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OPTIMIZATION OF COMPOSITION AND PRODUCTION TECHNOLOGY OF HIGH-DENSITY CONCRETE WITH CERAMIC AGGREGATE BASED ON DEPLETED URANIUM DIOXIDE

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ABSTRACT

Russian is researching the production and testing of concretes with ceramic aggregate based on depleted uranium dioxide (UO_2). These DU concretes (DUCRETE) are to be used as structural and radiation-shielded material for casks for A-plant spent nuclear fuel transportation and storage. This paper presents the results of studies aimed at selection of ceramics and concrete composition, justification of their production technology, investigation of mechanical properties, and chemical stability.

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INTRODUCTION

The current practice of ensuring the required gamma shielding and strength of metal-concrete casks is based on concrete density. For this purpose high-density rocks (magnetite, iron glance, barium sulfate, etc.) as well as scrap, scale, broken metal chips and others are introduced into concrete as coarse aggregates. The fine aggregate sand fractions in such concretes are usually crushed limonite, quartzite tailings, iron shot etc. Use of these coarse and fine aggregates as well as special technology procedures made it possible to increase concrete density up to ~ 4 gm/cm^3 at strength of ~ 79 MPa.

It is possible to increase efficiency, specific characteristics and safety of casks due to inclusion of very dense depleted uranium dioxide (UO_2) into concrete composition

Use of depleted uranium dioxide (UO_2) in metal-concrete casks, along with ensuring of required degree of gamma shielding, can also provide slowdown of fast neutrons due to high oxygen in depleted uranium dioxide (1.3 gm/cm^3). This allows capturing neutrons by thermal neutron absorption. This property is unique for such high-density shielding materials [1].

Furthermore, the idea of using depleted uranium as a concrete component presents a possibility to recycle this material, which has been treated as a waste and has not been involved into overall economic analysis up to now. But now this work establishes solutions to a number of problems connected with its DU storage, monitoring and etc.

Application of high-density concrete as structural and radiation shielding material in casks for SNF storage invokes a number of contradictory requirements. On the one hand its components should be not expensive and commercially available, on the other hand the material should provide high strength and density (that indicates the absorption degree of ionizing radiation), tolerable thermal conduction, thermo-, radiation and corrosion resistance, service life and water resistance.

Specific characteristics of UO_2's chemical activity because of its small size of particles and thus great specific surface area prevents the use of traditional methods of UO_2 introduction into concrete composition. Therefore the DU particles must be preliminary coarsened (aggregated) and UO_2 chemical resistance must be improved through additives.

Initially, the experiments on aggregation of powdered uranium dioxide for use as concrete aggregate and the experiments on concrete production were carried out at INEEL (USA) by Paul Lessing and William Quapp under the INEEL program for the USA DOE on use of depleted uranium [2]. They have developed the UO_2 sintering technology (ceramics production) with aggregates, which generate liquid phase under heating by interacting with uranium and with each other. During the sintering process the glass phase covers the oxide grains and fills the space between the grains forming a strong bond. At the same time UO_2 chemical resistance is improved and the aggregates of the required size are produced.

The technology of UO_2 concrete and ceramics production (DUCRETE and DUAGG) was patented by INEEL in the TETON TECHNOLOGIES (TTI) company in 1996 [3]. Then TTI cooperated with STARMET company on commercialization of the technology.

UO_3 was used as a source material for the experiments performed at INEEL and STARMET; at certain stages it was transformed into uranium protoxide-oxide U_3O_8, then uranium dioxide and UO_2 ceramics was produced by low-temperature reduction with hydrogen (safe-gas).

The source materials to produce UO_2 tested by INEEL and STARMET are available in the amount of ~ 5 % of the total volume. The rest 95 % are anticipated to be obtained using the “high-temperature” technology.

The experiments on ceramics production using the “high-temperature” UO_2 are carried out for the first time.

