Available online at www.sciencedirect.com
SCIENCE DIRECT®

C. R. Chimie 7 (2004) 1185–1190

COMPTES RENDUS CHIMIE

http://france.elsevier.com/direct/CRAS2C/

Full paper / Mémoire

Research and application of inorganic selective sorbents at Mayak PA

M.V. Logunov *, A.S. Skobtsov, B.V. Soldatov, A.P. Pazdnikov, Y.A. Voroshilov, Sergey I. Rovny

Mayak Production Association, Ermolaev Str, 18, Ozyorsk, Chelyabinsk Region, Russia, 456784

Received 1 December 2003; accepted after revision 11 May 2004

Available online 5 November 2004

Abstract

This work has been performed in order to identify selective inorganic sorbents for caesium and strontium. Thin-layer sorbents with nickel ferrocyanide embedded in an inert matrix were found to be the best for caesium. Sorbents including non-stoichiometric manganese dioxide were selected for strontium. Bench tests have been carried out on the purification of desalted water of SNF storage-pool from ^{137}Cs, and on the purification of contaminated natural water from ^{90}Sr. The facility for synthesizing the ferrocyanide sorbent with the registered mark 'Seleks-CFN' has been brought into operation. The sorbent ISM-S seems promising for ^{90}Sr decontamination. ***To cite this article: M.V. Logunov et al., C. R. Chimie 7 (2004)***.

Résumé

Recherches et applications sur l'utilisation de sorbants spécifiques à Mayak. Des sorbants sélectifs du césium et du strontium ont été identifiés. Pour le césium, le meilleur s'avère être le ferrocyanure de nickel, s'il est utilisé sous forme de couche mince. Pour le strontium, on a sélectionné des composés non stœchiométriques de dioxyde de manganèse. On a mené des tests visant à épurer en césium l'eau des piscines d'entreposage des combustibles nucléaires usagés, et en strontium des eaux contaminées. Une installation industrielle permettant de préparer le sorbant à base de ferrocyanure de marque « Seleks-CFN » a été réalisée. Le sorbant ISM-S semble prometteur pour la décontamination en strontium. ***Pour citer cet article : M.V. Logunov et al., C. R. Chimie 7 (2004)***.

Keywords: Decontamination; Caesium; Strontium

Mots clés : Décontamination ; Césium ; Strontium

* Corresponding author.
E-mail address: cpl@po-mayak.ru (M.V. Logunov).

1631-0748/$ - see front matter © 2004 Published by Elsevier SAS on behalf of Académie des sciences.
doi:10.1016/j.crci.2004.05.006

1. Introduction

The use of selective inorganic sorbents is one of the most up-to-date methods of radiochemical waste decontamination for aqueous low-level waste (LLW). Those of 'Mayak PA', coming from drainage system as well as water from spent-fuel assembly storage pool, are mainly contaminated with ^{137}Cs. Water of storage reservoirs of the 'Techa River Cascade' is mainly contaminated with ^{90}Sr [1]. Such multicomponent contaminated LLW predetermined the possibility of effective application of selective inorganic sorbents.

Mass distribution coefficients of ^{137}Cs for some synthetic and natural materials were measured in order to define the most prospective type of Cs selective sorbents [2]. The results of experiments are given in Table 1. Full-scale dynamic laboratory tests were also conducted on real desalted water from the spent-fuel assembly storage pool in order to select the best sorbent among those offering the more perspectives: ferrocyanides, phosphates, and zeolites. Filtration rate in top–down direction was supported with about 20 column volumes per hour. Results of the experiments are given in Fig. 1. The effective filtration cycle with a ^{137}Cs purification factor ≥ 10 was 30 thousand column volumes for zeolite CBF-10, and about 60 thousand column volumes for zirconium phosphate (T-3A). The effective filtration cycle on nickel ferrocyanides (NZA and T-35) was about 90 thousand column volumes. Thin-layer sorbent demonstrates better hydrolytic stability than composite sorbent.

This paper concerns experimental tests on ^{137}Cs and ^{90}Sr removal from some aqueous LLW.

