

ZEOLITE AS A COMPONENT OF BINDING MATERIALS FOR LIQUID RADIOACTIVE WASTE CONDITIONING

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The use of Portland cement in building structures for liquid radioactive waste immobilization does not prevent migration of the radioactivity through the walls of reinforced concrete constructions. Thus, the creation of new binding materials and development of up-to-date methods require constant effort. The sorption capacity of slag cement can be increased by adding a certain amount of finely dispersed sorbents. In alkaline medium, these sorbents (clay and zeolite) would also acquire binding properties that depend on the type of the sorbent. It was experimentally found that slag geopolymer concrete containing zeolite of size fraction of $<140 \mu\text{m}$ is characterized by the highest compressive strength limit (22 MPa). To cementation of LRW, slag and zeolite is added to make a compound. In the experiments, the concentration of salts in the LRW composition simulator was about 800 g/dm^3 . High salt concentration dramatically reduces the strength of the compounds, first of all, due to the presence of a significant number of sodium tetraborate crystals (sodium nitrate) that have the size over 3.5 mm. The crystal size can be reduced by introduction of $55\text{--}60 \text{ }^\circ\text{C}$ disperse zeolite into the simulator. When cooling, much smaller crystals are formed in the zeolite-simulator mixture than in the pure simulator. Then at about $40 \text{ }^\circ\text{C}$, slag is admixed to the mixture. The LRW simulator conditioning carried out according to the above scheme proved applicability of slag cement with zeolite admixture for LRW immobilization. It allowed to produce the compound with the setting time of 110 minutes and the compressive strength limit of $8\text{--}10 \text{ MPa}$. Zeolite and slag acquired binding properties due to the alkaline environment formed by NaOH and KOH that are components of the LRW simulator.

Keywords: radioactivity, radiation firmness, zeolite, cementation of LRW, speed of lixiviating, mechanical durability.

Introduction. An important step towards improving the state of the environment is the reliable conditioning and storage of liquid radioactive waste (LRW) of nuclear power plants. At present, it is admitted that the conditioning of LRW by their incorporation into the mineral matrix (cementation), despite the increase in volume, is a fairly common method due to the performing of simple operations [12, 6]. Cementation of LRW makes it possible to obtain compounds that meet the requirements of the normative document [4]. The parameters related to time are leaching rate and compressive strength limit after long period (90 days) of samples being in water. There is some uncertainty as to the changes that can occur in the compounds over time, which is comparable to half-life of radionuclides.

Observations show that the use of portland cement for the disposal of LRW does not provide certainty in the reliability of their localization for a long period of time [10]. At the enterprise «Radon» the percolation of active water through the walls of reinforced concrete structures was recorded [11]. This induces to search new approaches to the conditioning of LRW without the use of portland cement. In addition its production significantly contaminates the atmosphere

with carbon dioxide [5] that cannot be ignored in global warming.

On the other hand, in recent decades considerable attention has been paid to portland slag cement and slag alkali cement, in which the powdered slag of rapid cooling in an alkaline medium acquires the properties of the binding agent. Due to quality certificates, which indicate the chemical composition, granulometric characteristics and impurities, blast furnace slag of metallurgical combines can be used as a chemical reagent with certain properties that can be taken into account when it is applied. Practically slag increases the compressive strength limit and reduces the leaching rate of radionuclides [7]. Regarding the sorption properties of ground slag, this question was not widely considered, and therefore, when cementing LRW it is reasonable to introduce into slag geomaterials – sorbents in a dispersion form, the effect of which on the properties of slag compounds still to be studied. This is due to the fact that in the alkaline environment, as was investigated by Glukhovskiy and his colleagues [1, 2], mineral sorbents, and above all clays and zeolites, are transformed into binder and can be used to obtain the corresponding compounds. Concerning geocements, there is an opinion that they are much less leaching [8] and exhibit more durability than portland cement. In

addition, geococonetes increase their durability over time and can be made on water containing salt (sea water) and used both independently and as a coating for portland cement surfaces.

Since LRW contains a significant amount of alkalis, they (alkali) can be used in the manufacture of slag alkali geocement binders in new materials for the conditioning of LRW.

The purpose of the work was to study the possibility of conditioning of LRW by obtaining slag alkali geocement compounds using efficient geomaterials and alkalis present in the LRW simulator.

Experimental part. For the sampling the slag of the Mariupol Metallurgical Combine was used, which had the following properties.

