IMMOBILISATION OF CESIUM IN MATRICES BASED ON THE BLAST FURNACE SLAG INCORPORATING ZEOLITIC ADDITIVES

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Radioactive cesium and cobalt were sorbed from chloride solutions onto chemically treated, granular zeolitic tuff. The granular active (10 or 20 wt.%) and the disperse non active tuffs (10 wt.%) were incorporated into cement slurries based on the blast furnace slag and water glass solution before their casting into rectangular moulds (1 × 1 × 3 cm). The compressive strength of specimens after their placement for 42 days in humid atmosphere and subsequently for 42 days in corrosive alkaline or acid water solutions was comparable or slightly higher than the compressive strength of specimens cured in humid atmosphere for 28 days. Leaching test in corrosive liquids showed good retention of radionuclides in observed matrices. A decrease of the radioactivity of specimens was more pronounced only for samples placed in acid solutions.

INTRODUCTION

Cement matrices on Portland cements [1-8] as well as on the blast furnace slag basis [7-11] have been found appropriate for an immobilisation of the low and medium level radioactive wastes, including those containing cesium.

Double step procedures consisting in sorption of radionuclides to suitable inorganic [2,4,7,9,12], or organic [5,10] carriers and their incorporation into cement casts as fillers are seemed to be preferred in comparison to incorporation of the waste solutions into, or instead of the processing water in preparation of concrete mixtures.

In this contribution the suitability of a specific blast furnace slag (BFS) in a combination with natural zeolite in granular form was tested for the purpose of the immobilisation of radioactive wastes. Experimental data (leaching tests and a compressive strength measurements) are presented for cases in which radionuclides were initially adsorbed on a chemically treated clinoptilolite which was subsequently incorporated into referred cement casts. Chemical treatment of zeolite highly improves its sorption ability [13,14]. For comparison of results the additional untreated disperse clinoptilolite was contained in some casts.

EXPERIMENTAL PART

The as received milled, previously granulated blast furnace slag from Iron Works Košice, Slovakia, was used as the principal matrix former in all experiments. The amount of the water glass activator ($M_s = SiO_2/Na_2O = 1.9$; $\rho = 1.37$ g cm^{-3}) corresponded to 3.7 wt.% of Na_2O of the dry weight of BFS.

The zeolitic tuff from Nižný Hrabovec, Slovakia, containing 60% of the mineral clinoptilolite was treated by NaOH solution. The treatment consisted in soaking of the granular tuff (1.2 - 2.0 mm) at 80 °C for 4 hrs in 1M, 4M or 6M solutions respectively [13]. The solid material was washed several times by the distilled water and dried before further use.

The blends of individual components were cast into rectangular moulds (1 × 1 × 3 cm) and hydrated in a moist atmosphere at ambient temperature for specified time. The casts consisted invariably of 90 % of the BFS, 10 % of the dispersed (fine) zeolite and a solution of water glass and either 10, or 20 % of the granular (grob) active, or non active zeolite added during the mix formation, in excess to the content of previous solid components. The water / cement ratio varied in the interval 0.32 - 0.40.

Model solutions - CsCl (0.05 mol dm^{-3}), labelled as Cs^{137} and $CoCl_2.6H_20$ (0.05 mol dm^{-3}), labelled as Co^{60} have been used for the sorption of cesium and cobalt on pre-treated zeolites. The sorption took place at 20 °C for 24 hrs. The granular zeolites were treated by NaOH solutions (1, 4 and 6 mol dm^{-3}) and are further denoted as 1M, 4M and 6M zeolites respectively.

The radioactivity of the dry granular zeolites was measured by the scintillation detector SPK N01 (gamma automat NRG 603). From parallel measurements the σ values were inside the interval from 1.5 to 7.5 rel.%. The higher deviation was observed at lover values of radioactivity.

Leaching experiments were performed in the following three sets of experiments on casts previously specified (1 × 1 × 3 cm, surface area = 14 cm^2):

EA: Samples, after one day of hydration, were placed in water (W), in NaOH (B-base)(0.04 mol dm^{-3}), or in HCl (A- acid)(0.03 mol dm^{-3}) respectively.

