COMPARATIVE CHARACTERISTICS OF SELECTIVE SORBENTS FOR TREATMENT OF THE EVAPORATOR CONCENTRATES FROM NPP

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ABSTRACT

In this study the method for radionuclides selective sorption allowing to reduce a volume of radioactive waste many times has been investigated. The principle of the method is the following. Evaporator concentrates pass through sorbents, which selectively extract radionuclides. Cleaned from radionuclides, the evaporator concentrates representing a low hazardous chemical waste, are processed and stored at the site for industrial wastes. The influence of different parameters on sorption of cesium and cobalt by inorganic sorbents has been investigated. This radionuclides are the main one in the NPP evaporator concentrates. The pretreatment necessity of the evaporator concentrates before the sorption of cesium on ferrocyanide has been showed. The different sorbents, which produced in large scale, has been tested. The “Termoxid” is the best sorbent for cleaning the NPP evaporator concentrates from cesium.

INTRODUCTION

In the course of operation of NPP reactors of Russia and the Ukraine a huge amounts of evaporator concentrates have been accumulated. The tanks for their storage at all NPPs are practically filled to 70 % and more. Some NPPs use cementation, bituminization or deep evaporation as methods for treatment the evaporator concentrates from NPPs. These methods allow to transfer LRW into the rather inert form suitable for a disposal (storage). However, they do not allow to reduce a volume of a final radioactive product substantially (1).

The world practice begins to use a method of selective sorption for removal of radionuclides from LRW with low salt content. This method allows to reduce a volume of a final radioactive product by a factor of 100 or more.

The purpose of this work are the influence investigation of different parameters on sorption of main radionuclides evaporate concentrates, cesium and cobalt and choice of the most effective sorbents for cleaning waste from cesium.

WORK DESCRIPTION

We carried out the investigations in three stages.

At the first stage processes of cesium, cobalt radionuclides sorption by selective sorbents were studied on real evaporator concentrates from five NPPs of Russia and Ukraine (2, 3).

At the second stage the influence investigation of different parameters on sorption of cesium and cobalt from simulators of NPP evaporate concentrates were studied. The pretreatment necessity of the evaporator concentrates before the sorption of cesium on ferrocyanide were showed.

At the third stage different sorbent for cleaning real NPP evaporate concentrate from cesium after pretreatment were tested.

RESULTS

The evaporator concentrates from NPPs are represented by fluids of dark brown color with a specific odor. Their chemical composition is stipulated mainly by the presence of sodium and potassium nitrates, and for waste from VVER-type units also by borates. The ðÍ value of the evaporator concentrates from different NPP varies from 7 up to 13. The specific activity lies in the range between 1E-4 up to 2E-3 Cu/l and is stipulated mainly by the presence of cesium, cobalt and manganese isotopes.

The investigations on real evaporator concentrates were carried out at Balakovskaya , Khmelnitskaya, Kalininskaya , Leningrad and Kolskaya NPPs, which have two types of reactors: RBMK and VVER in operation. The sorbent tests under dynamic conditions were carried out on a plant, including two vessels, pump and three filters. Supernate of evaporator concentrates from NPP were pumped through three consistently connected filters filled with ferrocyanide sorbents.

The analysis of the received results shows:

- The specific activity of the evaporator concentrates on Cs137 reduced substantially, but it exceeds acceptable levels.

- The cobalt radionuclides removal by selective sorbents does not occur.

The absence of purification from radionuclides of a corrosive origin (Co, Mn), apparently, is explained by the form of a radioactive cobalt and etc. present in evaporator concentrate solutions. A radioactive cobalt, known as good complexformer, is present in the form of various organic complexes. The formation of organic complexes is caused by use of such substances, as EDTA, an oxalic acid, various detergents and so on during NPP operation. Coming in waste water, these substances form during evaporation the whole scale of various organic substances, which with radioactive cobalt form complexes nonsuspected to sorption.

The low efficiency of sorbents for cesium are apparently explained by poisoning influence of "organics" on sorbents and existing nonsuspected to sorption form cesium.

This assumption was confirmed by experiments on studying the influence of EDTA and oxalic acid ($H_2C_2O_4$) concentration on the sorption of a radioactive cobalt and cesium. The tests were conducted on simulators of NPP evaporate concentrate with salt content ~ 450 g/l and specific activity ~ 1E6 Bq/L under static condition. Hydrated zirconium phosphate (GFC) was used as sorbent for cobalt, and ferrocyanide for cesium. The concentration of EDTA and oxalic acid were 1E-5 - 1E-2 n.

