PROCESSING NPP BOTTOMS BY FERROCYANIDE PRECIPITATION

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ABSTRACT

The purpose of work is a laboratory test of a technological scheme for cleaning bottoms from radionuclides by use of ozonization, ferrocyanide precipitation, filtration and selective sorption. At carrying out the ferrocyanide precipitation after ozonization, the specific activity of bottoms by Cs^{137} is reduced in 100 - 500 times. It has been demonstrated that the efficiency of ferrocyanide precipitation depends on the quality of consequent filtration. Pore sizes of a filter has been determined to be less than 0.2 μm for complete separation of ferrocyanide residue. The comparison of two technological schemes for cleaning bottoms from radionuclides, characterized by presence of the ferrocyanide precipitation stage has been performed. Application of the proposed schemes allows reducing volumes of radioactive waste in many times.

INTRODUCTION

Bottoms are an evaporation product of various liquid radwaste, formed at NPP. Bottoms are solutions of a high salinity, contaminated with: decay products, radionuclides of the corrosion origin and various substances used for decontamination of equipment and maintenance of a water chemistry. Great amounts of bottoms are accumulated during operation of NPPs. Tanks for their storage are almost filled up. Used at some NPPs solidification methods for such waste can not be realized because of absence of storage sites for the final product. The situation requires an urgent resolution for the problem.

Recent years a method of selective sorption is used for processing the bottoms along with traditional methods (1) (cementation, bituminization). At Loivisa (Finland) bottoms after pH correction pass through a column with ferrocianide sorbent (2). Filtrate after sorption dump in the Baltic Sea. Thus, pollution of sea water both with chemical substances, and also with such radionuclides as Cs and Co occurs, because during selective sorption the cleaning of bottoms from Cs is incomplete, and cleaning from Co does not occur.

At SIA " Radon" NPP bottoms processing method, deprived of the specified drawbacks, is developed (3). According to the given method at first NPP bottoms are ozonied for destruction of non-absorptive form of Cs and especially Co, and also for oxidation of organic substances, poisoning sorbent. Then a deposit formed during ozonization, on which co-precipitation of Co^{60} occurs, is separated. Filtrate is passed through ferrocianide sorbent to extract Cs.

Bottoms cleaned from radionuclides are treated as an industrial waste.

The given technology was tested at Kola and Kalinin NPP. However, as the experiments which have been carried out on Kola NPP shown during cleaning bottoms from radionuclides by ozonization, filtration and selective sorption methods a plenty of the spent filters - containers with ferrocianide sorbent of high cost are formed. Therefore the aim of this work is to develop the basic technological scheme and to choose the equipment allowing to diminish the amount of the spent filters - containers with ferrocianide sorbent.

For realization of the given tasks the introduction of the various additives at a stage of the bottoms preliminary processing (ozonization and filtration) and ferrocyanide precipitation before a stage of selective sorption, and also some other approaches were tested.

The works were carried out at Kola NPP with use of bottoms from the first order tank EKO-5.

EXPERIMENTAL PART

Ozonization of bottoms was carried out on pilot plant, the scheme of which is given in Fig. 1. Before the experiment ~ 15 l of bottoms were pumped in the separating device through the orifice 5. The pump and ozonizer were started. During ozonization the following parameters were controled:

- pH;
- Optical density of sampling filtrate;
- Temperature;
- The rate of oxygen on ozonizer and concentration of ozone at outlet from ozonizer;
- specific activity of filtrate on Co^{60}, which was determined after preliminary extraction of Cs on ferrocianide sorbent.

