NPP Liquid Radioactive Waste Treatment with Selective Extraction of Radionuclides - 11272

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ABSTRACT

Several experiments to treat the major types of LRW from NPPs have been conducted. Ion-selective sorption for all kinds of radionuclides has been developed for purification of evaporator concentrates. The technology includes ozonization, filtration and selective sorption of Cs radionuclides. Ion-selective sorption technology has been tested in the laboratory and pilot plants and implemented on an industrial-scale at Kola NPP. Several methods, including dissolution with subsequent selective extraction of radionuclides, have been tested for the treatment of salt residue. Peroxide dissolution with subsequent ozonization and selective extraction of radionuclides has been proposed for treatment of ion-exchange resins. The technology of cotreatment for evaporator concentrates, salt residue and ion-exchange resins has been developed from the results of the work carried out.

The main liquid radioactive waste (LRW) generated during NPP operation are the following:

- evaporator concentrates;
- salt residue;
- spent media , mainly ion exchange resins.

The salt residue is a product, resulting from drying of evaporator concentrates, but it is not a conditioned product, therefore it was intentionally classified as LRW [1].

The comparative characteristics of treatment techniques for NPP evaporator concentrates are given in Table 1.

Table 1. Comparison of various evaporator concentrates treatment methods

№	Method of treatment	Volume reduction factor	Final product quality	Site of application
1.	Cementation	0.6-1.3	Satisfactory	Volgodonsk NPP
2.	Bituminization	1.5-2.5	Good	Leningrad NPP, Kalinin NPP
3.	Deep evaporation	2-3	Low	Novovoronezsh NPP
4.	Vitrification	3-4	High	SIA "Radon", Moscow
5.	Selective sorption	100	High	Lovisa, Finland

Selective sorption in terms of volume reduction factor has indisputable advantage in comparison with other methods. However, at the Lovisa NPP the evaporator concentrates are cleaned of caesium radionuclides only [2]. For the evaporator concentrates (EC) cleaning of all the radionuclides (Cs, Co, Mn and others) specialists from Moscow SIA "Radon" together with a number of organizations have developed the technology of ion selective sorption [3]. The essence of the technology consists of the following. The EC before selective sorption treatment are subjected to preliminary treatment which includes two stages: ozonization and separation of sediment.

The aim of pretreatment is:
- destruction of organic complexes, chelating Co, Mn and other radionuclides;
- destruction of organic substances that poison selective sorbents;
- removal of a formed residue collecting the major part (>99%) of Co, Mn and other radionuclides.

