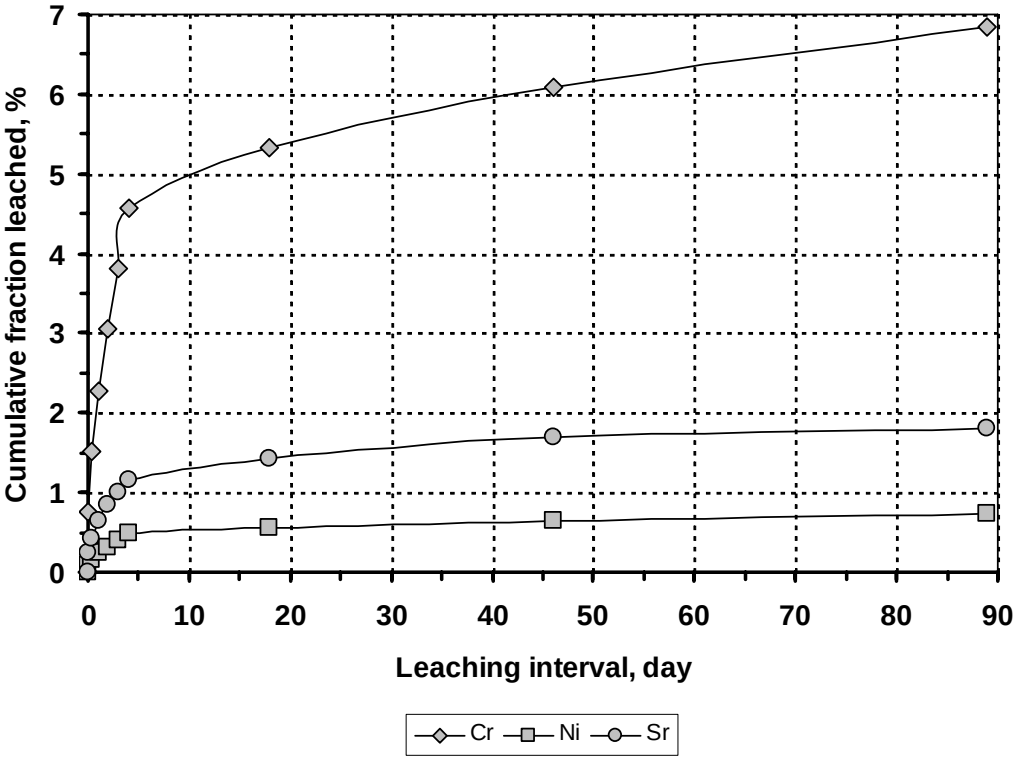


Figure 10 - Waste components cumulative fraction leached as a function of leaching interval

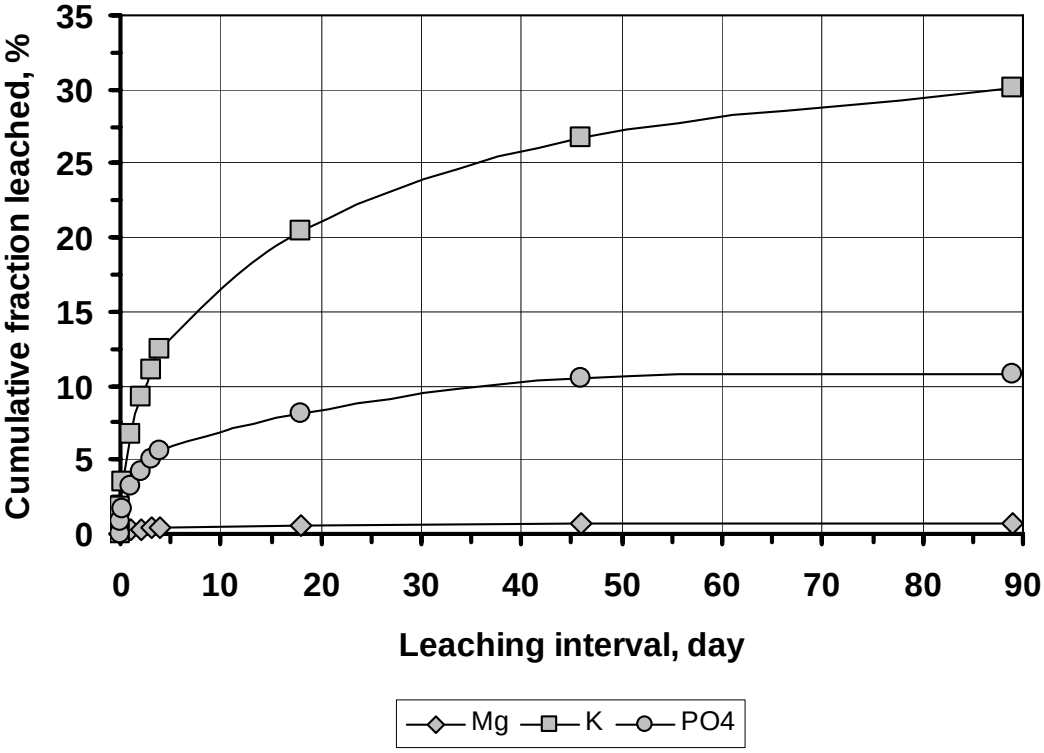


Figure 11 – Matrix components (Mg, K, PO_4) cumulative fraction leached as a function of leaching interval

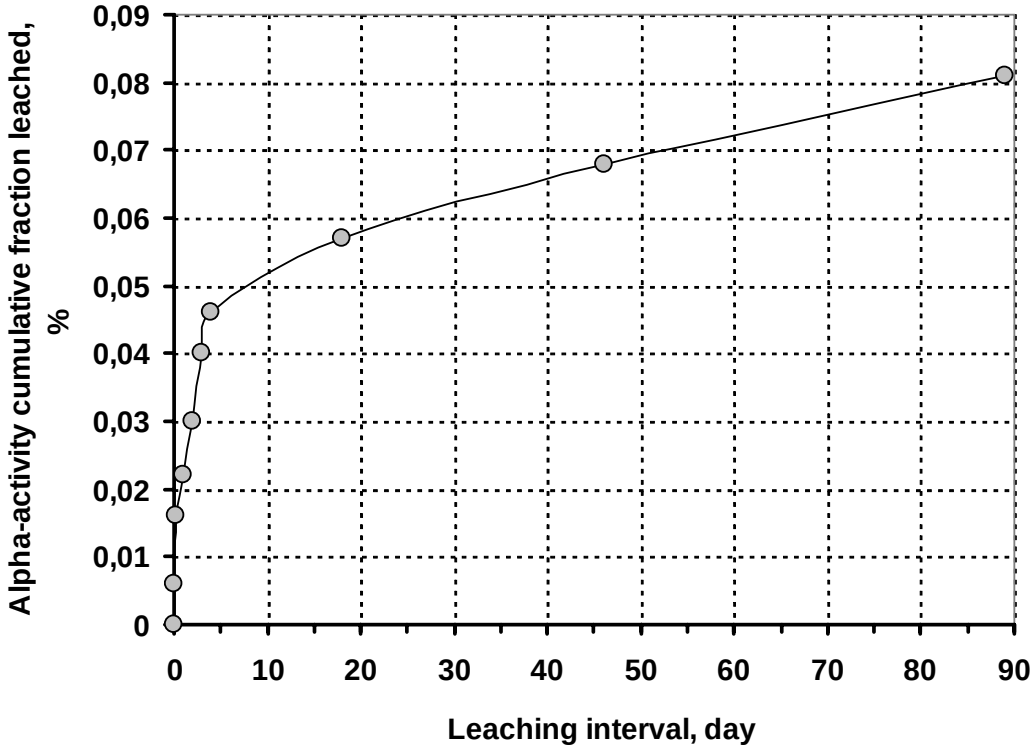


Figure 12 - Alpha-activity cumulative fraction leached as a function of leaching interval

Conclusion to Task 18.1

Advanced Ceramicrete technology for solidification of hot surrogate Mayak Stream 1&2 has been carried out. Hot Ceramicrete samples according to advanced process technique have been synthesized. Temperature during preparation of the samples has been monitored, the synthesis temperature maximum was not higher that 70 degrees C.

Ceramicrete matrix with solidified Streams-1&2 containing ^{137}Cs, ^{90}Sr, ^{129}I and alpha-emitting nuclides have a high chemical stability to leaching of the above radionuclides according to the test ANS 16.1. The Leaching Indexes proved to be higher than those obtained earlier, and they completely satisfied the requirements on a retention of the radionuclides: for ^{137}Cs ~13; for ^{90}Sr -11.1; for ^{129}I - 7.8; for alpha-emitting nuclides 12.9.

Samples of Ceramicrete matrix prepared by solidification of Streams-1&2 correspond to the required physical and strength properties. The loss of compressive strength of matrices after immersion test (90 days) is <25%. It was demonstrated that during solidification of modified Mayak Streams 1&2 composition of gas phase over solidified surface corresponds to that of ambient air, presence of radiolytic hydrogen was not detected.

TCLP Test showed that concentrations of environmentally hazardous elements (Cr, Ni, Sr) incorporated in the Advanced Ceramicrete matrix did not exceed acceptable limits and showed reliability of immobilization of these elements in the prepared Ceramicrete matrix.

Obtained results provide grounds for scaling Advanced Ceramicrete Technology and making hot Ceramicrete samples up to 20 L.

Task 18.2. Preparation and Testing of actual (hot) samples - 20 L scale

18.2.1. Mayak Stream 1 solidification (20 L scale)

Results obtained in Task 18.1 allowed to scale synthesis of hot Ceramicrete samples up to 20 L in accordance with advanced technology.

For preparation of 20 L hot samples, real solutions watering to safe level were used. Diluted high level alkaline supernatant was used as cesium radiant. As strontium radiant one of technological products was used. Iodine containing alkaline regenerate was used as source of ^{129}I. This solution was received from gas purification filter of radiochemical plant. As a result of three component mixing the solution with specific activity of ^{137}Cs – $7.2 \cdot 10^4$ Bq/L, ^{90}Sr – $3.85 \cdot 10^4$ Bq/L, ^{129}I – $1.24 \cdot 10^5$ Bq/L for preparation surrogate Mayak Stream 1 was obtained.

For preparation surrogate Stream 1 1226.4 g NaOH, 1202.4 g - $NaNO_3$, 412.5 g - $NaNO_2$, 648.6 g $Al(NO_3)_3 \cdot 9H_2O$, Na_2SO_4 – 45.8 g, NaCl – 21 g, NaF – 3.8 g, K_2CrO_4 – 109.5 g were dissolved in 5.46 L of radioactive solution. The acquired solution had volume 6.85 L and density 1.31 g/cm^3 . Its composition is given in Table 11.

Table 11

Modified Mayak Stream-1 properties

Components concentration, g/L									^{137}Cs, Bq/L	^{90}Sr, Bq/L	^{129}I, Bq/L
NaOH	Na^+	Al^{3+}	NO_3^-	NO_2^-	SO_4^{2-}	Cl^-	CrO_4^{2-}	TDS			
179.9	175.5	7.2	177.6	40.2	4.5	1.9	9.6	499	$5.76 \cdot 10^4$	$3.08 \cdot 10^4$	$9.92 \cdot 10^4$
TDS – total dissolved solids, g/L; ρ – solution density, g/cm^3; Σα – total activity of α-bearing nuclides, Bq/L											

Than, according to Ceramicrete advanced technology alkaline solution was neutralized by 768 mL phosphoric acid (1.69 g/cm^3, 14.7 M) up to pH 8. Nitrogen oxide release was observed during the process of neutralization. After neutralization color of the solution changed from primrose to olive caused by reduction of Cr(VI) до Cr(III) and the formation the precipitates of hydroxides $Al(OH)_3$, $Cr(OH)_3$. As a result solution with density 1.38 g/cm^3 was obtained.

Next 1365 g of dry granulated anion exchange resin AV-17 in chloride form (Cl-form) and 1210 mL of ferrocyanide sludge (ρ=1.17 g/cm^3, consisted of 114.9 g/L nickel ferrocyanide, 6.5 g/L – $Ni(NO_3)_2$, 140.6 g/L – KNO_3) were introduced into the neutralized

solution and it was mixed for 60 minutes to fix iodine and cesium. Density of this sludge became 1.30 g/cm^3.

Than, 750 g $Na_2S{\cdot}9H_2O$, dissolved in 1785 ml of water were introduced into the sludge at stirring. The color of the mixture became black due to precipitation of nickel sulfides. Obtained sludge had pH 10.5. To prevent eventual destruction of nickel ferrocyanide, 125 ml of concentrated nitric acid (12.4 M, density 1.35 g/cm^3) was added in order to stabilize pH at level below 9.

Finally initial radioactive solution was added into the sludge up to 11.7 L (Fig. 13). After all this operations sludge with density 1.26 g/cm^3 was used for Ceramicrete synthesis.

Figure 13 – Surrogate Stream 1 preparation

Magnesium oxide calcined at 1400 ^{o}C for 4 hours was used for synthesis of the ceramics. Boric acid in quantity 4 % was added to the compound to prolong solidification time. Wollastonite in quantity 15 % was added to the compound to increase compressive strength. The composition is described in Table 12.

Table 12

Composition for Stream 1 solidification

Composition					
MgO	KH_2PO_4	Stream 1	H_3BO_3	Wollastonite	Total
3,60 kg	10.83 kg	14.74 kg	1.28 kg	5.16 kg	35.61 kg
10.1 %	30.4 %	41.4 %	3.6 %	14.5 %	100 %

On the first step boric acid and potassium dihydrophosphate were dissolved during 2 hours until complete dissolution. Than wollastonite was added into mixture and stirred during 1 hour. Further MgO was dosed into sludge and stirring 30 min. Than sampling of 4 specimens with 2′ and 1′ diameters was taken place. Next 10 min mixture viscosity increased rapidly and the sample stiffening occurred.

After 4 weeks of maturing specimens were extracted from the moulds. Physical parameters of the samples are given in Table 13.

Table 13

Physical properties of the samples with Stream 1

Sample #	D, cm	H, cm	Weight, g	ρ, g/cm^3	Sample purpose	Compressive strength, kg/cm^2
1	2.5	5.0	42.68	1.74	for TCLP	88
2	2.5	5.1	43.29	1.73	for PCT	82
3	4.64	9.41	275.05	1.73	for ANS	-
4	4.64	9.24	272.08	1.74		-
5	34.0	22.6	35610	1.74	20.5 L sample	-

18.2.2. Mayak Stream 2 solidification (20 L scale)

In order to prepare surrogate Stream 2 the solution in volume 653 mL of $Fe(NO_3)_3$ in HNO_3 was taken, than it was neutralized by 311 mL concentrated NaOH (600g/L) and acid radioactive product containing alpha-emitting nuclides (AENP) was added up to 2220 mL. As a result radioactive Fe(III) hydroxide sludge with density 1.135 g/cm^3 was obtained.

The following salts were dissolved in 741 mL AENP - $Sr(NO_3)_2$ – 420.5 g, K_2CrO_4 – 10.2 g, $Ni(NO_3)_2 \cdot 6H_2O$ – 102.1 g and combined with the Fe(III) hydroxide sludge. Further 2720 mL nickel ferrocyanide suspension (nickel ferrocyanide – 115 g/L, $Ni(NO_3)_2$ – 6.5 g/L, KNO_3 – 140.6 g/L, ρ=1.17 g/cm$_3$) was added to the obtained sludge. As a result the volume of received radioactive sludge made 5680 mL.

Than 668,7 g $Na_2S \cdot 9H_2O$ previously dissolved in 1330 mL AENP was introduced into the sludge, whose color became black due to precipitation of nickel sulfide. Further pH was corrected to 10 by introducing 89 mL concentrated NaOH (600 g/L). At last AENP was added up to 11.1 L. The sludge with density 1.10 g/cm^3 and specific alpha-activity $1.15 \cdot 10^4$ Bq/L was used in ceramicrete synthesis. Chemical composition of the final sludge are presented in Table 14.

Table 14

Modified Mayak Stream-2 properties

Components concentration, g/L										Σα, Bq/L
Na^+	Sr^{2+}	K^+	Ni^{2+}	Cr^{3+}	$Fe(OH)_3$	SO_4^{2-}	NO_3^-	NFC	TDS	
24.0	15.7	13.6	2.36	0.25	19.7	24.2	82.6	28.2	210.7	$1.15 \cdot 10^4$
NFC - nickel ferrocyanide, g/L; TDS – total dissolved solids, g/L; ρ – solution density, g/cm^3; Σα – total activity of α-emiting nuclides, Bq/L										

Magnesium oxide calcined at 1400 ^oC for 4 hours was used for synthesis of the ceramics. Boric acid in quantity 2.5 % was added to the compound to prolong solidification time. Wollastonite in quantity 15 % was added to the compound to increase compressive strength. The composition is described in Table 15.

Table 15

Composition for Mayak Stream 2 solidification

Composition					
MgO	KH_2PO_4	Stream 1	H_3BO_3	Wollastonite	Total
4,92 kg	14.8 kg	12.21 kg	0.95 kg	5.72 kg	38.6 kg
12.8 %	38.3 %	31.6 %	2.5 %	14.8 %	100 %

At first boric acid and wollastonite was added subsequently with an one hour interval continuously stirring up. Than potassium dihydrophosphate was introduced and mixture stirred during 2 hour in order to reach the complete dissolution of the introduced components. At last, MgO was added and the obtained mixture was blended 30 minutes and than reaction mixture was poured in the moulds. For next 15 minutes stiffening of the composition occurred.

After 4 weeks of maturing the samples were extracted from the moulds. An exterior of the samples with solidified Stream 1&2 are shown in Fig. 14 and its physical parameters are given in Table 16.

Figure 14 – Ceramicrete samples with Mayak Stream 1&2

Table 16

Physical properties of the samples with Stream 2

Sample #	D, cm	H, cm	Ms, g	ρ, g/cm^3	Sample purpose	Compressive strength, kg/cm^2
1	2.5	5.17	45.66	1.80	for TCLP	81
2	2.5	5.23	45.93	1.79	for PCT	95
3	4.61	9.04	274.31	1.82	for ANS	-
4	4.61	10.10	304.90	1.81		-
5	34	23.4	38600	1.80	21.4 L	-

Chemical resistance of Ceramicrete has been assessed in concordance with three test procedures: ANS, TCLP and PCT. Leaching of ^{137}Cs, ^{90}Sr, Ce, ^{129}I, and Na, Cr, Ni, NO_3 was tested according to ANS 16.1, TCLP procedure was used for Ni, Cr, Ni, Sr, and PCT procedure was used for Mg, K, P and Na.

For test operation according to ANS 16.1 the made ceramics samples were hooked on a loop of copper wire.

18.2.3. Hazardous contaminants leaching study using TCLP test

The obtained compound was then used for TCLP tests. TCLP Test conditions are presented in Table 17. TCLP test results for different Ceramicrete samples are presented in Table 8.

Table 17

Summary of TCLP Test conditions

Liquid/Solid ratio, g/g	Leachant	Extraction time, hours	Sample weght, g	Particle size, mm	Test Vessel	Filter type
20	Extraction fluid #1	20	5	3-8	TFE-fluorocarbon	0.7 μm glass fiber
$S_{уд}$ – удельная площадь поверхности, $м^2/г$; * - Stream 1, ** - Stream 2						

Table 18

TCLP Test Results for Hot Ceramicrete Samples with surrogate waste Stream 1&2 (element content in mg/L)

Sample	pH of solution after testing	Loss of weight, %	Cr (0.85)*	Ni (1.0) *	Sr
Leachant	4.9	-	0.003	0.005	-
Stream-1	6.25	16.6	0.1	-	-
	6.06	15.2	0.1	-	-
average	6.16	15.9	0.1	-	-
Stream-2	6.85	11.4	0.1	0.75	9.3
	7.20	12.0	0.1	0.83	9.0
average	7.03	11.7	0.1	0.79	9.2
• UTS limits for these elements are shown in brackets					

TCLP test shows that Ceramicrete samples with solidified Mayak Stream 1&2 leach Ni, Cr into leachate in concentrations well below the UTS limits.

18.2.4. Matrix constituents, Na and NO_3 leaching study using PCT test

PCT test has been carried out with Ceramicrete samples synthesized using surrogate wastes. Ceramicrete samples were kept in molds during 4 weeks. Then these samples were extracted, their physical parameters were determined, and they were prepared for PCT leaching tests.

PCT Test conditions are presented in Table 19. PCT test results for different Ceramicrete Samples are presented in Table 20. 2 samples were used in parallel for the tests.

Table 19

Summary of PCT Test conditions

Liquid/ Solid ratio, g/g	Leachant	Test temperature, ^0C	Extraction time, days	Sample mass, g	Particle size,mm	Test Vessel	Filter type	S_{sp} , m^2/g
10	Distilled water	90	7	4	0.074-0.149	TFE-fluoro-carbon	0.7 µm glass fiber	14.7*
								16.2**
S_{sp} – specific surface area, m^2/g ; * - Stream 1, ** - Stream 2								

As shown in the table, reference Ceramicrete samples lost 33-44 % of their weight. Salt constituent of the wastes is not fixed chemically in the Ceramicrete matrix, therefore it should have been expected that soluble components of the wastes would completely transfer from powder samples into leachate. However, even in this case the loss of weight should not be such great as far as salt component make up about 15 % of the sample weight for Stream 1 and about 4 % for Stream 2. Thus, the considerable loss of weight is probably caused by leaching of structural components of the matrix. There are two reasons that may cause it. In our opinion, the main reason is a destruction of the original crystal structure of the sample under thermal effect. Thermographic analysis showed that Ceramicrete looses 22-25 % of weight in the range of temperatures from 70 to 90 ^oC. Apparently, it is connected with elimination of crystal water from the matrix and changes in original crystal structure of the material and its properties. Another reason is a mechanical destruction of the crystal structure that is forming around particles of unreacted magnesium oxide. As a result of the destruction of Ceramicrete crystals unreacted initial components are transferred into leaching medium.

PCT test data were used for leaching rate calculation of structure-forming constituents of the ceramics matrix (K, Mg, PO_4) and major salt components ($NaNO_3$). Results of the leaching rate calculation are obtained for the surface of powder material 14.7 m^2/g and 16.2 m^2/g. Data for different Ceramicrete samples are presented in Table 11.

Table 20

PCT Test Results for Ceramicrete Samples

Waste type	Leach rate, g/(cm^2·day)				
	Na	NO_3	K	Mg	PO_4
Stream 1	$1.72 \cdot 10^{-6}$	$2.86 \cdot 10^{-6}$	$1.78 \cdot 10^{-6}$	$5.70 \cdot 10^{-9}$	$5.71 \cdot 10^{-7}$
	$2.97 \cdot 10^{-6}$	$4.71 \cdot 10^{-6}$	$2.94 \cdot 10^{-6}$	$7.54 \cdot 10^{-9}$	$8.67 \cdot 10^{-7}$
Average	$\mathbf{2.37 \cdot 10^{-6}}$	$\mathbf{3.78 \cdot 10^{-6}}$	$\mathbf{2.36 \cdot 10^{-6}}$	$\mathbf{6.62 \cdot 10^{-9}}$	$\mathbf{7.19 \cdot 10^{-7}}$
Stream 2	$2.28 \cdot 10^{-6}$	$2.96 \cdot 10^{-6}$	$2.74 \cdot 10^{-6}$	$1.65 \cdot 10^{-9}$	$1.09 \cdot 10^{-6}$
	$1.84 \cdot 10^{-6}$	$2.26 \cdot 10^{-6}$	$2.10 \cdot 10^{-6}$	$1.44 \cdot 10^{-9}$	$8.15 \cdot 10^{-7}$
Average	$\mathbf{2.06 \cdot 10^{-6}}$	$\mathbf{2.61 \cdot 10^{-6}}$	$\mathbf{2.42 \cdot 10^{-6}}$	$\mathbf{1.55 \cdot 10^{-9}}$	$\mathbf{9.52 \cdot 10^{-7}}$

18.2.5. Testing of matrix with Mayak Stream 1 test according to ANS 16.1

In accordance with ANS 16.1 chemical resistance of Ceramicrete to leaching was studied at 20°C during 90 days (10 intervals). Twice-distilled water was used as leaching agent, the volume of the contact solution (leaching medium) was calculated for each sample taking into account its surface area according to requirements of the procedure to ensure solid surface/liquid volume ratio equal 1:10. Contents of waste components ^{137}Cs, ^{90}Sr, ^{129}I, Na, NO_3, SO_4 as well as matrix elements K, Mg, PO_4 were determined in the leaching medium. Realization of leaching test is presented in Fig. 15.

Figure 15 - Leaching test ANS 16.1 realization

Analysis of leaching curves (Fig. 16) has shown that waste macro-components (sodium, nitrates) are leached in considerable degree. For sodium and sulfates the results get close to the results obtained in previous investigations: 37 % and 18 %, respectively. Nitrates are leached almost completely up to 96 %.

Strength of chromium fixation with Ceramicrete was two orders of magnitude higher than sodium fixation strength (Fig. 17). Concentrations of chromium in leachate samples were ≤ 0.01 mg/L. In cases when concentration was < 0.01 mg/L the value of 0.01 mg/L was taken for calculations. Cumulative fraction leached have been calculated basing on these conservative assessments. Chromium cumulative fraction leached is stabilized on levels 0.67 %.

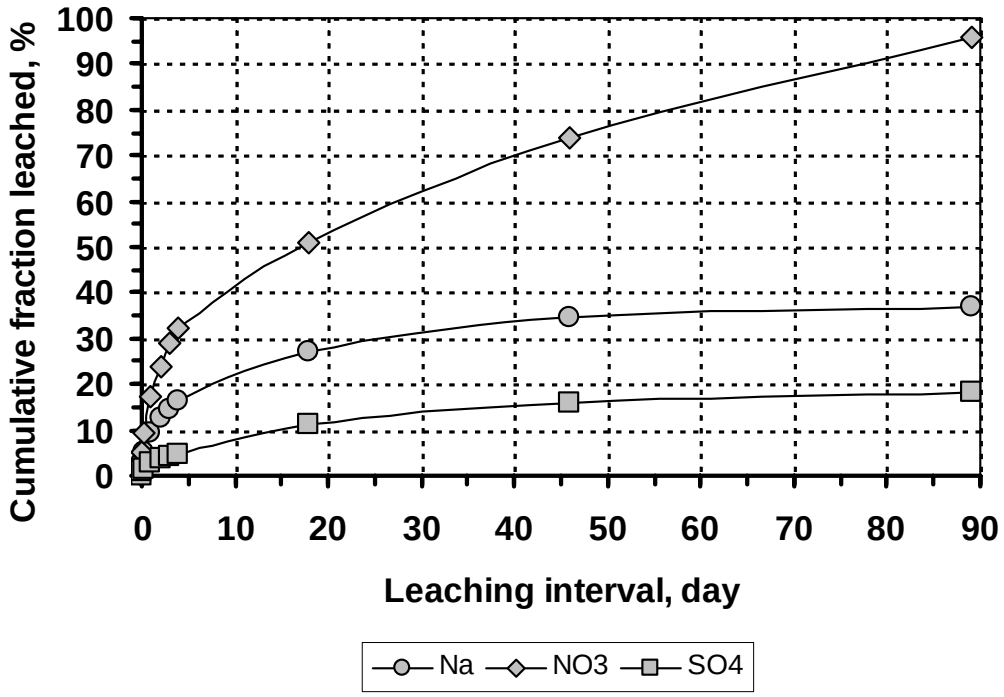


Figure 16 - Na, NO_3 and SO_4 cumulative fraction leached as a function of leaching interval

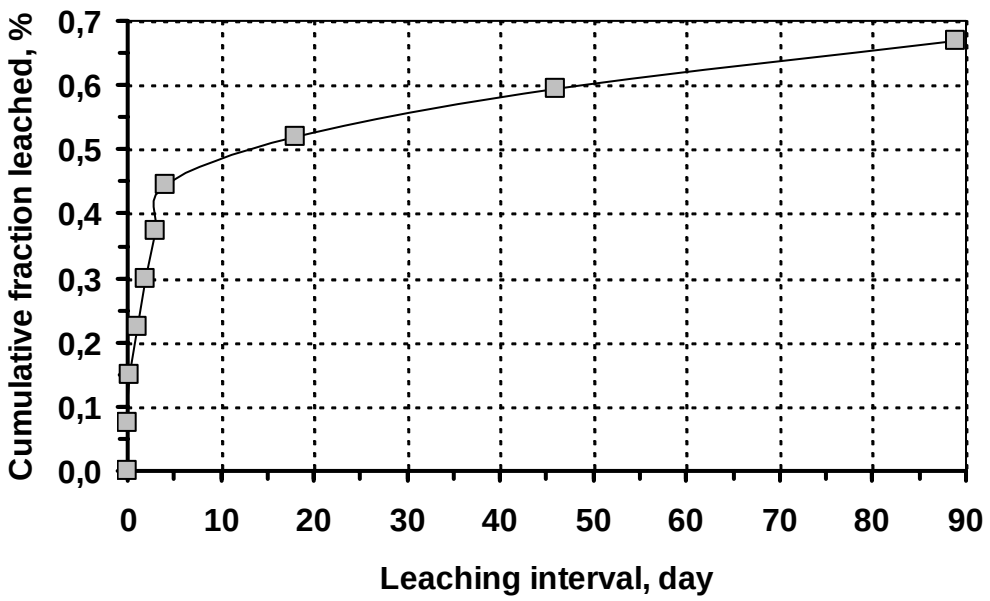


Figure 17 - Ni and Cr cumulative fraction leached as a function of leaching interval

Concentration measurements structure-forming constituents of the ceramics matrix (K^+, Mg^{2+}, PO_4^{3-}) in leaching medium have shown that contents of phosphates, potassium and magnesium changed within the ranges of 130-500 mg/L, 200-1400 mg/L, and 5-10 mg/L, respectively. Based on the data obtained cumulative fractions leached of the structure-forming constituents of Ceramicrete were determined. Results of the calculations

are presented graphically in Fig. 18. Potassium cumulative fraction leached is about 33 %, phosphate cumulative fraction leached is about 6 %, and magnesium cumulative fraction leached is about 0.6 %.

