

Processing of Spent Ion Exchange Resins in a Rotary Calciner - 12212

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ABSTRACT

Processing Russian nuclear ion exchange resin KU-2 using a "Rotary calciner was conducted. The resulting product is a dry free flowing powder (moisture content 3 wt.%, Angle of repose of $\approx 20^\circ$). Compared with the original exchange resin the volume of the final product is about 3 times less. . Rotary calciner product can be stored in metal drums or in special reinforced concrete cubicles.

After thermal treatment in a rotary calciner, the spent resin product can be solidified in cement yielding the following attributes:

- The cemented waste is only a 35% increase over the volume of powder product ;
- The volume of cement calciner product is almost 9 times less (8.7) than the volume of cement solidified resin ;
- The mechanical strength of cemented calciner product meets the radioactive waste regulations in Russia.

INTRODUCTION

Up to now Russian NPPs store a considerable amount of spent ion exchange resin (IER) in containers. The low radiation resistance of spent ion exchange resins and influence of biochemical decomposition do not support this practice for long-term safe storage.

Therefore compulsory conditioning of IER is needed for safe storage. The most common methods of spent radioactive IER conditioning on an industrial scale are cementation and bituminization.

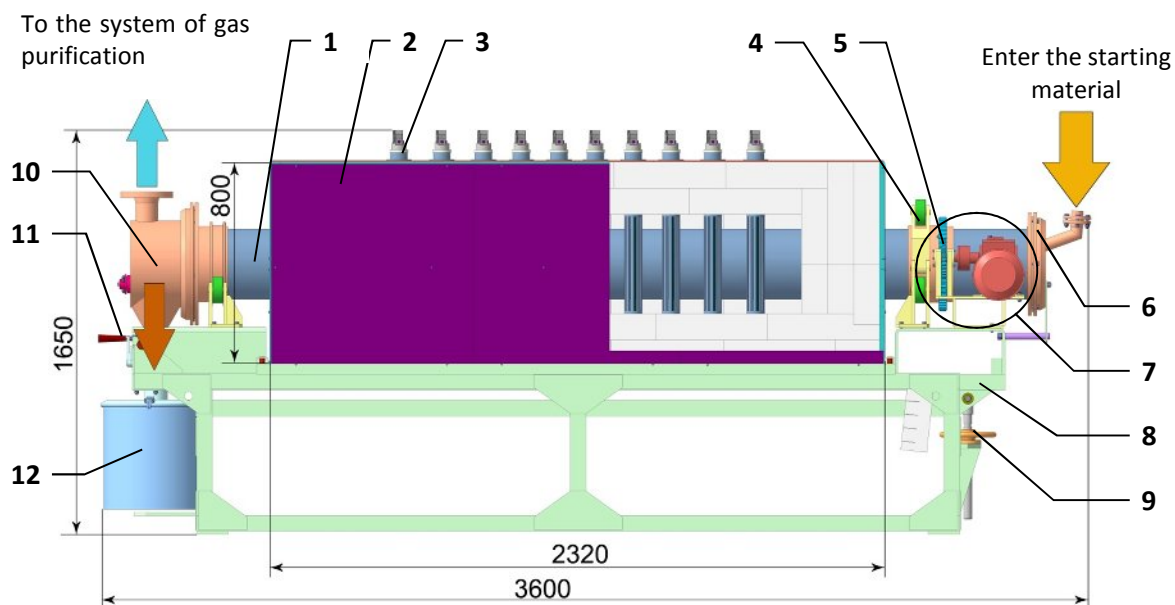
There are also suggestions for using high-temperature methods for IER processing (incineration and pyrolysis). The main advantages and disadvantages of existing methods for IER processing are shown in Table I.

Table I - Key advantages and disadvantages of existing IER processing methods.

Method	Advantages	Disadvantages
Bituminization	High waste loading (up to 40 wt.%)	The potential fire hazard of bituminous mass.
Cementation	The relative simplicity of the technological process. Ability to produce a solid low-soluble matrix.	The significant volume increase in the final product due to the limited waste loading , usually not more than 15wt.%.
Burning	The maximum possible decrease in the waste volume	The danger of atmosphere pollution from toxic products of combustion. Complex of gas-off cleaning equipment.

As an alternative or an addition to these technologies the method of calcification, which transforms resin pulp and liquid radioactive waste into dry and bulk powders.

JSC "VNIINM" conducted some experiments to determine the feasibility and the conditions to process Russian NNPs ion-exchange resin KU-2 by the calcination method.