After preliminary handling the solution is directed to the inorganic sorbents, loaded in filter-containers, for selective cesium removal. The filtrate obtained is solidified and stored as nonradioactive waste product. A block diagram of this process is shown in Figure 1.
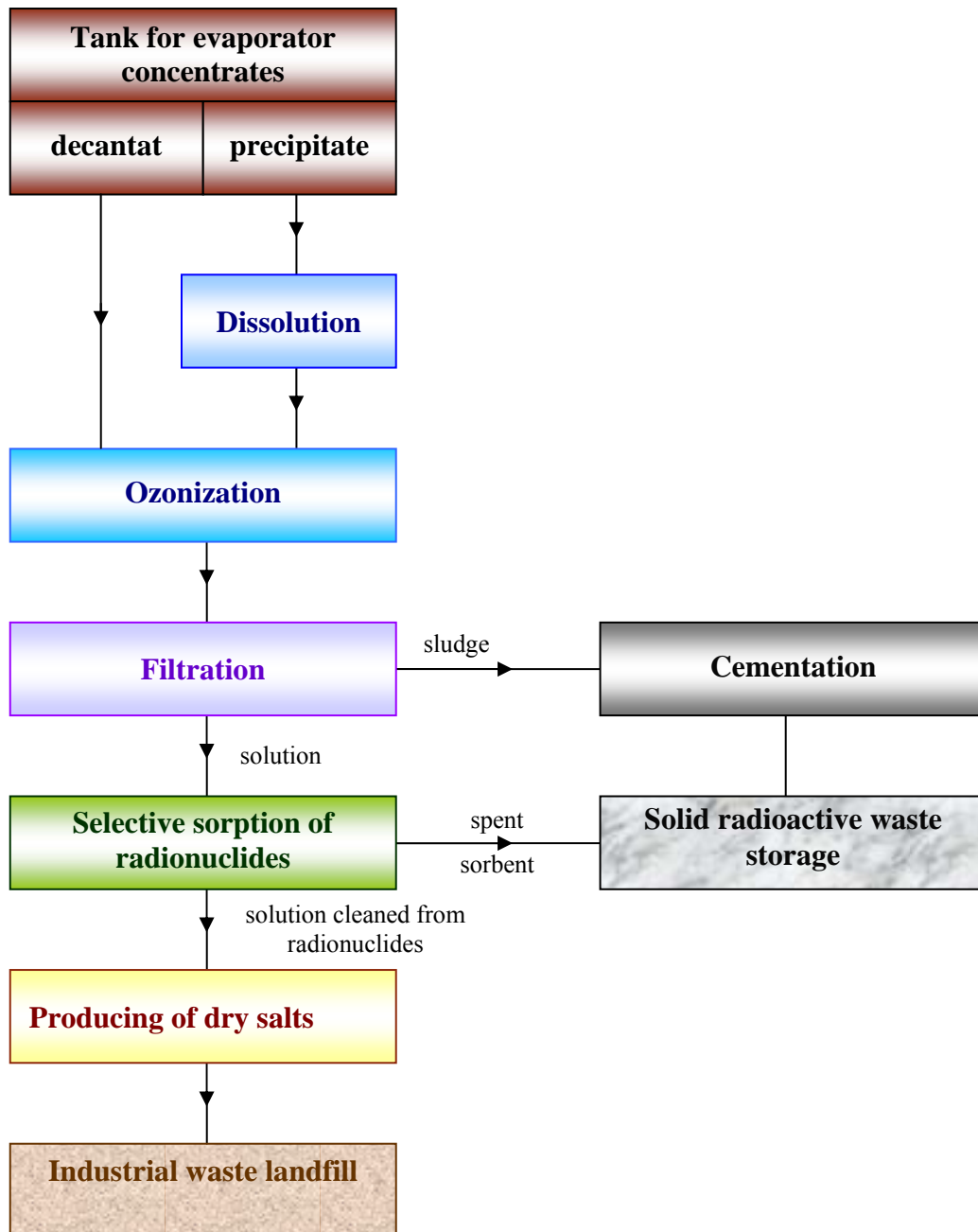
Fig. 1. Block diagram of the NPP evaporator concentrates treatment

This treatment method has been tested under laboratory conditions at various NPPs: Kalinin, BN-350, Novoronezsh, Leningrad, Kola and Kursk. The main "long-lived" radionuclides contained in the evaporator concentrates are $Cs^{137,134}$, Co^{60} and Mn^{54}. The experiments determined that the radionuclides are present in the evaporator concentrates are found not only in the ionic form, but also in the form of various complexes inactive to sorption. This is particularly true for Co^{60} and Mn^{54} radionuclides because various organic substances, such as EDTA, oxalic acid and others are present in the evaporator concentrates.

To transform radionuclides to the ionic form the evaporator concentrates were subjected to oxidation by introducing various oxidizing reagents, the most effective of which proved to be ozone. During ozonization the following processes were carried out: oxidation of the organic substances, destruction of the complexes connecting Co and Mn radionuclides as well as formation of a precipitate of oxides and hydroxides of transition metals present in the initial evaporator concentrate. It was observed that the residue co-precipitated Co and Mn radionuclides and at BN-350 – Sr^{90} and Alfa-nuclides also. Preliminary oxidation has allowed not only the removal of the specified radionuclides, but also a significant increase in efficiency of the subsequent selective sorption of Cs by ferrocyanide owing to elimination of the poisoning effect of organic substances.

Afterwards, this technology was tested on a bench scale at Kola NPP and NB-350, as well as on a pilot plant at the FEI, Obninsk (see tables 2 and 3).

Table 2. Bench test results of the NPP evaporator concentrates radionuclides treatment (bench test capacity < 10 l/hour).