2. Experimental results

2.1. ^{137}Cs decontamination

The data obtained allowed us to perform experimental industrial tests of the process of LLW decontamination from ^{137}Cs with water from the special drainage system of Mayak PA radiochemical facility, which annual water flow reaches 400 thousands m^3 [3]. Composition of water used in experimental industrial tests was as follows: not stable; pH value in the range from 7.7 to 8.2, water hardness from 4.65 to 10.2 mg equiv l^{-1}, calcium concentration from 46 to 117 mg l^{-1}, magnesium from 29 to 53 mg l^{-1}, sodium from 117 to 155 mg l^{-1}, nitrite ion from 624 to 1232 mg l^{-1}, ^{137}Cs activity was (7.03–13.4) × 10^3 Bq l^{-1}. Single synthesis of a large batch (about 8 m^3) of ferrocyanide sorbent NZS, which is a close analogue to NZA, was performed. Water purification unit was installed for purification of special drainage water on the basis of two filters and the existing manifold pipelines. Filters F-1 and F-2 contained 3.85 m^3 of NZS sorbent with size fraction from 0.2 to 0.3 mm per each filter. In F-2 NZS, sorbent was mixed with 0.77 m^3 of spent resin KU-2×8 to make a composition with improved hydrodynamic properties. Experimental sorption filters were operated at water flow rate equal to 25–30 m^3 h^{-1} or 7–8 column volumes per hour per

Table 1
Values of ^{137}Cs distribution factors depending on the composition of the initial solution

Sorbent	Caesium distribution factors (ml g^{-1}) from the solution			
	Water	0.1 M $NaNO_3$	1 M $NaNO_3$	0.05 M $Ca(NO_3)_2$
Vermiculite (Covdor)	4900 ± 1600	770 ± 180	80 ± 16	2500 ± 800
Clinoptilolite (Dzegvi)	5900 ± 400	9700 ± 600	200 ± 10	8600 ± 1600
Nickel ferrocyanide (NZA) [a]	4000 ± 900	3300 ± 300	2800 ± 600	5200 ± 2100
Nickel ferrocyanide (Seleks-CFN) [a]	2800 ± 400	7400 ± 500	26 000 ± 2400	24 200 ± 5200
Nickel ferrocyanide (T-35) [b]	5700 ± 1300	8200 ± 1400	15 700 ± 3000	8600 ± 2000
Titanium ferrocyanide (KNTZ) [b]	2500 ± 900	5500 ± 1400	4400 ± 1100	16 300 ± 4800
Iron ferrocyanide (FS-10) [b]	890 ± 160	2200 ± 300	10 700 ± 600	4000 ± 400
Zr phosphate (T-3A)	3900 ± 400	1900 ± 300	460 ± 30	4400 ± 1600
CFB-10 [c]	3600 ± 1000	450 ± 20	82 ± 46	4600 ± 300
CMP [c]	2200 ± 500	440 ± 30	70 ± 12	1700 ± 300
Sulfonic cation resin KU-2×8	8100 ± 800	180 ± 20	18 ± 5	16 ± 3

[a] Thin-layer ferrocyanides.
[b] Composite ferrocyanides.
[c] Zeolites.