EXPERIMENTAL WORK

Under ISTC Project # 2691 we investigated

- Properties of ceramics based on depleted uranium dioxide with mineral additives produced using “high-temperature” technology.
- Characteristics of concrete with ceramics aggregate based on depleted uranium dioxide.

OBJECTIVES OF THE STUDIES

The following samples were used in the studies:

- Samples of initial UO_2;
- Samples of source UO_2 manufactured under the mode similar to STARMET mode;
- Samples of the bond formed by mineral aggregates fabricated in accord with INEEL and VNIINM receipts;
- DUAGG samples – INEEL and VNIINM radiation shielding composition (RSC) fabricated using STARMET and VNIINM technologies.
- DUCRETE samples.

Chemical composition and some technological characteristics of the source UO_2 are described in Table 1.

Table 1 – Chemical composition of source UO_2 and its some technological characteristics

Analyzed elements and parameters	Value
U_Σ	87,77 %.by weight
Fe	<0,003 % by weight
Ni	<0,003 % by weight
Si	<0,003 % by weight
Mg	<0,003 % by weight
Al	<0,003 % by weight
Ca	<0,01 % by weight
P	<0,015 % by weight
F	<0,0006 %. by weight
F + Cl	<0,0012 % by weight
Water	0,1 % by weight.
Grain size	>0,4 μm
Total specific surface	3,4 m^2/gm
Bulk density (according to GOST 19440-96)	2,12 gm/cm^3
Bulk density after shaking down (according to GOST 25279-93)	2,70 gm/cm^3

The source UO_2 is a solid solution of oxygen ions implantation into the fluoride matrix of UO_2. The “a” parameter of the elementary cell of the source UO_2 is 5.447 Å, the oxygen factor is 2.16±0.08.

The bond production is based on Russian materials that have certificate of quality with identified mineral and chemical composition. The materials are delivered in the form of fine-dispersed powder with grain size of 150 μm max. The components of admixture for powdered UO_2 are not subjected to additional processing.

Water solution of polyvinyl alcohol of 11/2 grade GOST 10779-88 with density of 1.01 gm/cm^3 is prepared for using as a technological bond for pressing.

EXPERIMENTAL RESULTS

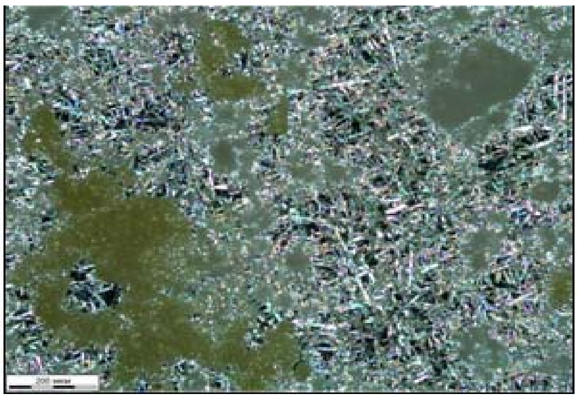
The following experiments were carried out:

1. the structure was studied of the glass-crystal matrix produced from Russian components according to the INEEL and VNIINM receipts,
2. a technology was developed to produce ceramics based on UO_2,
3. a material science testing of the UO_2 ceramics samples was carried out,
4. data were obtained related to mechanical characteristics of the UO_2 ceramic samples,
5. data were obtained on chemical resistance of DUAGG-INEEL, RSC-VNIINM and UO_2 samples,
6. parameters were identified to characterize RSC-VNIINM ceramics as the concrete aggregate,

7. receipt and production technology of concrete with UO_2 aggregate was developed.

The following experimental results were obtained.

1. According to the obtained data the INEEL and VNIINM binder samples are similar in structure. The INEEL bond consists of glass, titanium oxide, zirconium titanate, and zirconium oxide. The VNIINM bond includes also zirconium silicate. In both cases titanium oxide has two morphological varieties (see fig.1). It is easy to identify glass (black) and phase of rutile, titanium oxide (elongated grains with high interference color).