Site of tests	Specific activity of initial solution, Ci/l	Salt content, g/l	Specific activity of solution, Ci/l	
			After ozonization and filtration	After sorption
Kola NPP	$Cs^{137} - 2,1E-3$	520	$Cs^{137} - 2,0E-3$	$Cs^{137} - <1E-9$
	$Cs^{134} - 4,8E-4$		$Cs^{134} - 4,8E-4$	$Cs^{134} - <1E-10$
	$Co^{60} - 4,0E-5$		$Co^{60} - <1E-9$	$Co^{60} - <1E-9$
	$Mn^{54} - 2,0E-6$		$Mn^{54} - <1E-10$	$Mn^{54} - <1E-10$
MAEK, Actau	$Cs^{137} - 3,5E-3$	70,5	$Cs^{137} - 3,5E-3$	$Cs^{137} - 1,0E-9 \div 1,0E-10$
	$Co^{60} - 1,5E-6$		$Co^{60} - <1,0E-9$	$Co^{60} - <1,0E-10$
	$Sr^{90} - 2,0E-7$		$Sr^{90} - <1,0E-10$	$Sr^{90} - <1,0E-10$
	$\Sigma\alpha - 3,8E-7$		$\Sigma\alpha - <1,0E-10$	$\Sigma\alpha - <1,03E-10$
МАЭК, Actau	$Cs^{137} - 7,4E-3$	502	$Cs^{137} - 7,4E-3$	$Cs^{137} - 1,0E-9 \div 1,0E-10$
	$Co^{60} - 1,8E-6$		$Co^{60} - <1,0E-9$	$Co^{60} - <1,0E-10$
	$Sr^{90} - 1,3E-7$		$Sr^{90} - <1,0E-10$	$Sr^{90} - <1,0E-10$
	$\Sigma\alpha - 1,8E-7$		$\Sigma\alpha - <1,0E-10$	$\Sigma\alpha - <1,0E-10$

Table 3. Pilot plant test results of the evaporator concentrates (EC) radionuclide treatment
at the FEI, Obninsk
(pilot plant capacity 100 l/hour)

Type of LRW	Specific activity of initial solution, Ci/l	Salt content, g/l	Specific activity of initial solution, Ci/l	
			After ozonization and filtration	After sorption
EC from Kola NPP	$Cs^{137} - 9.1*E-5$	320	$Cs^{137} - 9.1*E-5$	$Cs^{137} - <1E-9$
	$Co^{60} - 3.7*E-7$		$Co^{60} - <1,0E-9$	$Co^{60} - <1E-9$
	$Mn^{54} - 3.1*E-7$		$Mn^{54} - <1,0E-9$	$Mn^{54} - <1E-10$
EC from Kalinin NPP	$Cs^{137} - 9.6*E-5$	150	$Cs^{137} - 9.6*E-5$	$Cs^{137} - <1*E-9$
	$Cs^{134} - 4.2*E-5$		$Cs^{134} - 4.2*E-5$	$Cs^{137} - <1*E-9$
	$Co^{60} - 1.1*E-5$		$Co^{60} - 1.5*E-9$	$Co^{60} - 1.1*E-9$
	$Mn^{54} - 5.9*E-6$		$Mn^{54} - <1*E-9$	$Mn^{54} - <1*E-9$

Bench and pilot plant tests have revealed that some process stages needed to be improved. In particular ozonization, to increase process efficiency:

1. Tests of various types of injectors and nozzles for LRW ozonization were carried out.

The most effective types of injector and nozzle creating the large mass exchange surface were chosen.

2. Tests on effect of an injector position relatively to tank containing LRW to be oxidized were carried out. It was found that for effective mass exchange the pipe between the injector and the tank with LRW should not have horizontal runs. On industrial-scale plant the individual injector should be installed on each tank.

3. Height of the injector above the tank may be varied from 0.2 up to 3 m. Optimum internal diameter of the pipe after the injector was determined. The depth of the pipe below the liquid level in the ozonization tank should be approximately 1 m.

4. In order to prevent foam carry-over while decantating during ozonization, it is necessary to introduce a defoaming agent at the start. The approximate defoaming agent consumption is 10 g/m^3 of decantate.