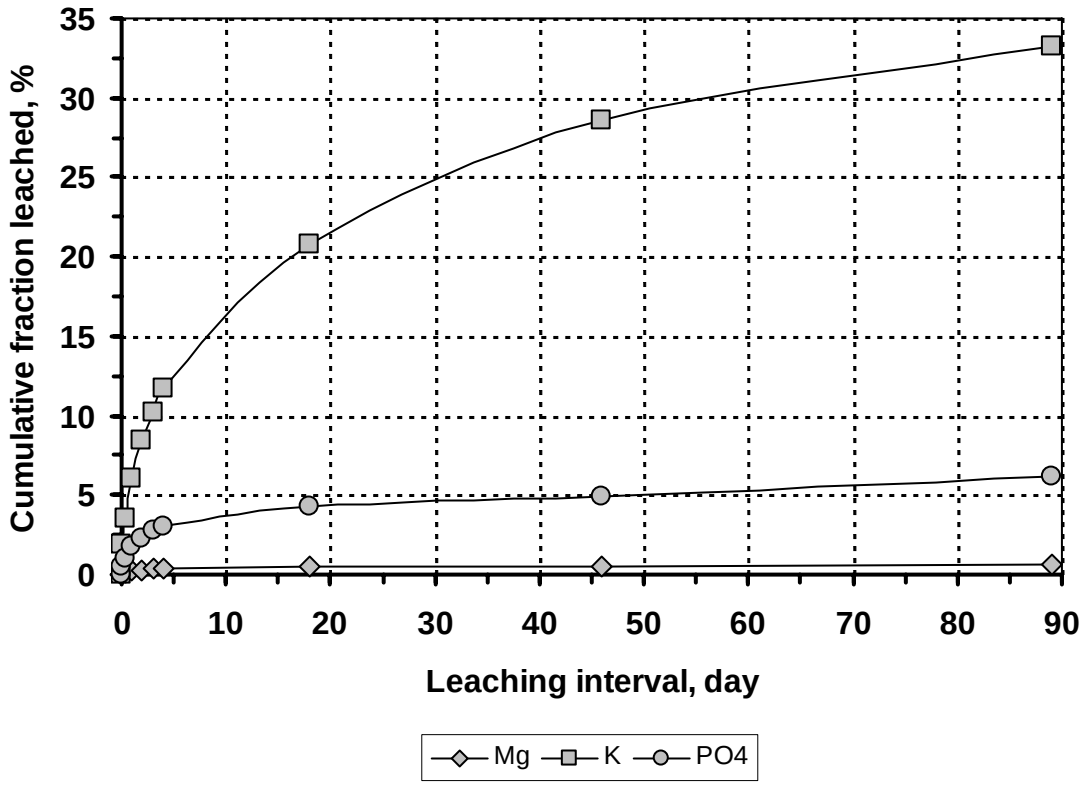


Figure 18 - Matrix components (Mg, K, PO_4) cumulative fraction leached as a function of leaching interval

Activity analysis of the leaching medium permitted to calculate cumulative fraction leached of Cs^{137}, ^{90}Sr, ^{129}I. The results of these calculations are presented in Fig. 19. For test time 0.8 % of ^{137}Cs contained in the Ceramicrete samples were leached into the leaching medium. At that 90 % of all ^{137}Cs passed into the leaching medium are washed out during the first 4 days. Leachability Index for ^{137}Cs was 11.42.

We must note, that ^{137}Cs fixation slightly decrease in comparison with laboratory scale study (report 18.1). We can suppose that the main reasons are quality of nickel ferrocyanide and procedure of solution pretreatment. Nickel ferrocyanide was synthesized closely before use and quality of reagents and synthesis may influence on final result (sorbent quality). On other hand solution pretreatment (creation of alkaline medium) give possibility to dissolved fresh nickel ferrocyanide sludge. All these reasons may provoke ^{137}Cs fixation decrease.

Cumulative fraction leached for ^{90}Sr was about 1.9 % (Fig. 19). Leaching of ^{129}I was one order greater then for other radionuclides and reached 33 % (Fig. 20), Leachability Index was 8.04. Leachability Indexes presented in Fig. 21.

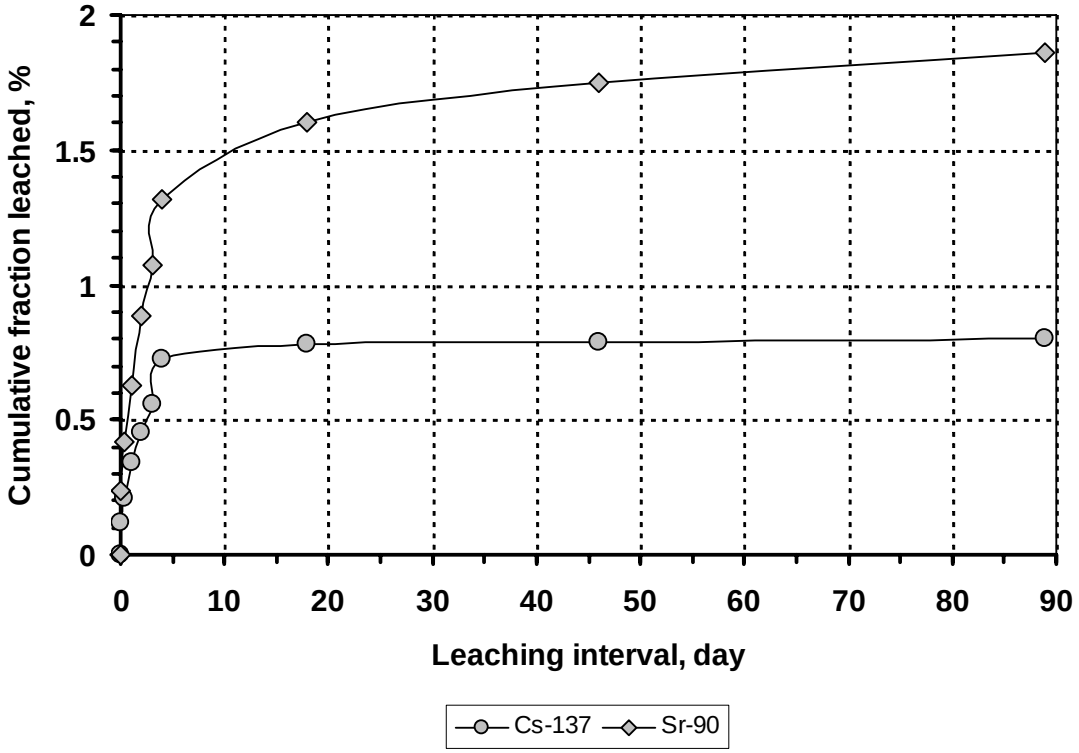


Figure 19 - ^{137}Cs and ^{90}Sr cumulative fraction leached as a function of leaching interval

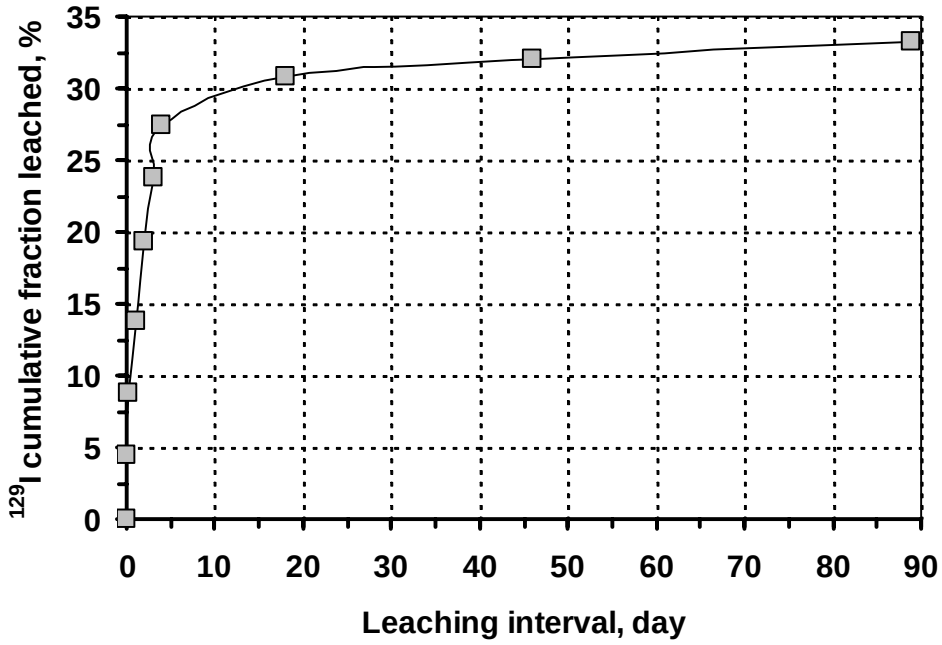


Figure 20 – ^{129}I cumulative fraction leached as a function of leaching interval

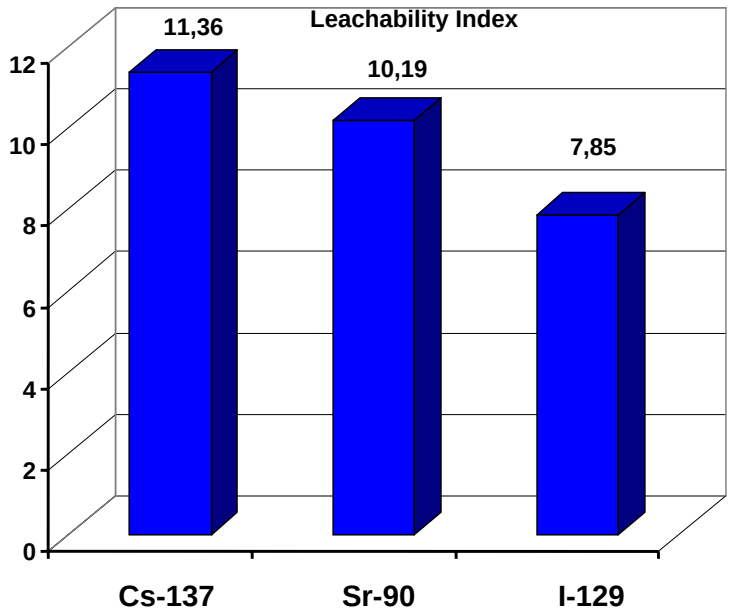


Figure 21 - ANSI 16.1 test results for matrix with Mayak Stream 1 (20 L scale)

18.2.6. Testing of matrix with Mayak Stream 2 test according to ANS 16.1

In accordance with ANS 16.1 chemical resistance of Ceramicrete leaching was studied at 20°C during 90 days. Twice-distilled water was used as leaching agent, the volume of the contact solution (leaching medium) was calculated for each sample taking into account its surface area in according to requirements of the procedure to ensure solid surface/liquid volume ratio equal 1:10. Activities of alpha-emitting radionuclides and contents of structure-forming matrix constituents (magnesium, potassium, phosphate) as well as of sodium, nitrates, strontium, chromium, nickel were determined in leaching medium. Chemical components of matrix were determined by the method of liquid chromatography.

On determining quantity of each component leached from matrix for test time its initial content in the leaching medium was taken into account.

Analysis of leaching curves (Fig. 22) have shown that waste macro-components (sodium, nitrates, sulphates) are leached in considerable degree. Nitrates cumulative fraction leached is about 82 %, sodium cumulative fraction leached is about 58 %, and sulphate is about 24 %.

Strength of chromium, nickel and strontium fixation with Ceramicrete was much better (Fig. 23). Concentrations of chromium, nickel and strontium in leachate samples were ≤ 0.01 mg/L. In cases when concentration was < 0.01 mg/L the value of 0.01 mg/L was taken for calculations. Cumulative fraction leached have been calculated based on these conservative assessments. Chromium, nickel and strontium cumulative fraction leached are reached 8 %, 0.9 % and 2 %, respectively.

Concentration measurements structure-forming constituents of the ceramics matrix (K^{+}, Mg^{2+}, PO_4^{3-}) in leaching medium have shown that contents of phosphates, potassium and magnesium changed within the ranges of 130-500 mg/L, 200-1400 mg/L, and 5-10 mg/L, respectively. Based on the data obtained cumulative fractions leached of the structure-forming constituents of Ceramicrete were determined were calculated. Results of the calculations are presented graphically in Fig. 24. Potassium cumulative fraction leached is about 23 %, phosphate cumulative fraction leached is about 9 %, and magnesium cumulative fraction leached is about 0.8 %.

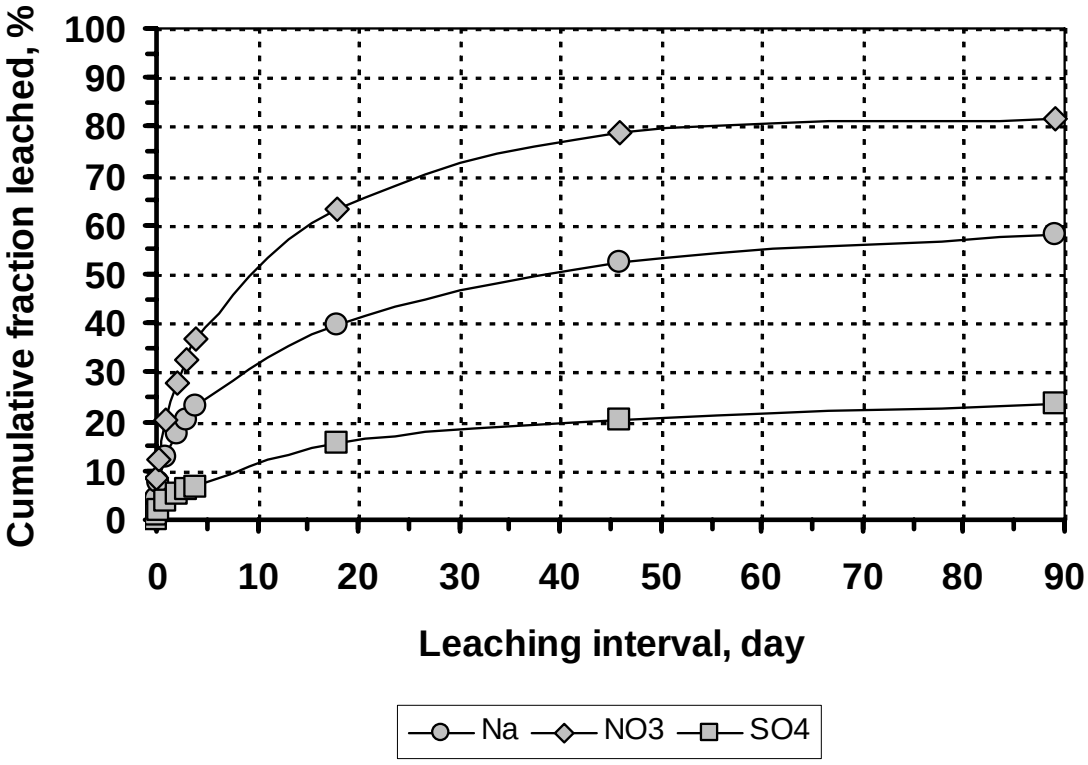


Figure 22 - Na, NO_3 and SO_4 cumulative fraction leached as a function of leaching interval

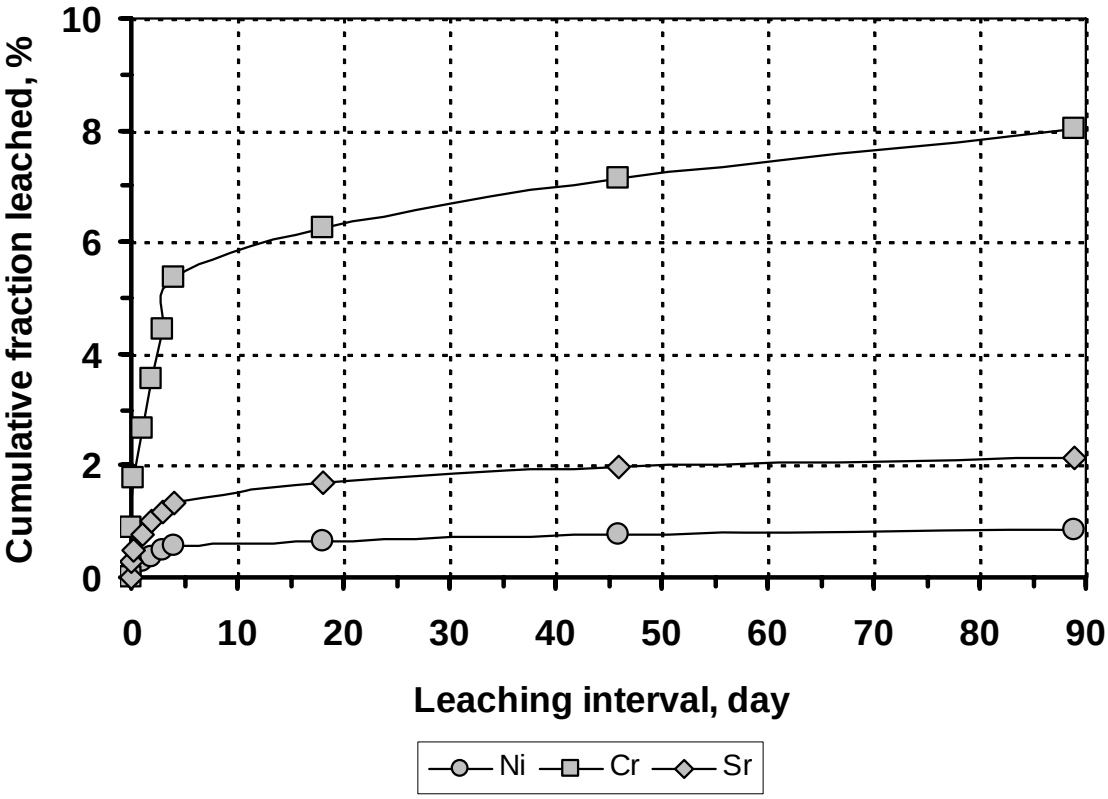


Figure 23 - Ni, Cr and Sr cumulative fraction leached as a function of leaching interval

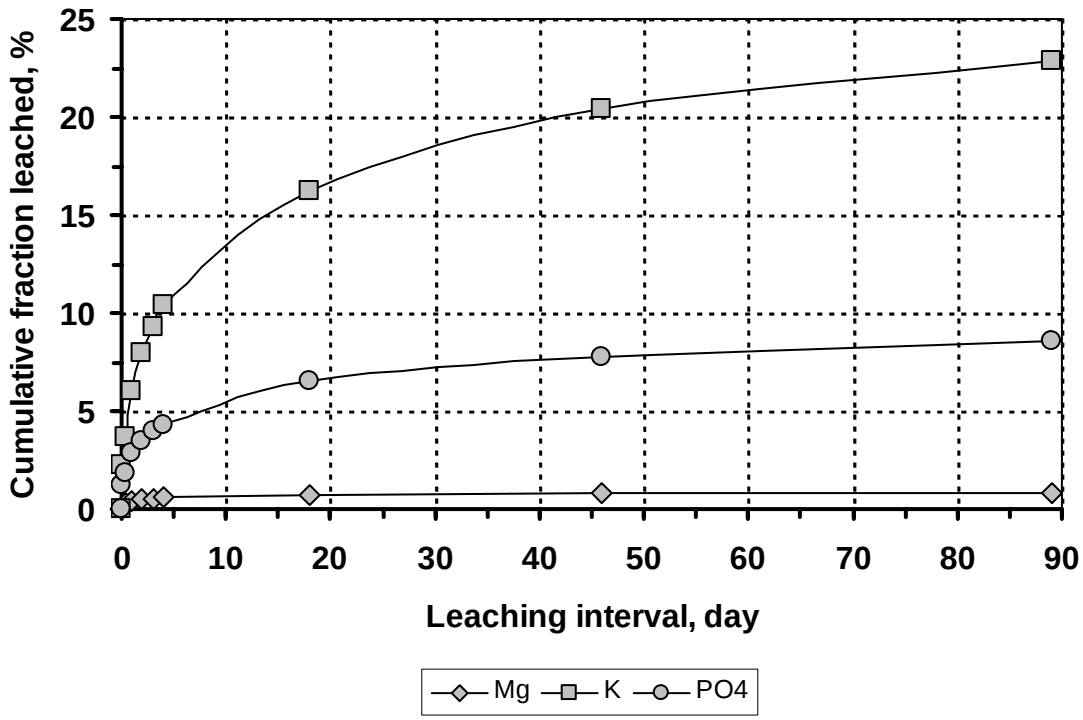


Figure 24 - Matrix components (Mg, K, PO_4) cumulative fraction leached as a function of leaching interval

Radiometric measurements of leaching medium have shown that activity changed from 0.3 to 1 Bq/L. Based on the radiometric measurements of the leaching medium cumulative fraction leached of α-emitting nuclides were calculated. During leaching test 0.57 % of total alpha-activity of the samples passed into leaching medium and leaching index of alpha-emitting nuclides was ~11.3. The tests have shown that for the first 4 days about 50 % of α-activity passed into the leaching medium. The results of these calculations are presented in Fig. 25. The data obtained permit to state that Ceramicrete fixes α-emitting nuclides rather strongly.

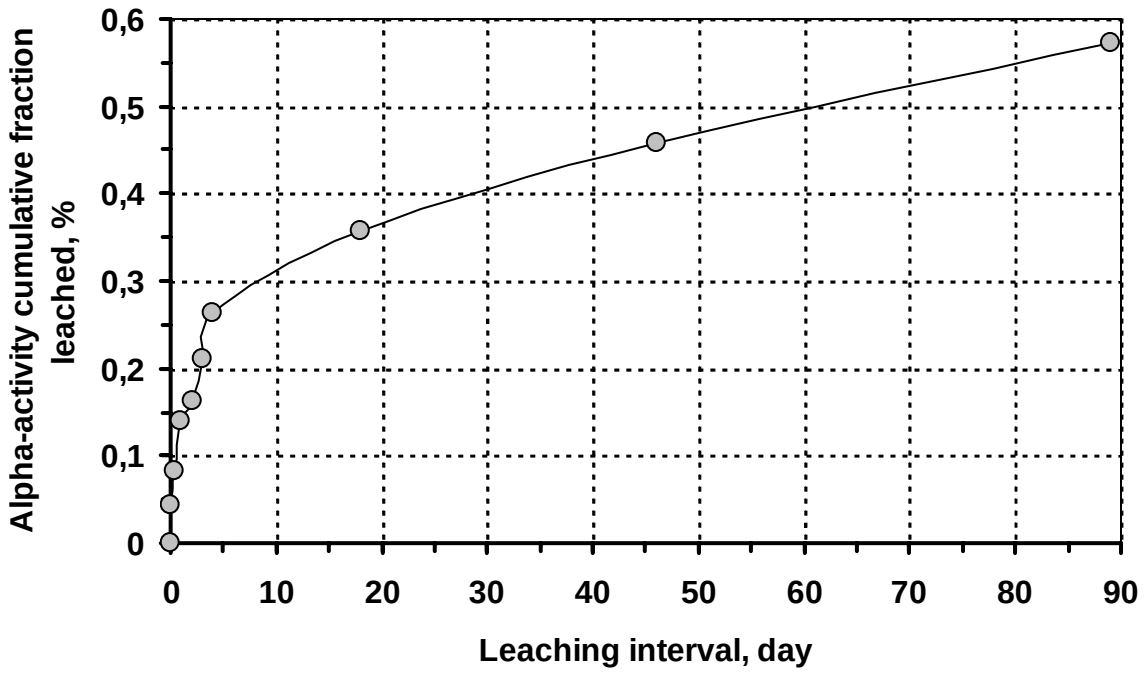


Figure 25 - Alpha-activity cumulative fraction leached as a function of leaching interval

Conclusion to Task 18.2

Advanced Ceramicrete technology for solidification of hot surrogate Mayak Stream 1&2 has been scale up to 20 L. Temperature during preparation of the samples has been monitored, the synthesis temperature maximum was not higher that 70 degrees C.

Ceramicrete matrix with solidified Streams-1&2 containing ^{137}Cs, ^{90}Sr, ^{129}I and alpha-emitting nuclides have a high chemical stability to leaching of the above radionuclides according to the test ANS 16.1. The Leachability Indexes proved to be higher than those obtained earlier, and they completely satisfied the requirements on a retention of the radionuclides: for ^{137}Cs 11.36; for ^{90}Sr 10.19; for ^{129}I 7.85; for alpha-emitting nuclides 11.3.

Samples of Ceramicrete matrix prepared by solidification of Streams 1&2 correspond to the required physical and strength properties. The loss of compressive strength of matrices after immersion test (90 days) is <25%. It was demonstrated that during solidification of modified Mayak Streams 1&2 composition of gas phase over solidified surface corresponds to that of ambient air, presence of radiolytic hydrogen was not detected.

TCLP Test showed that concentrations of environmentally hazardous elements (Cr, Ni, Sr) incorporated in the advanced Ceramicrete matrix did not exceed acceptable limits and showed reliability of immobilization of these elements in the prepared Ceramicrete matrix.

The data on hydrothermal leaching of structure-forming matrix components show that the prepared matrices containing modified Mayak Streams 1&2 are characterized by low values of normalized leaching rates both for main and impurity components of the matrices.

Obtained results provide grounds for Deployment Concept of Ceramicrete Technology for radioactive waste immobilization.

