Test Works of Treatment of Problematic Evaporator Concentrate from Kola NPP - 14081

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ABSTRACT

To decontaminate the problematic evaporator concentrate (EC) generated during the operation of the Kola NPP different treatment techniques using different additives, ozonization and filtration on simulated and real EC have been tested. Based on the results of this work a treatment technique to reduce the Kola NPP's problematic EC ^{60}Co values below < 410 Bq/kg. The essence of the EC treatment technique is as follows. First, the EC is ozonized at pH ~ 11.4 to reduce the COD (chemical oxygen demand) to less than 50 mg/l. Then, an additive is injected. The resulting precipitate is separated by filtration. The resulting precipitate is separated by filtration; the pH of the filtrate is adjusted up to ~ 10, and passes through the filter – a container with a ferrocyanide sorbent. Based on the results of the work obtained under laboratory conditions a successful experimental treatment of the EC of ECO - 4 I line on the industrial plant at the Kola NPP was carried out.

INTRODUCTION

In 2007, the scientific staff of JSC "RAOTECH", FSUE "Radon", JSC "Alliance - Gamma" and a number of other organizations, developed a technology and put into industrial operation a treatment plant for decontamination of the EC from the Kola NPP.
To decontaminate the EC at the Kola NPP methods of ozonization, filtration and selective sorption on ferrocyanides are used. The use of these methods reduces the specific activity of the accumulated EC from E+7 of ^{137}Cs and E+ 5 – 6 of ^{60}Co to less than 110 and 410 Bq/l respectively in the final solution, which meets the regulatory requirements. During the treatment of some types of the EC the specific activity in the final solution of ^{60}Co is 700-10000 Bq/l, which exceeds the regulatory requirements. This significantly reduces the efficiency of the treatment facility.
To solve this problem new modes of treatment with the introduction of additives have been tested. The work was carried out in two stages. In the first stage - on simulated EC. . In the second stage, the work was carried out on the problematic EC I - line of the Kola NPP of ECO-4.5, where the normal treatment regime does not provide the required decontamination of ^{60}Co.
During the work, in some modes on simulated and on real EC from the Kola NPP the necessary decontamination of ^{60}Co was acieved. Based on the results of the work obtained in the laboratory, a successful experimental treatment of the problematic EC of ECO - 4 I line on the industrial plant at the Kola NPP was carried out.

Methods of Analysis and Description of the Settings

Chemical analysis of the solutions was performed using the following methods:
Salt content – weight;
pH – using an ionomer «Ecotest– 2000»;
COD (chemical oxygen demand) - volumetric titration.

The radionuclide composition was determined using a gamma - spectrometer with a semiconductor detector. The ozonization of the problematic EC was carried out in a cylinder with volume of 0.5 l, equipped with a gas distributor of a porous ceramic. The ozone produced by the generator was passed through the EC at a temperature of 60^0C. During the ozonization the following parameters were controlled:

- Temperature;
- pH;
- COD;
- The optical density of the filtrate;
- The specific activity of the filtrate.

At the industrial plant of the Kola NPP the EC was subjected to the following treatment (see Fig.1). The decantate of the problematic EC or a solution of the precipitate is poured into one of the receiving tanks (items 70/1and 70/ 2). After heating and adjusting the pH, the TC was ozonized to a values < 50 mg/l of COD, and then to the constant specific activity of ^{60}Co to less than 410 Bq/kg. After that, the EC, with a suspension formed during ozonization, passes through a pair of pre-filters (items 71/1,3 and 71/2,4). The filtrate is routed into one of the filtrate tanks (items 72/1 and 72/2). The filtrate is passed through a membrane filter (73/1, 2) to remove fine particulate. The liquid in the permeate tank (items 74/1 and 74/2) is adjusted to a pH~10 and is then directed by the pump for the selective sorption containers for decontamination of $Cs^{137, 134}$.

Works Stages

Carrying out the Experiments on Simulated waste

The following LRW simulators were used :

- The problematic EC from the Kola NPP the I line of ECO 1 – 3 were oxidized with potassium permanganate, passed through a column with "Termoxid - 35“ and delivered to the FSUE “ Radon “;
- A mixture of decontaminated EC from the Kola NPP and EC from the Kalinin NPP was prepared in a ratio of 9/1.

