Test Treatment of Fulfilled TBP - 12084

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ABSTRACT

At SUE SIA "Radon" were carried out investigations and treatment of spent TBP, containing uranium with the help of the following methods:

- Impregnation of porous inorganic materials by spent TBP with the subsequent inclusion into the cement compound;
- Spent TBP cementation together with other LRW (inclusion of spent TBP into cement compound was 2%);
- inclusion of TBP into polymeric binder Nochar, Nochar, Pacific Nuclear Solutions, Indianapolis, USA;
- Impregnation of industrial porous materials with the subsequent treatment at plasma incineration facility at temperature up to 1600 ˚C. In such case takes place pyrolysis process and afterburning of organic content of spent extractant, as well as melting of its mineral content together with porous material. As a result slag incorporating radionuclides and phosphorus compounds is formed. The slag has a high chemical stability. With the help of the first method has been received cement compound with the inclusion of 20 weight % of spent TBP and during the pilot treatment about 1 m^3 of TBP has been solidified. Together with other LRW over then 10 m^3 of TBP has been solidified at the stationary cementation facility. Spent TBP inclusion into the polymeric binding material Nochar (N) has been carried out under laboratory conditions with a mass ratio TBP / Nochar from 1 / 1 till 20 / 1. At the plasma incineration facility has been processed about 1 m^3 of spent TBP. Comparative evaluation for the suggested methods of spent TBP treatment has been made.

INTRODUCTION

At the present time at NPPs and radiochemical sites has been accumulated a large amount of liquid radioactive waste (LRW) posing serious danger to the environment. Among them there are spent extractants, solvents and industrial oils. Besides there have been accumulated large amounts of spent extractants, among which TBP is the main one, at uranium producing plants. Now at SIA " Radon " are stored about 20 m^3 of spent TBP, containing uranium of 20 - 60 g/l (specific activity n E+5 Bq/l) , that demands the decision of the problem in the shortest terms.

There are no special facilities for spent TBP treatment in Russia. Possible technologies for such waste treatment, some of which have found the limited application abroad, are:

- Inclusion into matrix material (polymeric, cement).
- Thermal treatment (pyrolysis, incineration and so on).

At SUE SIA "Radon" were carried out investigations and pilot treatment of containing uranium TBP with the help of the following methods:

- Impregnation of porous inorganic material by spent TBP with the subsequent inclusion into the cement compound;

- TBP cementation together with other LRW (inclusion of spent TBP into cement compound was 2%);
- TBP inclusion into polymeric binder Nochar, Nochar, Pacific Nuclear Solutions, Indianapolis, USA;
- Impregnation of industrial porous materials with the subsequent treatment at plasma incineration facility at temperature less than 1600 ˚C. In such case takes place pyrolysis process and afterburning of organic content of spent extractant, as well as melting of its mineral content together with porous material. As a result slag incorporating radionuclides and phosphorus compounds is formed. The slag has a high chemical stability.

FACILITIES AND METHODS DESCRIPTION

At the first stage was determined absorbability of spent TBP by different porous materials under laboratory conditions. The porous material was poured out by excess TBP and kept for definite time. Absorption process ending was determined by the finish of air bubbling (ousting from sorbents pores). After that the excess of TBP was removed and calculated absorbability of the material by adsorbent mass change.

Conditioning of the adsorbents impregnated with TBP were carried out by impregnation or spill with cement solution under laboratory conditions. For cement solution spill these adsorbents were placed into cylinders 30 cm high and then cement solution was poured by portions into cylinders with their periodic vibration. For impregnation method cement solution was pumping through a glass pipe to a bottom of the cylinder filled with adsorbent with the help of peristaltic pump. After the conditioning process parameters selection the absorbents impregnated with TBP were treated at the cementation facility (fig. 1). Cement solution was prepared at mixer CM where preliminary cement and LRW had been measured out. Prepared solution was pumped into the container by the peristaltic pump equipped with devices for impregnation. Preliminary adsorbents were placed into the container and impregnated with TBP with the help of a batcher-pump.

Cementation of TBP together with other LRW was carried out at the cementation facility either. For that LRW, TBP and cement were measured out into the mixer and intermixed. The received cement solution was used for conditioning of SRW which had been preliminary placed into the container.

TBP solidification with the help of polymeric binder Nochar was carried out in 200 ml chemical glass. TBP with polymeric binder were mixed manually.

For a significant volume reduction porous material was impregnated with TBP with the following treatment at the plasma incineration facility “Pluton” (fig.2). The porous material impregnated with TBP was packed up into kraft-paper bags and loaded into the furnace together with other SRW.