Results of this testing are showed in the Table 1.

One can see, that oxalic acid does not influence on sorption of cobalt. If in absence of EDTA, the distribution coefficient for Co in the simulator of the evaporator concentrates onto GFC sorbent is 5 E3, at EDTA concentration more than 1E-4 n the sorption of cobalt does not occur practically. Cobalt exist in form of stable complex with EDTA and this form is nonsuspected to sorption.

So, to convert cobalt in suspected to sorption form it is necessary to destroy its complexes.

In the course of these experiments it was also found out, that the existence of the unabsorbed forms present in solutions is attributed also to radioactive cesium. In presence of

EDTA the distribution coefficient a cesium in the simulator of evaporator concentrates reduces by a factor of 5 - 10 times.

The distribution coefficients for Co in the simulator of the evaporator concentrates

Table 1

Concentration, n	EDTA		$H_2C_2O_4$		K_d , mL/g	
	Specific activity of initial solution, Bq/L	Specific activity of final solution, Bq/L	Specific activity of initial solution, Bq/L	Specific activity of final solution, Bq/L	EDTA	$H_2C_2O_4$
0	1.20E6	2.34E4	1.43E6	3.25E5	5.03E3	3.40E2
1E-5	1.04E6	4.48E5	1.36E6	1.72E5	1.32E2	6.91E2
1E-4	1.175E6	8.19E5	1.24E6	7.25E4	4.34E1	1.61E3
1E-3	1.058E6	1.00E6	1.33E6	5.82E4	5.80	2.19E3
1E-2	1.055E6	1.18E6	1.34E6	5.92E4	-	2.16E3

These circumstances, apparently are explained by the absence of sorption process of a radioactive cobalt and insufficient efficiency of cleaning the evaporator concentrates from a radioactive cesium by selective sorbents. Besides, in the evaporator concentrates there are many other organic substances, which have poisoning effect on sorbents. Therefore, before the sorption cleaning the evaporator concentrates all the complexes binding the radionuclides and also organic substances poisoning sorbents present in it should be previously decomposed.

In this study the destruction of mentioned substances in the evaporator concentrates from Kalinin NPP was carried out by oxidation with a potassium permanganate. Practically this resulted into complete extraction of a radioactive cobalt onto manganese dioxide arised during oxidation. After that oxidized evaporator concentrates were subjected to cleaning by ferrocyanide sorbents, which are of industrial production in the world. Among them the following sorbents were used: Fenix and Termoxid (Russia), HCF (Finland), KCoFeCN-PAN (Czech). Russian sorbents are ferrocyanide sorbents, put on the inorganic carrier material. In Czech sorbent polyacrylnitrile is used as the carrier material. Finnish sorbent is granulated potassium- cobalt ferrocyanide without the carrier material . It is used for cleaning the evaporator concentrates at the Loivisa NPP .

To determine sorption characteristics of different sorbents under dynamic condition pretreated real Kalinin NPP evaporate concentrate were pumped through filled sorbent column. The diameter of column was 1 sm and volume - 16 sm^3 . The process temperature was 30^0C, and flow rate - 2.5 bed volume per hour.

The sampling was made twice a day for measuring specific activity of the filtrate.

Test results are given in tables 2 and 3.

The comparison testing of these sorbents have showed, that sorbent Termoxid has the greatest resource. So, at initial specific activity of 1.3 E7 Bq/l on Cs137 (pH = 11.5) the decontamination factor after passing 300 column volume was: for Termoxid -5 E4, for Fenix - 2.7 E3, for KCoFeCN-PAN - 1 E3, for HCF - 6 E2. Height of a filtering layer for all experiments was 16 sm. Of course under operation condition height of a filtering layer will be higher (~ 600 - 800 mm). It will result into increase of decontamination factor and resource of sorbents. However, from the data obtained it is obvious, that sorbent Termoxid has the best sorption characteristics.