Ozonization was carried out with ozone-oxygen mixture generated by the device OPBK-60 at temperature $60 - 80\ ^0C$ in a circuit of the pump - ejector-separating device. The capacity of ozonizer was 60 g/hour. pH was adjusted in the range of 12 - 13 by addition 50 % NaOH solution.
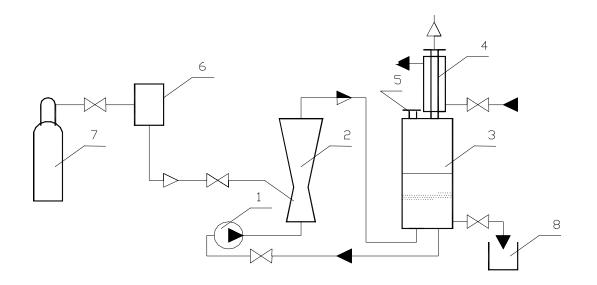

Fig. 1. The scheme of the pilot plant for ozonization of the bottoms.
1 - pump, 2 - ejector, 3 - dividing device, 4 – heat exchanger, 5 -orifice, 6 - ozonizer, 7 – vessel with the compressed oxygen, 8 – sampling.

The experiments on ferrocyanide precipitation were carried out by introduction of $Ni(NO_3)_2$ and $K_4[Fe(CN)_6]$ solutions at their different amounts , pH and time of processing.

Filtrate after ozonization and ferrocyanide precipitation was subjected to additional cleaning on ferrocyanide sorbent Termoxid T-35. Filtrate was passed through two consequently connected columns the volume of 20 ml and height of 22 cm each. The flow rate of filtration through columns was 200 ml/hour.

Results and their discussion

The results of the analysis of chemical and radionuclide composition of the samples are presented in Table I.

Table I. Chemical and radionuclide composition of bottoms.

Parameter	Units of measurements	Size
Density	Kg/m^3	1,34
Na^+	g/l	116
K^+	g/l	60
NO_3^-	g/l	408
H_3BO_3	g/l	9,9
Oxidability	$g\ O_2/l$	6
^{137}Cs	Bq/l (Ci/l)	$7,4*10^7\ (2,0*10^{-3})$
^{134}Cs	Bq/l (Ci/l)	$1,8*10^7\ (4,8*10^{-4})$
^{60}Co	Bq/l (Ci/l)	$1,1*10^6\ (3,0*10^{-5})$
^{54}Mn	Bq/l (Ci/l)	$5,6*10^4\ (1,5*10^{-6})$

Three sets of ozonization (15 l) of the bottoms under following conditions were carried out:
1 and 2 - without the additives;
3 - with the additive $Co(NO_3)_2$ 0,5 g/l.
Ozonization was finished when optical density of sampling filtrate constant in time was achieved. For definition of cleaning from Co^{60} the bottoms after ozonization and filtration were passed through a column with ferrocianide sorbent and spectrometer analysis was carried out. Filtering of samples from first two sets was carried out on the double paper filter «blue tape », and samples from the third set were filtered on the Millipore filter with the pore size 0,45 microns. The data on the bottoms cleaning from Co^{60} are given in table II.

Table II. Results of the bottoms cleaning from radionuclides by using ozonization, filtration and sorption.

N set	D_f	Specific activity, Bq/l (Ci/l)
1	1100	$1,0*10^3\ (2,7*10^{-8})$
2	750	$1,5*10^3\ (4,0*10^{-8})$
3	1800	$6,3*10^2\ (1,7*10^{-8})$

The ozone rate in all three sets was approximately the same and amounted 3 g O_3 on 1 g oxidability, which was equal to 6 g O_2/l.

One should point out that in spite 0f the fact that data of optical density sampling filtrate after ozonization are well correlated with specific activity sampling filtrate on Co^{60}, the ozonization is necessary to finish when specific activity sampling filtrate constant in time, but not optical density, is achieved. This assumption was confirmed by the following experiment. Total filtrate after ozonization and ferrocyanide precipitation of three sets (Cs^{137} - 2 E+5 Bq/l, Co^{60} - 1500 Bq/l) was subjected to additional ozonization at 60 ^{0}C with the addition of 0.5 g/l $Co(NO_3)_2$. The ozone rate amounted 0,1 g O_3 on 1 g oxidability, i.e. 3 % from the total ozone rate for oxidation of the bottoms. After additional ozonization the specific activity of filtrate was equal to 84 Bq/l. Thus optical density of filtrate has not changed practically.