Project Director Academician, Professor **Boris F. Myasoedov**

PROJECT STATUS REPORT:

Report Number: **RCO-10116-MO-03(ANL)**

Project Title:
"Ceramicrete Stabilization of Radioactive Salt-Containing Liquid and Sludge Waste"

Effective Date: **July 1, 2003**
Expiration Date: **May 19, 2008**

Reporting Period: December 2007 – May 2008

Based on the Tasks accomplished:

Mayak: **Task 19**

Moscow, 2007-2008

1. Mayak High Level Cs-containing Waste Solidification Process Description

Conceptual design has been developed based on the process steps and estimated quantities that were determined from the laboratory and pilot scale demonstration work for Mayak Stream 1 and Mayak Stream 2.

Mayak Stream 1 is alkali supernatant of sludge which is stored in tank for High Level Liquid Waste. Characteristics of Supernatant are presented in table 1.

Table 1
Characteristics of Supernatant

Component Concentrations, g/L									ρ, g/cm^3	Cs^{137}, Bq /L	Cs^{134}, Bq/L	Σα, Bq/L
NaOH	Na^+	Al^{3+}	NO_3^-	NO_2^-	SO_4^{2-}	Cl-	CrO_4^-	TDS				
213	173	8	99	38	13	6,3	6,7	450	1,28	$5{,}8\cdot10^{10}$	$3{,}4\cdot10^{7}$	$2{,}0\cdot10^{4}$

Based on the above trials to select a suitable ceramic process for MS-1, a sequence of steps was indicated for sample preparation that is likely to prove successful. The sequence is essentially neutralization - reagent addition - prior preparation - solidification. These four steps are needed for Mayak Stream 1 due to their pH characteristics, soluble hazardous chemical elements (Cr, Tc, and I states) and high salt content. The process is very simple and can be described as follows:

Neutralization. Research with the real and simulated solutions has shown that high alkali concentration promoted very rapid rate of Ceramicrete synthesis. To slow down the reaction rate to acceptable level, it is necessary to neutralize liquid wastes. MS-1 is partially neutralized to a pH = 5-8 using H_3PO_4. Solution temperature may rise to ~ 50-60° C and cooling is needed to ~ 20°-25° C. Temperature is controlled by the rate of neutralization, and can easily be kept well below the boiling point.

Reagent Addition. Small amounts of Nickel ferrocyanide (NFC), Na_2S, $SnCl_2$, and Ag-Z are added to precipitate insoluble compounds of Cs, and Cr, Tc and I, respectively, to form subsequent microencapsulation in the ceramic matrix. Temperature remains unchanged. Value of pH can be changed in alkali area (up to

10-11). To prevent nickel ferrocyanide from distruction pH value must be corrected below 9.5.

Solidification. Ceramicrete components (KH_2PO_4, H_3BO_3, $CaSiO_3$, MgO) is added into solution separately in order to provide complete dissolution of Boric acid and Monopotassium phosphate. Boric acid was used as retardant reaction. Boric acid and Monopotassium phosphate are dissolved during 2-3 hours under continuous stir due to high salt content of initial solution. After complete dissolution wollastonite and magnesium oxide are dosed. Than mixture stirred ~ 20 minutes (+/-) to effect reactions that convert waste constituents to insoluble compounds and ceramics, produce a ceramic matrix, and microencapsulate constituents.

2. Ceramicrete advanced process summary material balance

Ceramicrete advanced process material balance is determined by ceramicrete synthesis reaction.

$$MgO + KH_2PO_4 + 5\ H_2O \rightarrow KMgPO_4 \bullet 6\ H_2O$$

If a compound made of pure components is synthesized then the ratio of the reagents will be: MgO : H_2O : KH_2PO_4 = 1 : 2,25 : 3. But when we solidify waste we must take into account the solution density and the concentration of chemical components there.

According to data which were determined from the laboratory and pilot scale demonstration work formula for Mayak Stream 1 has some differences and is presented in table 2.

Table 2
Cheramicrete synthesis formula for Mayak Stream 1

Mayak Stream 1	MgO	KH_2PO_4	Wollastonite
41.5 % wt.	10.5 % wt.	31.5% wt.	15 % wt.

Concept is conservative, particularly in facility sizing, since the estimated volumes of immobilized waste are overestimates.

For this project, it was assumed that the waste will be delivered with a constant chemical content.

A conceptual diagram for immobilizing HLW – Mayak Stream 1 in Ceramicrete is depicted in Figure 1. The following description of the Mayak Stream 1 Ceramicrete advanced technology system (CATS) is based on processing 1000 m^3 at 7.5 M sodium every year at 70 percent total operating efficiency (TOE) (250 working day). All vessels are sized to hold their contents at 85 percent capacity, providing an operating/safety margin. Table 1 summarizes the material balance for processing 1000 m^3/year.

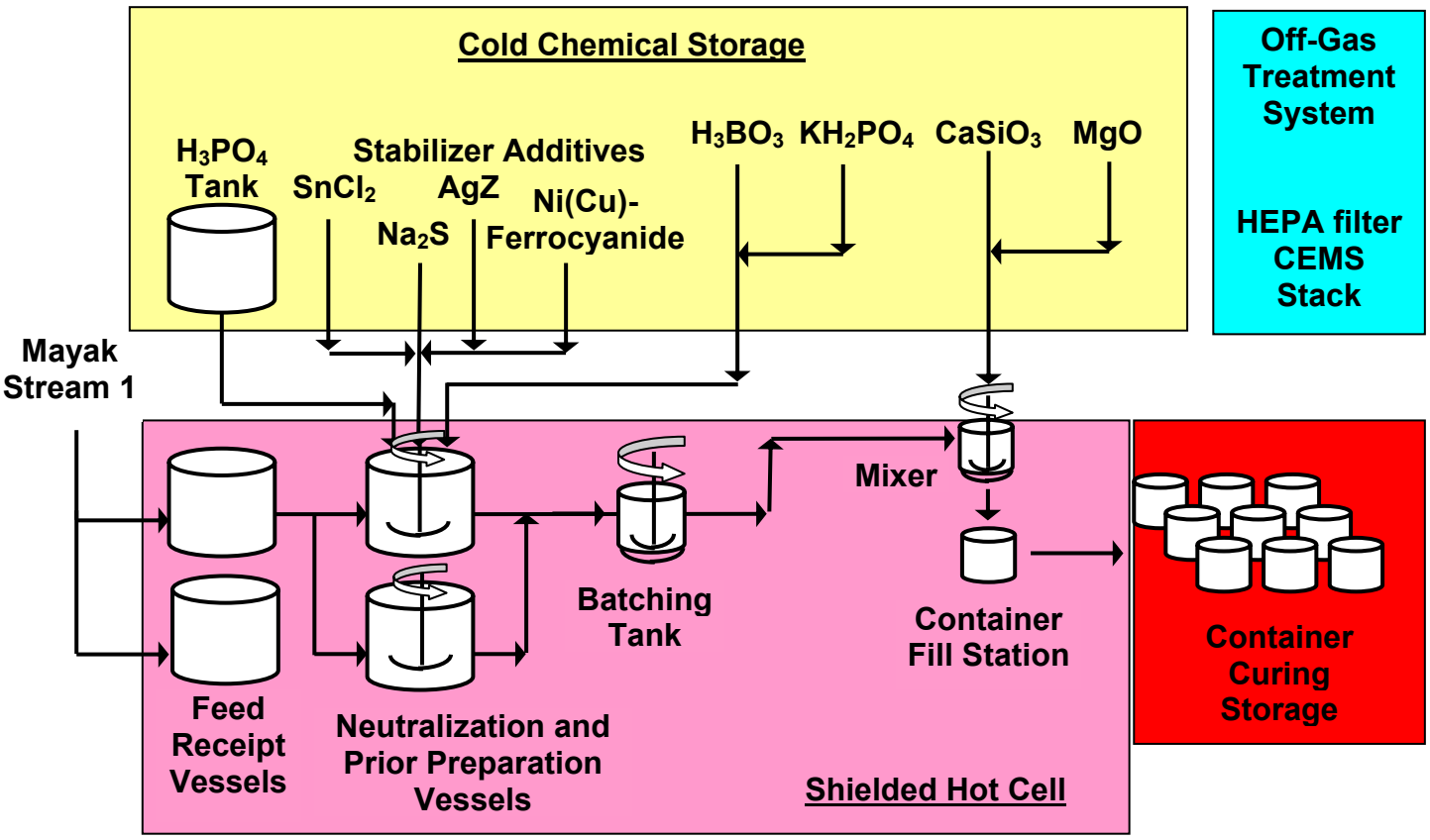


Figure 1 - Conceptual Flow Diagram of Mayak Stream 1 Immobilization

Table 3
Ceramicrete Immobilization of Mayak Stream 1 - Summary Material Balance

	Stream 1 MS-1	Stream 2 H_3PO_4	Stream 3 Neutralized MS-1	Stream 4 Reagents	Stream 5 Feed to Prior Preparation	Stream 6 H_3BO_3	Stream 7 KH_2PO_4	Stream 8 Calcium Silicate	Stream 9 MgO	Stream 10 Ceramicrete Immobilized MS-1
Quantity	1000,000 L	150,000 L	1150,000 L	27200 kg	1150,000 L	1.12+05 kg	1.18E+06 kg	5.02E+05 kg	3.93E+05 kg	3.74+06 kg
Density, g/mL	1.28	1.69	1.33		1.35			2.9		1.75
Analyte	moles	moles	moles	moles	moles	moles	moles	moles	moles	moles
Na^+	7.50E+06		7.50E+06	8.50E+05	8.35E+06					8.35E+06
PO_4^-		2.19E+06	2.19E+06		2.19E+06					2.19E+06
H^+		6.57E+06	6.57E+06		6.57E+06					6.57E+06
Ag 108				2.86E+04						2.86E+04
F 19				8.55E+04						8.55E+04
Sn 119				3.51E+04						3.51E+04
Cl				7.03E+04						7.03E+04
NFC				1.13E+05						
H_3BO_3						1.81E+06				
MgO									9.83E+06	
KH_2PO_4							8.68E+06			
$CaSiO_3$								4.33E+06		
Dosage of $SnCl_2$ and AgF is taken from CH2MHill report										

Summary material balance is presented for processing the maximum volume (1000 m^3) of MS-1 every year. Mass is equal for each of two reagents (sodium sulfide, stannous chloride) that are added. Boric acid is added as reaction retardant in quality of 3 % wt. from ceramicrete compound. Nickel ferrocyanide (in dry form) is dosed from calculation of 1 % wt. for ceramicrete compound.

2.1 Waste Receipt

The MS-1 is assumed to be received as a liquid waste stream into one of two, 5 m^3 capacity Feed Receipt Vessels (Tk-Fr-01/02) at the CTS. Feed Receipt Vessel is a tank for a batch of waste for daily operation of the system. Each of the MS-1 feed receipt vessels is sized to receive 4 m^3 Mayak Stream 1. One of the feed receipt vessels is used to receive MS-1 while the second vessel is transferring Mayak Stream 1 to the neutralization vessel.

The Vessels are equipped with level sensors, sampling system, gas-cleaning filter. Construction material of the vessels is stainless steel.

2.2 Partial Neutralization, Reagents Addition and Pretreatment

Approximately 2 m^3 of the Mayak Stream 1 are transferred every 4 hours from the feed receipt vessels to the neutralization and pretreatment vessels (Tk-Npt-01/02) of 3 m^3 capacity. The Vessels are equipped with level sensors, sampling system, gas-cleaning filter, mechanical mixer and inner cooling coil. Mechanical mixer intensifies heat transmission and mass exchange. Construction material of the vessels is stainless steel.

Approximately 0.15 L phosphoric acid of 85 wt % are added per 1 L of Mayak Stream 1 (300 L per batch) to adjust the mixture to pH 5-8. The addition of phosphoric acid also serves to convert most of the polyvalent metal cations to insoluble phosphate compounds and convert iodate (IO_3^-) to iodide (I^-) at this slightly acid condition.

Approximately 24 g of stabilizing reagents are added per 1 L of Mayak Stream 1 to the neutralization vessel at continuous mixing. These reagents, stannous

chloride ($SnCl_2$) and silver zeolite (Ag_2O-Al_2O_3-SiO_2, or Ag-Z in this report), are added as dry materials. The $SnCl_2$ reduces pertechnetate ($Tc(VII)O_4^{-2}$) to technetium pentoxide ($Tc_2(V)O_5$) or tetroxide ($Tc(IV)O_2$). The Ag-Z appears to have a cage structure that captures iodine and reacts to insoluble AgI. Nickel ferrocyanide is added in quantity up to 1.0 % wt. (from ceramicrite compound) for caesium radionuclides fixation. Nickel ferrocyanide can be used in dry form as well as fresh sludge. Approximately 80 kg of reagents are added per batch into the neutralization vessel.

After all this procedure Mayak Stream 1 will have density 1.35 and TDS about 500 g/L. Boric acid and monopotassium phosphate are added into Mayak Stream 1 in quantity 224 kg and 2360 kg, respectively and are stirred 2-4 hours to reach the complete dissolution.

After that temperature control takes place and cooling of solution if it is necessary.

2.3 Waste solidification into ceramicrete

After pretreatment treated MS-1 batch in volume of 1.15 m^3 is transferred through the batching tank to an immobilization subsystem where calcium silicate (wollastonite) or fly ash and magnesium oxide are mixed with the waste and discharged to disposal containers.

Batching tank (Tk-B-01) is a tank of 1.5 m^3 capacity for receiving and batching of wastes (1150 L) for one mixing operation. The tank is equipped with a level sensors, gas-cleaning filter, mechanical mixer, inner steam heating coil and weighing mechanism. Construction material of the tank is stainless steel.

A continuous, ribbon-type mixer is used to process the treated MS-1 and these dry reagents. The ribbon-type mixer is sized for producing ~2.1 m^3 (~3.7 MT) Ceramicrete batches. Approximately 502 kg of calcium silicate and 393 kg magnesium oxide are added per batch of treated MS-1 for immobilization, producing ~ 3750 kg (2100 L) of Ceramicrete. Approximately 312 MT of Ceramicrete-immobilized MS-1 is produced every month.

Sealing machine is used to place and seal a lid on a container with compound to ensure its impermeability.

2.4 Container Selection

The production rate of Ceramicrete-immobilized MS-1 is approximately 620 kg per hour (15 MT/day) at 70 % TOE, or approximately 885 kg per hour (21 MT/day) at 100 % TOE; i.e., a two-shift or three-shift operation to meet the specified generation rate. The density of the Ceramicrete waste form is approximately 1.75 MT/m^3. Table 2 lists the number of different types of containers with the Ceramicrete-immobilized MS-1 that would be produced per day. It is evident from Table 4 that 55-gallon drums or 85-gallon drums cannot be used for disposal of the Ceramicrete-immobilized MS-1, given the excessive number of containers generated per day. A larger container, such as a 50-yd^3 metal box, would greatly reduce container handling logistics, but could be difficult for Ceramicrete filling and curing and filled container transporting. Container requirements should be determined additionally.

Table 4
Disposal Container Evaluation

Ceramicrete production rate, m^3/day (kg/day)	Container type	Number per day
8.6 (15 000)	55-gallon metal drum (208 L)	46.0
	85-gallon metal drum (321 L)	29.8
	2.26-m^3 metal container	4.2
	50-yd^3 metal box (38.2 m^3)	0.225
Assumes 90 percent fill and 70 percent TOE		

Approximately 4 containers per day (at 70 percent TOE) will be produced, each containing 2.14 m^3 (3.75 MT at 90 percent fill) of Ceramicrete-immobilized MS-1. A unique labeled container will be positioned at the container filling station and loaded with Ceramicrete-immobilized MS-1. The filled containers will be sealed, surveyed (external contamination removed if necessary), and equipped with a Nucfil

013 TM filter (or equivalent) and a hydrogen recombination catalyst to mitigate hydrogen accumulation if it is needed. Tests have shown very low hydrogen generation, perhaps due to MgO which is known as hydrogen getter. On other hand the dense matrix allows hydrogen recombination.

2.5 Container Interim Storage

The Ceramicrete-immobilized MS-1 will cure within 24 hours of pouring into the 2.04-m^3 container. While the previous day's production is curing for 24 hours, the current day's production of containers will be accumulated at the CTS. Therefore, interim storage is provided for 2 days of production, and about 9 containers.

3. Deployment Concept

Major equipment list required for the Ceramicrete immobilization of the Mayak Stream-1 waste is identified in Table 5 and is based on the process description provided above. A preliminary facility concept drawing has been prepared depicting the equipment arrangement. The preliminary facility concept, Figure 4, includes an industrial-type structure housing the process equipment (40 feet by 20 feet), container interim storage pad (20 feet by 20 feet), an office/control room structure (20 feet by 50 feet), and locations for chemical reagent storage.

The industrial-type structure housing the process equipment is install in Shielded Hot Cell

Table 5
Preliminary Major Equipment List for Ceramicrete Immobilization of MS-2

Equipment	Quantity	Size, m (feet) (D × H)	Maximum Capacity (m^3)
MS-1 Feed Receipt Vessel (Tk-Fr-01/02) Stainless Steel Transfer Pump	2 2	1.7×2.4 (6×8) 100 gpm	5
Phosphoric Acid Chemical Storage Tank (Tk-Pa-01) Carbon Steel Transfer Pump	1 1	1.5×2 (5×7) 0 To 5 gpm	3.5
MS-1 Neutralization and Pretreatment (Tk-Npt-01/02) 304-L Stainless Steel Transfer Pump	2 2	2 2 1.5×2 (5×7) 100 gpm	3.5
Dry Stabilizing Reagent Hooper (BN-01/02/03/04) Carbon Steel Pneumatic Transfer	4	1.2 × 1.2 (4 × 4) 0.5 to 4 kg/minute	1
Boric Acid Hopper (BN-05) Carbon steel Pneumatic transfer		1.2×1.2 (4 × 4) 0.5 to 10 kg/minute	1
Monophosphate Potassium Hopper (BN-05) Carbon steel Pneumatic transfer		1.7×2.4 (6 × 8) 0.5 to 40 kg/min	5
Calcium Silicate Hopper (BN-07) Carbon steel Pneumatic transfer	1 1	1.7×2.4 (6 × 8) 0.5 to 40 kg/min	5
Magnesium Oxide Hopper (BN-08) Carbon steel Pneumatic transfer	1 1	1.7×2.4 (6 × 8) 0.5 to 40 kg/min	5
Batching tank (Tk-B-01) Stainless Steel	1	1.2×1.3 (4 × 4)	1.5
Ceramicrete Ribbon-type Mixer (ME-01) Carbon steel	1	2.14 m^3/batch	3
Sealing machine (SM-01)	1		

Table 5 (continued)

Equipment	Quantity	Size, m (feet) (D × H)	Maximum Capacity (m^3)
Container storage area with 10MT overhead crane	1	6×6×8 (20×20×25) (W x L x H)	9 containers
Underground Pipeline	N/A	4,500-ft	N/A
Dust Bag House	1	TBD	TBD
Process Off-Gas Treatment System	1	N/A	N/A
Facility Off-Gas Treatment System	1	N/A	N/A
Distributive Control System (DCS)	1	N/A	N/A
Office / Control Room area	1	6×15×12(20×50×40) (W × L × H)	90 m^2 (1,000 ft^2) 1080 m^3 (40,000 ft^3)
All vessels will be equipped with pressure, liquid level, specific gravity, low-level and high-level indicators instrumentation. Instrumentation and utilities are not listed.			

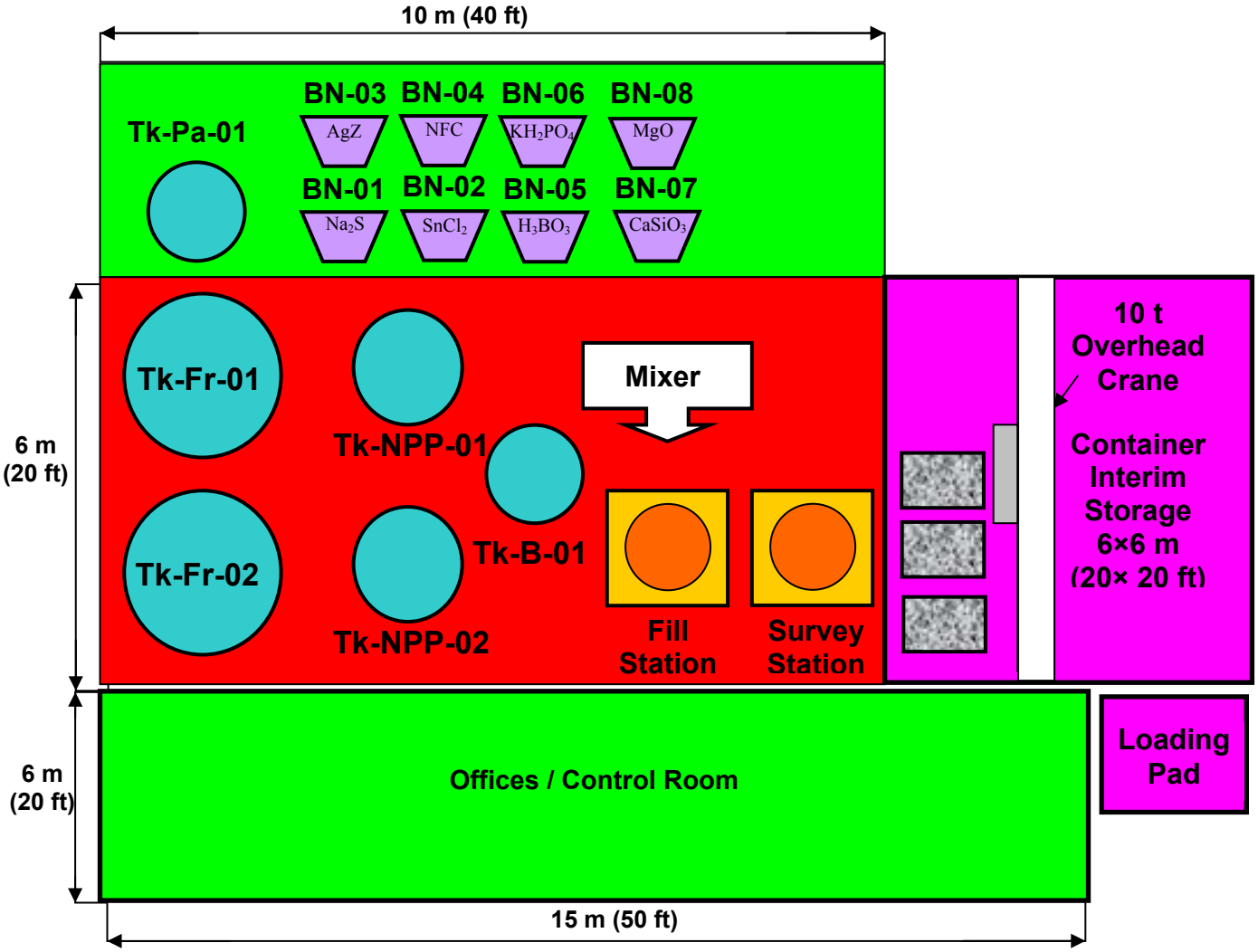


Figure 2 - Deployment Concept of Mayak Stream 1 Ceramicrete Immobilization

4. Integration with Other Mayak Facilities

The Ceramicrete Treatment Facility will need to process supernatant of HLLW tank storage. The Ceramicrete Treatment Facility must be located in area, near the HLLW storage to take advantage of available land and proximity and cost decrease. Some services, for example electrical or water supply, for the Ceramicrete Treatment Facility will be provided from existing services.

However, a specific location for the Ceramicrete Treatment Facility has not been selected. Mayak PA is an operating industrial enterprise, therefore the issue of adaptation of the process being implemented for the enterprise infrastructure requires design development to select an optimum decision. Obviously, the use of the existing infrastructure for new goals should not interfere with implementation of the main production program of the enterprise. Otherwise, construction of the reprocessing facility will require creation of new infrastructure. At present, the optimum decision is not obvious, that is why it is important to answer the question, whether to adjust stabilization process to the existing free spaces and networks or to build a new system, only after appropriate design and cost evaluation. Choice of specific location and determination of requirements for technical services can be defined in more detail during subsequent phases of the next project.

Issues relating to the process organization, transportation, storage, monitoring, and safety are determined and justified by the design depending on radioactive waste parameters (radionuclide composition, specific activity, period of potential hazard, physical and chemical properties), and taking into account environmental conditions of the storage facility location.

5. Cost estimate

The estimated cost for construction of the Ceramicrete Treatment Facility for immobilizing Mayak Stream 1 waste is $ 53 million. Details of this cost estimate are summarized in Table 5. This cost estimate includes a 50 percent contingency ($17.7 million), which is consistent with the level of uncertainty for a project at this stage.

The final waste form volume, and hence the containerization and disposal costs, can be optimized (for example in case of exception of wallostanite).

Table 6
Preliminary cost estimated for Ceramicrete Immobilization of Mayak Stream 1

Estimate Summary Description	Total Cost ($)
Other Project Costs	6,700,000.00
Program/Project Management	1,000,000.00
Technical Support	700,000.00
Preliminary Design	1,500,000.00
Pilot Testing	2,500,000.00
Regulatory Permitting/Approval	1,000,000.00
Engineering Support	620,000.00
Process System	300,000.00
Transfer Lines	120,000.00
Facilities / Utilities	200,000.00
Design	2,410,000.00
Process System	1,550,000.00
30 Percent Design	465,000.00
Final Design	900,000.00
Engineering During Construction	200,000.00
Transfer Lines	310,000.00
30 Percent Design	100,000.00
Final Design	200,000.00
Engineering During Construction	10,000.00
Facilities/ Utilities	550,000.00
30 Percent Design	150,000.00
Final Design	350,000.00
Engineering During Construction	50,000.00
Procurement	8,485,000.00
Process Equipment	2,990,000.00
Procurement	2,600,000.00
Procurement Support	390,000.00
Transfer Lines and Pits	5,150,000.00
Procurement	5,000,000.00
Procurement Support	150,000.00
Facilities/ Utilities	345,000.00
Procurement	300,000.00
Procurement Support	45,000.00

Table 6 (continued)

Estimate Summary Description	Total Cost ($)
Installation	15,745,000.00
Process System	1,535,000.00
Program Management/Construction Management (PM / CM)	300,000.00
Construction	1,200,000.00
Construction Support	35,000.00
Transfer Lines	3,210,000.00
PM / CM	150,000.00
Construction	3,000,000.00
Construction Support	60,000.00
Facilities/ Utilities	11,000,000.00
PM / CM	700,000.00
Construction	10,000,000.00
Construction Support	300,000.00
Readiness / Startup	560,000.00
Process System	400,000.00
Readiness/Startup	400,000.00
Transfer Lines and Pits	150,000.00
Readiness/Startup	150,000.00
Facilities/Utilities	10,000.00
Readiness/Startup	10,000.00
Subtotal	**35,380,000.00**
Contingency (50 Percent)	17,690,000.00
Escalation (not included)	
Total	**53,070,000.00**

6. Mayak alpha-containing sludge Solidification Process Description

Conceptual design has been developed based on the process steps and estimated quantities that were determined from the laboratory and pilot scale demonstration work for Mayak Stream 2 (MS-2).

Mayak Stream 2 is slightly alkali sludge which generate from Low Level Liquid Waste purification process. Characteristics of sludge are presented in table 7.

Based on the above trials to select a suitable ceramic process for MS-2, a sequence of steps was indicated for sample preparation that is likely to prove successful. The sequence is essentially pH correction – partial dewatering by evaporation - solidification. These not difficult three steps are needed for Mayak Stream 2 due to the absence of soluble hazardous chemical elements and another

radionuclides except alpha-emitters in sludge. The process is very simple and can be described as follows:

Table 7

Characteristics of Alpha-containing Sludge

Component Concentration, mg/L											ρ, g/cm^3	Σα, Bq/L
pH	$Fe(OH)_3$	Na^+	Ca^{2+}	Mg^{2+}	NO_3^-	NO_2^-	SO_4^{2-}	Cl^-	PO_4^{3-}	TDS		
10,5	18800	750	45	24	463	203	138	85	9	21200	1,02	$3{,}0 \cdot 10^5$
Σα – specific activity of alpha-emitted nuclides, Bq/L												

pH correction. Research with the real and simulated solutions has shown that high alkali concentration promoted very rapid rate of Ceramicrete synthesis. To slow down the reaction rate to acceptable level, it is desirable to correct pH below 10. Phosphoric acid can be used for that. Acid dosage is a very negligible that is why sludge temperature don't change.