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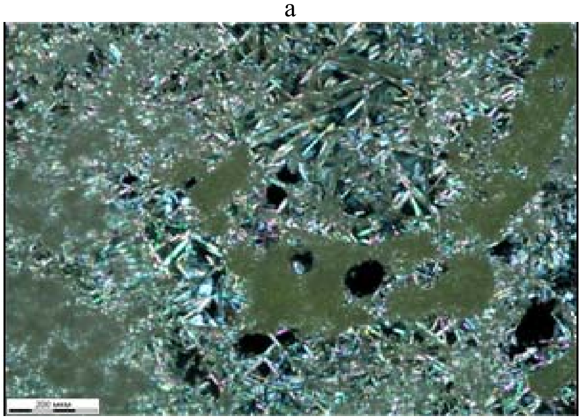

b

Fig. 1 Pictures of the INEEL (a) and VNIINM (b) bond samples

2. The samples of ceramics based on UO_2 were subjected to the technological testing. The obtained results prove the following:

- Preliminary mix of components of the glass forming adding actually does not affect the density of the finished samples,
- Increase of compacting pressure from 50 to 350 MPa results in increase of density after sintering, the further increase of compacting pressure causes density reduction. Optimum value of compacting pressure is in the range of 50 to 250 MPa,
- Reduction of density is caused by increasing heat rate during the sintering process. In some cases the density at sintering temperature of 1300 ^{0}C was less than at 1250 ^{0}C. This is caused by gaseous products generation (CO_2, H_2O) as a result of decomposition of the adding components and uranium dioxide reduction to stoichiometric composition during sintering, and due to capture of rare gas (Ar) in closed pores,
- Sintering provides DUAGG aggregate compacting due to capillary forces under wetting of uranium dioxide grains by amorphous glassy melt generating from the binder components,
- The DUAGG samples - INEEL, manufactured from Russian "high-temperature" UO_2 and adding are similar on characteristics (microstructure, phase composition, structural distribution of phases) to DUAGG – INEEL fabricated in the USA. At the same time such characteristics as density of "raw" and sintered pellets are different. The density of DUAGG-INEEL fabricated in the USA and VNIINM differs in approximately 10%, while porosity of the samples is the same. The difference is caused by variety of the density measurement methods,
- Density of DUAGG-INEEL ceramics sintered at 1250^{o}C manufactured in the modes similar to STARMET is 7.85-7.90 gm/cm^3.

3. UO_2 ceramics material science testing was carried out. According to the obtained results the ceramic samples have porous structure. The pore size varies much, but generally we can identify two size groups: 100-400 μm and 5-20 μm. Agglomerations of uranium dioxide grains form isometric isolations of 50-200 μm surrounded by glass. Identity of phases in the sintered UO_2 and ceramics based on UO_2 with admixtures proves that glass-formation processes under synthesis and formation of the glass protective phase in ceramics don't affect the structure of UO_2 – the basic component of ceramics. As a result of simultaneous processes of glass-formation and solid-phase synthesis for ceramics production the size of a source UO_2 cell is not significantly changed. Thus, the ratio U(4+)/U(6+), i.e. UO_2 oxygen coefficient of the synthesized ceramics is close to oxygen coefficient of the source UO_2. According to the results of measurements the oxygen factor of ceramics DUAGG – INEEL is – 2.06 ± 0.08, and VNIINM ceramics is 1.96 ± 0.08. Such values of the oxygen factor prove that during the ceramics synthesis the source UO_2 is reduced to composition, which is very close to stoichiometric UO_2.

4. Cylindrical samples of 10-mm diameter and 10-15mm height were used to test strength characteristics. The results of the RSC samples mechanical testing are tabled below.

Table 2 – Mechanical testing of the ceramic samples

#	Sample number	Code of the pilot lot	$\sigma_{0,2\ pressure.}$, MPa	$\sigma_{temporary\ pressure}$, MPa
1	1	DUAGG – INEEL «P9-1»	220	230
	2		160	170
2	1	DUAGG – INEEL «P9-2»	-	120
	2		120	140
3	1	DUAGG RSC-VNIINM «P10»	140	150
	2		160	180
4	1	DUAGG RSC–VNIINM «P11»	117	120
	2		210	220
	3		280	280

These data prove that VNIINM ceramics is competitive with DUAGG – INEEL in mechanical properties.