- 1 - retort, 2 - oven, 3 - heating element in a heat-resistant steel cover; 4 - roller bearing, 5 - gear, 6 - inlet flange, 7 - drive retort, 8 - frame; 9 - adjustment screw, 10 - exit flange, 11 - rotary gate, 12 - receiving container

The original resin pulp enters into the calciner retort. The retort (pos. 1) is a rotating pipe varying from 2 to 5 ° tilt angle. To heat the retort the three-section oven with slit heaters is used (pos. 2). Calciner performance is up to 25 l / h of evaporated moisture. The maximum temperature on the inner surface of the retort is not more than 700 ° C. The rotation of the retort (at a rate of 3 to 20 rpm) is driven by a gear system (pos. 7) with variable speed. Pulp moving through the heated retort segment is evaporated, dried

and calcined . The final product (calcined) is loaded into a receiving container (pos. 12). The resulting gas-steam phase enters into the system of gas purification.

Calciner technical parameters:

Volume capacity (for vaporized moisture), l / h	25±3.
Maximum temperature of the retort heating, °C.....	700.
Retort rotational speed, rpm	3-20.
The retort tilt angle, degree.....	0 - 5.
<u>Overall dimensions, mm:</u>	
- Length	3350;
- Width.....	1140;
- Height.....	1417.
<u>Retort of overall dimensions, mm:</u>	
- Length	3200;
- Heated length.....	1700;
- Outside diameter, mm	273;
- Inner diameter, mm.....	257.

To determine the chemical reactions occurring during the thermal processing of ion-exchange resin the method of differential thermal analysis (DTA) was used.

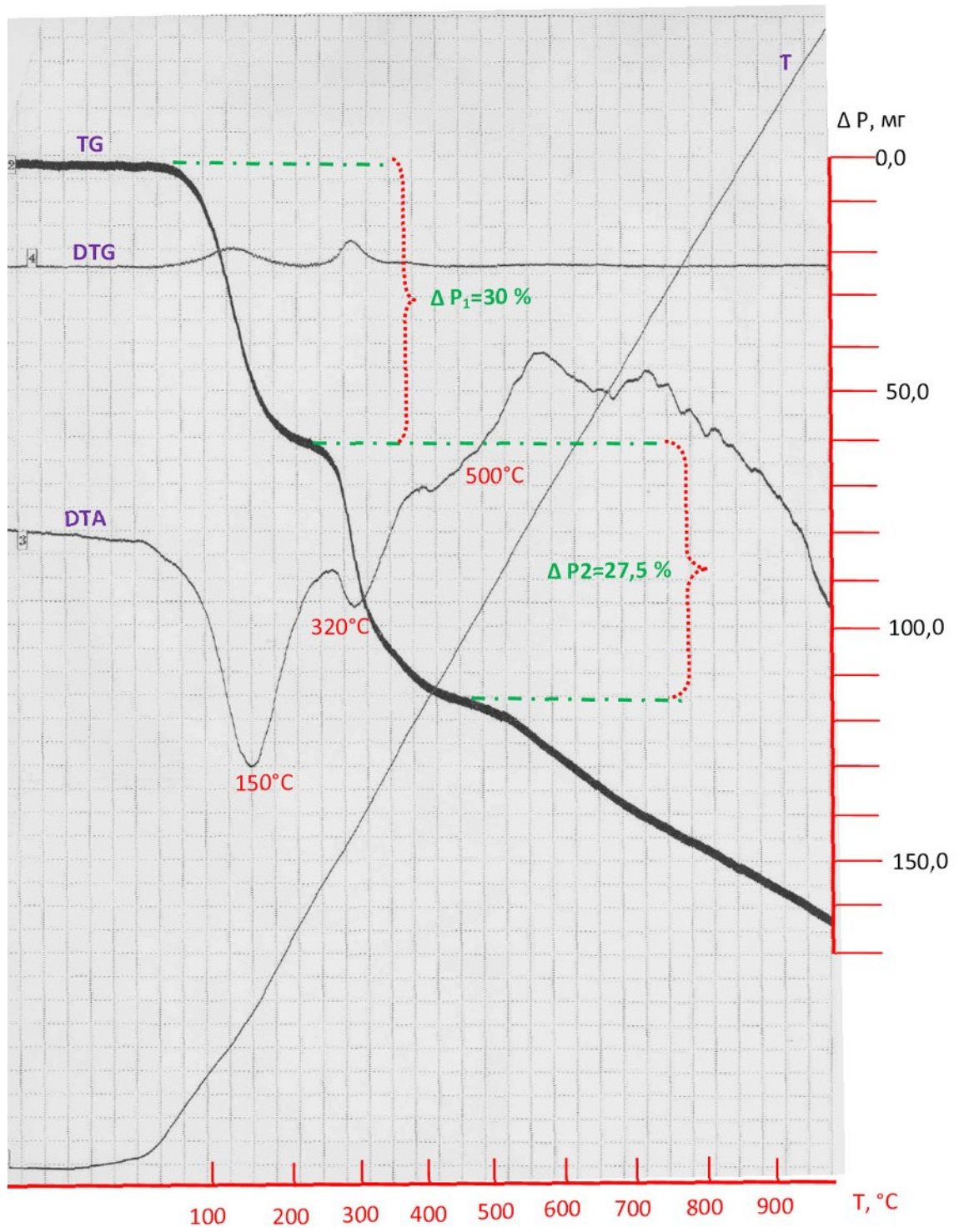
The curves of thermographic resin analysis (Picture II) shows that the largest mass loss upon heating the resin (57.5 wt. %) occurs at a temperature of 500 ° C.