EB: The pH of the original medium of HCl (0.03 mol dm^{-3}) was changed after 14 days of leaching by adding HCl to pH 2.

EC: Samples, after 28 days of hydration in the humid atmosphere, were placed into solution of HCl (0.2 mol dm^{-3}).

RESULTS AND DISCUSSION

Individual characteristics of the BFS used are given in Table I. Its suitability for the preparation of alkaline concrete was approved in [15]. The granulometry of the disperse zeolitic tuff is given in Table II and chemical and mineralogical composition of NaOH treated and untreated granular zeolitic tuff is given in Table III.

The radioactivity of zeolitic tuff (further referred as zeolite), treated by $CsCl_2$ and $CoCl_2$ solutions is given in Table IV. It is seen from this Table that the alkaline pre-treatment of the original zeolite is an efficient way in increasing its sorptive capacity. Unexpected is finding that the sorptive capacity increases with an extent of a decomposition of the clinoptilolite structure.

Bulk densities and mechanical properties of samples with non active incorporated granular zeolites are given in Table V. The mechanical strength of samples decreases in a row: non filled matrix, matrix filled with zeolite 1M, zeolite P (primary, untreated), zeolite 6M and zeolite 4M respectively. Increased portion of zeolite decreases the mechanical strength of samples. The results show on the other hand that the mechanical strength of composites with P-zeolite, or 1M-zeolite is relatively high, above approx. 58 MPa after 28 days of hydration.

Table I. Chemical composition and physical properties of the blast furnace slag

Chemical composition		Physical properties
Oxide	(wt.%)	
SiO_2	37.81	Density: = 2.78 g cm^{-3}
Al_2O_3	7.03	Spec. surface = 290 m^2 kg^{-1}
Fe_2O_3	0.73	(Blaine)
CaO	41.42	Glass content = 94 %
MgO	8.89	Granulometric composition(wt.%)
MnO	0.48	> 0.1 mm 0.1 -0.063 mm 0.063 - 0.04 mm
S	0.87	3.0 21.6 57.2
LOI	0.61	< 0.04 mm
		18.2

Table II. The granulometry of the disperse zeolite

Particle size (mm)	> 0.1	0.1 -0.063	0.063 -0.04	< 0.04
Fraction (wt.%)	13.6	33.2	28.3	24.9

Table III. Chemical and mineralogical composition of the original and the pretreated zeolites

Zeolite	Sample	Chemical composition (wt.%)						
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	LOI
Original	P	68.25	11.66	1.17	3.62	1.30	0.70	11.45
Treated	1M	62.83	12.47	1.30	3.97	1.77	2.14	12.32
in	4M	43.75	14.44	1.76	5.05	1.91	7.82	23.51
NaOH	6M	36.30	15.43	1.87	4.29	1.39	9.54	29.28

Mineralogical composition

P : Clinoptilolite, Quartz
1M : Clinoptilolite, Quartz
4M : Albite, Quartz, amorphous phase
6M : Albite, Quartz, Jadeite, Paragonite

Table IV. Radioactivity of zeolites

Zeolite	Radioactivity (counts g^{-1} 100 s^{-1})		
	Cs	Co	Cs + Co
P (orig.)	7 980	860	8 840
1M	10 650	1 180	11 830
4M	15 440	1 460	16 900
6M	17 750	1 450	19 200

Table V. Bulk densities and the strengths of specimens

Sample	Bulk density (g cm^{-3})		Bending strength (MPa)		Compress. strength (MPa)		Porosity (vol.%)
	7 days	28 days	7 days	28 days	7 days	28 days	
No addit.	2.11	2.12	3.0	12.0	48	80	3.8
P - 10%	2.07	2.08	2.2	6.7	41	68	6.1
P - 20%	2.01	2.05	2.7	6.0	45	65	6.4
1M - 10	2.06	2.08	1.9	10.4	43	70	
1M - 20	2.02	2.04	1.6	8.9	34	58	
4M - 10	1.96	1.97	1.4	5.0	26	40	
4M - 20	1.83	1.86	0.8	3.6	16	30	7.4
6M - 10	1.96	1.98	3.2	7.7	30	43	
6M - 20	1.89	1.91	1.1	3.3	26	36	