Partial Dewatering by Evaporation. Mayak Stream 2 is the sludge with low TDS. That is why exist possibility to decrease final volume of solidificated waste. For that initial liquid waste must be partially dewatering. The result of partially dewatering is waste volume reduction. The potential to maximize waste loading was studied using real alpha-containing waste. The results of the alpha-containing sludge evaporation are shown that volume can be reduced up to 10 times and paste-like vat residues resulting from process. However such product is difficult to transfer. In the case of two times volume reduction fluid sludge is obtained and can be transferred easy for another operation. This solution was used in conceptual design of Mayak alpha-containing sludge Solidification.

Solidification. Ceramicrete components (KH_2PO_4, H_3BO_3, $CaSiO_3$, MgO) is added into solution separately in order to provide complete dissolution of Boric acid and Monopotassium phosphate. Boric acid was used as retardant reaction. Boric acid and Monopotassium phosphate are dissolved during 1-2 hours under continuous stir. After complete dissolution wollastonite and magnesium oxide are dosed. Than mixture stirred ~ 20 minutes (+/-) to effect reactions that convert waste constituents to insoluble compounds and ceramics, produce a ceramic matrix, and microencapsulate constituents.

7. Ceramicrete process summary material balance

According to data which were determined from the laboratory and pilot scale demonstration work formula for Mayak Stream 2 has some differences from original and presented in table 8.

Table 8
Cheramicrete synthesis formula for Mayak Stream 2

Mayak Stream 2	MgO	KH_2PO_4	Wollastonite
35.0 % wt.	13.0 % wt.	39.0 % wt.	13 % wt.

For this project, it was assumed that the waste will be delivered with a constant chemical content.

A conceptual diagram for immobilizing ILW – Mayak Stream 2 in Ceramicrete is depicted in Figure 3. The following description of the Mayak Stream 2 Ceramicrete technology system (CTS) is based on processing 800 m^3 every year at 70 percent total operating efficiency (TOE) (250 working day). All vessels are sized to hold their contents at 85 percent capacity, providing an operating/safety margin. Table 9 summarizes the material balance for processing 800 m^3/year.

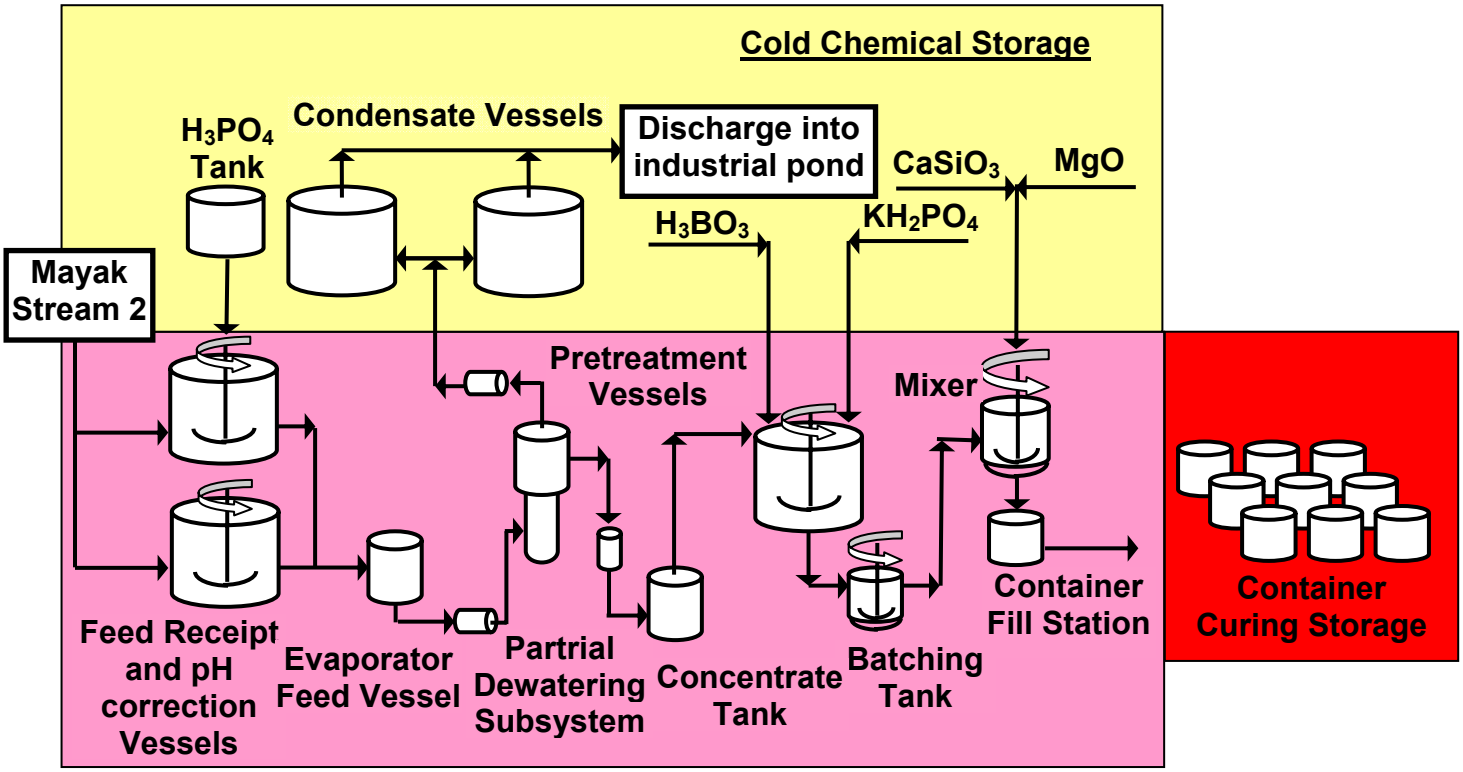


Figure 3 - Conceptual Flow Diagram of Mayak Stream 2 Immobilization

Table 9
Ceramicrete Immobilization of Mayak Stream 2 - Summary Material Balance

	Stream 1 MS-2	Stream 2 H_3PO_4	Stream 3 Neutralized MS-1	Stream 4 Feed to evaporator	Stream 5 MS-2 Concentrat	Stream 6 Condensat	Stream 7 H_3BO_3	Stream 8 KH_2PO_4	Stream 9 Calcium Silicate	Stream 10 MgO	Stream 11 Ceramicrete Immobilized MS-2
Quantity	800,000 L	5,000 L	805,000 L	805,000 L	400,000 L	405,000 L	2.97+04 kg	4.65E+05kg	1.55E+05 kg	1.55E+05kg	1.22+06 kg
Density, g/mL	1.02	1.02	1.02	1.02	1.04	1.00			2.9		1.80
Analyte	moles	moles	moles	moles	moles		moles	moles	moles	moles	moles
Na^+	2.61E+04		2.61E+04	2.61E+04	2.61E+04						5.05E+06
PO_4^-		7.30E+04	7.30E+04	7.30E+04	7.30E+04						2.19E+06
H^+		2.19E+05	2.19E+05	2.19E+05	2.19E+05						6.57E+06
Fe	1.41E+05		1.41E+05	1.41E+05	1.41E+05						2.86E+04
H_3BO_3							4.79E+05				
MgO										3.88E+06	
KH_2PO_4								3.42E+06			
$CaSiO_3$									1.34E+06		

Summary material balance is presented for processing the maximum volume (800 m^3) of MS-2 every year. Boric acid is added as reaction retardant in quality of 2.5 % wt. from ceramicrete compound. Nickel ferrocyanide (in dry form) is dosed from calculation of 1 % wt. for ceramicrete compound

7.1 Waste Receipt and pH correction

The MS-2 is assumed to be received as a liquid waste stream into one of two, 5 m^3 capacity Feed Receipt and pH correction Vessels (Tk-Frc-01/02) at the CTS. Feed Receipt and pH correction Vessel is a tank for a batch of waste for 2-3 day operation of the system. Each of the MS-2 feed receipt and pH correction vessels is sized to receive 4 m^3 Mayak Stream 2. One of the feed receipt vessels is used to receive MS-2 and pH correct while the second vessel is transferring Mayak Stream 2 to the evaporator feed vessel. Approximately 0.006 L phosphoric acid of 85 wt % are added per 1 L of Mayak Stream 2 (24 L per batch) to adjust the mixture down to pH 10.

The Vessels are equipped with level sensors, sampling system, gas-cleaning filter and mechanical mixer. Construction material of the vessels is stainless steel.

7.2 Partial dewatering by evaporation

Approximately 2.5 m^3 of the MS-2 are transferred every 8 hours from the feed receipt and pH correction vessels to the evaporator feed vessel (Tk-Ef-01) of 3 m^3 capacity. The Vessel is equipped with level sensors, sampling system and mechanical mixer. Construction material of the vessels is stainless steel.

The 800 m^3 batch of MS-2 is transferred to a vacuum-operated, forced circulation evaporator where excess water is removed to minimize the waste volume. The volume of the MS-2 is reduced by approximately 50 % during evaporation, yielding ~400 m^3 of concentrated sludge. This is conservative in that a greater volume reduction was shown to be achievable with Ceramicrete.

The evaporator process condensate (~9 m^3 per batch) is collected into one of two condensate vessels (Tk-Cd-01). Each condensate vessel (capacity ~ 10 m^3 (2650

gallons) can store condensate generated in 5 days (working week). Two condensate collection vessels are employed to allow one vessel to be receiving condensate while the other vessel is being sampled and discharged. The condensate after activity control is discharged into industrial pond (< 5 Bq/L) or in Low Level Liquid Stream (> 5 Bq/L), which transferred for purification.

The evaporator process concentrate (~1.25 m^3 per batch) is collected into concentrate vessel (Tk-Cc-01). The concentrate vessel (capacity ~ 1.5 m^3) can store concentrate generated in 8 hours. The vessel is equipped with level sensors, sampling system and mechanical mixer.

The evaporator subsystem is sized to process 3 lpm of MS-2 and consists of a high-volume pump, heat exchanger, evaporator vessel, condenser, 2.5 m^3 capacity evaporator feed vessel, and 1.5 m^3 capacity concentrate receipt vessel.

7.3 Waste pretreatment

Approximately 1.25 m^3 of the MS-2 concentrate are transferred every 8 hours from the concentrate vessel to the waste pretreatment vessel (Tk-Wt-01). The waste pretreatment vessel (capacity ~ 1.5 m^3) can store concentrate generated in 8 hours. Boric acid and monopotassium phosphate are added into concentrate Mayak Stream 2 in quantity 93 kg and 1450 kg, respectively and are stirred 1-2 hours to reach the complete dissolution.

The waste pretreatment is equipped with level sensors, sampling system and mechanical mixer.

7.4 Waste solidification into ceramicrete

After pretreatment concentrate MS-2 batch in volume of 1.25 m^3 is transferred through the batching tank to an immobilization subsystem where calcium silicate (wollastonite) or fly ash and magnesium oxide are mixed with the waste and discharged to disposal containers.

Batching tank (Tk-B-01) is a tank of 1.5 m^3 capacity for receiving and batching of wastes for one mixing operation. The tank is equipped with a level

sensors, gas-cleaning filter, mechanical mixer and weighing mechanism. Construction material of the tank is stainless steel.

A continuous, ribbon-type mixer is used to process the concentrate MS-2 and these dry reagents ($CaSiO_3$, MgO). The ribbon-type mixer is sized for producing ~2.1 m^3 (~3.7 MT) Ceramicrete batches. Approximately 482 kg of calcium silicate and 482 kg magnesium oxide are added per batch of concentrate MS-2 for immobilization, producing ~ 3807 kg (2100 L) of Ceramicrete. Approximately 100 MT of Ceramicrete-immobilized MS-2 is produced every month.

Sealing machine is used to place and seal a lid on a container with compound to ensure its impermeability.

7.5 Container Selection

The production rate of Ceramicrete-immobilized MS-2 is approximately 200 kg per hour (5 MT/day) at 70 % TOE, or approximately 285 kg per hour (7 MT/day) at 100 % TOE; i.e., a two-shift or three-shift operation to meet the specified generation rate. The density of the Ceramicrete waste form is approximately 1.80 MT/m^3. Table 10 lists the number of different types of containers with the Ceramicrete-immobilized MS-2 that would be produced per day. It is evident from Table 4 that 55-gallon drums or 85-gallon drums cannot be used for disposal of the Ceramicrete-immobilized MS-1, given the excessive number of containers generated per day. A larger container, such as a 50-yd^3 metal box, would greatly reduce container handling logistics, but could be difficult for Ceramicrete filling and curing and filled container transporting. Container requirements should be determined additionally.

Approximately 1-2 containers per day (at 70 percent TOE) will be produced, each containing 2.14 m^3 (3.8 MT at 90 percent fill) of Ceramicrete-immobilized MS-2. A unique labeled container will be positioned at the container filling station and loaded with Ceramicrete-immobilized MS-1. The filled containers will be sealed, surveyed (external contamination removed if it is necessary), and equipped with a Nucfil 013 TM filter (or equivalent) and a hydrogen recombination catalyst to

mitigate hydrogen accumulation if it is needed. Tests have shown very low hydrogen generation, perhaps due to MgO which is known as hydrogen getter. On other hand the dense matrix allows hydrogen recombination.

Table 10
Disposal Container Evaluation

Ceramicrete production rate, m^3/day (kg/day)	Container type	Number per day
2.7 (4900)	55-gallon metal drum (208 L)	14.8
	85-gallon metal drum (321 L)	9.6
	2.26-m^3 metal container	1.3
	50-yd^3 metal box (38.2 m^3)	0.07
Assumes 90 percent fill and 70 percent TOE		

7.6 Container Interim Storage

The Ceramicrete-immobilized MS-2 will cure within 24 hours of pouring into the 2.26-m^3 container. While the previous day's production is curing for 24 hours, the current day's production of containers will be accumulated at the CTS. Therefore, interim storage is provided for 2 days of production, and about 4 containers.

8. Deployment Concept

Major equipment list required for the Ceramicrete immobilization of the Mayak Stream-2 waste is identified in Table 11 and is based on the process description provided above. A preliminary facility concept drawing has been prepared depicting the equipment arrangement. The preliminary facility concept, Figure 4, includes an industrial-type structure housing the process equipment (50 feet by 20 feet), container interim storage pad (20 feet by 13 feet), an office/control room structure (20 feet by 50 feet), and locations for chemical reagent storage.

Table 11
Preliminary Major Equipment List for Ceramicrete Immobilization of MS-2

Equipment	Quantity	Size, m (feet) (D × H)	Maximum Capacity (m^3)
MS-2 Feed Receipt and pH correction Vessel (Tk-Frc-01/02) Stainless Steel Transfer Pump	2 2	 1.7×2.4 (6×7) 100 gpm	5
Phosphoric Acid Chemical Storage Tank (Tk-Pa-01) Carbon Steel Transfer Pump	1 1	0.5×1 (2×3) 0 To 5 gpm	0.2
Evaporator feed vessel (Tk-Ef-01) 304-L Stainless Steel Transfer Pump	1 1	 1.5×2 (5×7) 100 gpm	3
Concentrate Vessel (TK-Cc-01) 304-L Stainless steel Transfer pump			1.5
Evaporator – 304-L stainless steel Re-boiler (E-01) Vapor-liquid separator vessel (EV-01) Primary condenser (E-02) Secondary condenser (E-03) Recirculation pump Concentrate pump	 1 1 1 1 1 1		
Condensate Vessel (TK-PCd-01/02) 304-L Stainless steel Transfer pump	2		10
Waste pretreatment vassel (Tk-Wt-01) 304-L Stainless steel Transfer pump	1		1.5
Boric Acid Hopper (BN-01) Carbon steel Pneumatic transfer		1.2×1.2 (4 × 4) 0.5 to 10 kg/minute	1
Monophosphate Potassium Hopper (BN-02) Carbon steel Pneumatic transfer		1.7×2.4 (4 × 4) 0.5 to 40 kg/min	5
Calcium Silicate Hopper (BN-03) Carbon steel Pneumatic transfer	 1 1	1.3×1.5 (6 × 8) 0.5 to 50 kg/min	2
Magnesium Oxide Hopper (BN-04) Carbon steel Pneumatic transfer	1 1	1.3×1.5 (6 × 8) 0.5 to 50 kg/min	2

Table 11 (continued)

Equipment	Quantity	Size, m (feet) (D × H)	Maximum Capacity (m^3)
Batching tank (Tk-B-01) Stainless Steel	1	1.2×1.3 (4 × 4)	1.5
Ceramicrete Ribbon-type Mixer (ME-01) Carbon steel	1	2.14 m^3/batch	3
Sealing machine (SM-01)	1		
Container storage area with 10MT overhead crane	1	6×4×8 (20×13×25)	4 containers
Underground Pipeline	N/A	4,500-ft	N/A
Dust Bag House	1	TBD	TBD
Process Off-Gas Treatment System	1	N/A	N/A
Facility Off-Gas Treatment System	1	N/A	N/A
Distributive Control System (DCS)	1	N/A	N/A
Office / Control Room area	1	6×15×12 (20×50×40) (W×L×H)	90 m^2 (1,000 ft^2) 1080 m^3 (40,000 ft^3)
All vessels will be equipped with pressure, liquid level, specific gravity, low-level and high-level indicators instrumentation. Instrumentation and utilities are not listed.			

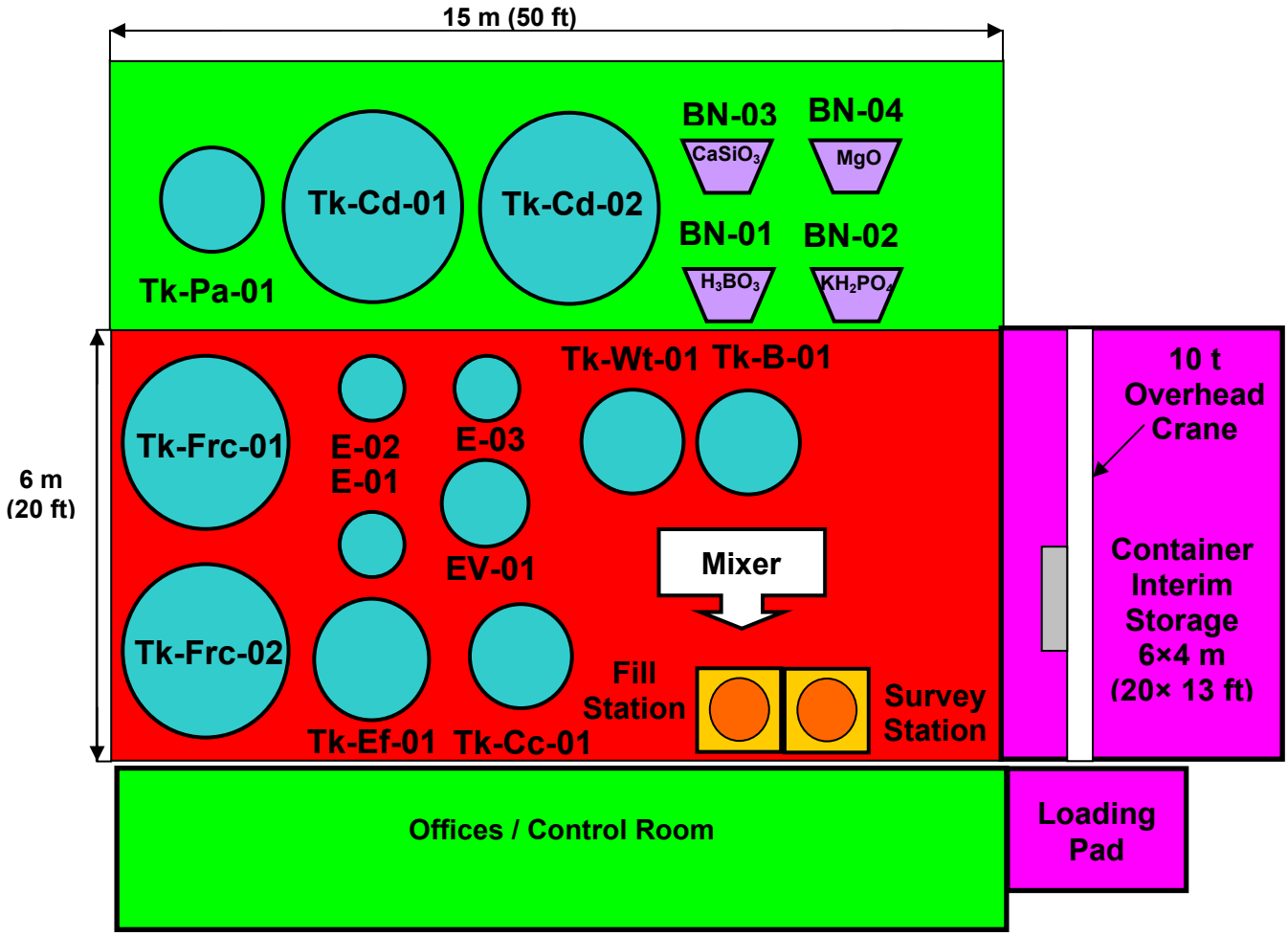


Figure 4 - Deployment Concept of Mayak Stream 2 Ceramicrete Immobilization

9. Integration with Other Mayak Facilities

The Ceramicrete Treatment Facility will need to process slightly alkali sludge which generate from alpha-containing Low Level Liquid Waste purification process

The Ceramicrete Treatment Facility must be located in area, near the Low Level Liquid Waste purification facility advantage of proximity and cost decrease. Some services, for example electrical or water supply, for the Ceramicrete Treatment Facility will be provided from existing services.

However, as in case of HL supernatant choice of specific location and determination of requirements for technical services can be defined during subsequent phases of the next project.

10. Cost estimate

The estimated cost for construction of the Ceramicrete Treatment Facility for immobilizing Mayak Stream 2 waste is about $ 30 million. Details of this cost estimate are summarized in Table 5. This cost estimate includes a 50 percent contingency ($ 9.9 million), which is consistent with the level of uncertainty for a project at this stage. The final waste form volume, and hence the containerization and disposal costs, can be optimized (for example in case of exception of wallostanite).

Table 6
Preliminary cost estimated for Ceramicrete Immobilization of Mayak Stream 1

Estimate Summary	
Description	**Total Cost ($)**
Other Project Costs	4,200,000.00
Program/Project Management	1,000,000.00
Technical Support	200,000.00
Preliminary Design	1,000,000.00
Pilot Testing	1,500,000.00
Regulatory Permitting/Approval	500,000.00
Engineering Support	620,000.00
Process System	300,000.00
Transfer Lines	120,000.00
Facilities / Utilities	200,000.00

Table 6 (continued)

Estimate Summary Description	Total Cost ($)
Design	2,100,000.00
Process System	1,000,000.00
30 Percent Design	300,000.00
Final Design	600,000.00
Engineering During Construction	200,000.00
Transfer Lines	310,000.00
30 Percent Design	100,000.00
Final Design	200,000.00
Engineering During Construction	10,000.00
Facilities/ Utilities	500,000.00
30 Percent Design	150,000.00
Final Design	300,000.00
Engineering During Construction	50,000.00
Procurement	3,620,000.00
Process Equipment	2,250,000.00
Procurement	2,000,000.00
Procurement Support	250,000.00
Transfer Lines and Pits	1,150,000.00
Procurement	1,000,000.00
Procurement Support	150,000.00
Facilities/ Utilities	220,000.00
Procurement	200,000.00
Procurement Support	20,000.00
Installation	7,785,000.00
Process System	1,535,000.00
Program Management/Construction Management (PM / CM)	300,000.00
Construction	1,200,000.00
Construction Support	35,000.00
Transfer Lines	750,000.00
PM / CM	100,000.00
Construction	600,000.00
Construction Support	50,000.00
Facilities/ Utilities	5,500,000.00
PM / CM	300,000.00
Construction	5,000,000.00
Construction Support	200,000.00
Readiness / Startup	560,000.00
Process System	400,000.00
Readiness/Startup	400,000.00
Transfer Lines and Pits	150,000.00
Readiness/Startup	150,000.00
Facilities/Utilities	10,000.00
Readiness/Startup	10,000.00
Subtotal	**19,695,000.00**
Contingency (50 Percent)	9,847,500.00
Escalation (not included)	
Total	**29,542,500.00**

11. Performance specifications

Performance specifications – criteria for waste feed for the stabilized waste; requirements for off-gas, shielding, containers, handling, etc.

The principal criterion that should be taken into account in this project at present is a requirement to admissible specific activity of the compound. It is 1.7×10^{14} Bq/m3 (~9.0×10^{13} Bq/kg) for ^{137}Cs, 2.6×10^{14} Bq/m3 (1.4×10^{14} Bq/kg) for ^{90}Sr, and 3.7×106 Bq/kg for uranium and transuranium alpha-emitting radionuclides with half-life period more then 5 years

For wastes containing a mixture of radionuclides the total concentration is defined as "a sum of fractions" by division of the concentration of each nuclide by corresponding admissible concentration. The sum of fractions should not exceed 1.0.

The upper (conservative) value of $3.7\cdot10^{6}$ Bq/kg for uranium and transuranium alpha-emitting radionuclides with half-life period more then 5 years is acceptable only for single packages with radioactive waste in condition that their mean specific activity in subsurface burial do not exceed 370 Bq/kg.

The process should be safe in terms of fire and explosion hazard and should not be accompanied with toxic component generation.

Requirements for the containers (construction materials, weight, dimensions, design, and mechanical properties) as well as for the waste packages in general are established by the design of the subsurface burial place.

12. Regulatory and Mayak site requirements

Process requirements are based on the following regulatory documents:

Radiation Safety Standards SP 2.6.1.758-99 (NRB-99)

Basic Sanitary Rules for Radiation Safety (OSPORB-99)

Sanitary and Epidemiological Rules and Standards (SanPiN 2.6.1. 07 – 03) "Hygienic Requirements for Design of Nuclear Enterprises and Facilities"

Sanitary Requirements for Collection, Storage, Transportation, and Disposal of Solid Radioactive Waste at “Mayak” PA (ST TRO – M) Method Recommendations, MU 2.6.1.24-04

“Radioactive Waste Disposal. Principles, Criteria, and Basic Safety Requirements” (NP-055-04)

Average effective dose of personnel exposure (group A personnel) should not exceed 20 mSv per year for any successive 5 years. In the course of 5 years a single excess of exposure dose is allowed but not higher than 50 mSv/year.

Levels of radioactive contamination for carriers and outer surface of packages and shielding containers should not exceed values presented in Table 3.5.1. OSPORB-99.

Table 2.

Levels of radioactive contamination for carriers and outer surface of packages and shielding containers

Contaminated subject	***Type of contamination***			
	Fixed		Unfixed	
	α-activity	β- activity	α- activity	β- activity
Outer surface of shielding containers	Inadmissible	Inadmissible	Unregulated	200
Inner surface of shielding containers	1	100	Unregulated	2000
Outer surface of package	1	100	Unregulated	2000

Radioactive waste storage facilities should be located at enterprises generating the wastes. Type and design of the facility as well as storage conditions should be based on type and characteristics of wastes, aim and duration of storage, climatic, geologic, hydrogeological, and seismic characteristics of the site where the storage facility is situated.

Radioactive waste storage facilities should be equipped with exhaust ventilation functioning around-the-clock and a system of observation wells for monitoring of possible groundwater contamination.

