

INCINERATION OF WET ION EXCHANGE RESINS MIXED WITH METAL FUEL

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ABSTRACT

A technology of thermochemical treatment of wet ion exchange resins (IER) mixed with powder metal fuel (PMF) has been developed. Metal powder (Mg, Ca, Al, etc.) included in PMF reacts with moisture generating enough heat to break down IER. To burn-out the products of IER decomposition and hydrogen resulting from the reaction of the metal with the moisture, the air is injected into the combustion chamber.

A pilot plant has been designed and constructed. Results of the investigation have shown a high efficiency of the technology developed. Slags remained in the combustion chamber confine radionuclides in the fixed form in amounts of 90 % or more of Cs-137 and up to 95 % of Sr-90 and Co-60.

INTRODUCTION

Ion exchange resins (IER) are widely used in water purification facilities of nuclear power plants and nuclear research centers. In this connection during operation of, for instance, nuclear power reactor of 1000 MW spent granular IER in amounts of more than 40 m³ is generated over the course of a year (Table I).

**Table I. Performances of granular IER “produced” by the nuclear power
reactor of 1000 MW (1)**

Source of IER	Volume of IER, m ³ /yr.	Activity, Bq	Specific activity, Bq/l
Cooling pond	2.0	$3.7 \cdot 10^{11}$	$1.9 \cdot 10^8$
Reactor			
• chemical control system	8.5	$2.1 \cdot 10^{14}$	$2.4 \cdot 10^{10}$
• bypass purification	4.8	$3.7 \cdot 10^{13}$	$7.4 \cdot 10^9$
Steam generator			
• leakages treatment	8.5	$7.4 \cdot 10^{11}$	$8.9 \cdot 10^7$
• condenser (deep purification)	9.9	$1.9 \cdot 10^{11}$	$1.9 \cdot 10^7$
“Contaminated” waste (deep demineralization)	2.8	$1.9 \cdot 10^{11}$	$6.3 \cdot 10^7$
“Decontaminated” waste (deep demineralization)	5.7	$3.7 \cdot 10^{11}$	$6.7 \cdot 10^7$

IERs most generally used are copolymers of styrene and divinylbenzene (2). Among them cationites KU-2-8 and its foreign analogs HCR-W, HCR-S, HGR-W, HGR-W2 (Dowex), IR-120, IR-

122, IR-130C, IR-132C (Amberlite) which contain fixed ions - sulfogroup $-\text{SO}_3\text{H}$ (H-form of a resin) or $-\text{SO}_3\text{Na}$ (Na-form, resin KA-11) are in wide use.

As an example of anionites the ion exchange resin AV-17, containing quaternary aminogroups and its analogs SBR, SBR-P (Dowex), IRA-400, IRA-420C, IRA-440C (Amberlite) may be cited.

Major radionuclides contained in the spent IERs are Cs-137, Sr-90, Co-60, Ru-106 and Mn-54 with a half-life of 30, 29, 5.3, 1 and 0.85 years respectively (1,3).

INCINERATION OF IER (TRADITIONAL METHODS)

To reduce initial volume and produce a product suitable for safe storage and disposal, the spent IERs are treated by special methods, among which the heat treatment by incineration in excess of the air (4) deserves attention.

Essentially all countries having nuclear technologies are developing methods and facilities for reprocessing wet IERs by incineration (see, for instance, (5-7)).

Since a wet resin does not burn, to incinerate IER by the traditional ways, removal of the moisture from the IER is previously required. This process consumes 2255 kJ/kg of water. Further process can be considered as combustion of polystyrene, which is the main constituent of IER.

According to present views, the process of polystyrene combustion is thought of as initial destruction of original substance to liquid state, subsequent evaporation and combustion of its vapors (8,9). Volatile products of polystyrene destruction at 400°C are a mixtures of a monomer, dimer, trimer and other compounds with the monomer (~94 mol. %) predominating. At high temperatures the larger fragments have a chance to pass into products of evaporation (prior to decomposition into a monomer). From different data activation energy of the release of a monomer, dimer and trimer from polystyrene is 230 - 270 kJ/mole, heat of gasification of polystyrene ranges between 1000 and 2000 kJ/kg (8).

Combustion of vapors above the surface of the melt proceeds under diffusion regime. Diffusion burning out of separate granules (drops) in the medium of gaseous oxidizer follows the law of Sreznevsky: $d_k^2 = d_{k0}^2 - kt$, where d_{k0} , d_k - initial and current diameter of a drop, k - constant of linear rate of burning out, for polystyrene $k = 57.6 \text{ cm}^2/\text{s}$ (8), t - time. The theory of diffusion combustion is sufficiently well-developed (10). However, this idealized process is very far from an actual pattern of the process of IER combustion in a bulk layer where products of IER destruction fill hollows between granules with the resulting formation of a large body of melt with granules incorporated into it. Combustion proceeds actually over the melt surface with leakage of the latter. Besides, this process is time consuming.