In terms of the filtration stage:

Since the residue formed during ozonization of the evaporator concentrates has poly-disperse structure, it was proposed to separate the residue in two stages. As a coarse filter the following filters were tested:

- bulk filters;
- bag filter with various filter materials;

As a fine filter the following filters were tested:

- various designs of devices with TRUMEN type membranes (flat frame-type, disk-shaped with rotating mixer, with rotating dics of the Zolushka type);
- ceramic filters.

According to the test results for the industrial -scale plant, the course filter we selected for use is a bag filter with a filtering material made of stainless steel mesh with pore diameter 5-10 microns in two layers. The fine filter selected for use is a ceramic filter with pore diameter 0.1 microns.

In terms of a selective sorption stage:

Taking into account high cost of filter-containers the use of a sorbent in them should be the most effective. To solve this problem various circuits of connection of filters filled with Termoxid-35 sorbent were tested.

Circuit I:

Filter connection is serial;

Quantity of filters – 2

Characteristic of a sorbent – there is a fresh sorbent in both filters.

Circuit II:

Filters connection is serial;

Quantity of filters – 2

Characteristic of a sorbent:

In the first filter there is a sorbent previously used in the second filter during testing the circuit I until the filtrate specific activity after the second filter exceeded 110 Bq/l for Cs^{137}.

In the second filter there is a fresh sorbent.

Circuit III:

Filter connection is parallel-serial;

In the first position there are two course filters connected in parallel. In the second position there is one filter. And connection of the filter in position 2 is carried out when a filtrate specific activity after the first set of filters reaches the value of 110 Bq/l for Cs^{137}. This will eliminate the temporary poisoning effect on sorbent in filter 2.

Application of connection circuits I and III assumes use of the sorbent filter in a position 2 without biological protection. Specific activity of the spent sorbent from this filter has to be at the level making it possible to remove spent sorbent by hydro-unloading. The cost of such filter will depend on cost of a sorbent that will reduced operating expenses significantly.

During tests under laboratory conditions on the oxidized evaporator concentrates from Kalinin NPP the amount of sorbent to limit effluent to 110 Bq/l for Cs^{137}, in column volumes (calculated per volume of the first column or some first columns):

under circuit I: 978-1088 (average value 1033);

under circuit II: 260-530 (average value 395);

under circuit III: 1339-1398 (average value 1369).

All the technological and technical approaches except for optimization of sorption stage have been realized at Kola NPP on industrial -scale plant for the evaporator concentrates treatment. To date, about 1000 tons of non-radioactive salts have been produced. A radioactive waste reduction factor of 80 has been achieved..

As already noted, salt residue produced during deep evaporation of the NPP evaporator concentrates is an unconditioned product. Its storage at NPP sites represents a serious threat for the environment. Laboratory experiments on treatment the evaporation residue from Novovoronezsh NPP were carried out. Composition of the salt residue is represented in Tables 4, 5.

Table 4. Chemical composition of the salt residue, mass. %

Na^+	K^+	Ca^{2+}	Fe^{2+}	Al^{3+}	NO_3^-	CO_3^-	Cl^-	BO_3^-	SiO_2
12 - 20	1 - 4	3 - 5	< 1	< 1	18 - 23	10 - 15	< 1	25 - 33	1 - 5

Table 5. Radionuclides composition of the salt residue, Bq/кg

$\Sigma \beta$ по ^{137}Cs	$\Sigma \beta$ по $^{90}Sr+^{90}Y$	$\Sigma \beta$ по Y^{90} $E\beta > 1,0$ МЭВ	$\Sigma \alpha$ по Pu^{239}	Cs^{137}	Cs^{134}	Co^{60}
$7,5\bullet10^6$	$4,3\bullet10^6$	$4,2\bullet10^4$	$<1,5$	$6,7\bullet10^6$	$6,6\bullet10^3$	$2,9\bullet10^3$

At SIA "Radon" Moscow three options for the NPP salt evaporation residue treatment were proposed and tested.

1-st way consists of salt residue dissolution and then its treatment, including oxidation, separation of the sediment obtained and selective treatment on ferrocyanide sorbents.

2-nd way consists of fusion of the salt residue, addition of glassforming additives and melting of borosilicate glass in a melter such as a "cold crucible".