Transportation of waste packages should be performed in containers using special carriers and taking into account package activity, dimensions, and weight.

Planned γ dose rate on the surface of the storage walls should not exceed 6 micro sieverts per hour if it is located on site, 1.2 micro sieverts per hour if it is located in the site buffer zone, and 0.06 micro sieverts per hour if it is constructed outside the buffer zone.

Type and design of the facility as well as storage conditions should be based on type and characteristics of wastes, aim and duration of storage, climatic, geologic, hydrogeological, and seismic characteristics of the site where the storage facility is situated.

SRW and LRW storage facilities should be a system of observation wells for monitoring of possible groundwater contamination.

Burial of radioactive waste is used for safe isolation of conditioned radioactive wastes from human activities for the whole period of potential hazard of the waste without intention of their further removal.

Under the period of potential hazard of radioactive wastes one should understand a period of time buy the end of which the activity of radionuclides in the waste reduces to the values which do not require restrictive measures for isolation and radiation protection and when the monitoring of the wastes as a source of exposure can be stopped.

A principle of multi-barrier protection should be a basis for environmental safety of radioactive waste disposal. It is based on the combined use of natural (geologic) and man-made (artificial) barriers on the way of radionuclide migration from the storage facility.

Depending on the features of multi-barrier protection waste disposal is related to the following types:

- subsurface disposal (shallow land burial)

- waste disposal in geologic formations

Disposal in surface or shallow (up to 50 m) burials provides keeping of radioactive wastes in vaults where man-made barriers play the main role in waste isolation. Natural barrier (host rock) plays a role of protection in case of radioactive accidents.

Project Director Academician, Professor **Boris F. Myasoedov**

PROJECT STATUS REPORT:

Report Number: **RCO-10116-MO-03(ANL)**

Project Title:
"Ceramicrete Stabilization of Radioactive Salt-Containing Liquid and Sludge Waste"

Effective Date: July 1, 2003
Expiration Date: May 19, 2008

Reporting Period: **December, 2007 – May, 2008**

Based on the Tasks accomplished: **Task 20**

Moscow, 2008

Task 20
Microstructure and phase evaluation at Mayak

1. Background

The main goal of current work was examination of physical-chemical properties of "hot" (radioactive) Ceramicrete samples prepared according to advance technology in the laboratory scale using the Scanning Electronic Microscope (SEM), and X-ray Phase Analysis technique. In the frame of realization of the Report#20 we focused on two most important tasks: (1) to observe the homogeneity of samples above during solidification; and (2) to appreciate a phases evaluated during ceramic matrix formation. For these purposes the "Chemical Bore" (The Emission Electronic Spectroscopy) had been used. The results obtained are discussed below.

2. Preparation of "hot" samples

Stream 1 solidification. In order to prepare "hot" samples, real solutions watering to safe treatment level were used:

- Cs-137 with specific activity $1.46 \cdot 10^7$ Bq/L obtained from alkaline supernatant by dilution;
- Sr-90 with specific activity $1.51 \cdot 10^6$ Bq/L got from a technological products;
- I-129 with specific activity $2.26 \cdot 10^6$ Bq/L selected from alkaline regenerative solution of filter gas purification from radiochemistry plant.

For preparation surrogate **Stream 1** 34 g NaOH, 33.4 g - $NaNO_3$, 11.5 g - $NaNO_2$, 18 g $Al(NO_3)_3 \cdot 9H_2O$, Na_2SO_4 – 1.27 g, NaCl – 0.59 g, NaF – 0.11 g, K_2CrO_4 – 3.04 g were dissolved in 153 mL of radioactive solution. The acquired solution had volume 190 mL and density 1.31 g/cm^3. Its composition is given in Table 1.

Table 1
Modified Surrogate Mayak Stream 1 properties

Components concentration, g/L									^{137}Cs, Bq/L	^{90}Sr, Bq/L	^{129}I, Bq/L
NaOH	Na^+	Al^{3+}	NO_3^-	NO_2^-	SO_4^{2-}	Cl^-	CrO_4^{2-}	TDS			
179.9	175.5	7.2	177.6	40.2	4.5	1.9	9.6	499	$1.46 \cdot 10^7$	$1.51 \cdot 10^6$	$2.26 \cdot 10^6$
TDS – total dissolved solids											

Than as provided by Cermicrete advanced technology, provided at the GEOKHI RAS, alkaline solution was neutralized by 25 mL phosphoric acid (ρ=1.69 g/cm^3) up to pH=8. Nitrogen oxide release was observed during the process of neutralization. After it

color of the solution changed from primrose to olive caused by reduction of Cr(VI) до Cr(III) and the formation the precipitates of hydroxides $Al(OH)_3$, $Cr(OH)_3$. Next 34 mL of nickel ferrocyanide suspension (ρ=1.17 g/cm^3, consisted of 114.9 g/L nickel ferrocyanide, 6.5 g/L – $Ni(NO_3)_2$, 140.6 g/L – KNO_3), 37.9 g of dry granulated anion exchange resin AV-17 in chloride form (Cl^- -form) were introduced into the neutralized solution and it was blended for 60 minutes to fix caesium and iodine. Than, 21.0 g $Na_2S{\cdot}9H_2O$, dissolved in 50 ml of initially prepared radioactive solution were introduced in obtained mixture stirring up. Its color became black due to precipitation of nickel sulfide. Obtained sludge had pH 10.5. To prevent nickel ferrocyanide from eventual destruction, 4 ml of concentrated nitric acid (12.4 M, density 1.35 g/cm^3) was added in order to stabilize pH at level below 9. Finally initially prepared radioactive solution was added up to 355 mL. Obtained mixture had density 1.26 g/cm^3 and was used in Ceramicrete synthesis. Magnesium oxide calcined at 1400 ^oC for 4 hours was used for synthesis of the ceramics. Boric acid in quantity 4 % was added to the compound to prolong solidification time. Wollastonite in quantity 15 % was added to the compound to increase compressive strength. The composition is described in Table 2. Boric acid and wollastonite were added subsequently with an one hour interval continuously stirring up. Than monopotassium phosphate was introduced. Mixture was stirred during 2 hours in order to reach the complete dissolution of the introduced components. Further, MgO was added and the obtained mixture was blended 50 min and than was poured in the moulds. For next 10 min stiffening of the composition occurred.

Table 2
Composition for Stream 1 solidification

Composition					
MgO	KH_2PO_4	Stream 1	H_3BO_3	Wollastonite	Total
109.7 g	328.4 g	447.3 g	38.7 g	156.9 g	1081.0 g
10.1 %	30.4 %	41.4 %	3.6 %	14.5 %	100 %

After 4 weeks of maturing the samples were extracted from the moulds. Physical parameters of the samples with solidified Stream 1 are given in Table 3.

Table 3

Physical properties of the sample 462 with Stream 1

Sample №	D, cm	H, cm	Weight, g	ρ, g/cm^3	Specific strength, kg/cm^2
462	2.5	5.2	44.08	1.73	90

Stream 2 solidification. In order to prepare surrogate Stream 2 the solution $Fe(NO_3)_3$ in HNO_3 14.7 mL in volume was taken, than it was neutralized by 7mL NaOH (600g/L) and radioactive product containing alpha-emitting nuclides (AENP) was added up to 50 mL. As a result radioactive Fe(III) hydroxide sludge with density 1.135 g/cm^{3}was obtained. The following salts were dissolved in 16.7 mL AENP - $Sr(NO_3)_2$ – 9.47 g, K_2CrO_4 – 0.3 g, $Ni(NO_3)_2{\cdot}6H_2O$ – 2.3 g and combined with the Fe(III) hydroxide sludge. Further 61.3 mL nickel ferrocyanide suspension (nickel ferrocyanide – 115 g/L, $Ni(NO_3)_2$ – 6.5 g/L, KNO_3 – 140.6 g/L, ρ=1.17 g/cm^3) was added to the obtained sludge. As a result the volume of received radioactive sludge achieved 128 mL.

Than 15.06 g $Na_2S{\cdot}9H_2O$ previously dissolved in 30 mL AENP was introduced into the sludge, whose color became black due to precipitation of nickel sulfide. Further pH was corrected to 10 by introducing 10.2 mL NaOH (600 g/L). At last AENP was added up to 250 mL. The sludge with density 1.10 g/cm^3 and specific alpha-activity $1.29{\cdot}10^5$ Bq/L was used in ceramicrete synthesis. Its chemical content is presented in Table 4.

Table 4

Modified Surrogate Mayak Stream 2 properties

Components concentration, g/L										Σα, Bq/L
Na^+	Sr^{2+}	K^+	Ni^{2+}	Cr^{3+}	$Fe(OH)_3$	SO_4^{2-}	NO_3^-	NFC	TDS	
24.0	15.7	13.6	2.36	0.25	19.7	24.2	82.6	28.2	210.7	$1.29{\cdot}10^5$

NFC - nickel ferrocyanide, g/L; TDS – total dissolved solids, g/L; ρ – solution density, g/cm^3; Σα – total activity of α-emitting nuclides, Bq/L

Magnesium oxide calcined at 1400 ^oC for 4 hours was used for synthesis of the ceramics. Boric acid in quantity 2.5 % was added to the compound to prolong solidification time. Wollastonite in quantity 15 % was added in order to increase compressive strength. The composition is described in Table 5.

Table 5
Composition for Stream 2 solidification

Composition					
MgO	KH_2PO_4	Stream 2	H_3BO_3	Wollastonite	Total
110.8 g	333.4 g	275.0 g	21.5 g	128.8 g	869.5 g
12.8 %	38.3 %	31.6 %	2.5 %	14.8 %	100 %

Boric acid and wollastonite was added subsequently with an one hour interval continuously stirring up. Than monopotassium phosphate was introduced. The solution was stirred during 2 hour in order to reach the complete dissolution of the introduced components. After it, MgO was added and the obtained mixture was blended 30 minutes and than was poured in the moulds. For next 20 min stiffening of the composition occurred. After 4 weeks of maturing the samples were extracted from the moulds. An exterior of the sample with solidified Stream 2 and its physical parameters are given in Table 6.

Table 6
Physical properties of the samples with Stream 2

Sample №	D, cm	H, cm	Weight, g	ρ, g/cm^3	Compressive strength, kg/cm^2
461	2.5	5.1	45.04	1.80	97

The photos of the samples studied are shown in Fig. 1

Figure 1 - Ceramicrete samples with solidified surrogate of Stream 1 (1), and 2 (2)

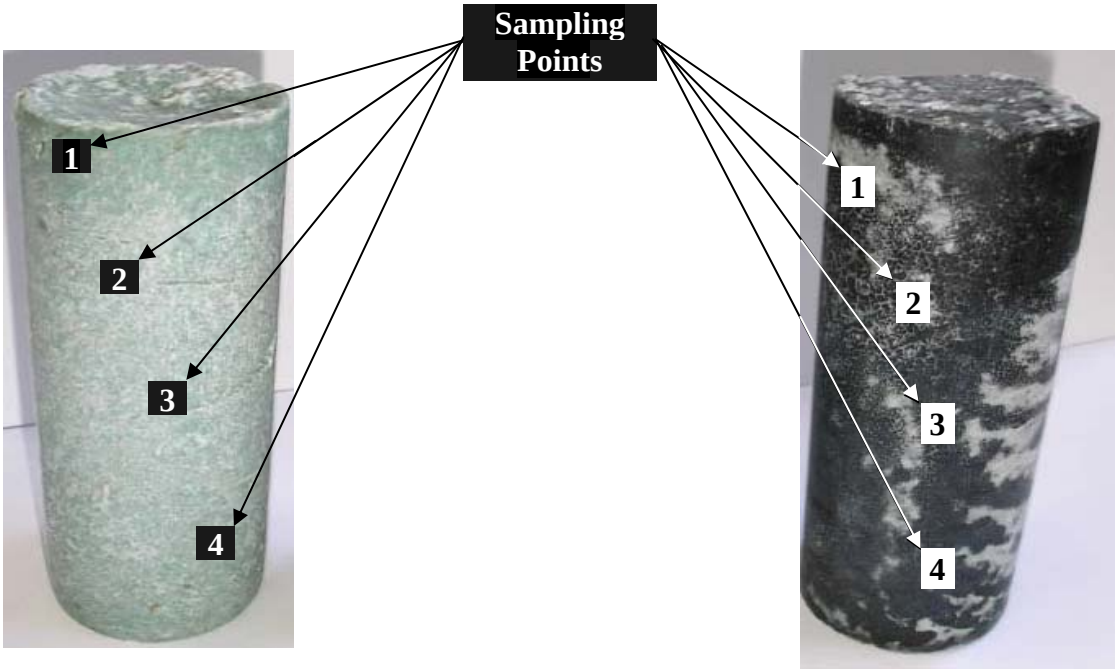
3. Microstructure and phase evaluation at Mayak

For experiments we selected four specimens from Ceramicrete samples with immobilazed Stream 1 and 2. The volume of each sample was about 1 cm^3. For SEM experiments we recorded two microphotos for each sample in the different points 1 and 2 The numbering of the specimens is presented in the Table 7.

Table 7
List of specimens numbering

Specimen with Stream 1 #462	Sample #462(1)		Sample #462(2)		Sample #462(3)		Sample #462(4)	
	Point 1 462(1)1	Point 2 462(1)2	Point 1 462(2)1	Point 2 462(2)2	Point 1 462(3)1	Point 2 462(3)2	Point 1 462(4)1	Point 2 462(4)2
Specimen with Stream 2 #461	Sample #461(1)		Sample #461(2)		Sample #461(3)		Sample #461(4)	
	Point 1 461(1)1	Point 2 461(1)2	Point 1 461(2)1	Point 2 461(2)2	Point 1 461(3)1	Point 2 461(3)2	Point 1 461(4)1	Point 2 461(4)2

The locations of Samples #(1) – (4) in the Specimens #462 and Samples (1) – (4) in the Specimens #461 are shown in the Fig. 2



Specimen #462 (Stream 1) **Specimen #461 (Stream 2)**

Figure 2 - The locations of Samples #(1–4) in the Specimen #462 and Samples (1–4) in the Specimen #461

In every case we recorded the microphotos of both matrix of numbered sample, and the material of granules of an anionite AV-17, incorporated into the Ceramicrete matrix as a necessary component.

For each samples we recorded the microphotos with the resolutions from x10 to x1250 times.

For determination of a phase evaluation of a Specimens #462 and Specimens #461, included the Stream 1, and Stream 2 sludge, respectively, the "chemical bore" based on the electronic emission spectroscopy had been applied. During the experiments for each Sample (1–4) from Specimens #462, and #461 the Quantitative Analysis Results for all the chemical elements had been carried out. Detection limit of the elements founded in the sample was >0.1% of atoms against of total amount of all the atoms presented in the sample. The chemical analysis obtained in two points has been averaged and presented in the summarized tables. From the chemical analysis data it was found that ratios of the content of elements include on the matrix selected in Point 1 and Point 2 in any cases are about ±10%. This information shows a great homogeneity of matrix prepared.

3.1. Specimen #462 (Stream 1).

The general view of the Specimen #462 surface. At the beginning of the experiments we recorded the microphotos of a Sample #462 incorporated with Stream 1 sludge with the different resolution from 10 to 160. The obtained results are shown in the figures below:

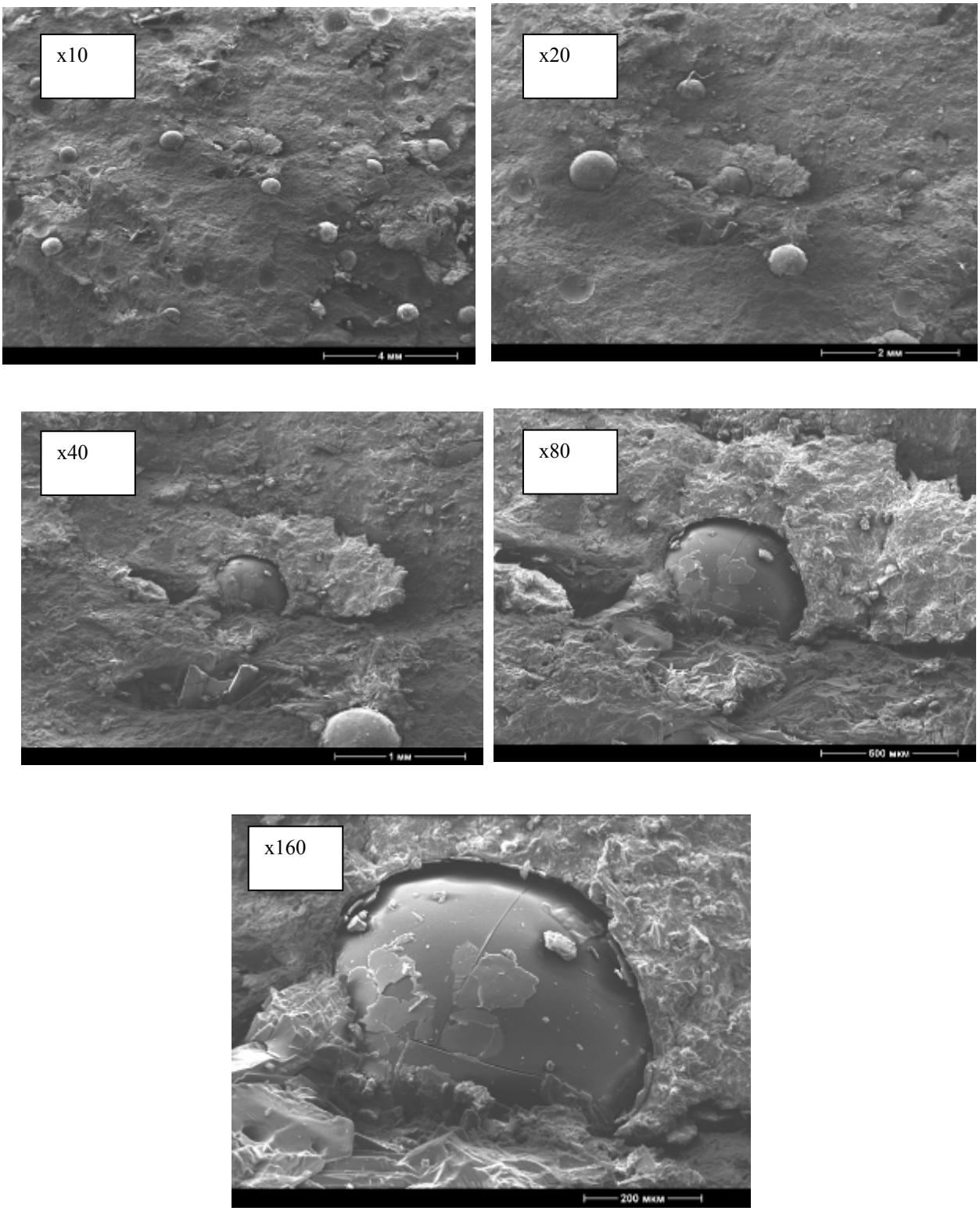
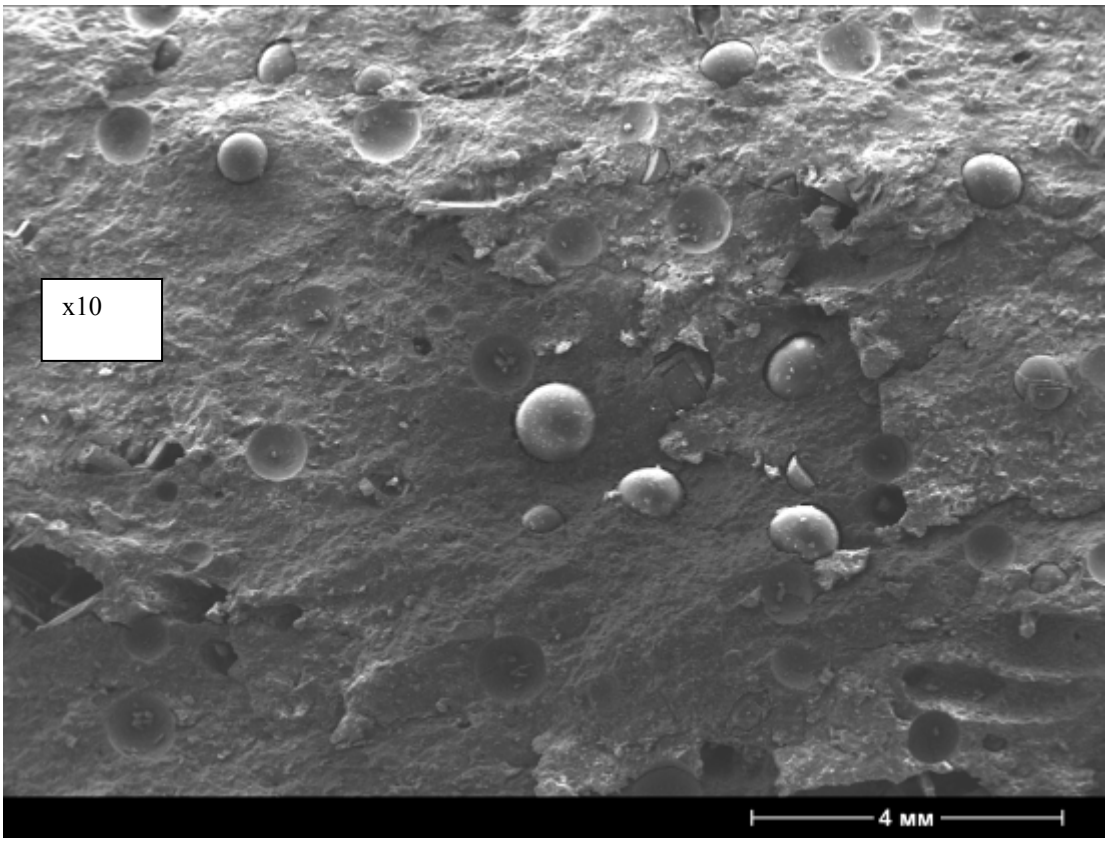


Figure 3 - The general view of the Specimen #462 surface

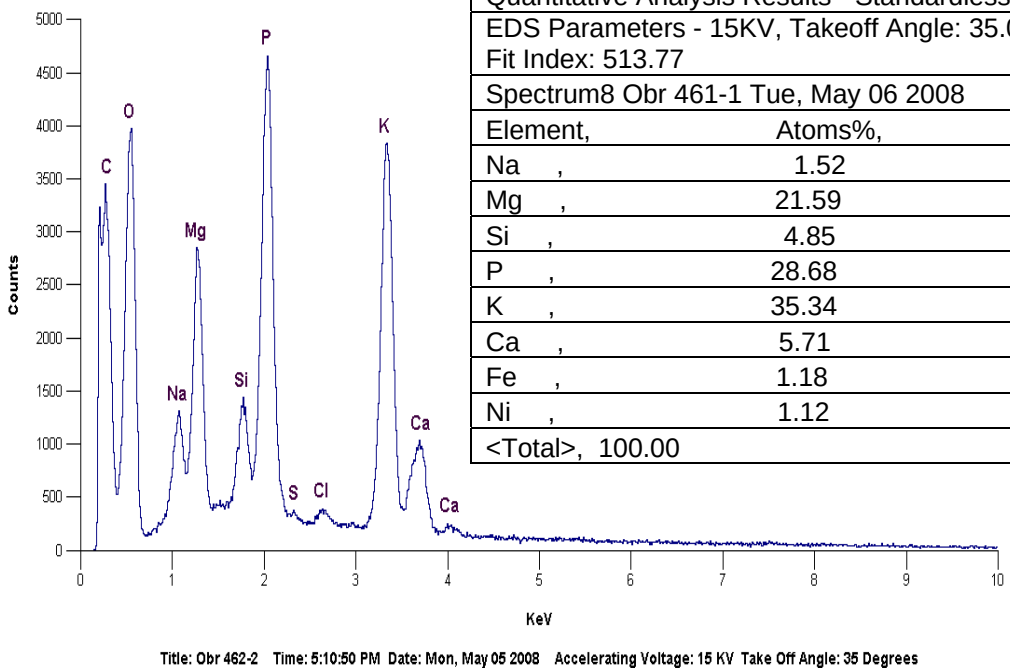
From the data obtained we concluded that the Ceramicrete matrix incorporated the Stream 1 sludge with the adjusted loading has a high solidity. The visible cracks in the matrix material and around the anionite AV-17 granules could not obtain. The granules above fixed by Ceramicrete matrix very strongly. Consequently, we can conclude that irradiation of Ceramicrete matrix, goes from high radioactive elements, not result the structural degradation.

The chemical content of the Specimen #462 Samples (1) – (4) shown from two Points for each samples. For determination of a chemical content of the Ceramicrete matrix with immobilized Stream 1 the SEM Quantitative Analysis Results for all the chemical elements had been carried out. This part contains four sections from section (1) to section (4). Every section includes one microphoto of a surface, and results of a chemical analysis of corresponding samples (tables with the element analysis of the matrix used from two points of sample). The number of the section corresponded with the number of samples used.

Specimen #462 Sample (1)

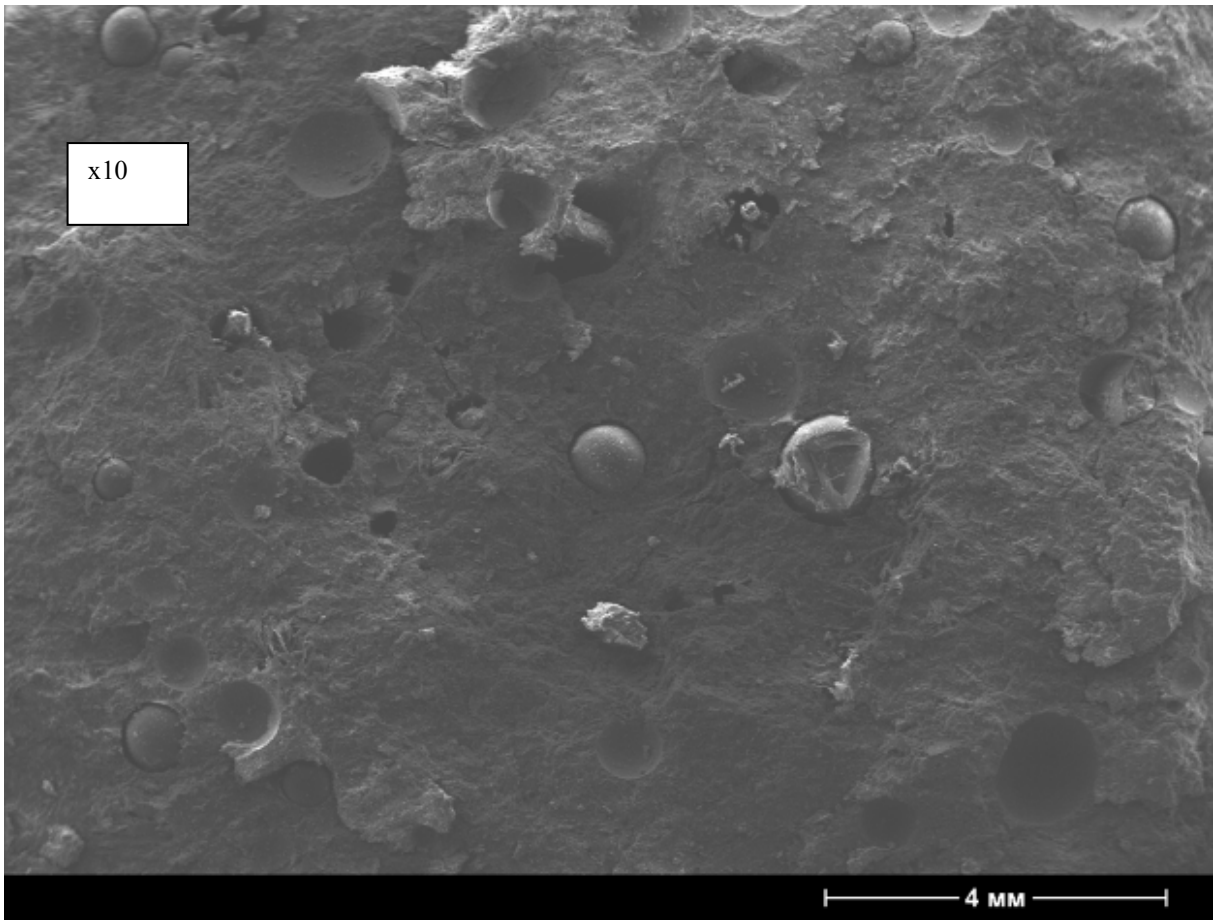


Specimen #462 Sample (1) The average data summarized from Points 1 and 2.