Chemical composition: SiO₂ – 36,53; Al₂O₃ – 7,92; Fe₂O₃ – 0,24; MnO – 0,1; CaO – 42,94; MgO – 9,47; S – 0,54; (Na₂O + K₂O) – 1,29; TiO₂ – 0,47.

Qualitative characteristics:

Mass fraction of moisture – 0,1 %;

The residue on the sieve is 0,08–1,25 %;

Specific surface area is 288 m²/kg.

Bentonite, glauconite, kaolinite, saponite and zeolite in a dispersed state with a particle size less (100–140) μm were tested as geomaterials (the composition of the samples is given in Table 1). For the measurement of the strength of the slag alkali geocement, beams were made, which included the same amount of geomaterials and had a size (4 × 4 × 16) cm. The pre-

pared beams were placed in the atmosphere of saturated water vapor for 7 days, later they were withdrawn and dried during (5–10) days in the room at a temperature (14–18) °C.

The compressive strength limit was determined by described method [9]. During the experiments it was established that the presence in the slag alkali geocement of one or another sorbent significantly influences such a parameter as the compressive strength limit (Fig. 1).

It can be seen from the figure that slag alkali geocement has the greatest strength in the case when zeolite is used as a geomaterial in a fraction of <140 microns. Taking into account that, further experiments were carried out with Sokirnitsky zeolite, the main characteristics of which are given below.

The simulator of the vat residue, which was mixed with slag and zeolite, approached the LRW composition of Zaporizhzhya NPP. Additionally, the surfactant “SHCHYT” was introduced into the simulator and a stable cesium nitrate was added in the amount necessary to exceed the measurement error by a two-beam atomic absorption spectrophotometer (AA 8500F “Jarrel-H”). The simulator of the vat residue had the following composition (Table 4).

The study of the behavior of the simulator showed that after mixing all the components (salts) with water, the temperature of the mixture rises to (55–60) °C. At this temperature, all the salts that are part of the simulator are in a dissolved state. Gradual decrease

Table 1. Sample composition for compression resistance limit testing, %

Reagent	SZ-10	SZ-17	SZ-18	SZ-19	SZ-20
Slag	43,4	46,4	47,2	47,5	46,8
Bentonite	21,7	–	–	–	–
Zeolite	–	23,2	–	–	–
Glauconite	–	–	23,6	–	–
Kaolin	–	–	–	23,8	–
Saponite	–	–	–	–	23,4
NaOH + KOH	3,0	3,2	3,3	3,4	3,2
Water	31,8	27,1	25,6	25,4	26,5

Note: dash a substance was not used.

Table 2. Chemical composition of zeolite (Sokyranskyi zeolite plant’s certificate)

Elements	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	NiO ₂	CaO	MgO	P ₂ O ₅	K ₂ O + Na ₂ O	F	Cu
Content, %	71,5	13,1	0,9	0,2	2,1	1,1	0,0	5,0	0,0	0,0

Table 3. Physical characteristics of zeolite

Physical characteristics	Density, kg/dm ³	Specific surface area, m ² /kg	Porosity, %	Ion-exchange capacity, mEq/g	Thermal stability, °C	Content of the main substance, %
Value	2,37	50–65	44	1,50	700	70

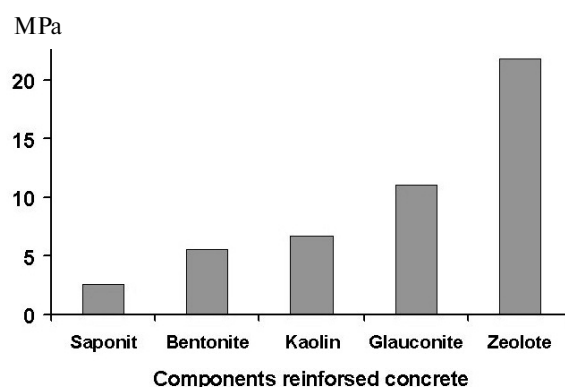


Fig. 1. Compression resistance limit of slag-alkaline reinforced concrete

Table 4. The salt composition of the simulator of the vat residue, % wt

Elements	Na ₂ B ₄ O ₇ × 5H ₂ O	NaNO ₃	NaCl	KOH	NaOH	Fe ₂ O ₃	NH ₄ OH	CsNO ₃	Surfactant
Content	60,1	13,1	0,5	3,4	21,7	0,5	0,2	0,1	0,4

Table 5. Interpretation of X-ray photographs of salts deposited from the simulator