The mass loss is a result of the removal of "chemically bound" water contained in the hydrophilic functional groups of resin.

With a further increase of temperature above 500 °C it is observed a series of exothermic effects at the DTA curve (pic.II) that are associated with combustion and thermal decomposition of the resin.

Therefore, to avoid formation of toxic gaseous products (dioxins) formed at thermal decomposition of the resin, the maximum temperature of calcination reprocessing should not exceed 500 ° C.

The technological parameters of IER calcinations conducted at the laboratory rotary calciner are shown in Table III.



Picture II – IER KU-2 thermogramme

Table III - The main technological parameters of the KU-2 IER calcination reprocessing.

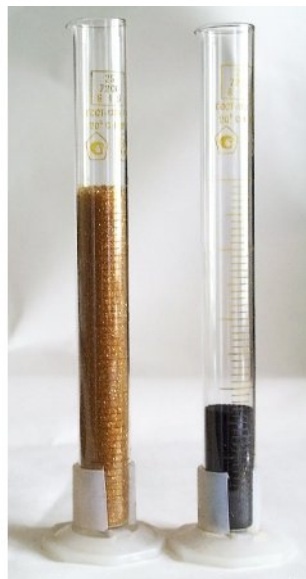
Characteristic	Value
The maximum temperature of the process, ° C	500
Retort rotational speed, rev / min	10
The pulp conveying speed, l / h	7,2
The ratio of Solid\Liquid in initial pulp	1:5

The structure and characteristics of the product obtained in the result of the KU-2 IER calcinations are shown in Pictures III-IV and Table III.



Picture III –The structure of resin calcinations

**The initial resin
(moisture content ~ 30 wt.%)**



Processed resin

The coefficient of volume reduction is $\approx 3,1$

Picture IV - The volume of initial and final products

Table III - Main calcinate characteristics

Fraction size, mm				Solidity, g/cm ³	Tilt angle	Moisture content, wt. %
0,5	0,25	0,125	< 0,125			
Fractional composition, mass. %				0,57	≈ 20°	≈ 3
2,8	66,2	26,4	4,6			

Cementation can be used to convert the product obtained from thermal processing of IER to provide a suitable waste form for storage or disposal.

Some laboratory samples were prepared to assess the possibility of using the cementation of the processing IER.

A mixture of Portland cement PC-500-D0 and sorption additives (bentonite) in a ratio of 9:1 by weight was used.

The processed IER waste loading in the cement product ranged from 25 to 35 % by weight.

The mechanical strength, water resistance and frost resistance of laboratory prepared samples was determined.

The main characteristics of the cement product containing processed resin are presented in Table IV and Picture IV.

Table IV - Main characteristics of the cement compounds obtained by IER reprocessed cementation.

Waste loading, mass. %	The content of bentonite, mass. %	Water/cement ratio	Mechanical strength, MPa		
			1	2	3
25,0	10,0	0,65	15,7	21,5	25,0
28,3	10,0-	0,75	13,8	21,5	20,2
35,0	10,0	1,1	8,0	12,4	11,6

Notes:

1 – the mechanical strength of the samples was determined after a 28 day cure in air;