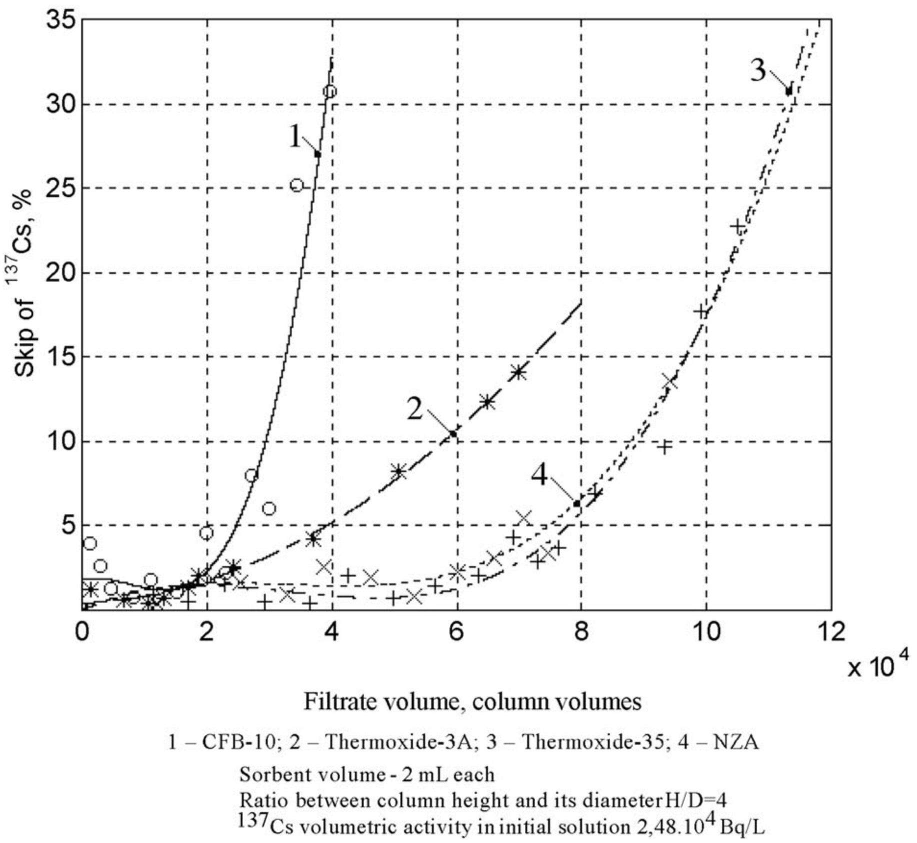

Fig. 1. Result curves for sorption of ^{137}Cs on inorganic sorbents.

each filter. The results of experimental industrial testing are given in Table 2. Data prove that in the process of application of sorption filters at selective caesium extraction units (with a purification factor ≥ 10), about 85 m^3 of special drainage water was decontaminated. The best results were achieved using filter F-2 with added KU-2×8. About 1.96 TBq of ^{137}Cs were extracted from LLW in total. ^{137}Cs concentration in the

Table 2
Results of experimental-industrial tests of drainage water decontamination from ^{137}Cs with NZS sorbent

Operation stage	Filters	Filtrate volume		Average ^{137}Cs activity in the filtrates (Bq l^{-1})	Water decontamination factor from ^{137}Cs	Amount of extracted ^{137}Cs (GBq)	Radiation background (μSv s^{-1})	
		m^3	Column volume				Over resin	Near apparatus
1	F-1	3266	848	347	15	15.9	0.60	0.30
	F-2	3266	848	151	35	16.6	0.14	0.30
2	F-1	17 470	4537	296	77	392.2	4.00	0.30
	F-2	17 470	4537	128	178	392.2	6.00	0.50
3	F-1	8649	2246	825	45	316.0	8.00	0.80
	F-2	8649	2246	181	206	321.5	10.0	1.00
4	F-1	14 011	3639	3922	4.2	175.8	–	–
	F-2	15 931	4138	403	37	256.4	18.0	1.60
5	F-2	11 740	3049	507	10.1	54.4	–	–
Total result	F-1	43 396	11 272	1576	14.2	899.9	8.00	0.80
	F-2	57 056	14 820	292	64	1041.1	18.0	1.60

filtrates exceeded only slightly the admissible level for discharged industrial water during the major part of the test. An additional purification factor was obtained on routine ion-exchange treatment. Thus, discharged water was practically not contaminated with ^{137}Cs.

Experimental-industrial facility Seleks-CFN for the synthesis of ferrocyanide sorbent of NZS-type with an output up to 12 t/year was built up at Mayak PA with consideration of successful results of experimental industrial tests of synthesis and water purification process. Seleks-CFN sorbent synthesis is based on saturation of granular silica gel or other porous material, loaded into sorption column, with nickel and ferrocyanide ions. Water solutions of nickel ammoniate or potassium ferrocyanide are used. A sparingly soluble compound, nickel-potassium ferrocyanide, forms as a result of such a treatment in silica gel pores.

Seleks-CFN facility was commissioned in 1999 and it works in periodic mode when it is necessary. About 1420 kg of Seleks-CFN sorbent were synthesized in the course of the facility operation. The effective pH of contaminated water for Seleks-CFN sorbent is in the range 2–12. Statistic exchange capacity for caesium is up to 30 mg g^{-1}. Half-exchange time is 2.1 min.