No.	Salt sample		Na ₂ B ₂ O ₄ × 8H ₂ O (reference data, ASTM 9-11)	
	Intensity of the x-rayed peaks	Interplaner distance	Intensity of the x-rayed peaks	Interplaner distance
1	14	5,73	10	5,87
2	25	5,41	30	5,30
3	13	4,79	80	4,72
4	9	4,49	—	—
5	15	3,74	50	3,73
6	24	3,47	70	3,46
7	100	2,86	100	2,86
8	17	2,78	40	2,76
9	28	2,65	90	2,67
10	56	2,33	40	2,34
11	18	2,26	30	2,26
12	9	1,89	40	1,88
13	11	1,84	20	1,84

Note: dash the are not date.

of the temperature of the mixture occurs to about 27 °C, after which it is observed increase to 38 °C. In the mixture, crystals of sodium metaborate begin to form (Table 5).

With further cooling to a temperature of (16–18) °C, the part of crystals grows to a size of more than 4 mm; in the mixture, the amount of alkalis and water decreases; the mixture crystallizes and the introduction into such bulk a binder becomes much more complicated, the starting time of the setting of compounds shortens, their compressive strength limit decreases.

If at the imitation temperature of 60 °C, disperse zeolite in a fraction <140 microns in the ratio to slag (imitation) as 1 : 10 is added, then the cooling process changes. The mixture is cooled to 41 °C, and then, if there are centers of crystallization – particles of zeolite – a large number of small crystals are formed in the mixture and its temperature increases to 44 °C.

Further the temperature gradually decreases, the small crystals slightly increase to sizes much smaller than in the case without zeolite (Fig. 2). The temperature range during cooling of the simulator and in the presence of zeolite is shown in Fig. 3.

These results were taken into account when obtaining a compound containing an simulator with

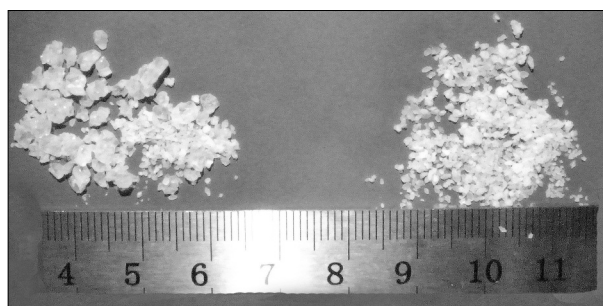


Fig. 2. Sodium metaborate crystals: *a* – without zeolite additive in the simulator, *b* – with zeolite additive

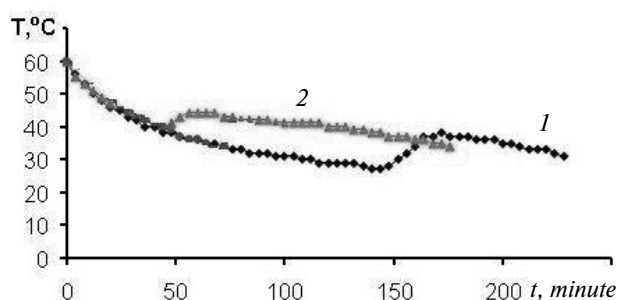


Fig. 3. Temperature pattern during the simulator (*1*) cooling and with zeolite (*2*) additive

alkaline properties, a slag that became astringent in alkaline medium, and a zeolite that functioned not only as a sorbent of radionuclides, but also was the initiator of crystallization at higher temperature.

Composition of the compound, %:

Simulator Salt – 23,8

Slag – 47,6

Zeolite – 4,8

Water – 23,8.

The initial temperature of the simulator was 58 °C, at 50 °C zeolite was added into the simulator, while cooling to 40 °C – slag. If the slag is mixed in at a high temperature, then the setting period is significantly reduced. Obtained according to the given scheme, the compound started to set after 110 minutes, and finished after 210 minutes. Measuring the compressive strength limit gave the result: 10 MPa and 8 MPa, which is almost twice the normalized value of this parameter [4]. The study of leaching rate of stable Cs showed that the average values of leaching rate reached the normative parameter of 10⁻³ g/(cm² day) at 85 days from the beginning of the experiment, while at an interval estimation in the interval (21–28) day, the leaching rate was 1,4 g / (cm² day), which almost corresponds to the normalized parameter.

The conducted research is the first approach to solving the issue of conditioning of LRW by incorporating them into slag alkali geocement matrices which resistance to irradiation, as well as frost resistance and water resistance, is yet to be thoroughly investigated. This is especially true for the study of changes in normalized parameters over a long period of time.

Conclusions.