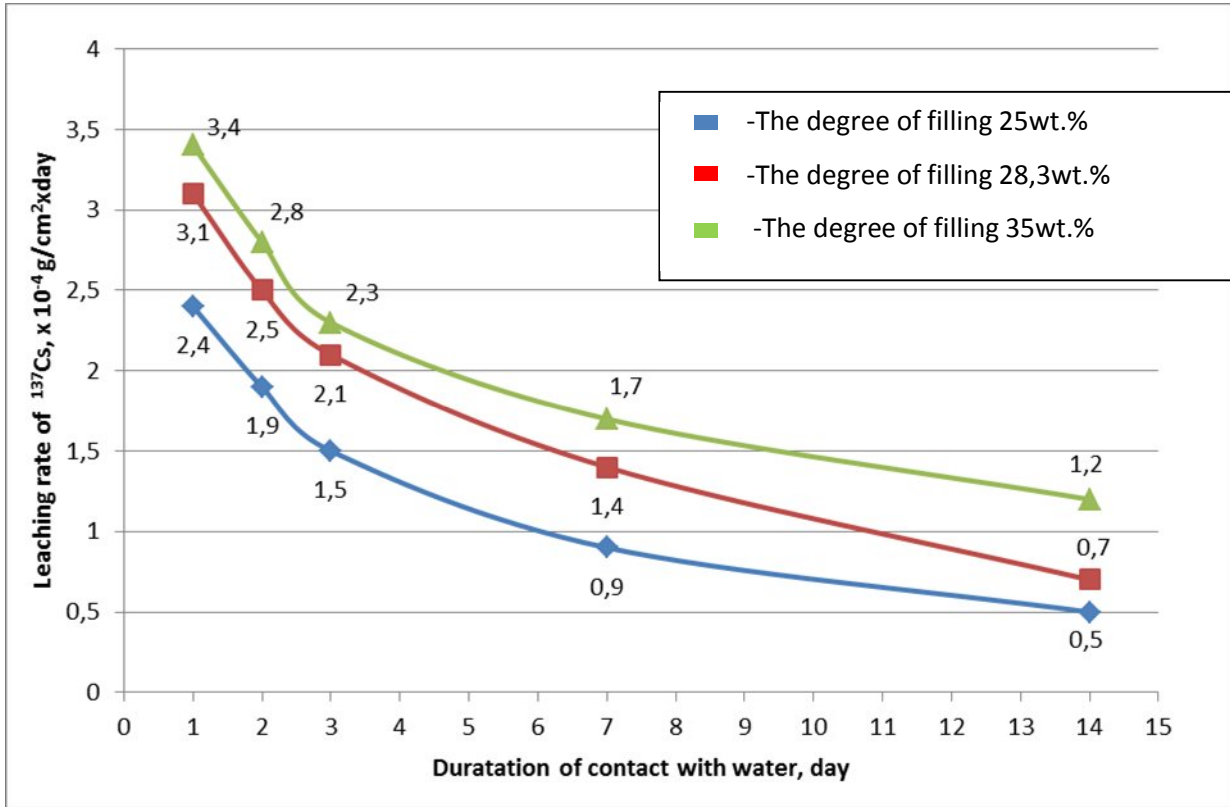
2 – the mechanical strength of the samples was determined after frost resistance testing (after 30 cycles of freezing and thawing);

3 - the mechanical strength of the samples was determined after water resistance testing (placed into water for 90 days).

The Table 4 data analysis shows that the cemented calcined IER product is characterized by the compressive mechanical strength.

Compressive strength for all the samples is significantly higher than Russian regulatory requirements (4.9 MPa).

Water resistant of the cement samples (Picture V) also meets regulatory demands and does not exceed the value of 4.10 g/sm² per day (regulatory demands - not worse 10⁻³g/sm²h per day).



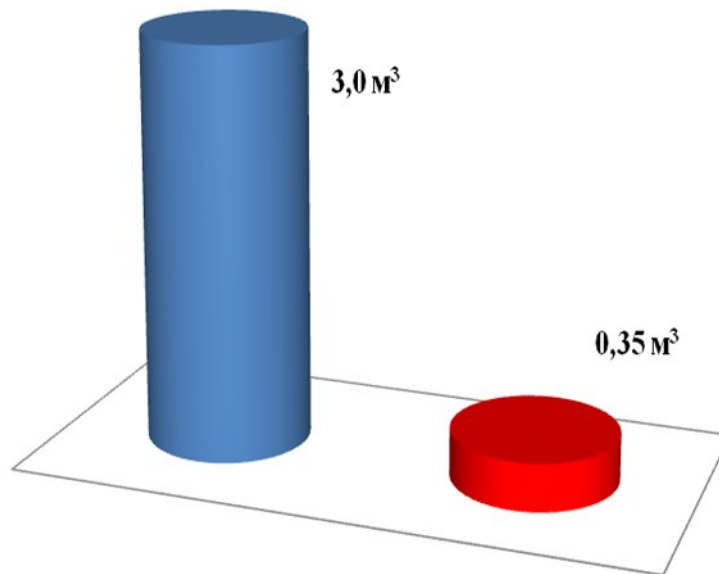
Picture V - The leaching rate of Cs-137 from cement products



The results show that cementation of IER calcined product produces an acceptable waste form.

At the same time, a volume reduction of almost 9 (8.7) over cementation of IER is achieved (Picture VI).

Similar results have been obtained from thermal processing of IER of S-940 and PFA – 460 grades.

The experimental results show the feasibility and effectiveness of the calcination method for spent IER processing which recommends this technology for IER conditioning.



-  - Unit, obtained by cementing a resin 1 m³ of natural moisture content (filling - 15 wt.%)
-  - Unit, obtained as a result of cementing calcinate received from 1 m³ of resin (filling - 35 wt.%)

Picture VI – Comparison of cement units obtained from 1 m³ of IER KU -2