The results of the analysis of the decontaminated EC from the Kola NPP are shown in Table. 1.

Table 1. The radionuclide and chemical composition of the decontaminated EC from the Kola NPP

Number of tank	Total salt content, g/dm^3	COD, mgO_2/dm^3	pH	Specific activity, Bq/dm^3	
				^{137}Cs	^{60}Co
ECO - 1	171	< 100	8.8	120	5,2 E+ 3
ECO - 2	490	< 100	9.4	200	4,8 E+ 3
ECO - 3	483	< 100	9.6	120	1,37 E+3

To isolate the cobalt several processing modes were tested:
The first mode was as follows :

- Adjusting of pH to ~ 1 - 2, introduction of the Fe^{+3} solution, heating to 60^0C;
- separate the resulting sediment of the filtration;
- Ozonization of the EC at pH=1 – 2 to the constant COD value ;
- Adjusting of pH to 11.4;
- Ozonization of the EC at pH=11,4 to the constant specific activity of ^{60}Co;
- Filtration at pH=11.4;

The test results of ozonization of the decontaminated EC of the Kola NPP in the first stage are shown in Table 2.

Table 2. Results of ozonization of decontaminated EC from the Kola NPP

No. of tank	Introduction of Fe^{+3}	Separation of the sediment before the process of ozonization , pH	pH of the ozonization	COD		Specific activity on ^{60}Co, Bq/kg		K_d on Co^{60}
				before	after	Before	after	
ECO-1	-	-	11.4	<100	<100	5200	3500	1,49
ECO-2	-	-		<100	<100	4800	4500	1,07
ECO-3	-	-		<100	<100	1370	1100	1,25
ECO-1	+	+, 1	1/11,4	<100	<100	5200	370	14,1
ECO-2	+	+, 1	1/11,4	<100	<100	4800	1500	3,2
ECO-3	+	+, 1	1/11,4	<100	<100	1370	390	3,51

As seen, the separation of the precipitate formed as a result of the Fe^{+3} introduction allows further improvement in the efficiency of decontamination of ^{60}Co from EC. Apparently, the components of the EC are transferred into the sediment which prevents the complete destruction of the ^{60}Co complexes, and its transition into a precipitate of the ozonization. The proposed method allows decontamination of the EC of ECO-1 and ECO-3 to values lower than the reference (410 Bq/kg), but does not allow decontamination of the EC of ECO-2. Co^{60} can be in the EC as a complex with – EDTA and in the form of other more stable complexes. For example, in the presence of the chromates as CoCrK, where K is a chelator. Then adding the lead ions into the solution can yield the following reactions:

$$CoCrK + CrO_4^- + Pb^{+2} = CoCrK + PbCrO_4$$
$$CoCrK + CrO_4^- + Pb^{+2} = CoPbK + PbCrO_4$$

That is, there is a loss of chromates in the sediment as lead chromate and substitution of the chrome with lead in the complex. Under the influence of ozone on the complex in the presence of sulfate the following reaction may occur :

$$SO_4^{-2} + CoPbK + O_3 = Co(OH)_{2,3} + PbSO_4 + \text{decomposition products K}$$

That is, there is destruction of the complex and precipitation of the cobalt as well as the lead sulfate.

The second mode of simulated EC treatment is as follows. The ozonation was carried out in an alkaline medium to value of 50 mg/l of COD, and then deposition of the chromates, filtering the sediment, introduction the collector Co $(NO_3)_2$ and ozonization to a constant in time specific activity of ^{60}Co. For the deposition of the chromates, a lead nitrate solution was used. The results of the filtrate analysis obtained in different decontaminated fractions from the main radionuclides of the EC in the second mode are shown in Table.3.

Table 3. Results of the analyzes the filtrates ECO-1 and ECO – 2

No. of tank	pH of the ozonization	COD		Specific activity on ^{60}Co, Bq/kg		K_d on Co^{60}
		Before	after	before	after	
EKO-1	11,4	<100	<100	5200	25,7	202
EKO-2	11,4	<100	<100	4800	91	52,7

As shown in Table 3, holding the processing of the second mode allows decontamination of EC to values of ^{60}Co below the required <410Bq/kg.