The decontamination factors (Df) of Fenix and KCoFeCN-PAN
Feed specific activity on ^{137}Cs – $1.3*10^7$ Bq/L

Table 2

Fenix				KCoFeCN-PAN			
Volume, mL	Bed volumes	Specific activity of filtrate, Bq/L	Df	Volume, mL	Bed volumes	Specific activity of filtrate, Bq/L	Df
200	12	$1.5*10^2$	$8.7*10^4$	160	10	$1.2*10^3$	$1.1*10^4$
900	56	$1.9*10^3$	$6.8*10^3$	810	50	$1.3*10^4$	$1.0*10^3$
1170	73	$2.5*10^3$	$5.2*10^3$	1120	70	$4.2*10^4$	310
1870	116	$1.4*10^2$	$9.3*10^4$	1830	114	$4.7*10^4$	277
2150	134	$2.1*10^3$	$6.2*10^3$	2100	130	$4.0*10^4$	325
2800	175	$1.5*10^3$	$8.7*10^3$				
3020	188	$1.8*10^3$	$7.2*10^3$				
3190	199	$1.3*10^3$	$1.0*10^4$				
3930	245	$2.2*10^3$	$5.9*10^3$				
4210	263	$2.8*10^3$	$4.6*10^3$				
4460	278	$3.2*10^3$	$4.1*10^3$				
4730	295	$4.8*10^3$	$2.7*10^3$				
5430	339	$2.2*10^4$	591				
5700	356	$3.5*10^4$	371				

Other advantages of Termoxid are:

- high chemical resistance, that allows to use it in the wide range of ðÍ values and salt concentrations;
- high mechanical strength, that allows to use it in device with hydraulic discharge;
- high radiation resistance;
- the compatibility with various matrix materials, that allows to treat a spent sorbent (if necessary) by methods of cementation or vitrification.

The sorbents mentioned are used or can be used for cleaning such LRW, as:

- evaporator concentrates from NPP;
- fuel storage pond water;
- LRW, arised from treatment of spent nuclear fuel.

However, for cleaning of mentioned LRW it is necessary to use sorbents in a combination with such methods as oxidation, ño-precipitation and filtration.

CONCLUSION

Before the sorption cleaning the evaporator concentrate NPP all the complexes binding the radionuclides and also organic substances poisoning sorbents present in it should be previously decomposed.

The decontamination factors (Df) of Termoxid and HCF
Feed specific activity on ^{137}Cs – $1.3*10^7$ Bq/L

Table 3

Termoxid				HCF			
Volume, mL	Bed volumes	Specific activity of filtrate, Bq/L	Df	Volume, mL	Bed volumes	Specific activity of filtrate, Bq/L	Df
400	25	32.4	$4.0*10^5$	750	47	$8.7*10^2$	$1.5*10^4$
1080	68	$6.7*10^2$	$1.9*10^4$	990	62	$1.1*10^3$	$1.2*10^4$
1790	112	14	$9.3*10^5$	1620	101	$2.0*10^3$	$6.5*10^3$
2070	129	$2.0*10^2$	$6.7*10^4$	1880	118	$4.3*10^3$	$3.0*10^3$
2740	171	$1.3*10^2$	$1.0*10^5$	2640	165	$6.7*10^3$	$1.9*10^3$
2960	185	$1.6*10^2$	$8.1*10^4$	2930	183	$6.9*10^3$	$1.9*10^3$
3170	198	$2.2*10^2$	$1.4*10^5$				
3720	233	$3.0*10^2$	$9.9*10^4$	3630	227	$1.0*10^4$	$1.3*10^3$
3980	249	$1.3*10^2$	$2.2*10^5$	3870	242	$1.1*10^4$	$1.2*10^3$
4630	289	$3.5*10^2$	$8.6*10^4$	4090	256	$1.2*10^4$	$1.1*10^3$
4820	301	$3.4*10^2$	$5.0*10^4$	4750	297	$2.4*10^4$	542
5480	343	$1.7*10^2$	$1.0*10^5$	5040	315	$2.1*10^4$	619
5750	359	$2.1*10^2$	$8.6*10^4$				
5940	371	$2.1*10^2$	$8.6*10^4$	5940	371	$2.5*10^4$	520
6170	386	$1.0*10^2$	$1.8*10^5$				
6840	428	$1.2*10^2$	$1.5*10^5$				
7100	444	$3.1*10^2$	$5.8*10^4$				

2. The sorbent Termoxid has the best sorption characteristics for cleaning evaporator concentrates NPP from cesium.

V. REFERENCES

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