LEACHING EXPERIMENTS

Corrosion and the mechanical strength of specimens

The weight changes of samples in corrosive liquid media are given in Table VI. The samples kept in water and in the basic solution show initially an increase in the weight with a maximum increment at 7 days (from 0.8 % at 1M zeolite to 3.0 % at 4M zeolite). Later on, up to 14 days, there follows a decrease in weight of samples with a "stabilisation" of weight changes in the next period of testing. The changes reflect to some extent porosity of samples and a content of the filler (granular zeolite).

The greatest changes occurred in an acid solution (at constant pH=2) with a weight decrease reaching 7 wt.%.

After 42 days of the exposition in the corrosive liquid the mechanical strength of samples did not decrease at all with an exception of the 20 % of 4M zeolite kept in the acid solution. In majority of cases the strength was equal, or higher than the 28 days strength of samples prior to their corrosive tests. An extreme observed was the strength of the basic matrix - 108 MPa at approx. 3 months of hydration including 42 days in the aggressive acid medium. The results are summarised in Table VII.

Table VI. Cummulative weight changes of composites suspended in corrosive liquids

Solution	Exp. (days)	Kind of zeolite additive with its specified content (wt.%)								
		0	P-10	P-20	1M-10	1M-20	4M-10	4M-20	6M-10	6M-20
N	7	0.1	0.7	0.8	0.7	1.0	2.3	2.8	1.2	1.4
	14	-0.1	0.3	0.6	0.4	0.7	1.7	2.1	0.9	0.8
	21	-0.2	0.3	0.7	0.4	0.7	1.7	2.2	0.8	0.7
	28	-0.2	0.3	0.7	0.4	0.7	1.8	2.3	0.8	0.6
	35	-0.2	0.3	0.7	0.4	0.7	1.8	2.3	0.8	0.6
	42	-0.2	0.3	0.7	0.4	0.7	1.8	2.3	0.8	0.6
B	7	-0.1	1.1	1.0	0.9	1.3	1.9	3.1	1.2	1.3
	14	-0.1	0.9	0.5	0.5	0.9	1.5	2.3	0.7	0.6
	21	-0.2	0.9	0.5	0.5	0.9	1.4	2.3	0.7	0.5
	28	-0.3	0.9	0.4	0.5	1.0	1.5	2.5	0.7	0.3
	35	-0.3	0.9	0.4	0.5	1.0	1.5	2.5	0.7	0.3
	42	-0.3	0.9	0.4	0.5	1.0	1.5	2.5	0.7	0.3
A	7	-0.8	-0.5	-0.2	-0.5	0.3	1.0	1.7	-0.1	0.4
	14	-2.4	-2.2	-2.1	-2.6	-1.8	-0.9	-0.3	-2.1	-1.4
	21	-3.7	-3.5	-3.2	-4.1	-3.5	-2.4	-1.5	-3.4	-3.1
	28	-5.1	-5.4	-5.1	-6.4	-5.6	-4.1	-3.4	-5.1	-5.1
	35	-5.7	-5.9	-5.8	-6.8	-6.1	-4.7	-4.1	-5.8	-5.7
	42	-6.2	-6.6	-6.5	-7.2	-6.4	-5.2	-4.5	-6.3	-6.0

Table VII. Mechanical strength of samples exposed in the corrosive medium (28 days)

Granular zeolite		Compressive strength (MPa) Corrosive solution		
Sample	Content (wt.%)	N	B	A
	0	93	90	108
P	10	78	80	72
P	20	61	69	68
1M	10	66	83	72
1M	20	69	68	61
4M	10	59	55	48
4M	20	39	33	24
6M	10	57	57	57
6M	20	40	44	38

Radioactivity

The initial radioactivities of composites are summarised in Table VIII. Figures 1*a*, 1*b* and 1*c* show changes in the radioactivity of samples with 20 % of zeolites during their leaching in water, NaOH and HCl respectively (experiment EA). The highest decrease in the radioactivity was observed at leaching in HCl (0.03 mol dm^{-3}), especially at leaching of samples containing 4M and 6M zeolite.