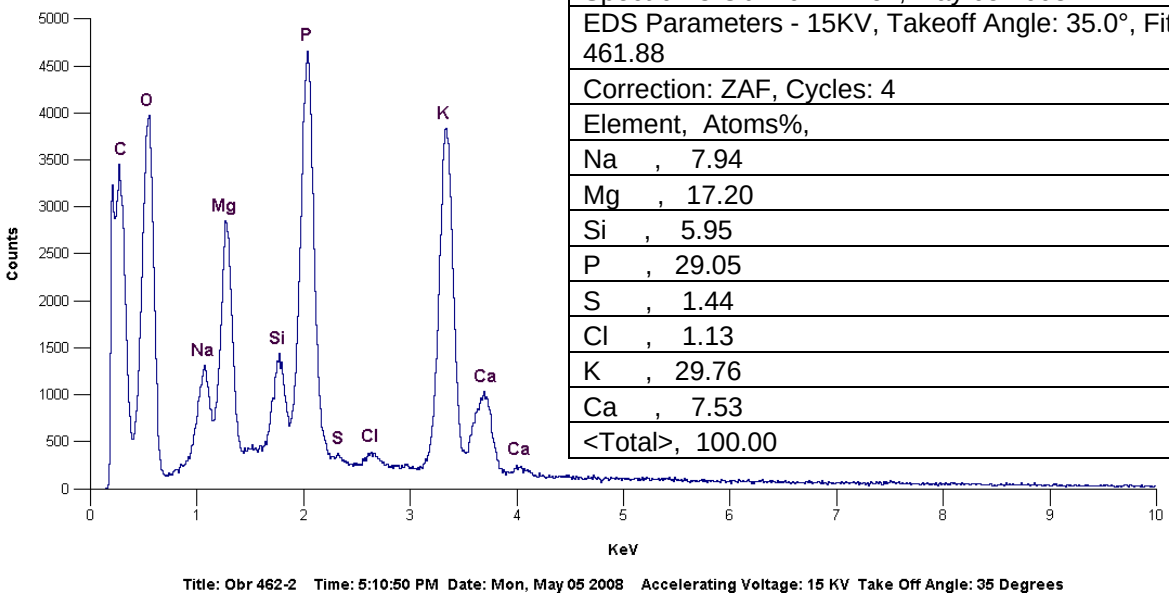


Quantitative Analysis Results - Standardless Analysis	
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 513.77	
Spectrum8 Obr 461-1 Tue, May 06 2008	
Element,	Atoms%,
Na ,	1.52
Mg ,	21.59
Si ,	4.85
P ,	28.68
K ,	35.34
Ca ,	5.71
Fe ,	1.18
Ni ,	1.12
<Total>, 100.00	

Specimen #462 Sample (2)

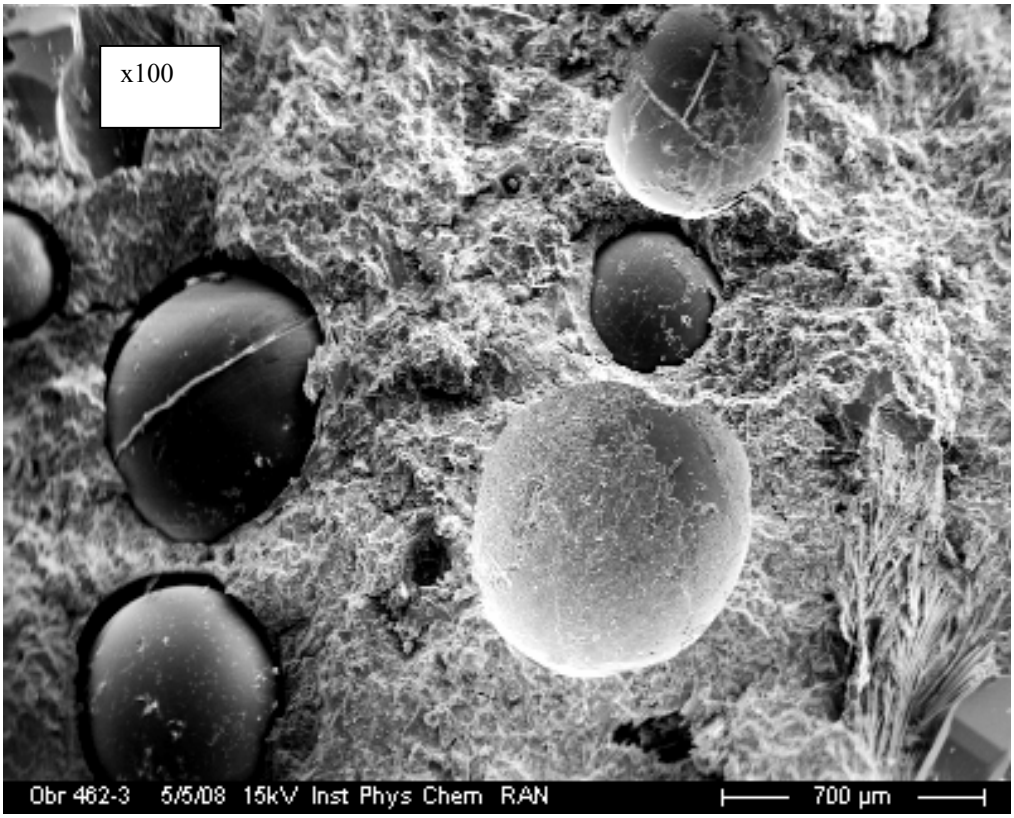


Specimen #462 Sample (2) The average data summarized from Points 1 and 2.

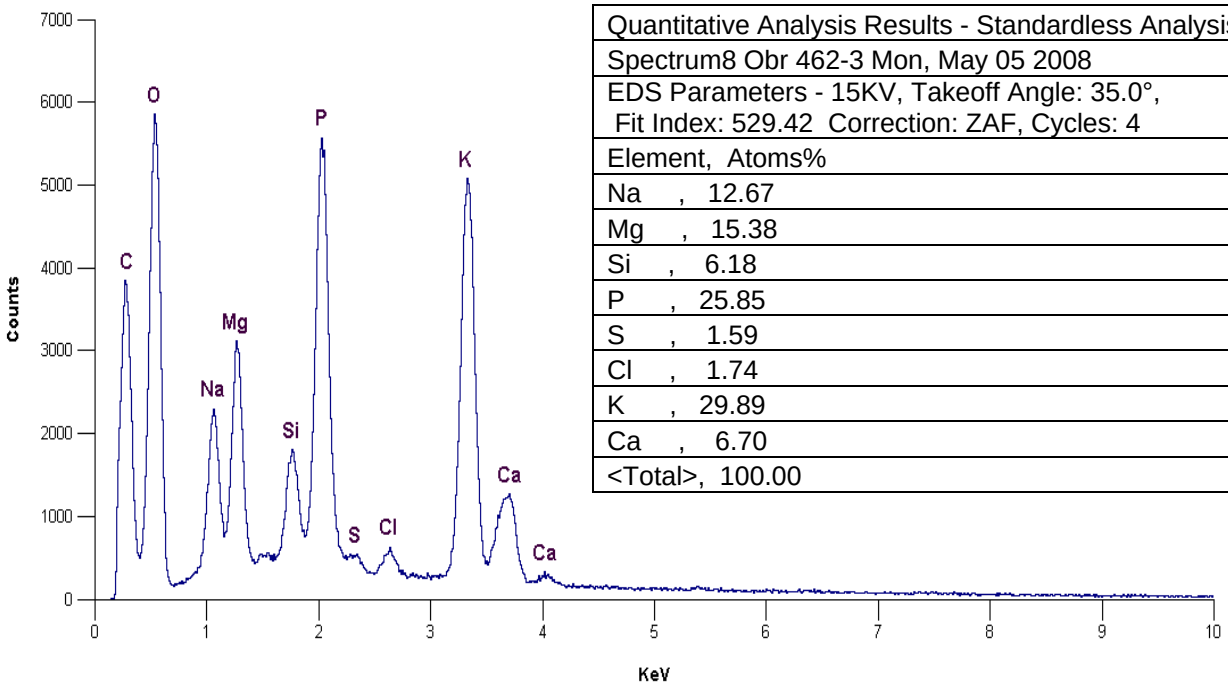


Quantitative Analysis Results - Standardless Analysis :
Spectrum8 Obr 462-2 Mon, May 05 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 461.88
Correction: ZAF, Cycles: 4
Element, Atoms%,
Na , 7.94
Mg , 17.20
Si , 5.95
P , 29.05
S , 1.44
Cl , 1.13
K , 29.76
Ca , 7.53
<Total>, 100.00

Specimen #462 Sample (3)

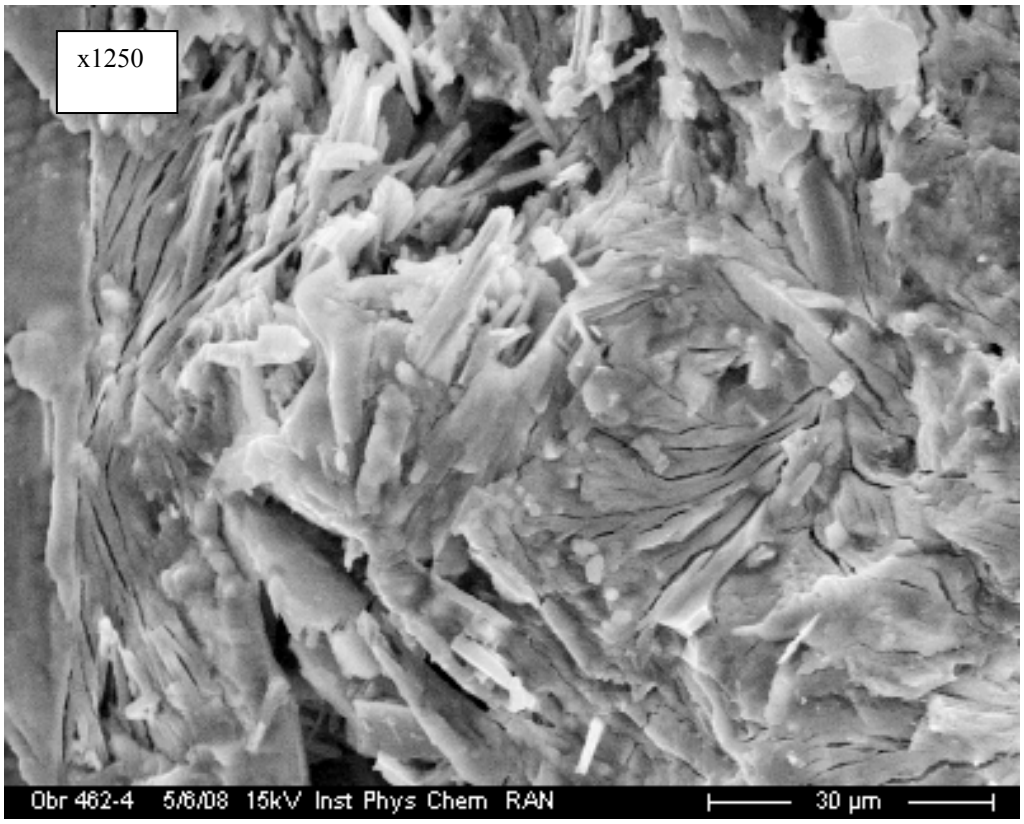


Specimen #462 Sample (3) The average data summarized from Points 1 and 2.

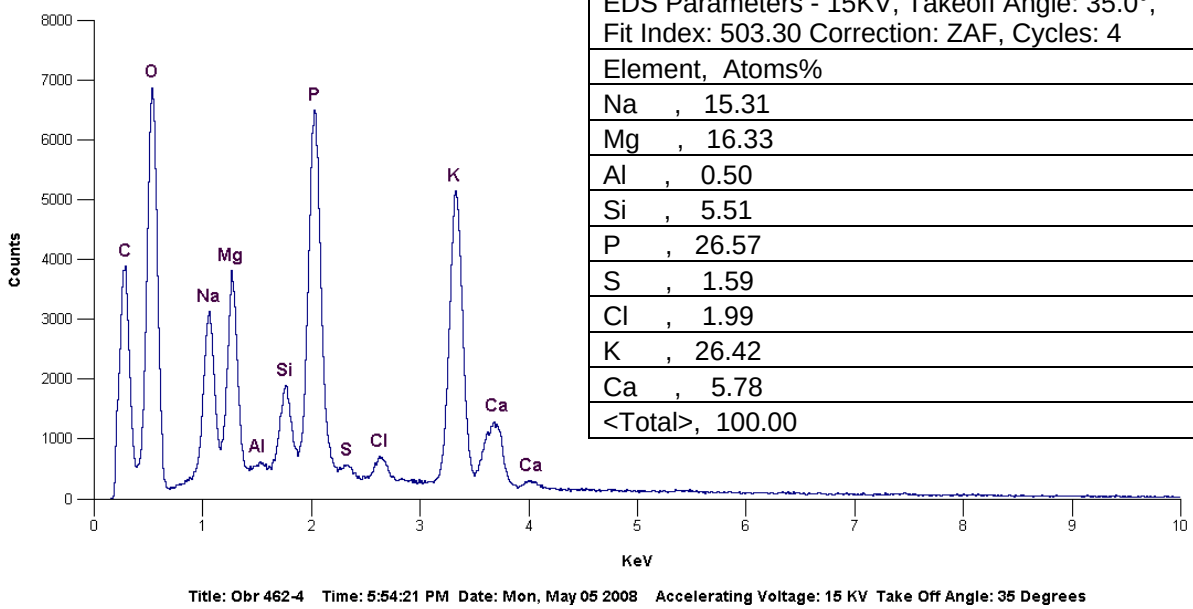


Quantitative Analysis Results - Standardless Analysis
Spectrum8 Obr 462-3 Mon, May 05 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 529.42 Correction: ZAF, Cycles: 4
Element, Atoms%
Na , 12.67
Mg , 15.38
Si , 6.18
P , 25.85
S , 1.59
Cl , 1.74
K , 29.89
Ca , 6.70
<Total>, 100.00

Specimen #462 Sample (4)
Ceramicrete Matrix incorporated the Stream 1 sludge.

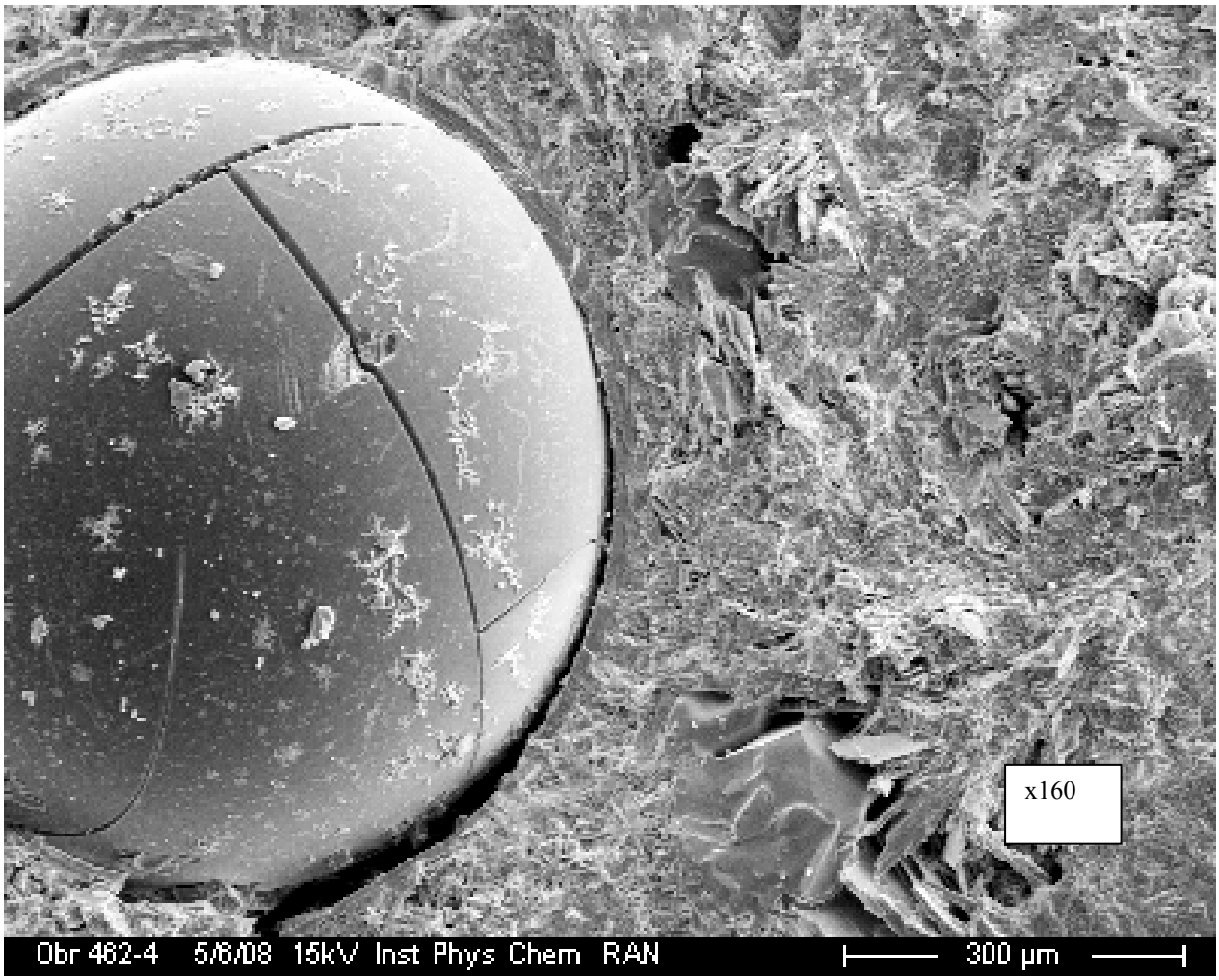


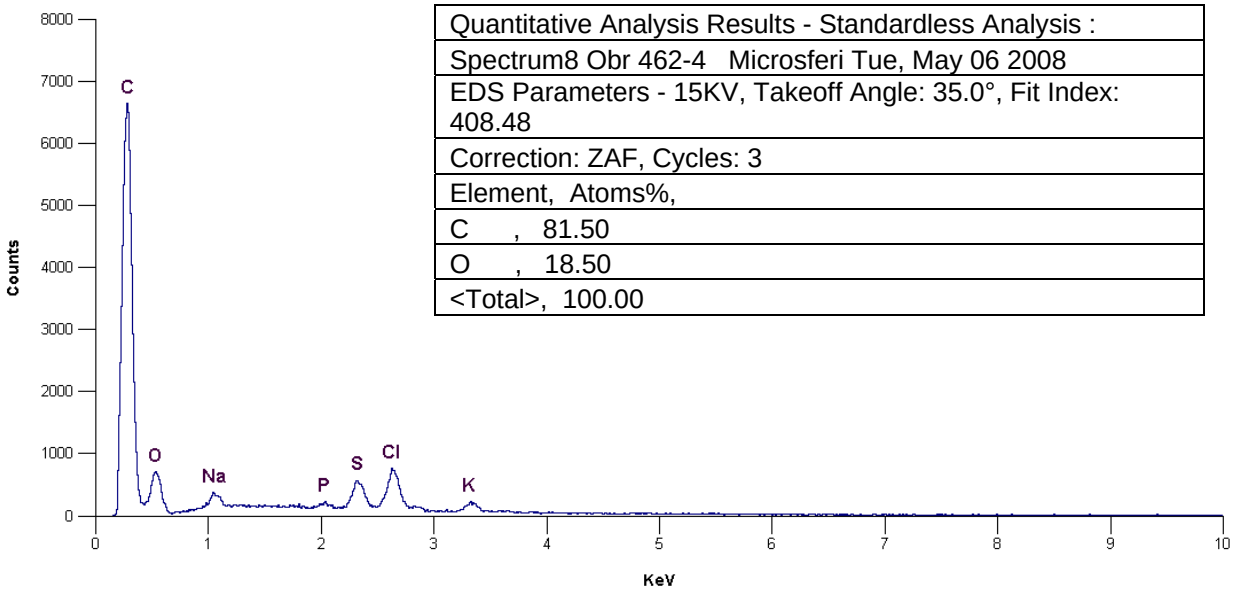
Specimen #462 Sample (4). Ceramicrete Matrix incorporated the Stream 1 sludge.
The average data summarized from Points 1 and 2.



Quantitative Analysis Results - Standardless Analysis :
Spectrum8 Obr 462-4 Mon, May 05 2008; EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 503.30 Correction: ZAF, Cycles: 4
Element, Atoms%
Na , 15.31
Mg , 16.33
Al , 0.50
Si , 5.51
P , 26.57
S , 1.59
Cl , 1.99
K , 26.42
Ca , 5.78
<Total>, 100.00

Specimen #462 Samples (4) Point 3.
The AV-17 anionite granule in the Ceramicrete Matrix incorporated the Stream 1 sludge.



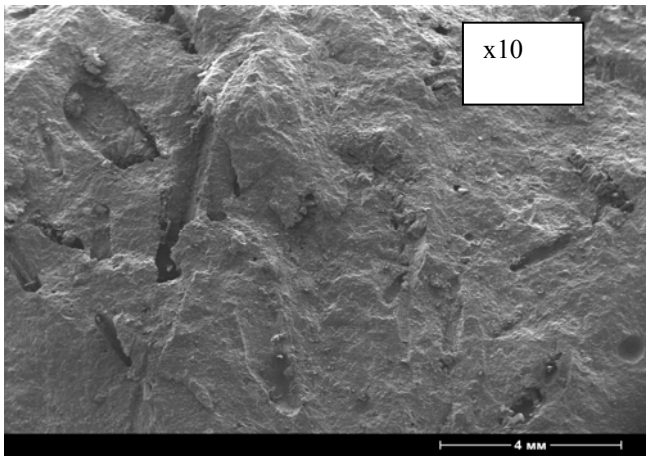


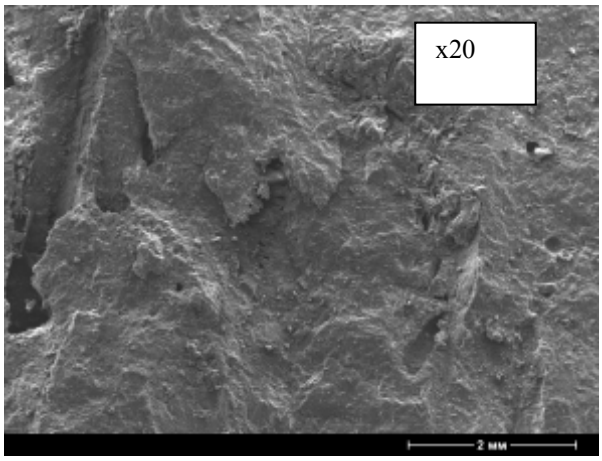
Quantitative Analysis Results - Standardless Analysis :
Spectrum8 Obr 462-4 Microsferi Tue, May 06 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 408.48
Correction: ZAF, Cycles: 3
Element, Atoms%,
C , 81.50
O , 18.50
<Total>, 100.00

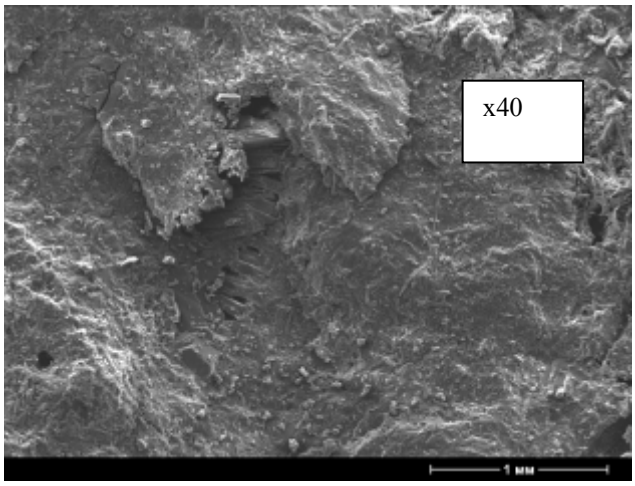
As a results of experiments had been found, that in all Samples (1) – (4) the matrix formation elements (P, K, Mg, O) are detected. Moreover, the different elements including in the matrix used have been detected: Ca and Si (from the Wollastonite – the necessary for Ceramicrete compound). The Na, Al, S, Cl also have been detected in the specimen # 462 from the waste forms: NaCl, $Al(OH)_3$, Na_2SO_4.

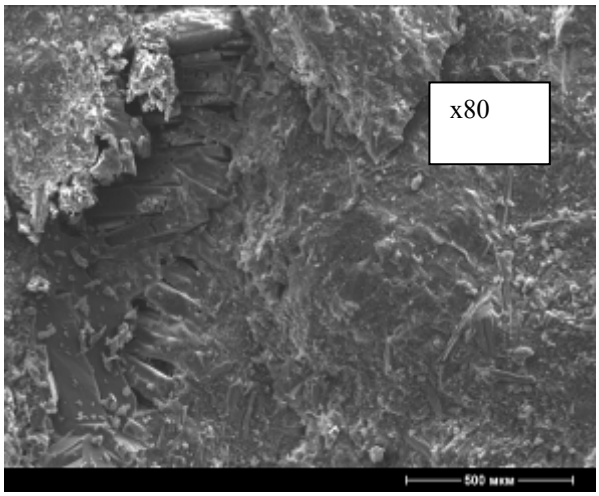
3.2. Specimen #461 (Stream 2).