3-rd way consists of dissolving the salt residue, oxidation of the solution obtained, removal of radionuclides by collectors and the separate handling of formed deposit and the solution. The deposits containing more than 99 % of the activity are directed to vitrification, and the solution is directed either to a concentrates dryer or to cementation.

All three options have been tested. The highest radwaste volume reduction factors can be achieved in 1 of 3 ways.

For treatment of spent ion exchange resins (IER) it is known [4]:

- immobilization into various matrixes;
- thermal methods;
- dissolution under various conditions by using oxidizers.

IER dissolution in hydrogen peroxide at an elevated temperature was tested. It was found that oxidation was not complete, therefore additional oxidation of the resulting solution by ozone was proposed. A block diagram of this process is shown in Fig.2.
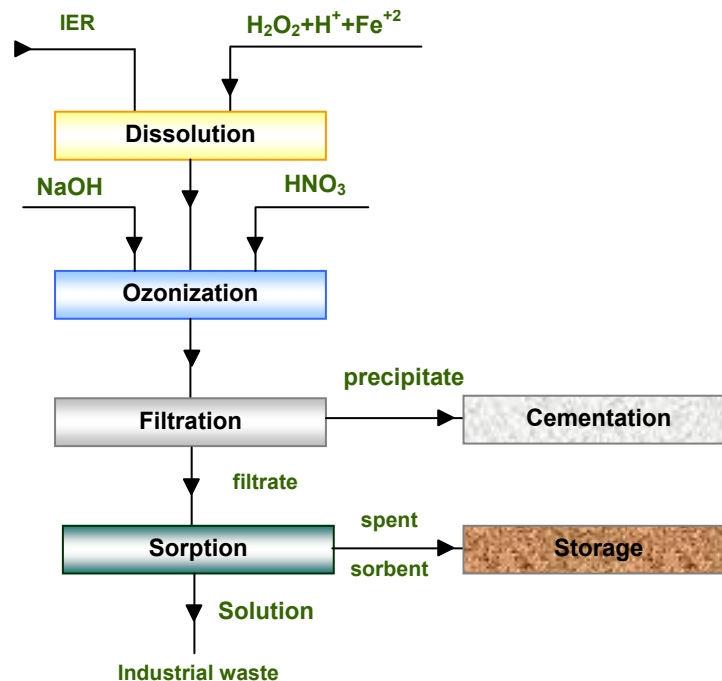
Fig. 2. Block diagram of spent IER treatment.

Laboratory experiments were carried out on real IER from Kursk NPP representing a mixture of ion exchangers KU-2 and AV-17 and having a specific activity in Bq/kg for: Cs^{137} – 1.7E+7, Co^{60} –1.0 E+7.

Bench tests were carried out on ion exchange resins from "Radon". The resin specific activity in , Bq/kg was: Cs^{137} – 2.3 E+5, Co^{60}- 2.0 E+3 and evaporator concentrates from Kalinin NPP, in Bq/kg was: Cs^{137}- 1.7 E+7, Co^{60} – 2.0 E+5. The IER were processed on a bench scale both separately and together with the evaporator concentrates.

Bench tests consisted of 4 units for:

- dissolution of IER;
- ozonization;
- filtration;
- sorption.

In the course of the experiments it was found that combined treatment of IER and EC on a bench scale using methods mentioned above would result in radwaste volume reduction of more than 50 times. The resulting solution from treatment was a non-radioactive waste.