It has been established that in the conditioning of simulator of boron liquid radioactive waste (LRW) slag alkali geocements can be used, in which together with slag as a geomaterial-sorbent and carrier of crystallization centers zeolite is used in a fraction of <140 microns, and alkaline medium for slag gaining of astringent properties is obtained in compound due to the use of alkali in the LRW simulator.

2. When the LRW is conditioned in accordance with given scheme, there is a gradual decrease in temperature with a few degrees fluctuations. This, together with a long period before the setting start, may allow the cementing of LRW directly in containers for the storage of solid radioactive waste.

3. Experiments on the preparation of slag alkali geocements showed that the compressive strength limit of samples in which zeolite powder was used as a geomaterial in a fraction of <140 microns significantly exceeded this parameter obtained using powdered kaolinite, bentonite, saponite and glauconite.

4. When obtaining compounds, it is reasonable to introduce zeolite into the LRW simulator separately from slag to the beginning of spontaneous crystallization of metaborate.

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Цеоліт у складі зв'язуючих для кондиціонування рідких радіоактивних відходів

У випадку застосування портландцементу у будівельних конструкціях для іммобілізації рідких радіоактивних відходів (РРВ) через деякий час спостерігається проникнення активності крізь стінки залізобетонних конструкцій, і тому пошук нових зв'язувальних матеріалів та методів їх застосування привертає постійну увагу. Установлено, що у лужних умовах мелений доменний шлак набуває в'язкості. Бетон із застосуванням шлаку має високу міцність та низьку швидкість вилугування. Сорбційні властивості шлаколужних цементів у досліджах були підвищені шляхом додавання до них високодисперсних сорбентів. У лужному середовищі такі сорбенти (глини та цеоліт) набували зв'язувальних властивостей. Експериментально встановлено, що найвищу межу міцності до стиснення (22 МПа) мають шлаколужні геобетони, у складі яких є цеоліт у фракції <140 мкм. Для цементування РРВ (концентрація солей ~800 г/дм³) поєднували зі шлаком і цеолітом, унаслідок чого утворювався компаунд. Міцність компаундів за такого вмісту солей різко зменшувалась, зокрема через наявність кристалів метаборату натрію розміром понад 4 мм. Зменшити розмір кристалів вдалося завдяки внесенню в імітат дисперсного цеоліту за температури (55–60) °С, а за температури ~40 °С до суміші

додавали шлак і перемішували. Виконане за цією схемою цементування імітату РРВ дало змогу отримати компаунд з початком тужавлення 110 хв, межею міцності на стиск (8–10) МПа і задовільною швидкістю вилуговування.

Ключові слова: радіоактивні відходи, цеоліт, шлаколузні цементи, цементування, радіаційна стійкість, швидкість вилуговування, механічна міцність.

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Цеолит в составе вяжущих для кондиционирования жидких радиоактивных отходов

В случае применения портландцемента в строительных конструкциях для иммобилизации жидких радиоактивных отходов (РРВ) через некоторое время наблюдается проникание активности сквозь стенки железобетонных конструкций, поэтому поиск новых вяжущих материалов и методов их применения остается актуальным. Известно, что в щелочной среде измельченный доменный шлак приобретает вяжущие свойства. Бетон при использовании шлака имеет высокую прочность и низкую скорость выщелачивания. Сорбционные свойства щелочных цементов в опытах были повышены путем добавления к ним высокодисперсных сорбентов. В щелочной среде эти сорбенты (глины и цеолит) приобретают вяжущие свойства. Экспериментально установлено, что наивысший предел прочности на сжатие (22 МПа) имеют шлакощелочные геобетоны, в состав которых входит цеолит фракции <140 мкм. Для цементирования РРВ (концентрация солей ~800 г/дм³) соединяли со шлаком и цеолитом, вследствие этого получали компаунд. Прочность компаунда с таким содержанием солей резко уменьшалась, из-за присутствия кристаллов метабората натрия размером более 4 мм. Уменьшить размер кристаллов удалось при помощи внесения в имитат дисперсного цеолита при температуре (55–60) °С, а при температуре ~40 °С к смеси добавляли шлак и перемешивали. Выполненное по этой схеме цементирование имитата РРВ дало возможность получить компаунд с началом схватывания 110 мин, пределом прочности на сжатие 8–10 МПа и удовлетворительной скоростью выщелачивания.

Ключевые слова: радиоактивные отходы, цеолит, шлакощелочные цементы, цементирование, скорость выщелачивания, механическая прочность.

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