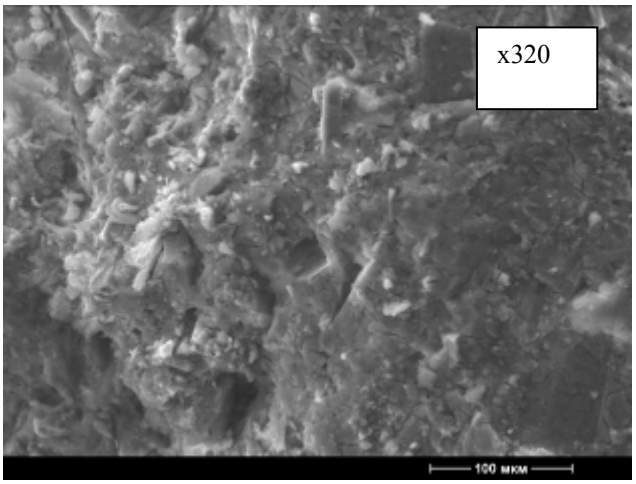
The general view of the Specimen #461 surface. At the beginning of the experiments we recorded the microphotos of Specimen #461 (Sample 1), incorporated the Stream 2 sludge with the different resolution from 10 to 1250. The obtained results are shown in the figures below:

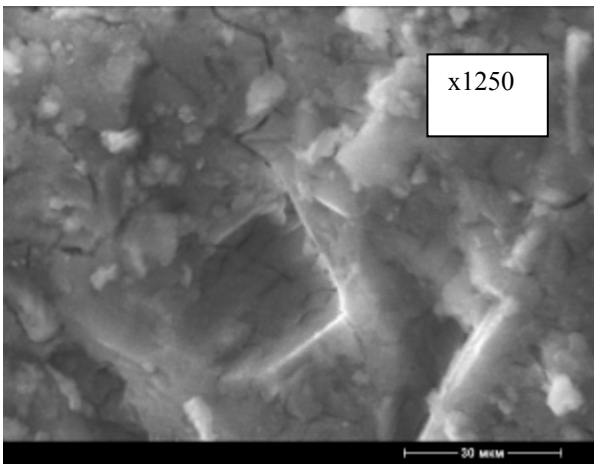








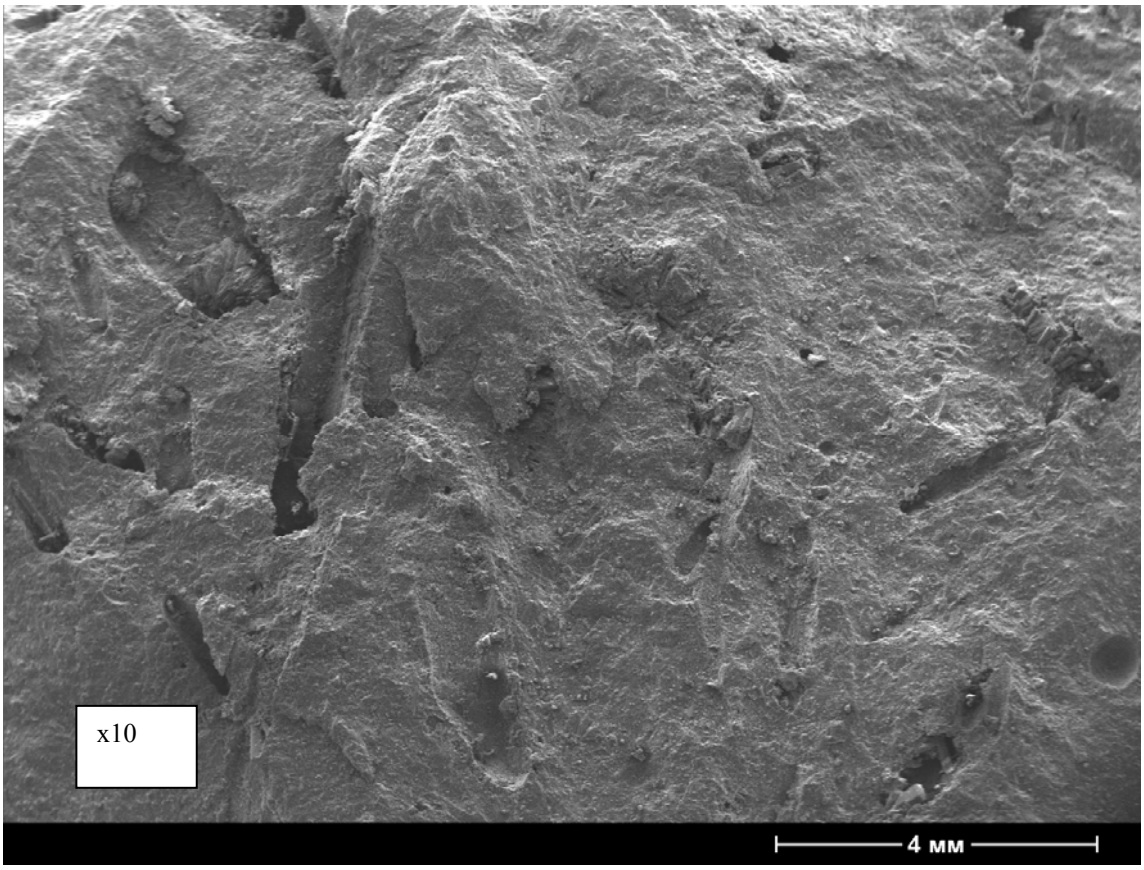




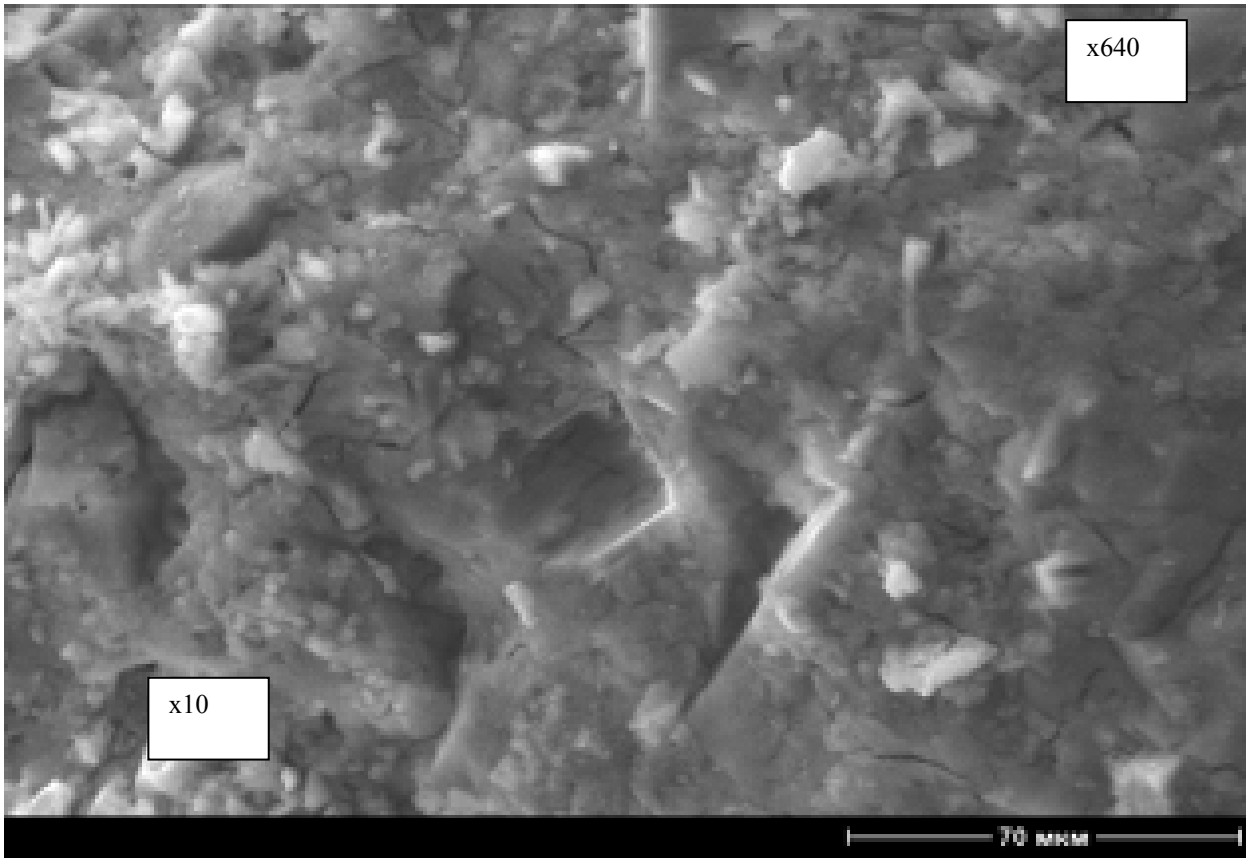
From the data obtained we concluded that the Stream 2 Ceramicrete matrix with the adjusted loading also has a high solidity in comparison with the Specimen #461. The visible cracks in the matrix material and around the anionite AV-17 granules could not obtain. We have never seen conspicuous cracks in the Specimen #461 even under the resolution of a matrix equal x1250! The granules above fixed by Ceramicrete matrix also very strongly. Consequently, we can conclude that irradiation of Ceramicrete matrix, goes from the high radioactive elements, not result in structural degradation.

The chemical content of the Specimen #461 Samples (1) – (4) shown from two Points for each samples. For determination of chemical content of the Stream 2 Ceramicrete matrix the SEM Quantitative Analysis Results (Non-standard Analysis) for all the chemical elements had been carried out. This part also contains four sections from section (1) to section (4). Every section includes one or two microphoto of a surface, and results of a chemical analysis of corresponding samples (tables with the element analysis of the matrix used from two points of sample). The number of the section corresponded with the number of samples used.

Specimen # 461 Samples (1).

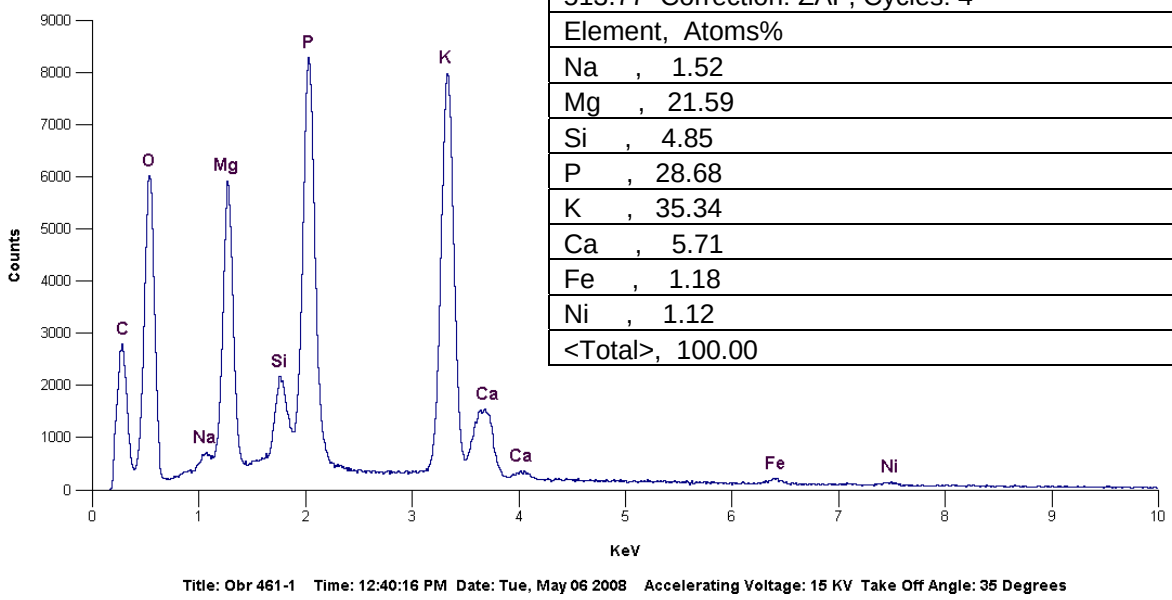


Specimen # 461 Samples (1).

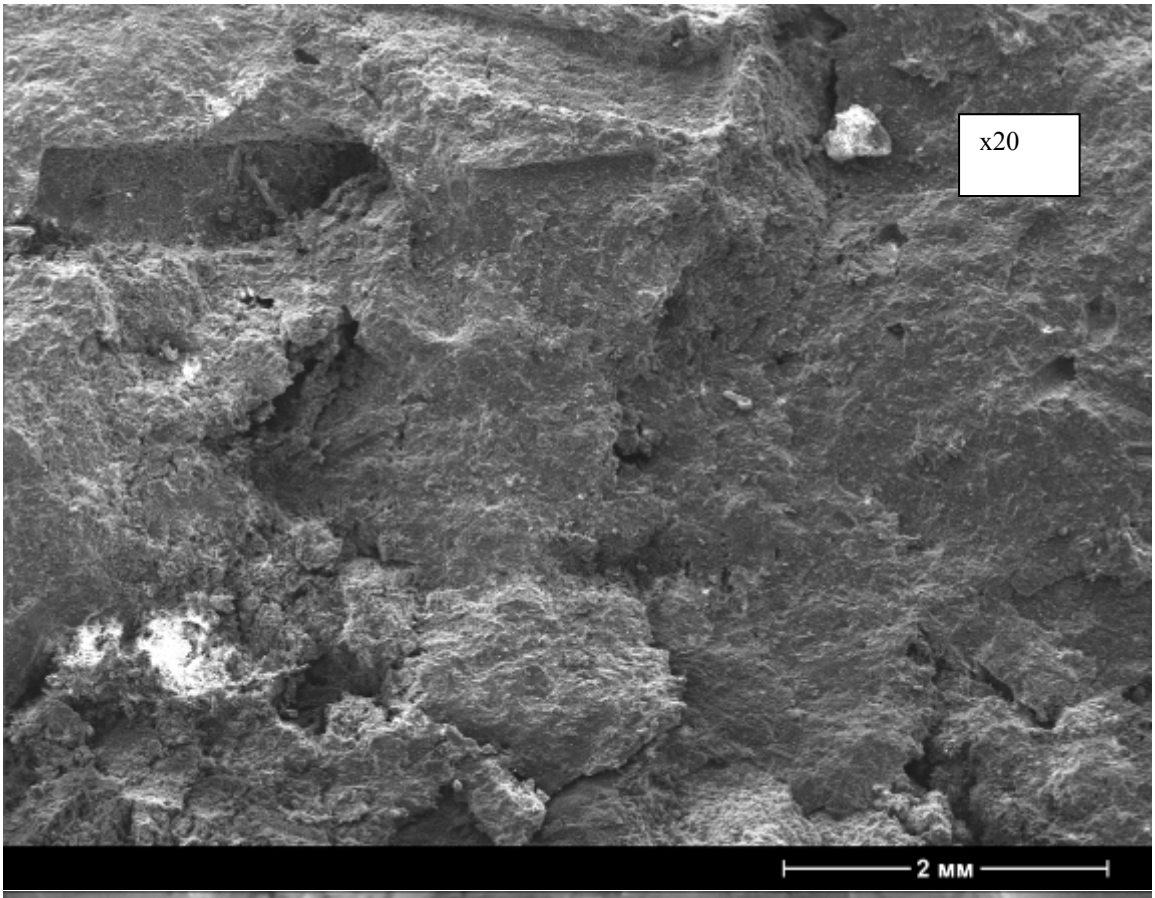


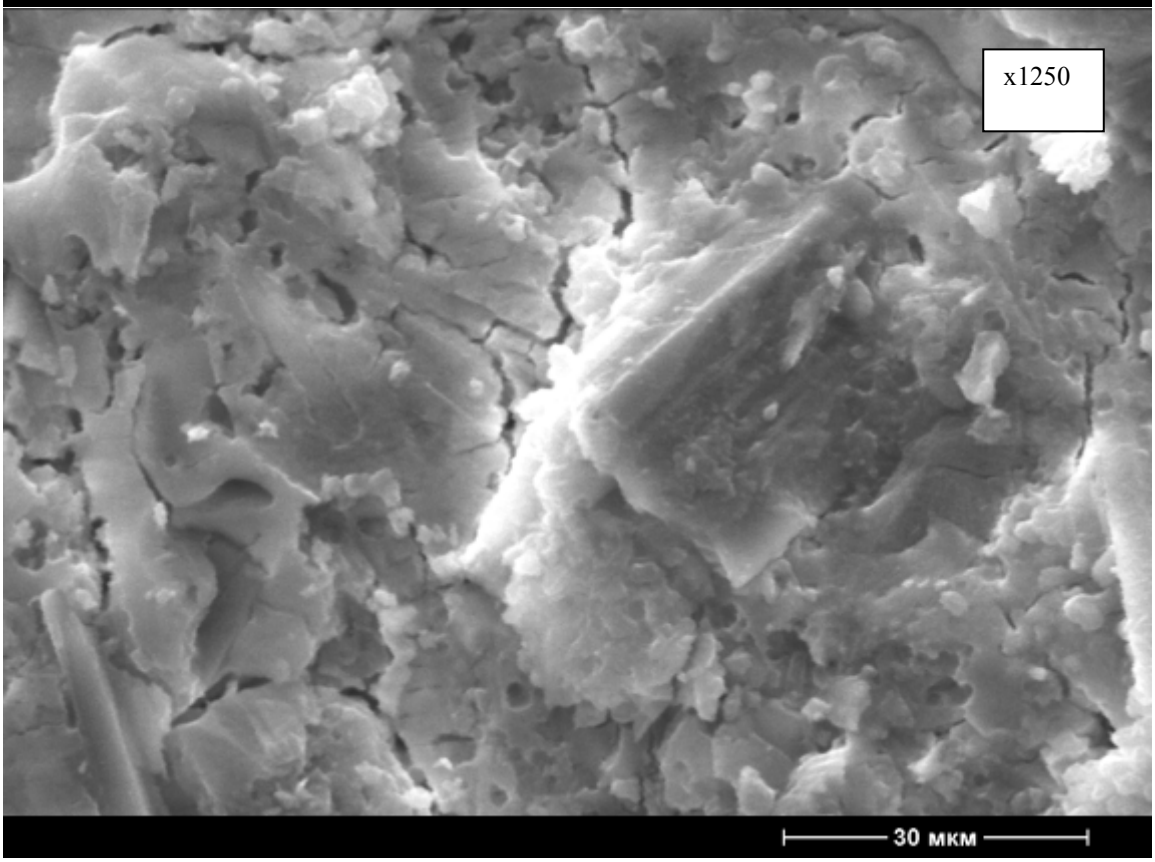
Specimen # 461 Samples (1). The average data summarized from Points 1 and 2.

Quantitative Analysis Results - Standardless Analysis :
Spectrum8 Obr 461-1 Tue, May 06 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 513.77 Correction: ZAF, Cycles: 4
Element, Atoms%
Na , 1.52
Mg , 21.59
Si , 4.85
P , 28.68
K , 35.34
Ca , 5.71
Fe , 1.18
Ni , 1.12
<Total>, 100.00

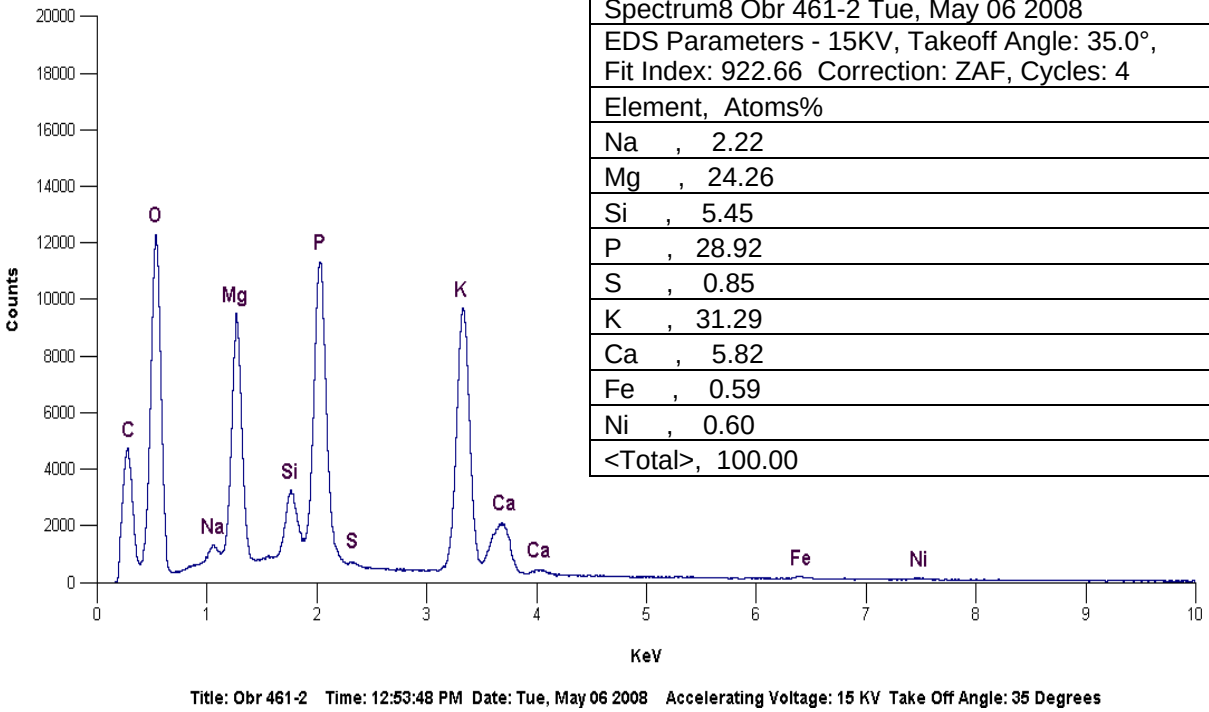


Specimen # 461 Samples (2)



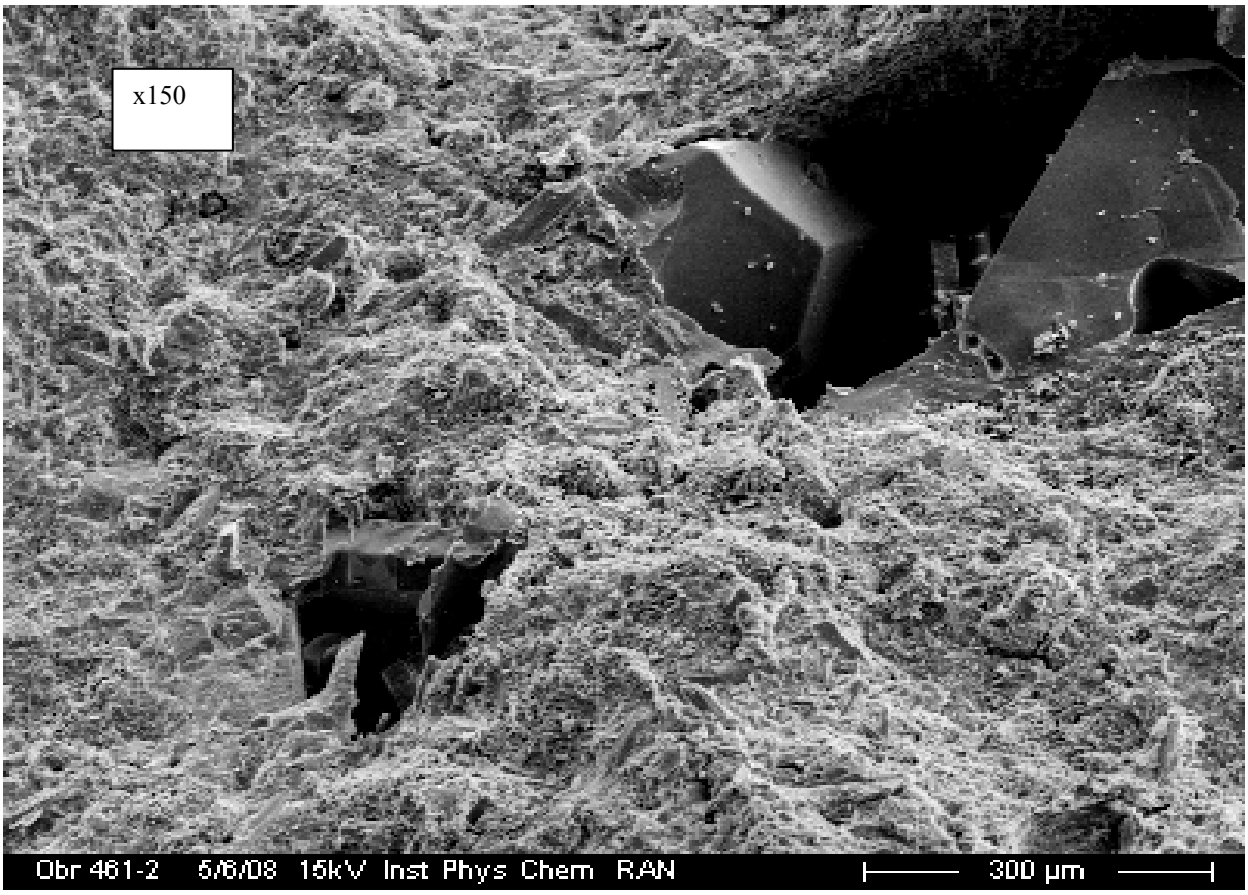


Specimen # 461 Samples (2). Matrix. The average data summarized from Points 1 and 2.

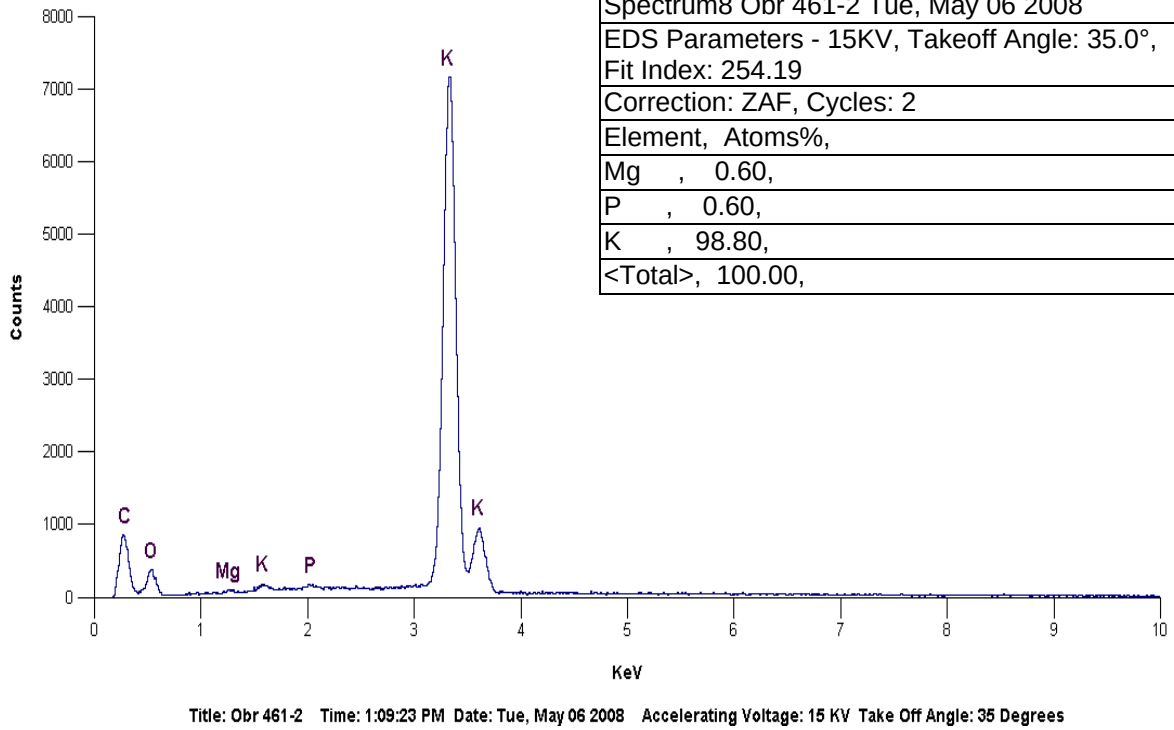


Quantitative Analysis Results - Standardless Analysis :
Spectrum8 Obr 461-2 Tue, May 06 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 922.66 Correction: ZAF, Cycles: 4
Element, Atoms%
Na , 2.22
Mg , 24.26
Si , 5.45
P , 28.92
S , 0.85
K , 31.29
Ca , 5.82
Fe , 0.59
Ni , 0.60
<Total>, 100.00

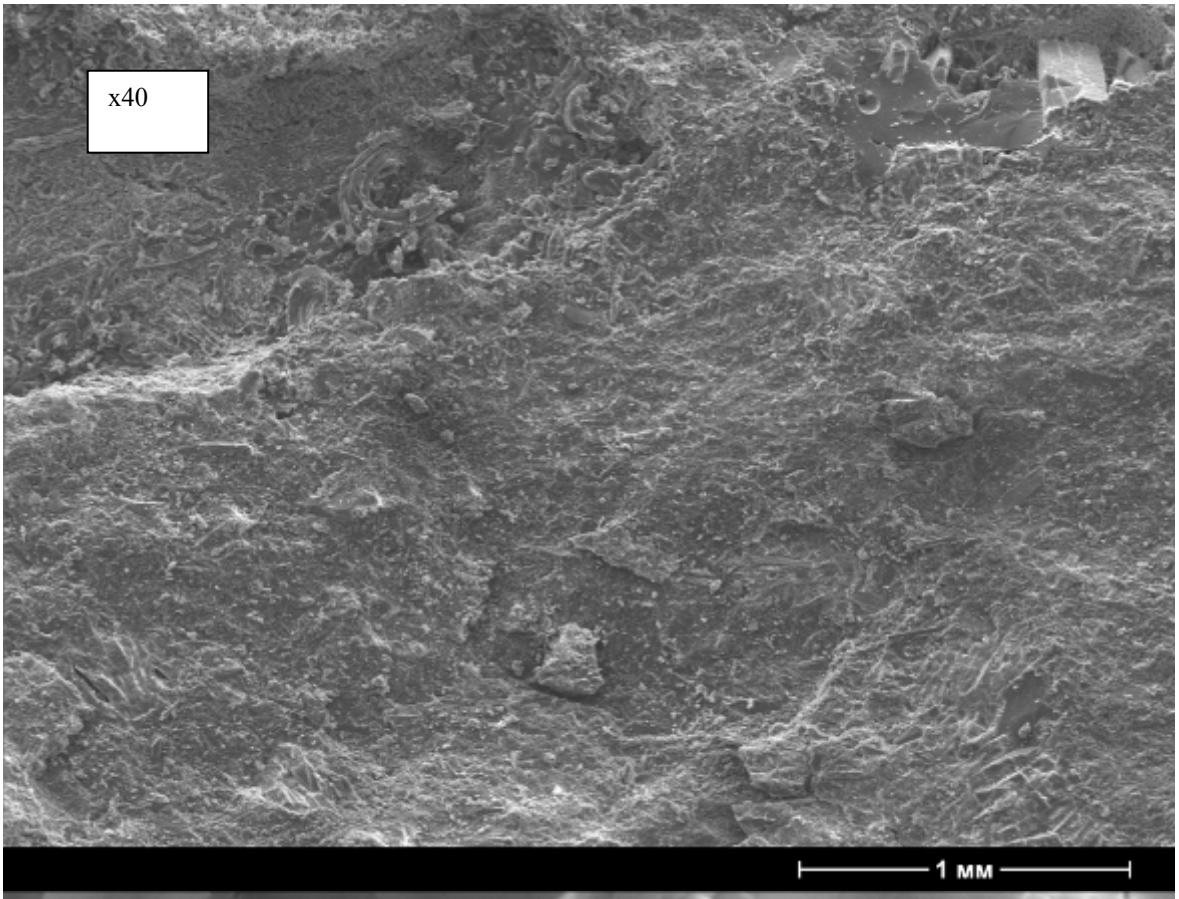
Specimen #461 Samples (2). AV-17 granule.