RESULTS AND DISCUSSION

It is a commonly known fact that organic LRW inclusion into hydraulic binding agents is limited.. As a rule the inclusion rate does not exceed 5%. Impregnation of porous adsorbents with organic LRW and their subsequent inclusion into matrix material is one of the possible ways of inclusion rate increase. Industrial adsorbents which meet the following requirements were used as materials for preliminary impregnation by TBP:

- TBP absorbability (more than 0,5 g of TBP / 1 g of adsorbent);
- Compatibility with cement solution;
- Melting temperature less than 1500 ^{0}C
- Low cost.

Also as a porous material was used haydite which had been received by Radon as SRW.

Radionuclide composition of TBP and haydite are presented in Table I and results of TBP absorbability for different materials are presented in Table II.

Table I. Radionuclide composition of spent TBP and the haydite

	Σβ	Σ α	Th^{232}	Ra^{226}	U^{238}	U^{235}
Haydite	8.3 E+3	4.4 E+4	7.1 E+1	9.3 E+2	-	-
spent TBP	1,39·E+5	5,0·E+4	3.7 E+2	6.6 E+1	2,4·E+5	1,1·E+4

Table II. Mass absorbability of TBP by different adsorbents

Material type	TBP absorbability per 1 g of adsorbent
Mineral adsorbent S-VERAD	3,14
Akvaionite with mineral substances content 50 mass%	0,80
Akvaionite with mineral substances content 95 mass%	0,73
Pulverulent ion exchange	0,70
Diatomite-1	1,65
Haydite	0.65
Foamglass	1,26

As shown in the table some of the materials have quite high TBP absorbability including the haydite which should also be conditioned.

Impregnated with TBP adsorbents can be included into matrix material by the following ways [1, 2]:

- At different types of mixers;
- At a container equipped with a stirring rod
- At a container by high penetrating matrix material

As the last way is the simplest it has been chosen as a basic one. Two variants of its implementation under laboratory conditions have been tested. The first variant consists in the following: inorganic binding material is supplied to the top of impregnated with TBP adsorbent layer placed into the cylinder . The second one consists in binding material supply by peristaltic pump through a pipe disposed in the middle of the cylinder to the bottom-most part. As binding materials Portland cement and fine powder Portland cement with special additives were used. Water-to-cement ratio was changed in the range from 0,5 to 0,8 and a height of impregnated with TBP adsorbent layer was changed in the range from 5 to 30 cm. An even filling of the whole cylinder volume (H= 30 cm) by the cement solution was the main criterion of receiving conditioned final product. The process of cylinder filling with cement solution was inspected visually because a glass cylinders which have been used for tests completing. The results are presented in a table III.

Table III. The results of conditioning by cement solution

The way of cementation	Adsorbent	Cement type	Water to cement ratio (W/C)	Presence of vibration	Impregnation height, cm	Dehydration	Proposal for further use
Spill	S-VERAD	PC	0,6	+	7	-	cannot be used
Spill	S-VERAD	PC	0,8	+	10	-	cannot be used
Spill	H	PC	0,6	-	5	-	cannot be used
Spill	H	PC	0,6	+	18	-	cannot be used
Spill	H	PC	0,8	-	15	-	cannot be used
Spill	H	PC	0,8	+	30	10	can be used
Impregnation	H	FPC	0,6	-	30	2	can be used
Impregnation	H	FPC	0,8	-	30	8	can be used
Impregnation	H	PC	0,8	-	30	30	cannot be used

H – haydite
PC – Portland cement
FPC – fine powder cement

As indicated in the table above inclusion of impregnated with TBP adsorbent into cement matrix is possible then as an adsorbent haydite1 is used. Besides spill method can be realized only with vibration and high W/C ratio (0,8). Impregnation method can be realized then fine powder cement and W/C ratio in the range from 0,6 to 0,8 are used. In cases then Portland cement was used high dehydration was observed.

Since the impregnation rate had been specified the process of haydite impregnated with TBP conditioning was carried out at the cementation facility (fig.1) in two containers (V = 2,7 m^3). For the impregnation process was used cement solution based on fine powder cement and

W/C ratio 0,6. Both containers contents were successfully conditioned. Mass inclusion of TBP into cement compound was 21%. Cement compound strength exceeded 8 MPa in 28 days.

Together with other LRW over 12 m^3 of TBP have been processed at the cementation facility. The obtained cement solution based on TBP was used for large-dimensioned SRW conditioning. Although only 2 mass % of TBP have been included into cement compound three types of RW were conditioned in one container – SRW, LRW and organic LRW (spent TBP) therefore this technology can be used.