A subsequent addition of HCl after 14 days of leaching (experiment EB, Figure 2) resulted in the stepwise drop of the radioactivity for samples containing 20% of zeolite without a change in the radioactivity in the next period of leaching.

The results of leaching experiments (EC) in Figure 3, at which the samples had been solidified in the wet atmosphere prior to leaching tests, manifested only small decrease in radioactivity in spite of the placement of samples in the comparatively strong acid.

Table VIII. Initial activities of composites

Granular zeolite		Sample weight (g)	Average activity (counts 100 sec^{-1})
Sample	Content (wt.%)		
P	10	7.07	4 740
P	20	6.70	10 580
1 M	10	6.70	6 890
1 M	20	6.29	12 030
4 M	10	6.19	8 490
4 M	20	5.93	15 930
6 M	10	6.52	8 750
6 M	20	6.35	16 510

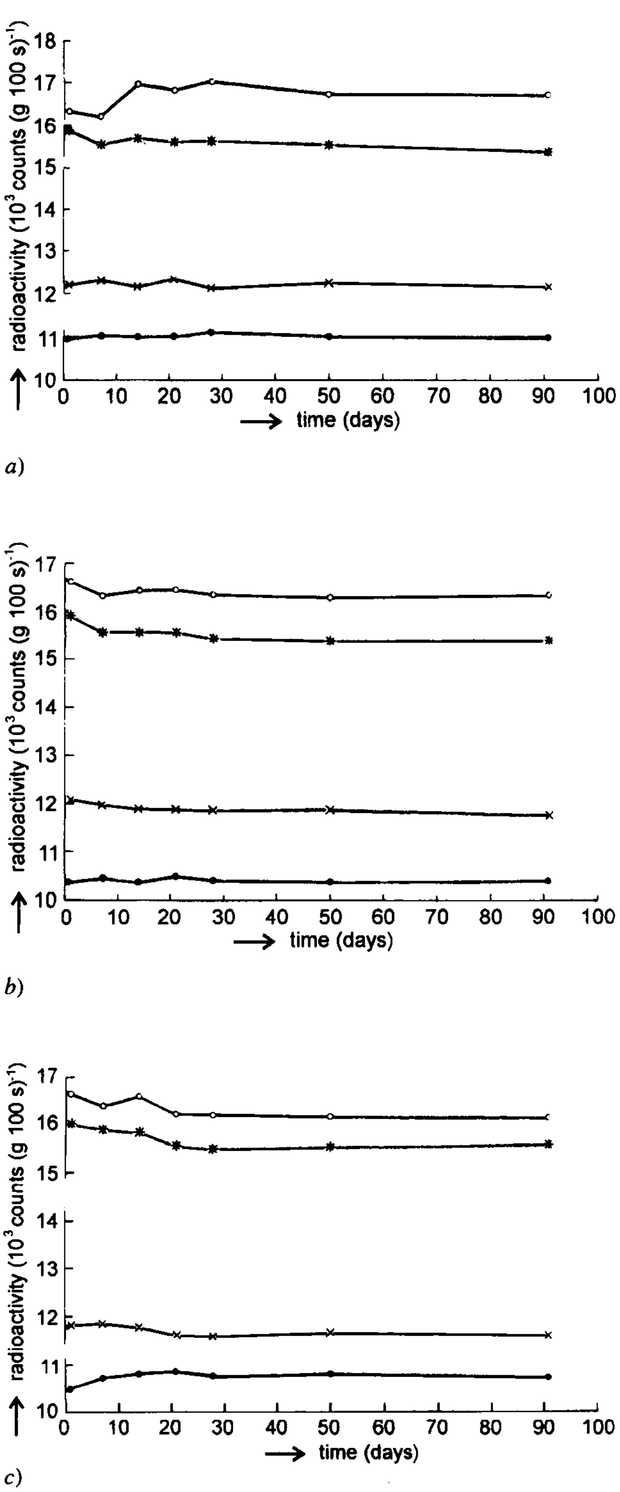


Figure 1. Radioactivity of samples containing 20 % of zeolites after an exposure