The experiments carried out on different scales enabled the development of a treatment circuit (see Fig. 3) for processing LRW accumulated at NPPs (PWR reactors). This treatment circuit is also able to process secondary wastes generated from solid radwaste (SRW) incineration (spent scrubber solution from a gas purification system) and spent decontamination solutions.
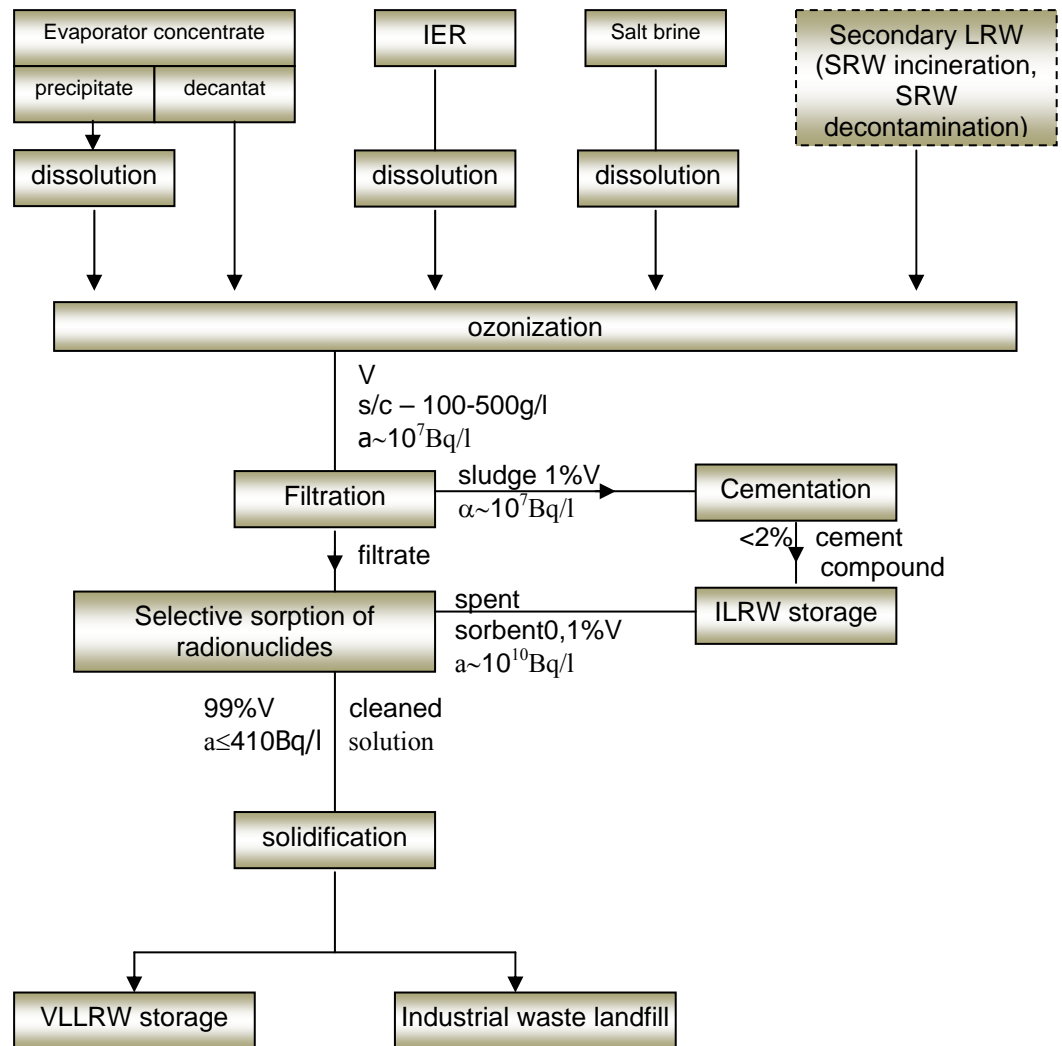
Evaporator concentrate
precipitate	decantat

IER

Salt brine

Secondary LRW (SRW incineration, SRW decontamination)

dissolution

dissolution

dissolution

ozonization

V
s/c – 100-500g/l
$a\sim10^7$Bq/l

Filtration

sludge 1%V
$\alpha\sim10^7$Bq/l

Cementation

<2% cement compound

filtrate

Selective sorption of radionuclides

spent sorbent0,1%V
$a\sim10^{10}$Bq/l

ILRW storage

99%V
$a\leq410$Bq/l

cleaned solution

solidification

VLLRW storage

Industrial waste landfill

Fig. 3. Block diagram of LRW treatment from NPP (PWR)

Conclusions

1.   Selective removal of radionuclides can be used for treatment of both homogeneous and heterogeneous low and intermediate level radwaste .

2.   Application of selective removal of radionuclides in LRW treatment allows:

•   reduced volumes of conditioned radwaste to be directed to storage facilities;

•   the vast majority of the solidified product to be categorized as non- radioactive waste or very low level radwaste (VLLRW), which greatly reduces the cost of subsequent storage and overall waste management costs.

References

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