Carrying out the Works at the Kola NPP

Laboratory Experiments

In the laboratory experiments on the release of ^{60}Co from the problematic EC from the Kola NPP the EC ECO-4, ECO-5 I-line of the Kola NPP were used. The analysis of the initial EC is presented in Table.4.

Table 4. The radionuclide and the chemical composition of the EC

No. of tank	Specific activity, Bq/kg			Salt content, g/l	COD, mg/l
	^{60}Co	^{134}Cs	^{137}Cs		
ECO - 4	1,89 E5	1,65 E6	2,9 E7	584	4950
ECO - 5	1,61 E5	1,60 E6	3,62 E7	470	5450

After dilution the EC was subjected to e ozonization at 60^0C under various conditions in a measuring cylinder using an ozonizer with a capacity of 10 g/h of ozone. After carrying out the ozonization and the ferrocyanide deposition the EC was passed through a "blue ribbon" filter.
The filtrates were sent to the γ-spectrometric analysis. In addition to decontamination of cobalt – 60, deposition of chromates present in the EC at different stages of ozone treatment were measured. For the deposition of the chromates a solution of the lead nitrate was added
.
Experiments were performed under the following conditions:

1. An ozonization in an alkaline medium to values of COD<50mg/l without isolation of chromates;
2. ozonization in an alkaline medium to COD<50 mg /l + chromate deposition in the end of ozonization with subsequent separation of the precipitate from the ozonization and the chromates;
3. ozonization in an alkaline medium to values of COD 80 -100 mg /l + chromate deposition + filtering sediment + introduction of the collector Co $(NO_3)_2$ + ozonization to a constant in time specific activity on ^{60}Co.

The results of analysis of the filtrates obtained in the different modes of ozonization, are shown in Table. 5

Table 5. Results of analysis of the filtrate obtained in the different modes of ozonization

No. of tank	Optical Density of filtrate after the precipitation of chromates D	Dilution with water	Mode of treatment	Specific activity of the filtrate, Bq/kg	
				^{137}Cs	^{60}Co
ECO – 4	0,24	1 : 3	1	8,41 E4	1,42 E4
ECO – 4	0,015	1 : 3	2	1,82 E4	1,07 E4
ECO – 4	0,015	1 : 3	3	2,67 E4	27,6
ECO – 5	0,015	1 : 3	3	1,21 E4	43,4

As seen from Table. 5, with almost complete separation of the chromates (D = 0.015) the EC from ECO - 4 and ECO - 5 can be decontaminated to ^{60}Co values lower than the control. Thus, the work done on the treatment of the problematic EC from the Kola NPP, confirmed the sequence of treatment steps needed to decontaminate the EC to the regulated levels for ^{60}Co .

This processing is as follows.

- Ozonization of the EC at pH=11.4 to COD less than 50 mg/l;
- The introduction of the lead nitrate solution;
- Separation of the precipitate formed by filtration;
- Introduction the collector;
- Ozonization of the EC at pH=11-11.4 to the constant in time specific activity on ^{60}Co;
- Filtration at pH=11-11.4;
- Adjusting of pH to 9 - 10;
- Sorption on ferrocyanide sorbent.

Experimental Treatment at the Industrial Plant

An experimental treatment at the industrial plant was performed on a mixture of EC from ECO - 4 and drain water. About 3 m^3 of drain water was added to 1 m^3 of EC from ECO - 4. The sequence of treatment operations was as follows, see fig 1. In the receiving tank (item70/1) a mixture was prepared, adjusted pH to 11.4 and started the ozonization. During the ozonization the value of pH was maintaining about 11.4 by adding a solution of acid or alkali. When reaching values < 50 mg/l of COD, the ozonization was stopped.
The lead nitrate solution was poured into receiving tank (item 70/1) in doses of 50 l, stirred using a pump for 10 - 15 minutes in the circuit: (item70/1and the eductor pump, E1). The sediment formed during the ozonization and the introduction of the lead nitrate were filtered, so that the filtrate after the pre-filters (items71/1,3) enter receiving tank 70/2. After the completion of filtration of the tank 70/2 the calculated amount of cobalt nitrate solution was added. Ozonized the solution in the circuit: tank 70/2 – educator pump E2 to reduce the specific activity of cobalt-60 in the filtrate sample less than 410 Bq/kg. The resulting solution was filtered through the pre-filters 71/2, 4 into the filtrate tanks (items 72/1 or 72/2). The filtrate was passed sequentially through two sorbent filters - containers filled with ferrocyanide sorbent. The specific activity of the resulting solution was, 12 Bq/kg ^{137}Cs and 33 Bq/kg ^{60}Co. Thus, the experimental confirmed the correctness of the chosen treatment.