Further the influence of accurate filtration on Co^{60}removal from ozonized bottoms were inverstigated. For this purpose after ozonization of bottoms from the 2-d set and filtration through the paper filter the additional filtration through the Millipore of filter 0,45 microns was carried out. The content of ^{60}Co on the Millipore filter and in filtrate after ozonization was determined. The following results were obtained:

On the Millipore filter   - 3,7*10-9 Ci,
In filtrate after ozonization   - 1,8*10-9 Ci (1,2*10-8 Ci/l).

Thus, the additional filtration allowed to extract twice more ^{60}Co, than it was remained after ozonization, and total factor of cleaning was 2500, that is 3,3 times more, than without filtration through Millipore filter.

Thus, it is necessary to carry out ozonization of NPP bottoms under following conditions:
- pH = 12 - 13;
- Temperature of process - 60 - 80 ^{0}C;
- Concentration of $Co(NO_3)_2$ - 0,5 g/l;
- when specific activity of sampling filtrate on ^{60}Co constant in time is achieved the process is completed, and separation of deposit formed at ozonization can be carried out on filters with the pore size < 0,45 microns.

The experiments on ferrocyanide precipitation were carried out at various pH, at various ratios of reagents , joint and separate separation of a deposit after ozonization and ferrocyanide precipitation in several stages. At the first stage bottoms after ozonization from the first set was taken. After performing ferrocyanide precipitation at various pH deposits were filtered. Filtration was carried out through the double paper filter «blue tape ». At pH 12,3 Cs is not precipitated practically, and in a range pH 9 - 10,8 the factors of cleaning on Cs 130 - 200 were obtained. The solutions $K_4Fe(CN)_6$ и $Ni(NO_3)_2$ were brought in stoichiometry ration to obtain 1 g/l of $NiK_2Fe(CN)_6$.

Bottoms after ozonization of the first set were investigated also on cleaning from ^{137}Cs and ^{60}Co depending on pH at separate filtering of a deposit after ozonization and ferrocyanide precipitation. A filtration after ozonization was carried out at pH 12,3, and after ferrocyanide precipitation at different pH. Both filtrations were carried out through the double paper filter « a blue tape ». Ferrocyanide precipitation was carried out in stoichiometry of reagents. The factors of cleaning from ^{137}Cs and ^{60}Co in a range pH 8,7 - 10,4 varied unsignificantly and amounted 170 - 280 on ^{137}Cs, and - 450 - 590 on ^{60}Co. At pH 11,5 cleaning of bottoms from ^{137}Cs and ^{60}Co was much worse.

The release of ^{137}Cs at ferrocyanide precipitation with a different ratios of reagents was investigated. Ferrocyanide precipitation was carried out in four various conditions:
1 - 50 % surplus of $Ni(NO_3)_2$ at pH=9;
2 - 50 % surplus $K_4Fe(CN)_6$ at pH=9;
3 - in stoichiometry of reagents at pH=9;
4 - introduction of reagents at pH=12,1, and then correction up to pH=9.

As a result of these experiments was established, that:
- The separation of deposits after ozonization and ferrocyanide precipitation can be carried out both separately, and jointly;
- ferrocyanide precipitation allows to diminish specific activity of bottoms on Cs^{137} after ozonization more than in 100 times;
- Sufficient concentration of a ferrocyanide deposit is 1 g/l;
- pH = 8, 7 - 10;
- For simplification of deposit separation it is necessary to carry out precipitation at surplus of $Ni(NO_3)_2$;
- The introduction of reagents and correction of pH can be carried out in any sequence.