a) - in the neutral medium N (water) - experiments EA; *b*) - in the basic medium, B: NaOH (0.04 mol dm^{-3}) - experiments EA; *c*) - in the acid medium, A: HCl (0.03 mol dm^{-3}) - experiments EA
• - P, × - 1M, * - 4M, o - 6M

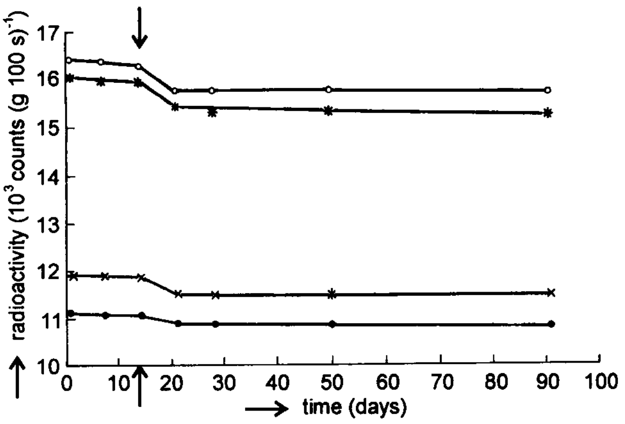
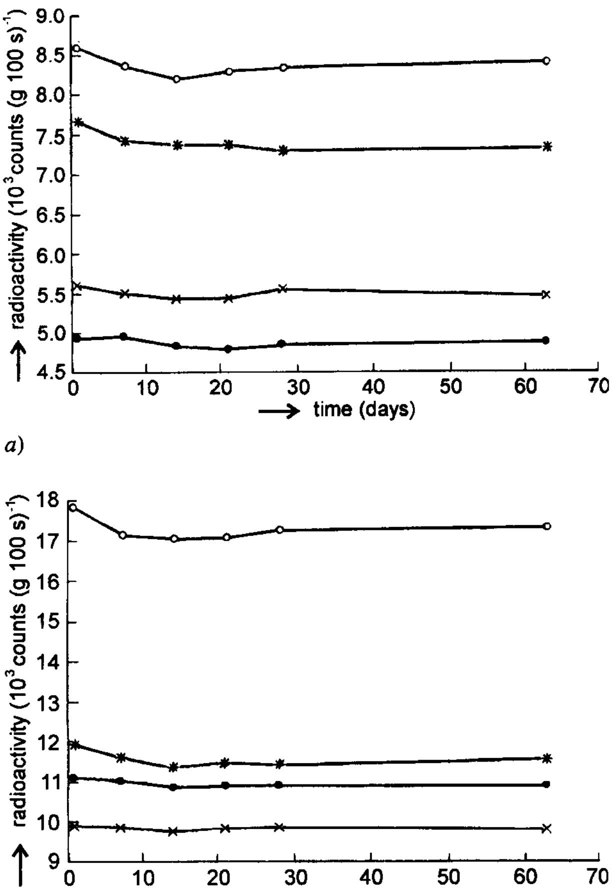


Figure 2. Radioactivity of composites containing 20 % of zeolites after an exposure in the acid medium readjusted after 14 days of leaching - experiment EB
• - P, × - 1M, * - 4M, o - 6M



a)

b)

Figure 3. Radioactivity of samples leached in HCl (0.2 mol dm^{-3}) after the previous 28 days hydration in a humid atmosphere - experiment EC
a) composites with 10 % of zeolite; *b*) composites with 20 % of zeolite
• - P, × - 1M, * - 4M, o - 6M

CONCLUSIONS

The mechanical strength of prepared composites is favourable and shows good compatibility of zeolitic additives to a basic matrix of the blast furnace slag and of the water glass activator.