A process technology and a prototype of the industrial facility for decontamination of desalted water of spent-fuel assembly (SFA) storage pool were developed using this sorbent. A pilot sorption facility with sorbent volume of 65 l was mounted on the slotted covering of the pool. The column itself was placed at the depth about 3 m, which provided sufficient radiation shielding. In order to decontaminate the maximum volume of water in the storage pool, water was taken for treatment and purified water was discharged from the column in the opposite loci of the storage pool. Sorption column was used with bottom up flow rate from 2.5 m^3 h^{-1} to 6.0 m^3 h^{-1}. The results of the experiment are presented in Table 3. They show that 22 885 m^3 of water were filtered through the sorbent during the experiment, which is equal to about 253 thousand column volumes. High water purification efficiency and column hydrodynamic characteristics were stable during the whole filtration cycle. Activity of the initial water decreased 5 times for ^{137}Cs. Preliminary calculation show that 2.07TBq of ^{137}Cs were deposited in the column. The data show that Mayak PA developed an effective process of SFA storage-pool water decontamination from ^{137}Cs.

2.2. *^{90}Sr decontamination*

The most advanced oxy-hydrate sorbents whose composition is based on non-stoichiometric manganese dioxide were studied for purification of non-saline natural waters from ^{90}Sr in static and dynamic conditions. The following sorbent types were used: ISM-S with composition $(Na, K)_xMnO_y$, where $x = 0.25$ to 0.3 and $y = 1.9$ to 2.1, as well as ISM-SP, which is the same sorbent, fixed in a matrix of inert medium (perchlorovinyl). Method was developed and sorbents were synthesized in Russia in the city of Perm under the leadership of Professor V. Volkhin [4]. The

Table 3
Results of experimental/industrial tests of water treatment process in the storage pool using Seleks-CFN sorbent

Operation stage	Filtrated water volume, m^3	Radionuclide activity in initial water (Bq l^{-1})		Radionuclide activity in filtrate, (Bq l^{-1})	Water decontamination factor from ^{137}Cs
		^{137}Cs	^{134}Cs	^{137}Cs	
1	3706	1.49×10^5	1.73×10^3	2.53×10^3	59
2	3601	1.49×10^5	1.40×10^3	5.0×10^3	30
		9.93×10^4	1.20×10^3	3.33×10^3	30
3	2990	1.12×10^5	1.07×10^3	3.27×10^3	34
4	2423	8.80×10^4	–	1.20×10^3	73
5	2901	7.47×10^4	600	< 100	> 700
6	2687	5.30×10^4	313	387	140
		4.67×10^4	400	213	220
7	1239	5.90×10^4	667	333	180
8	2370	5.49×10^4	733	667	82
		5.70×10^4	667	333	170
9	968	3.0×10^4	333	467	64
Total	22 885				