5. The data were obtained on chemical resistance of DUAGG-INEEL, VNIINM and UO_2 sintered at 1300 ^{0}C for cooling conditions within 890…2500 hours at 70 ^{0}C and 150 ^{0}C in distilled water (pH~6) and water extract from cement solution (pH ~13,5).

Weighing of the samples after drying over P_2O_5 shows mass increase. Mass increase of the samples tested in distilled water is caused by filling of deep pores with water, which is not entirely removed during the drying. The greater values of mass increase for the samples tested in cement extract solution are also a result of salt precipitation onto the sample surface.

These results prove that uranium is dissolved in distilled water only in the sample from pure uranium dioxide (without admixtures), when other ceramic samples are tested the uranium is not detected in water. In DUAGG-INEEL and VNIINM testing Al, B and Si were detected in water, probably due to leaching from glassy phases. Analyses of cement leachate solution show that all samples subjected to the testing are resistant to uranium leaching. In DUAGG- INEEL and VNIINM samples there was increased boron leaching (in comparison with distilled water) that can be caused by high alkalinity of the solution.

6. The following parameters characterizing VNIINM ceramics as a concrete aggregate are identified:

- Average density 7.84 gm/cm^3,
- Compression strength 265MPa ,
- Uniformity of grain strength 5.1%,
- Water absorption 0.33%.

Based this information, material science, technological and corrosion testing aimed at studying characteristics of uranium dioxide ceramics as a concrete component in order to fabricate experimental samples of DUCRETE the radiation shielded composition of VNIINM (rf-2) is recommended for future use. The VNIINM ceramics (rf-2) is very competitive to DUAGG-INEEL based on physical parameters, and some times it even exceeds the INEEL parameters. In addition, VNIINM ceramic fabrication requires minimal component composition that reduces its cost.

The following production mode is required to obtain the best characteristics of the radiation-shielded composition (RSC)-VNIINM (rf-2):

- Mixing of RSC components;
- Pressing of RSC half-finished product with a force of 150 MPa;
- Crushing of RSC half-finished product to obtain the required fraction composition;
- Drying in the atmosphere of Ar + 7% H_2 for 1 hour at 700 ^{0}C, heating with a rate of 6 ^{0}C/min, cooling with a rate of 26 ^{0}C/min;
- Sintering of crushed RSC for 1 hour at 1250 ^{0}C, heating with a rate of 7.5^{0}C/min, cooling with a rate of 17 ^{0}C/min.

This technological mode offers advantages in comparison with STARMET production technology, as it does not include the stage of sintered briquette crushing. Excluding of this procedure allows reducing of energy consumption and avoiding of dust containing UO_2.

Figure 2 and 3 present production technologies of ceramics using the STARMET and VNIINM modes.