Leaching experiments are hopeful and show good retention of observed radionuclides in samples exposed to corrosion in alkaline and neutral water solutions.

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IMOBILIZÁCIA CÉZIA V MATRICIACH VYSOKOPECNEJ TROSKY S OBSAHOM ZEOLITOV

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V práci sa študovala vhodnosť matríc na báze troskových spojív pre imobilizáciu rádioaktívneho cézia a kobaltu. Cézium aj kobalt sa dopredu sorbovali z roztokov na chemicky upravený zrnitý prírodný zeolit, ktorý sa pri príprave spojivovej kaše použil ako plnivo v množstvách 10 a 20 hmot. %. Zložkou spojivovej zmesi bol tiež neaktívny disperzný zeolit (10 hmot. %). Základom spojiva bola mletá, granulovaná vysokopecná troska z VSŽ Košice aktivovaná roztokom vodného skla.

Chemická úprava zeolitu, ktorá výrazne zvýšila jeho sorpčnú kapacitu sa zaistila jeho varom v roztokoch NaOH (2M, 4M a 6M roztok).

Na zatuhlých spojivových kašiach (tvar teliesok 1×1×3 cm) sa zmerala ich korózna stálosť pri uložení vo vode, v kyslom aj alkalickom vodnom prostredí. Vyhodnotila sa zmena ich mechanickej pevnosti.

Po lúžení vzoriek vo vode, alkalickom aj kyslom roztoku sa stanovil pokles rádioaktivity vzoriek a posúdila sa účinnosť imobilizácie.

Hoci chemická úprava zeolitov zvyšuje sorpčnú kapacitu, nevedie k poklesu mechanickej pevnosti pripravených teliesok. Táto aj po koróznych skúškach je stále dostatočne vysoká.

Najvyšší pokles aktivity aj mechanickej pevnosti teliesok sa zaznamenal pri ich uložení v silne kyslom vodnom prostredí (pH = 2).

CORROSION OF ADVANCED CERAMICS

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Corrosion, that is chemical interaction of a material with its environment, usually involving degradation of its properties, has recently been a subject of increasing attention in all fields of materials science. Relatively fewer studies have been devoted to the corrosion of ceramics, in particular as compared to the subject of corrosion of metals, this being due to the high stability of oxide-based ceramics and to the much more limited possibilities of influencing the processes involved. In spite of this, corrosion of ceramics has been gaining in significance, as indicated by several more recent monographs. The interest is nowadays focused especially on advanced ceramics, because corrosion of the more traditional materials (such as glasses and refractories) has been dealt with in detail during the last decades.

During the 4th European Ceramic Conference in Riccione, Italy, a Special Session was held on the corrosion of advanced ceramics, promoted by he Institute for Advanced Materials of the Joint Research Centre at Petten in the Netherlands. The invited and contributed papers from the conference are now published as proceedings whose introduction presents two review papers: The Corrosion of Ceramics : Where Do We Go from Here? (by F.L. Riley), and Approaches to Standardization: High Temperature Oxidation and Hydrothermal Corrosion of Silica Forming Ceramics (by K.G. Nickel and Y.G. Cogotsi).

The chapter called Oxidation contains ten papers devoted to the behaviour of non-oxide ceramics, in particular nitride and carbide ones, at high temperatures in oxidation atmospheres. Another section was concerned with high-temperature gaseous corrosion. The corrosive media were air containing water and sulphur oxides, atmosphere containing carbon oxides and HCl, and the last paper dealt with degradation of SiC-based materials in high-temperature combustion environments. Two studies were devoted to corrosion of non-oxide ceramics in liquid metals. The section on Low Temperature Aqueous Corrosion includes five papers dealing with the behaviour of oxide and non-oxide ceramics under hydrothermal conditions and in minerals acids.

The Volume gives a very good survey of knowledge on the most frequently occurring corrosion mechanisms, and presents recent results achieved in key areas of advanced ceramic materials. The Proceedings can be recommended in particular to people working in ceramic research, to advanced university students and to engineers designing special materials working in corrosive environments and in extreme conditions.

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