To carry out experiments on additional cleaning with sorbent after ozonization and ferrocyanide precipitation ozonied bottoms were filtered through the double filter « a blue tape », then pH was corrected by a nitric acid up to 9, $K_4Fe(CN)_6$ and $Ni(NO_3)_2$ with surplus of Ni were added at 1 g/l of a deposit. The formed deposit was separated on the double filter « blue tape ». The specific activity of filtrate was equal to: ^{137}Cs - $1,2*10^{-5}$ Ci/l, ^{60}Co - $3,9*10^{-8}$ Ci/l.

But, as the further experiments on sorption Cs from bottoms after ozonization and ferrocyanide precipitation shown, the filtration on «blue tape » is unsufficient. At realization of sorption on Termoxid-35 through two consequently connected columns factor of cleaning from Cs constituted only 30 - 200 on two columns (see table. III).

Table III. Sorption ^{137}Cs from bottoms after ozonization and ferrocyanide precipitation

Volume		Specific activity, Bq/l (Ci/l)	
ml	Bed volumes	After 1 column	After 2 column
625	16	-	$2,3*10^4(6,1*10^{-7})$
1125	56	$2,9*10^4(7,9*10^{-7})$	-
1985	100	-	$5,9*10^3(1,6*10^{-7})$
4000	200	-	$4,8*10^3(1,3*10^{-7})$
4100	205	$4,1*10^4(1,1*10^{-6})$	-

The assumption was made, that Cs slips through sorbent not in ionic form, but on small particles of a deposit. We carried out researches on sorption with Termoxid T-35 after filtration through various filters. For this purpose bottoms after ozonization, ferrocyanide precipitation and the filtration through the paper filter were filtered through 6 types of filters additionly: 0,15 mcm, 0,25 mcm, 0,45 mcm, 0,65 mcm, 0,05 - 0,1 mcm. After filtration sorption on Termoxid was carried out. The results are given in table IV.

Table IV. Influence of accurate filtration.
Initial specific activity ^{137}Cs - $1,1*10^5$ Bq/l ($3,0*10^{-6}$ Ci/l)

Pore size of filter,mcm	Specific activity, Bq/l (Ci/l)	D_f
Direct sorption	$3*10^2(8*10^{-9})$	370
0,65	$<40(<1,8*10^{-9})$	>2750
0,45	$<27(<7,3*10^{-10})$	>4100
0,25	$1,0*10^3(2,7*10^{-8})$	110
0,15	$31(8,4*10^{-10})$	3500
0,05-0,1	$38(1,0*10^{-9})$	2900

As it can be concluded, membrane with pore size less than 0,65 microns is sufficient for practically complete removal of Cs. However, as the further experiments shown, even after a filtration through a membrane with pore size 0,45 microns secondary ferrocyanide precipitation at interaction filtrate with ferrocyanide sorbent occurs. Therefore for separation of ferrocyanide deposit it is possible to recommend a filtration through membranes with a pore size < 0,2 microns.

To check this assumption separation of a deposit after ozonization and ferrocyanide precipitation carried out on a membrane with pore size 0,05-0,1 microns. Filtrate with specific activity $1.1.10^5$ Bq/l on ^{137}Cs was passed through two consequently connected columns with Termoxid T-35. The sorption curves are given in table V.

Table V. The sorption curves after ozonization, ferrocyanide precipitation and filtration (0.1mcm)

Bed volumes	After 1 column		After 2 column	
	A, Bq/l	D_f	A, Bq/l	D_f
24	-	-	<15	$<7,3*10^3$
34	-	-	<27	$<4,1*10^3$
108	<15	$<7,3*10^3$	-	-
230			<15	$<7,3*10^3$
293	39	$2,8*10^3$	-	-
1165	-	-	62	$1.8*10^3$
1347	$1.3*10^2$	$8.5*10^2$	-	-
1415	-	-	33	$3.3*10^3$

Thus, the corrected technological scheme of cleaning NPP bottoms from radionuclides can be realized as follows:
1. Correction pH of NPP bottoms by a solution of alkali up to 12 - 13;
2. ozonization up to constant in time specific activity of sampling filtrate on ^{60}Co;
3. correction pH up to 8 - 10 with nitric acid, addition of reagents for performing ferrocyanide precipitation;
4. Separation of a deposit on filter with pore size < 0.2 mcm;
5. Selective sorption of Cs from filtrate.