Inclusion of TBP into polymeric binding material despite their high cost is attractive because of the possibility of high filling level with TBP. For the experiments binding material Nochar (N) has been used. Ratio of N/TBP was in the range from 1:1 to 1:20. At ratios from 1:1 to 1:4 TBP was poured into glass containing Nochar material with subsequent manual mixing whereas at ratios from 1:6 to 1:20 Nochar was poured into glass with TBP. At small ratios the final product volume depended on mixing intensity and greatly exceeded Nochar volume. The product structure in this case was not monolithic. At high ratios final product structure was monolithic and the final volume was almost equal to initial TBP volume. At a ratio N/TBP from 1:6 – 1:8 the final product did not change its form during glass inclination for 90˚ for one day. At a ratio of more than 1:10 the final product changed its form. At present time experiments of final product properties investigation are being carried out (leashing rate of radionuclides, mineral oils etc.).

Thermal treatment of organic LRW allows to reduce the volume sufficiently although in this case occurs the problems with radionuclides carrying over to gas flow, equipment corrosion and gas purification system operation. . In order to reduce the abovementioned problems thermal treatment has been divided into two stages – the first one was preliminary adsorbent impregnation with TBP, the second thermal treatment at a temperature 1500˚C.

In the beginning impregnated with TBP adsorbents were heated at a muffle furnace at a temperature of 1500˚C for two hours and soaking for half an hour at 1500˚C. As adsorbents for this method implementation were used:

- Market foam concrete based on Portland cement (ρ=400 kg/m^3)
- S-VERAD
- Foam concrete blocks of diatomaceous clay
- Haydite contaminated with uranium

The results of the experiments which were carried out under laboratory conditions have shown that at a temperature 1500 ˚C forms a slag there remain over 99% of Uranium and over 90% of phosphorus compounds. The melt viscosity with the use of some types of adsorbents was not enough for melt pouring from the melting zone into containers therefore additional charging was selected for impregnated with TBP sorbent which mass % did not exceed 30. Subsequent to the results of laboratory experiments for pilot treatment at "Pluton" facility [3] have been chosen the following adsorbents:

- Market foam concrete blocks with dimensions of 20x20x20 cm
- S-VERAD adsorbent with additional charging of granules 0,2-1 mm
- Foam concrete blocks of diatomaceous clay with dimensions 20x10x5 cm
- Granulated form Haydite (4-5mm)

Preliminary impregnated with TBP adsorbent at kraft sacks were loaded into the furnace (fig.2) by terms with other SRW. The results of foam concrete blocks of diatomaceous clay impregnated with TBP treatment presented in Table IV. Altogether at "Pluton" facility have been treated about 1 m^3 of spent TBP.

Table IV. Spent TBP treatment at "Pluton" facility

	Packages	kg	%	m^3
The total amount of treated RW	546	2750,65		27,3
Among them				
combustible:	382	1357,25	49,3	19,1
Wood	31	129,1		1,55
Ventilation filter	252	794,35		12,6
Paper, pasteboard	61	298,1		3,05
Rags, overalls, garbage	27	87		1,35
Rubber	1	10,6		0,05
Plastics	10	38,4		0,5
Incombustible:	108	972,2	35,3	5,4
Glass wool	35	132,3		1,75
Construction waste	17	163,4		0,85
Metal components	3	8,4		0,15
Silt	23	430,5		1,15
Reagents	1	7,3		0,05
Glass	2	7,4		0,1
Foodstuff (berries)	28	225		1,4
TBP, foam concrete blocks, fluxing additions	56	421,2	15,3	2,8

Consequently spent TBP can be processed by the following methods:

- Impregnation of inorganic adsorbent with TBP with the subsequent inclusion into cement matrix
- Inclusion into cement compound together with other LRW
- Inclusion into polymeric binding material
- Impregnation of inorganic adsorbent with the following thermal treatment.

Comparative evaluation for abovementioned ways of treatment for 1 m^3 of TBP solution and 1 m^3 of haydite is presented in Table V.

As the Table shows the cheapest way of treatment is thermal treatment because of the low materials cost although operating costs in this case are the highest.

Table V. Comparative evaluation for suggested methods of treatment for 1 m^3 of haydite (H) and 1 m^3 of TBP.