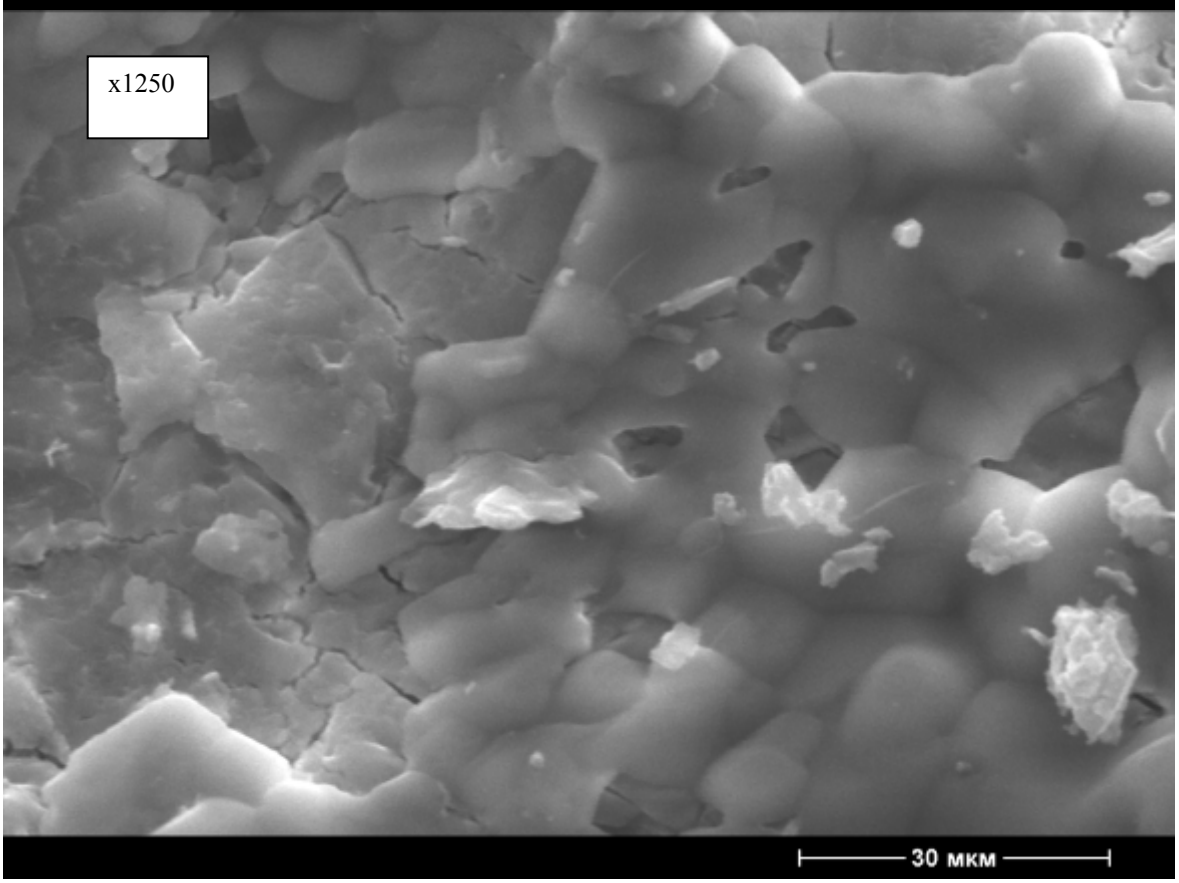


Quantitative Analysis Results - Standardless Analysis
Spectrum8 Obr 461-2 Tue, May 06 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 254.19
Correction: ZAF, Cycles: 2
Element, Atoms%,
Mg , 0.60,
P , 0.60,
K , 98.80,
<Total>, 100.00,

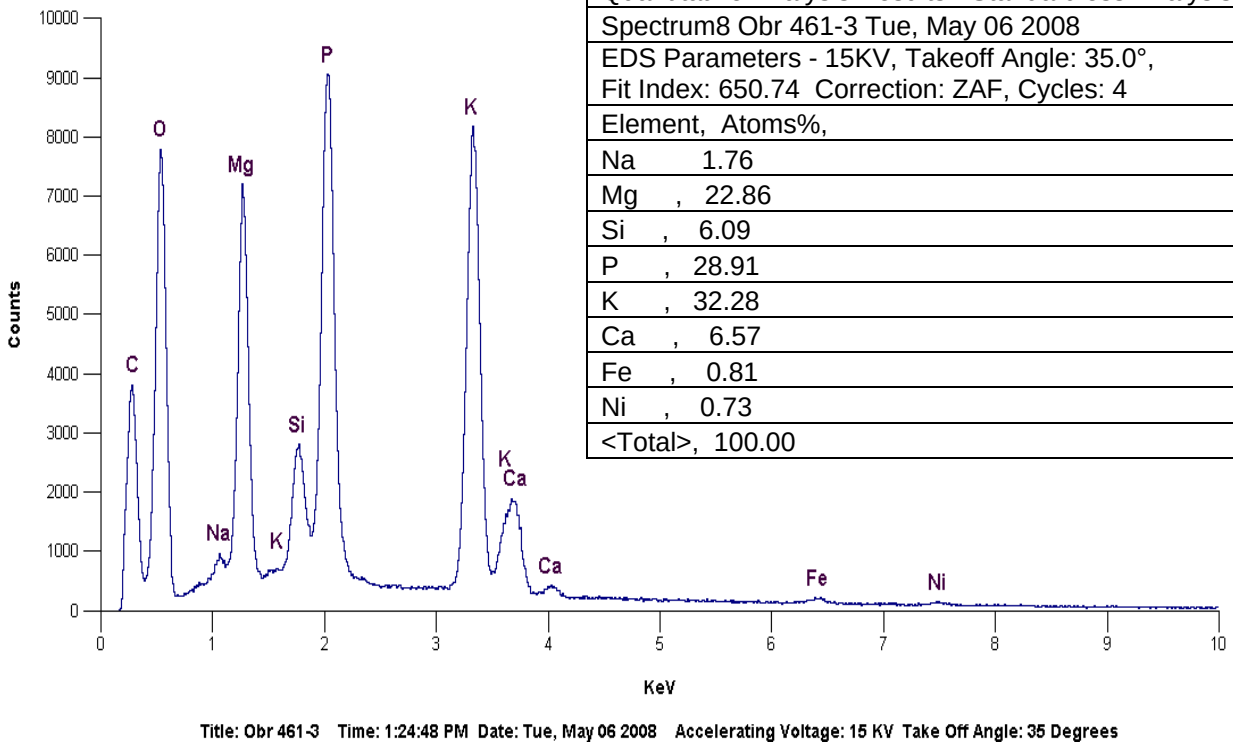


Specimen #461 Samples (3)



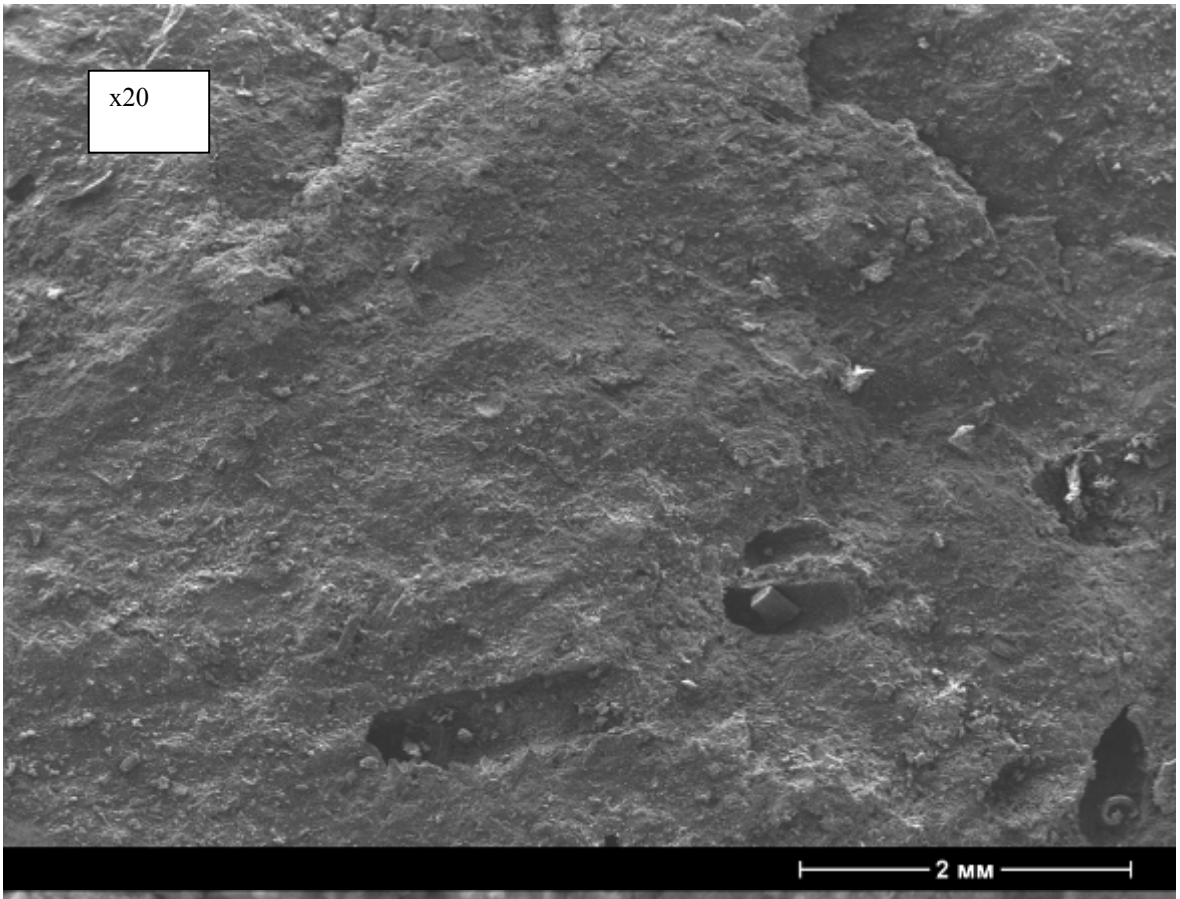


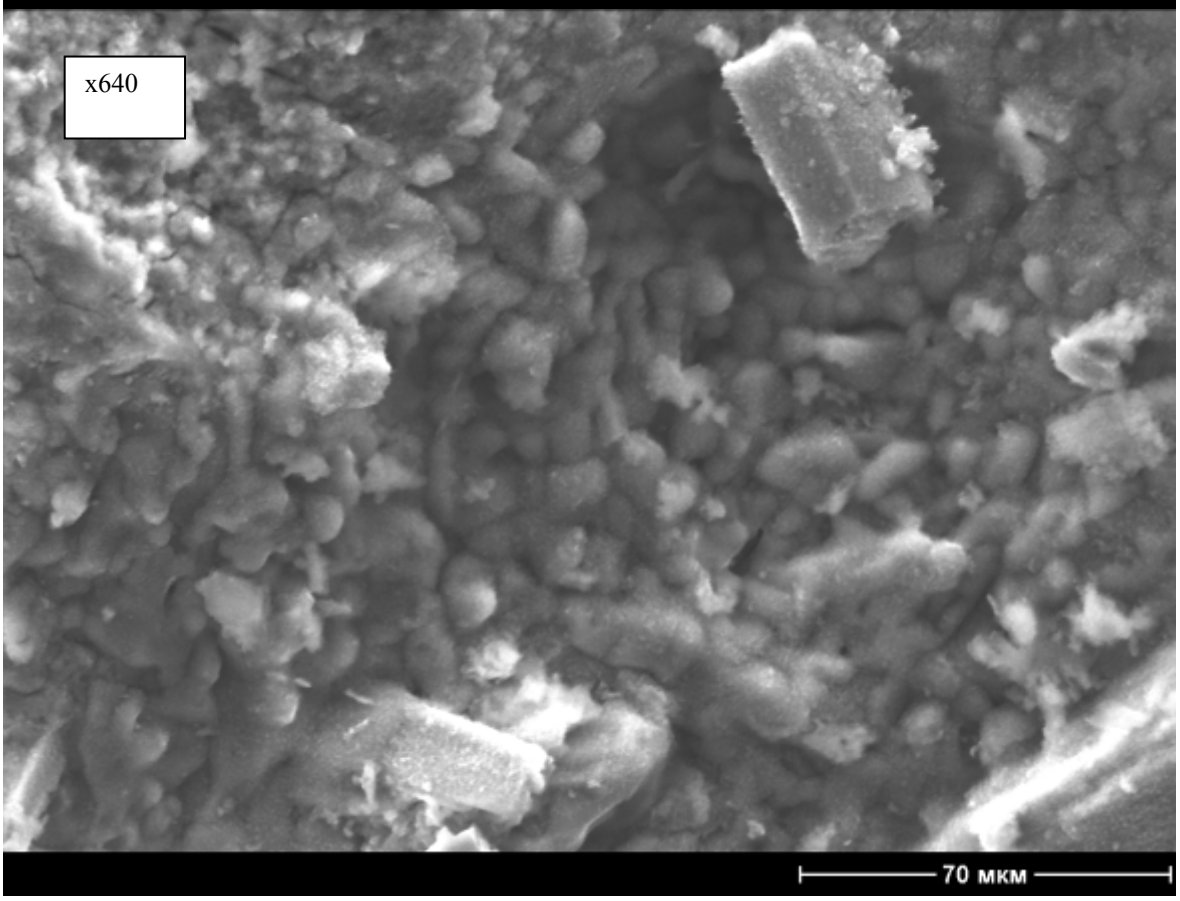
Specimen #461 Samples (3). Point 1



Quantitative Analysis Results - Standardless Analysis :
Spectrum8 Obr 461-3 Tue, May 06 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 650.74 Correction: ZAF, Cycles: 4
Element, Atoms%,
Na 1.76
Mg , 22.86
Si , 6.09
P , 28.91
K , 32.28
Ca , 6.57
Fe , 0.81
Ni , 0.73
<Total>, 100.00

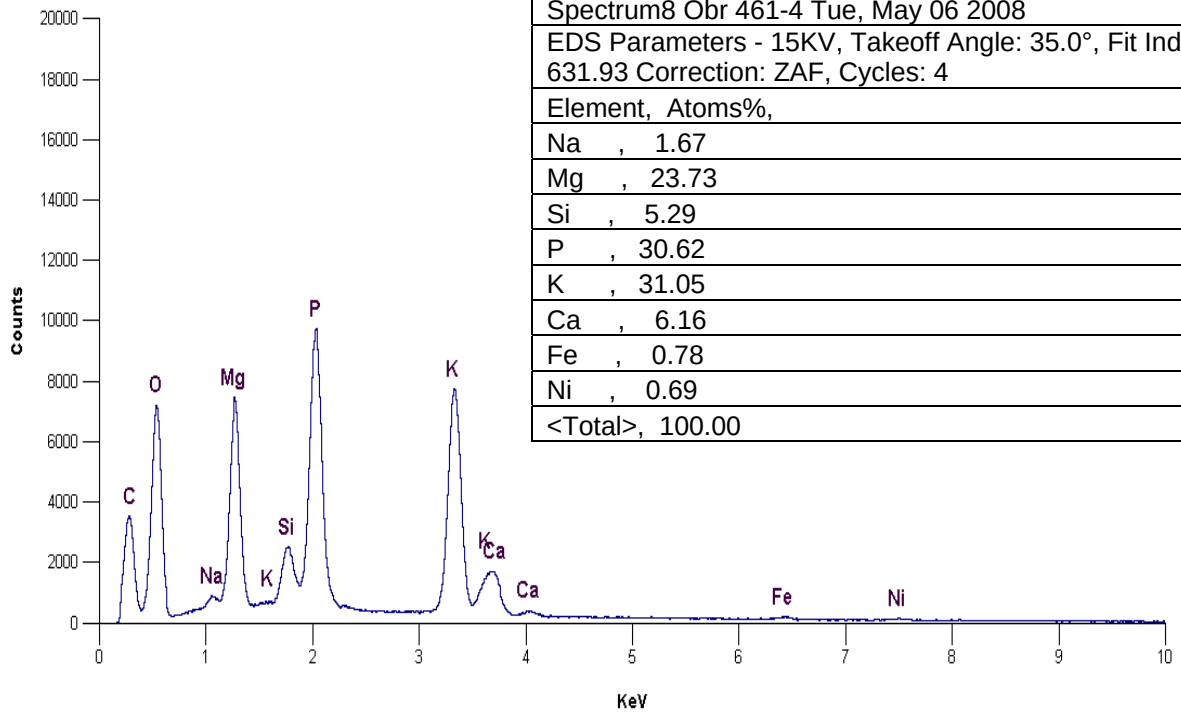
Specimen #461 Samples (4).





Specimen #461 Samples (4). The average data summarized from Points 1 and 2.

Quantitative Analysis Results - Standardless Analysis :
Spectrum8 Obr 461-4 Tue, May 06 2008
EDS Parameters - 15KV, Takeoff Angle: 35.0°, Fit Index: 631.93 Correction: ZAF, Cycles: 4
Element, Atoms%,
Na , 1.67
Mg , 23.73
Si , 5.29
P , 30.62
K , 31.05
Ca , 6.16
Fe , 0.78
Ni , 0.69
<Total>, 100.00



Title: Obr 461-4 Time: 1:37:08 PM Date: Tue, May 06 2008 Accelerating Voltage: 15 KV Take Off Angle: 35 Degrees

As a results of experiments had been found, that in all Samples (1) – (4) the matrix formation elements (P, K, Mg, O) were detected. Moreover, the different elements including in the matrix used have been detected: Ca and Si (from the Wollastonite – the necessary for Ceramicrete compound). The Na, Al, S, Cl, Fe, Ni also have been detected in the Specimen#462 from the waste forms: NaCl, $Al(OH)_3$, Na_2SO_4. $Fe(OH)_3$, nickel ferrocyanide and $Ni(NO_3)_2$.

4. X-ray Structure Analysis of the Specimens # 462 and #461 with Solidified Stream 1 and Stream 2

The main goal of this work was to identify and evaluate the solid state phases, which were obtained during solidification of the Ceramicrete samples with the Stream 1 and 2. The peculiar meaning of this work consists with application of a radioactive tracers during solidification of Ceramicrete matrix with Stream 1 and 2.

The X-ray radiographs of the Ceramicrete specimens with loading 41.4 % of Stream 1 and 31.6% of Stream 2 respectively are shown in the Fig. 3 and 4.

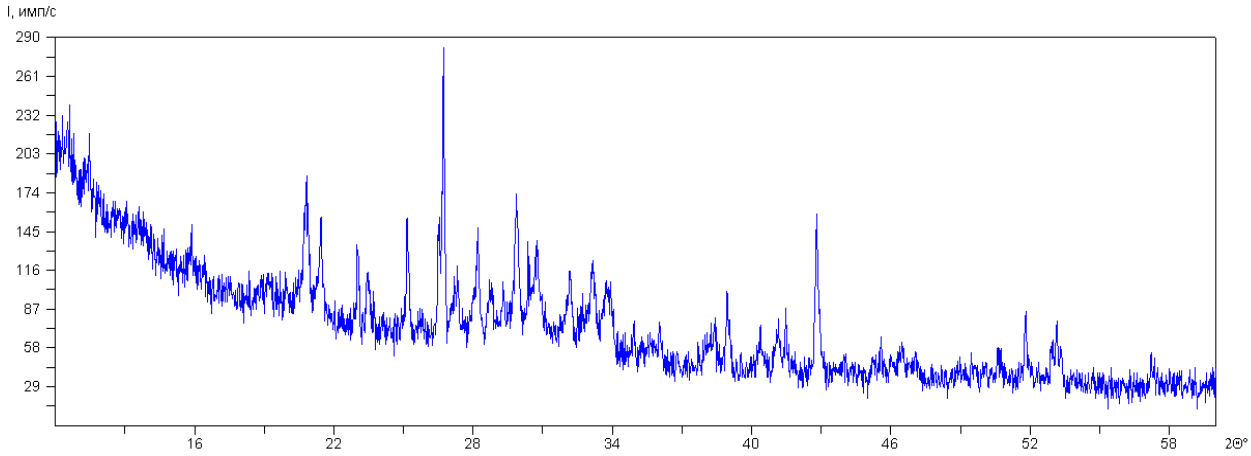


Figure 3 - X-ray photograph of Ceramicrete with immobilized Stream 1 Specimen # 462

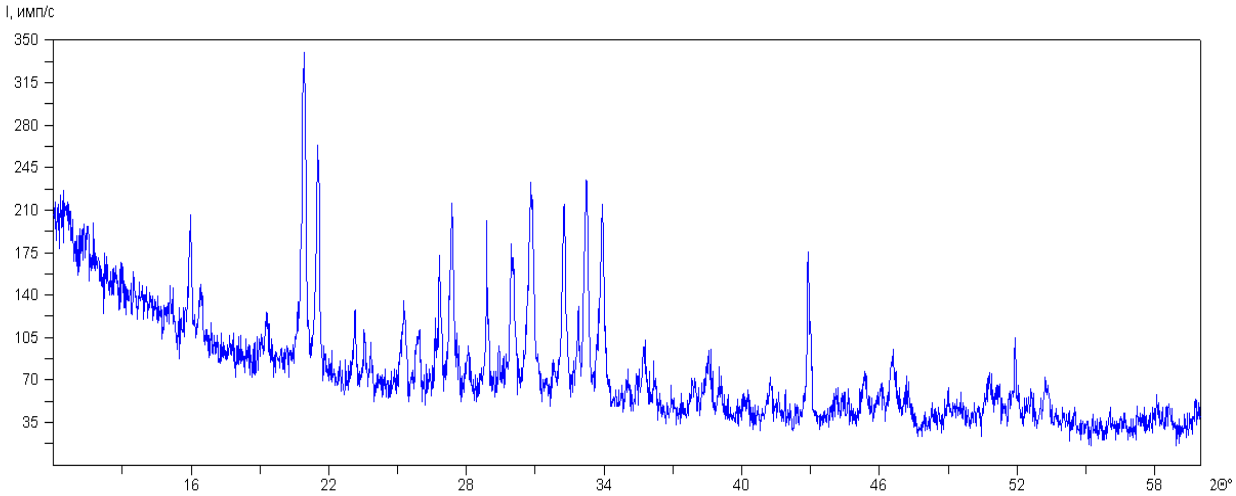


Figure 4 - X-ray photograph of Ceramicrete with immobilized Stream 2 Specimens # 461

From the X-ray data it was found that the interaction of MgO and K_2HPO_4 during solidification with Streams 1 and 2 had been leaded incomplete. In the Ceramicrete matrix we found the reflexes corresponding with the start compound MgO which have a peak at 42.79 ($2\Theta^o$). The distinctive feature of Ceramicrete with waste streams is presence of a reflex at 3.036 Å. The primary reflection of $Na_2HPO_4 \cdot 2H_2O$ is present here.

The Ceramicrete sample with immobilized Stream 2 also is characterized by the presence of reflexes $Na_2HPO_4 \cdot 2H_2O$.

The reflexes and consequently presence of $Na_2HPO_4 \cdot 2H_2O$, in the ceramicrete can be explained by reaction of $NaNO_3$ with H_3PO_4 (neutralization reagent) and KH_2PO_4 (a binder component). There can be a consecutive reaction between Na_2HPO_4 and MgO with an appearance of $MgNaPO_4$ in the system.

Conclusions:

1. It was found that the Ceramicrete Specimens incorporated the Streams 1 and 2 sludges with the adjusted loading about 41.6 and 31.6%, respectively, have a high solidity. The visible cracks in the matrix materials and around the anionite AV-17 granules included could not obtain. The granules mentioned above fixed by Ceramicrete matrix very strongly. Consequently, we can conclude that irradiation of Ceramecrete matrix, goes from the high radioactive elements, not result the structural degradation.

2. Based on the chemical analysis of specimens #462 and #461 used it was shown that these matrix included the formation elements (P, K, Mg, O), but in the different samples their correlations are different. These ratios of the content of elements included are about ±10%. This information shows a great homogeneity of matrix prepared. In the list of the elements founded, expect the matrix formation elements, we detected also Ca and Si (from the wollastonite – the necessary for Ceramicrete compound); Na, Al, S, O, Cl, Fe, Ni also have been detected in the Specimen#642 from the waste forms: NaCl, $Al(OH)_3$, Na_2SO_4. $Fe(OH)_3$, nickel ferrocyanide and $Ni(NO_3)_2$. The unintelligible results also were found from analysis of an AV-17 granules, in which we obtain the great amount of K.

3. The X-ray radiographs of the Ceramicrete specimens with loading 41.4 % of Stream 1 and 31.6% of Stream 2, respectively showed that the realization of the advance technology, created at GEOHKI, leads to formation of excellent ceramic matrix with high amount of radioactive streams up to 40% and more. Really, during the interaction with start compounds MgO and KH_2PO_4 with the present of H_3BO_3 and Wollastonite this process run with high speed under the controlled regimes. That fact that the Ceramicrete matrix with 30-40% of Streams 1 and 2 have a crystalline form, not amorphous matter, allows to permit that these matrix should be very stable, reliable for incorporation of a radionuclides.

Project Director Academician, Professor **Boris F. Myasoedov**