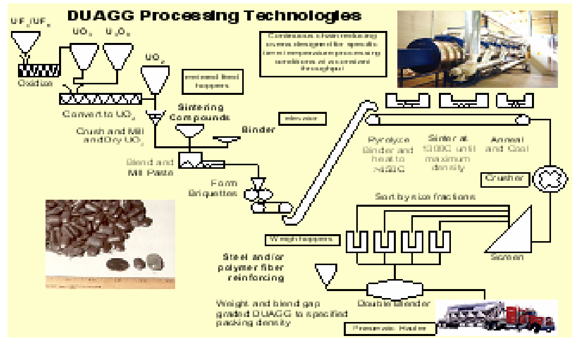

Fig. 2 Ceramics production using the STARMET technology

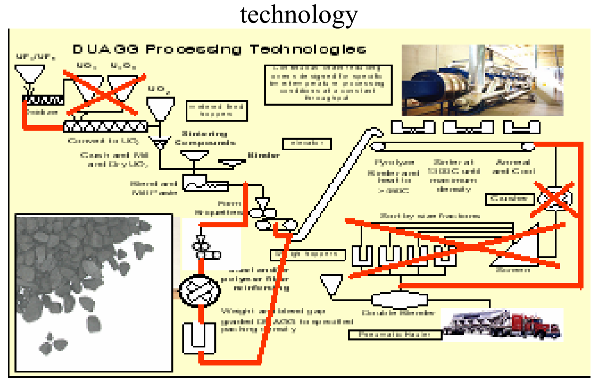

Fig. 3 Ceramics production using the VNIINM technology

7. Development of UO_2 concrete receipt and production technology is based on the following parameters:

- Average density (volume mass) – 6 gm/cm^3 min;
- Workability of concrete mixture should meet standard requirements;
- Concrete mixture should not segregate under technological procedures (fabrication and compression).

The obtained experience on concrete aggregate production from UO_2 proves that production of ceramic fine fraction (less than 1mm) is the most expensive and labor intensive. So several concrete compositions were subjected to the testing. The concrete receipts included two types of the aggregate finest fraction:

- UO_2 sand;
- Steel crushed shot #05;

Several experiments were carried out using concrete without fine fraction.

After the series of experiments we recommend the following compositions for further investigations.

Table 3 – Concrete composition

	Composition 1		Composition 3	
	Mass, kg (per m^2)	Volume, l	Mass, kg (per m^2)	Volume, l
Portland cement M500-D0	450	143	450	175
Water	170	170	161	193
Plasticizer	5	2	5	2
UO_2 aggregate:				
Fraction 5…10 mm	2500	275	2500	275
1,25…5 mm	1230	135	1230	104
0,63-1,25 mm	1240	137	1240	251
0,15…0,63 mm	1240	137		
Crushed steel shot #5			1050	144
Calculated volume mass	~ 6800	999,0	~6640	1001,0
Calculated water/cement ratio	0,37		0,36	
Actual parameters of concrete mixture quality				
Workability on cone slump, cm	5 cm		4.8	
Average density (volume mass), gm/cm^3	6.58		6.42	
Characteristics of concrete mixture	Mixture is uniform, without segregation		Mixture uniform without segregation	

The procedure of DUCRETE production is the following:

- Mixing the RSC-VNIINM fractions (composition # 3 includes shot) with Portland cement;
- Plasticizer adding and mixing;
- Water adding and mixing.

The DUCRETE mixtures prepared in the concrete mixing machine were placed into the moulds (concrete forms) of 40x40x160mm (3 units per each receipt) and 70x70x70mm (3 units per each receipt), and then were pressed under vibration.

After 48 hours the moulds were dismantled. DUCRETE samples were tested after their cure in wet sawdust for 28 days.

Compressive strength of the concrete was tested using cubic samples of 70x70x70mm pursuant to GOST 10180-90. The results of the testing are shown in the Table 4.

Table 4 – Concrete strength

# of the sample	RECEIPT 1 Strength, MPa	# of the samples	RECEIPT 3 Strength, MPa
1-1	67.0	3-1	65.9
1-2	71.2	3-2	67.8
1-3	66.8	3-3	64.9
mean	69.1	mean	66.9

Note: Pursuant to GOST 10180-90 if three samples are tested, then the average concrete strength is determined using the two greatest values.

SUMMARY

1. Experiments prove the possibility to develop concrete aggregate based on depleted uranium dioxide produced under "high-temperature" technology. The produced depleted uranium dioxide provides the required density, strength and chemical resistance, and its production technology is rather simple.
2. We have developed the receipt and production technology for concrete with ceramic aggregate based on depleted uranium dioxide. The produced concrete samples provide density of more than 6gm/cm^3 and their compressive strength is more than 60 kg/cm^2

The work continues.

NOMENCLATURE

Depleted **U**ranium **Con**c**rete (DUCRETE)**
Depleted **U**ranium **Agg**regate **(DUAGG)**

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