Conditioning method	Basic technological parameters	Amount of materials for 1m^3 H+1m^3TBP	Cost of materials for 1m^3 K+1m^3TBP, Rub.
Haydite is disposed at the container, TBP cementation together with other LRW	2 w/w % TBP at cement compound (CC)	Protective metallic container (PMC) - 8,47 pcs. Cement -24.5 ton	873426,4 94325 Total: 967751,4

Haydite impregnated with TBP is included into cement matrix	0.45 g TBP/ g of H W/C=0.8	PMC-1,13 pcs. Cement -0,4 ton	116525,6 1540 Total: 118065,6
Haydite is disposed at the container, TBP is solidificated by polymeric binding material (PBM)	PBM/TBP=1:8 by weight	PMC - 0,75 pcs PBM - 102,4 kg	77340 102400 Total: 179740
Haydite impregnated with TBP is solidificated at 1500˚C	0.56 g TBP/ g of H, K_v = 5 T-1500^{0}C	PMC – 0,19 pcs.	19592,8

CONCLUSIONS

1. Have been proposed and carried out several ways of spent TBP treatment under laboratory conditions:

- Impregnation of inorganic adsorbent with TBP with the subsequent inclusion into cement matrix
- Inclusion into cement compound together with other LRW
- Inclusion into polymeric binding material
- Impregnation of inorganic adsorbent with the following thermal treatment

2. Over 15 m^3 of spent TBP solution contaminated with U - 235 and U - 238 have been processed at the abovementioned facilities

3. Comparative evaluation of materials cost for the suggested methods of spent TBP solution treatment has been made.

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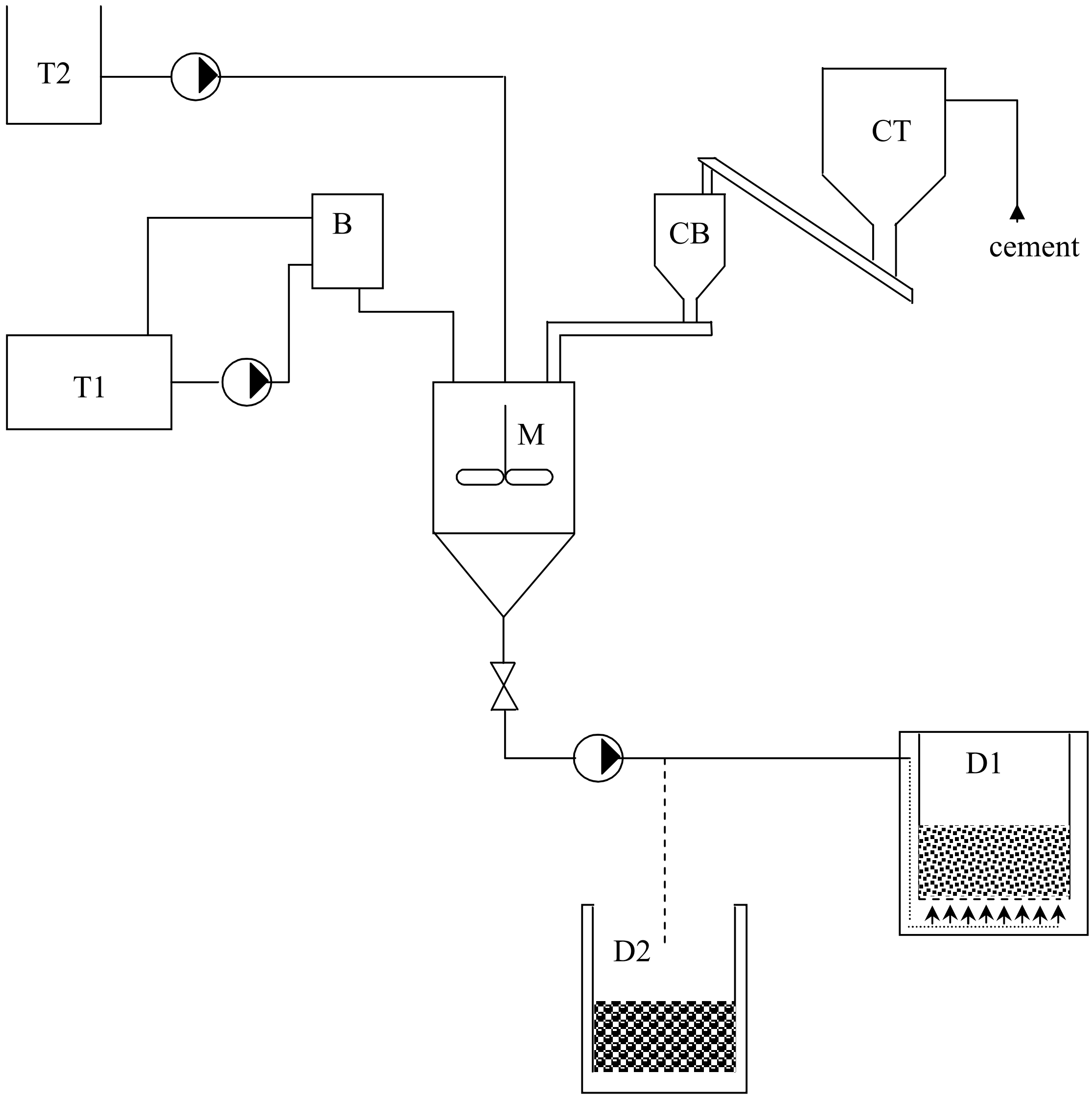