Let's compare two ways of cleaning NPP bottoms from radionuclides:
1 - ozonization, filtration, selective sorption;
2 - ozonization, ferrocyanide precipitation, filtration, selective sorption.

Both these ways can be realized on one plant. The main differences of ways consist in the following. According to the first way 99 % of Cs is introduced in sorbent, present in the filter - container, and according to the second one 99 % of Cs is included in a deposit after ferrocyanide precipitation, which is incorporated in cement matrix and is placed in the ferro-concrete container such as NZK.

Let's try to make a rough comparison of two ways according to expenditure.
Conditions of comparison:
- bottoms of Kola NPP;
- Volume - 2400 m^3;
- Average specific activity - 1,25 Ci/m^3;
- Total activity - 3000 Ci.

The material balance of both ways is given in table VI.

Table VI. The material balance of both ways

Material	1 way			2 way		
	Quantity	cost, thousand rubles	total cost, thousand rubles	Quantity	cost, thousand rubles	total cost, thousand rubles
NaOH	38,6 t	7	270,2	39 t	7	273
HNO_3	20 t	3,25	65	20 t	3,25	65
$K_4Fe(CN)_6$	–	–	–	2,4 t	175	420
$Ni(NO_3)_2$	–	–	–	2,16 t	52	112,3
Sorbent	24 m³	250	6000	2,4 m³	250	600
Cement	52 t	0,85	44,2	52 t (520*)	0,85	44,2 (442*)
Filter - container	200	100	20000	20	50	1000
Container NZK	29,2	15	438	29,2 (292*)	15	438 (4380*)
Total:			**26817,4**			**2955,5 (7295,3*)**

 * - taking into account the radiation doze rate estimation

As it can be concluded from the data, given cost of expenditure on the second way is much less. But in both ways the total cost is determined by cost of filters – containers significantly.
How it is possible to cut the costs?

According to the first way it is to refuse from expensive filters - containers and to use the filters with sorbent, which are present against the stationary shield. The spent filters with sorbent should be transported in the storage for solid waste in the returnable transport container.
The second way is a simplification of the filter - container and the use of stationary shield, refusal from containers NZK and use of 200-liter barrels for cement compound, transportation of filters - containers and barrels in the returnable transport container. The last can be universal both for a barrel, and filters - containers on both ways.

It is also necessary to discuss the location of the deposit from ozonization and ferrocyanide precipitation after mixing it with cement. Possible versions:
- container NZK;
- 200 - liter barrel.

According to the Russian norms the radiation doze rate from the transport container should not exceed 10 mrem/hour at the distance of 1 m.

As rough calculations of radiation doze rate on distance 1 m from the container NZK show, it is possible to fill in the container with cement compound having the following restriction on specific activity. The maximal specific activity should not exceed $1.3 *10^{-2}$ Ci/l. It will result that the deposit after ferrocyanide precipitation can be concentrated during filtration only in 10 times. Hence, deposit volume delivered for cementation will grow, and amount of containers produced during filling with cement compound will increase in 10 times. The latter will result not only in increase of cost of processing, but also of temporary storage.

Thus, taking into account large technological reliability of 1-st way and smaller expenditure of the2-nd way, it is expedient:
- To create universal plant allowing realization of both ways;
- To use the filter with geometry 200 - liter barrel equipped with stationary bioprotection according to both ways as the device for selective sorption of Cs;
- To pour the cement compound in 200 - liter barrels;
- To transport the spent filters - containers and filled barrels in the returnable transport container designed for realization of both ways;
- To perform the final choice of a way during operation of the plant.

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