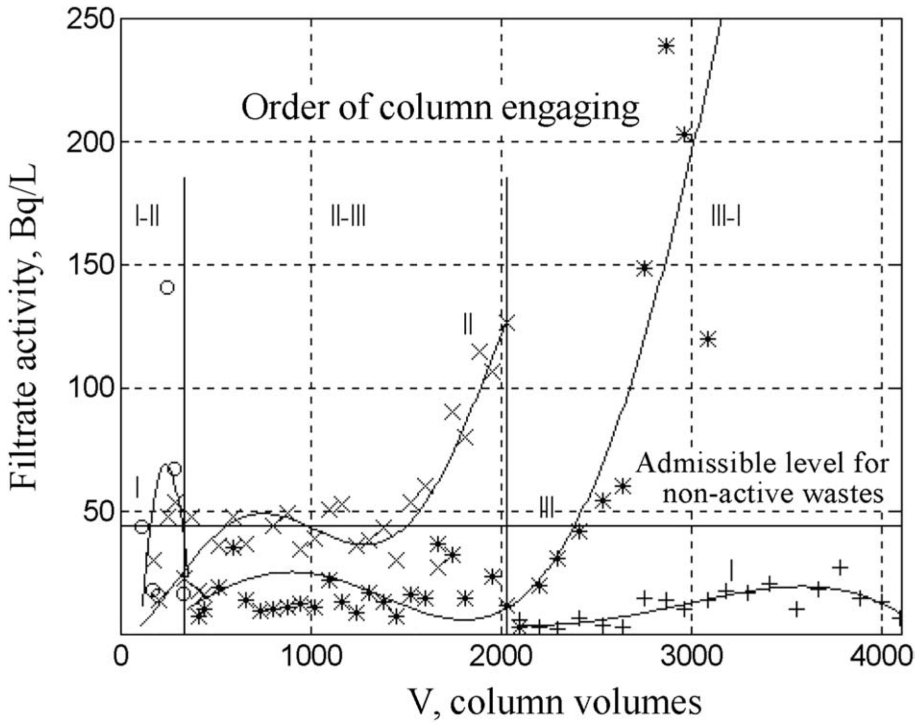

Fig. 2. Output curves of ^{90}Sr depending of columns engaging in the process.

peculiar feature of these sorbents in comparison with well-known natural and synthetic samples on the basis of manganese oxy-hydrate is their ability for reversible sorption of strontium.

It was defined experimentally that the pH range from 6 to 10 with maximum at pH 6.9 is optimal for ^{90}Sr sorption with ISM-S sorbent. Radionuclide desorption is possible in acid medium up to pH 1 to 2 [4]. The results of laboratory investigations allowed us to perform experimental industrial tests.

Three 3.5-l sorption columns (I to III) filled with the sorbent ISM-SP were used. One additional column was filled with a layer of quartz sand for mechanic filtration of the contaminated water (pH ~ 8, total beta-activity about 3.3 kBq l^{-1}, ^{90}Sr activity around 1.6 kBq l^{-1}, water hardness –4.5 to 5.4 mg equiv l^{-1}) before being directed toward the sorption columns. Contaminated water went top–down with a flow rate of 30 to 35 column volume h^{-1} trough two concatenated columns. Desorption was obtained with a 0.3-mol l^{-1} solution of HNO_3 and regeneration with a 0.2 mol l^{-1} solution of NaOH. Output curves of strontium are presented in Fig. 2 depending of the columns engaged in the process. Optimum results were obtained for columns III–I. This shows that column performances are different depending on packaging. Over 7 m^3 (~2000 column volumes) of radioactive contaminated natural water were decontaminated in the course of the third test cycle (engaging columns III–I) to the admissible level water discharge.

The obtained results make it possible to conclude that the ISM-SP (ISM-S) sorbent is quite prospective for the decontamination of natural waters from Sr and it can serve as a basis for development of a respective process technology with a mode sorption–desorption–regeneration. Thus, Mayak PA experts have considerable experience in the use of inorganic selective sorbents for applied tasks of radiochemistry.

3. Conclusions

1. Thin-layer ferrocyanide sorbents are the most effective for low-level waste ^{137}Cs decontamination.

2. 'Mayak' PA is experienced in synthesis of thin layer ferrocyanide sorbents; purification techniques for special drainage saline water and spent-fuel storage-pool non-saline water are used at the experimental industrial scale.

3. For ^{90}Sr decontamination of natural contaminated water, sorbents based on non-stoichiometric manganese dioxide were tested and recommended for use.

References

[1] Y.V. Glagolenko, E.G. Dzekun, E.G. Drozhko, G.M. Medvedev, S.I. Rovny, A.P. Suslov, Radiat. Saf. Probl. 2 (1996) 7.
[2] Y.A. Voroshilov, Y.V. Glagolenko, D.N. Kolupaev, K.K. Korchenkin, M.V. Logunov, A.P. Pazdnikov, E.R. Sabitov, A.S. Skobtsov, Radiat. Saf. Probl. 1 (2001) 32.
[3] A.I. Bardov, Y.A. Voroshilov, N.P. Zemlina, M.V. Logunov, N.N. Prokofyev, B.V. Soldatov, Radiochemistry 41 (1999) 451.
[4] Y.A. Voroshilov, M.V. Logunov, N.N. Prokofyev, N.P. Zemlina, Radiochemistry 45 (2003) 62.