Fig. 1. Basic diagram of cementation facility

T1 – LRW tank; T2 – TBP tank, B – batcher for LRW; M – mixer; CB – cement batcher; CT – cement tank; D1 – container for impregnation, D2 – container for spill with cement solution

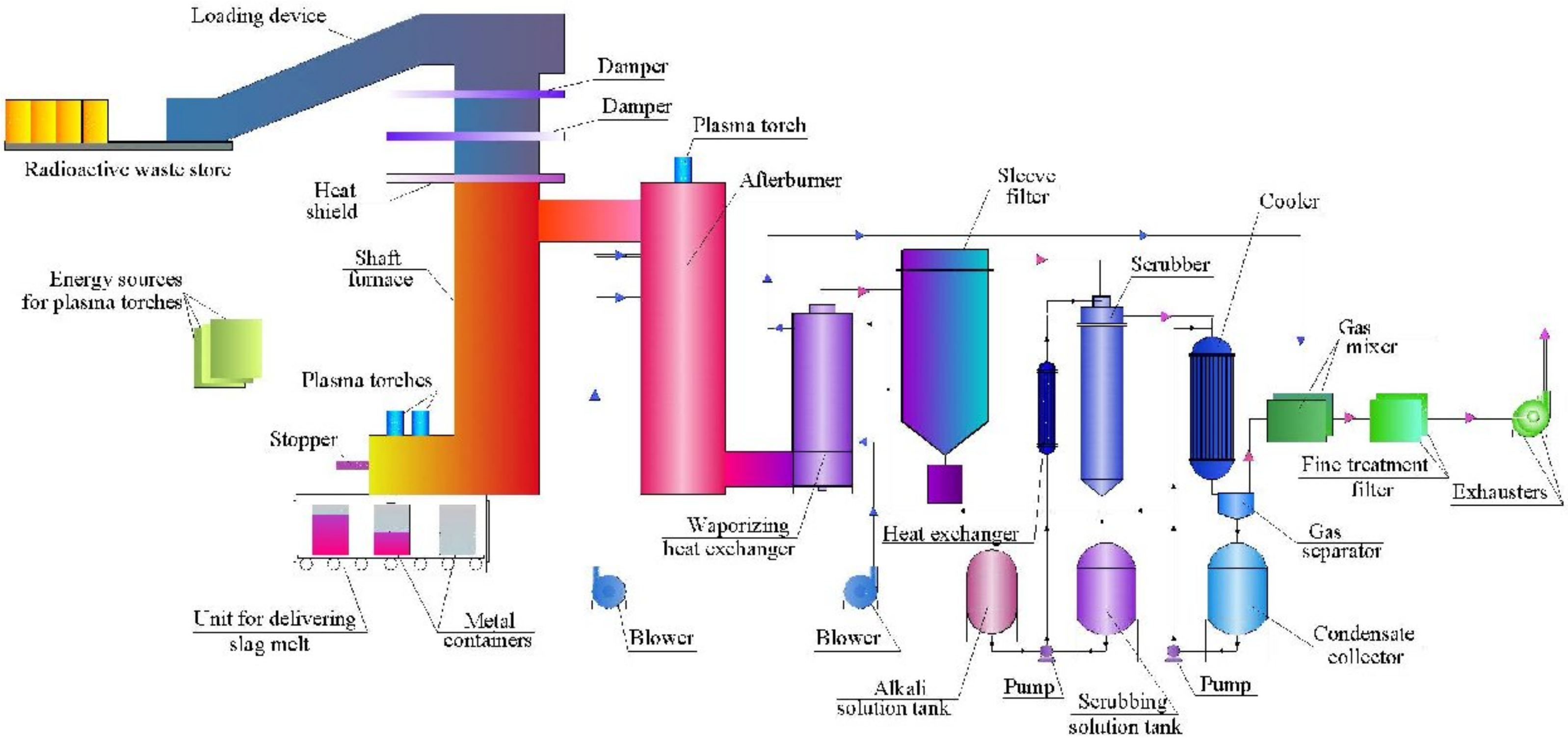

Fig 2. Basic diagram of “Pluton” plasma facility.