CONCLUSIONS

1. Studies on decontamination of ^{60}Co from the problematic EC at the Kola NPP were carried out on simulated and real EC in different modes.
2. A new processing mode for problematic EC was proposed and successfully tested on the industrial plant at the Kola NPP which allows the EC decontamination of ^{60}Co to values lower than the required <410 Bq/kg.

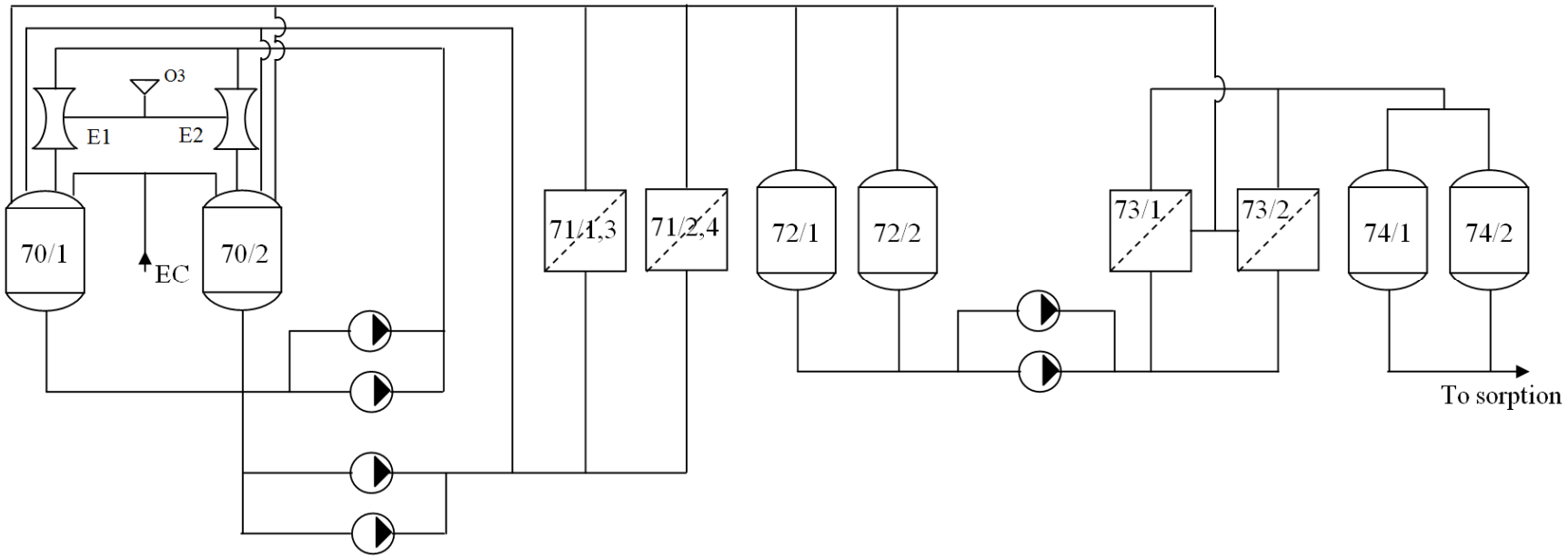

Figure 1. Schematic diagram of the EC treatment at the Kola NPP

70/1,2 – receiving tank; 71/1,2,3,4 – pre-filter, 72/1,2 – filtrate tank; 73/1,2 – membrane filter; 74/1,2 – permeate tank; E1,2 – educctors