The basic problems arising in the traditional incineration of IER are connected with operation of gas purification systems and corrosion of the equipment. Corrosion activity of off-gases produces high loading on the purification apparatuses, which eventually raises considerably the price of the incineration process. That is the reason why the traditional methods of IERs incineration are relatively expensive and are not widely used (4).

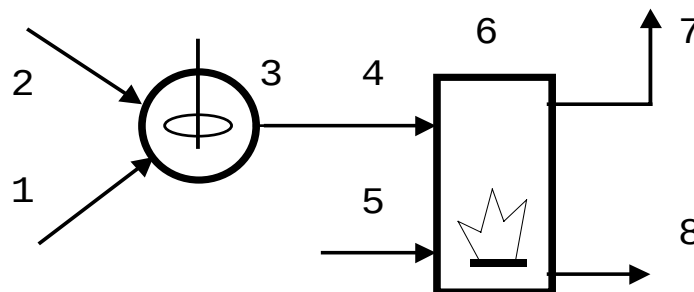
THERMOCHEMICAL TREATMENT OF IER MIXED WITH METAL FUEL

Moscow SIA "Radon" has proposed and developed a new technology of thermochemical treatment of wet IER using PMF (11,12). Powder of a metal capable of reacting (burning) with water constitutes the major fraction of PMF (Table II).

Table II. Characteristics of stoichiometric burning of some hydroreacting metals with water

Metal	Heat of combustion, kJ/kg	Equilibrium temperature, K
Mg	13000	2747
B	19550	1898
Al	15050	2872
Si	10170	2278
Ti	7720	2326

Scheme of the process of incineration of IER mixed with PMF is presented in Fig. 1.

**Fig. 1. Scheme of the process of IER thermochemical treatment**

1 - feed of wet IER, 2 - PMF feed, 3 - mixer, 4 - mixture feed, 5 - air feed, 6 – thermochemical reactor, 7 - off-gases, 8 - ash residue.

Wet IER and PMF previously mixed in the appropriate ratio are fed into a furnace where the mixture is initiated and its combustion proceeds. A metal powder contained in PMF is in the immediate contact with granules of IER and reacts with moisture included in them with the resulting release of a great quantity of heat (see Table II) which is enough for the moisture to evaporate and IER to be gasified. Moreover, the reaction of PMF with the surface of granules of IER prevents the coalescence of these latter and serves to the retention of porosity of the bulk being incinerated.

To burn out the products of IER gasification and hydrogen resulting from the reaction of the metal with the moisture, the air is supplied to the combustion chamber. Parameters of the combustion process in the furnace may be controlled by changing the air flow rate. The combustion proceeds with the formation of gas phase and ash residue. The process in the furnace is so organized that radionuclides contained in the wet resin are converted into low-volatile compounds of ash residue.

THERMODYNAMIC SIMULATION OF TERMOCHEMICAL PROCESS

To perform preliminary analysis of temperature conditions of thermochemical treatment, phase and chemical composition of resulting products of the thermochemical treatment, the method of thermodynamic simulation is used in this study. Program complex ASTRA.4 has been used as the simulation mean (13).

In the first place, temperature conditions of combustion of the mixture IER - PMF depending on the moisture content were studied. For an ion exchange resin in the system under study we used the cationite KU-2-8. The MTKD-45 type fuel including metal powder, burning activator and technological additive was selected as the powder metal fuel. The results obtained allow us to choose the necessary temperature conditions of the treatment of a resin depending on its initial moisture content. From the

viewpoint of intensification of the combustion of a resin, high temperatures are desirable, but this will promote the carry-over of highly volatile radionuclides with the gas phase. Moreover, in the system in question high temperatures are achieved with the great contents of PMF (over 25 - 30 %) that is not profitable. The wanted results can be obtained for the reasonably low PMF content of a source mixture with the air being injected into a combustion chamber of a furnace. Figure 2 shows the variation of the equilibrium combustion temperature of a mixture consisting of 20 % of PMF and a resin with moisture 0 (dry), 50 and 75 % with the air excess coefficient α . The combustion temperatures differ greatly at $\alpha < 1.5$, and for larger flow rates of air this difference is practically unnoticeable.

Some combustion characteristics of dry and wet IERs mixed with 20 % of PMF are given in Table III. (L_0 - air quantity in kg necessary for complete burning of 1 kg of the mixture, and Q - heat quantity in kJ generated in combustion of 1 kg of the mixture in stoichiometry with the air.)

Table III. Some characteristics of the combustion of IER mixed with 20 % of PMF

Characteristics	Dry resin	Resin with moisture 50 %	Resin with moisture 75 %
L_0 , kg/kg	11.3	6.0	3.3
Q , kJ/kg	38600	22000	13750

On the basis of the thermodynamic and experimental simulation results an operating range was chosen of the incineration process of wet IERs mixed with PMF.

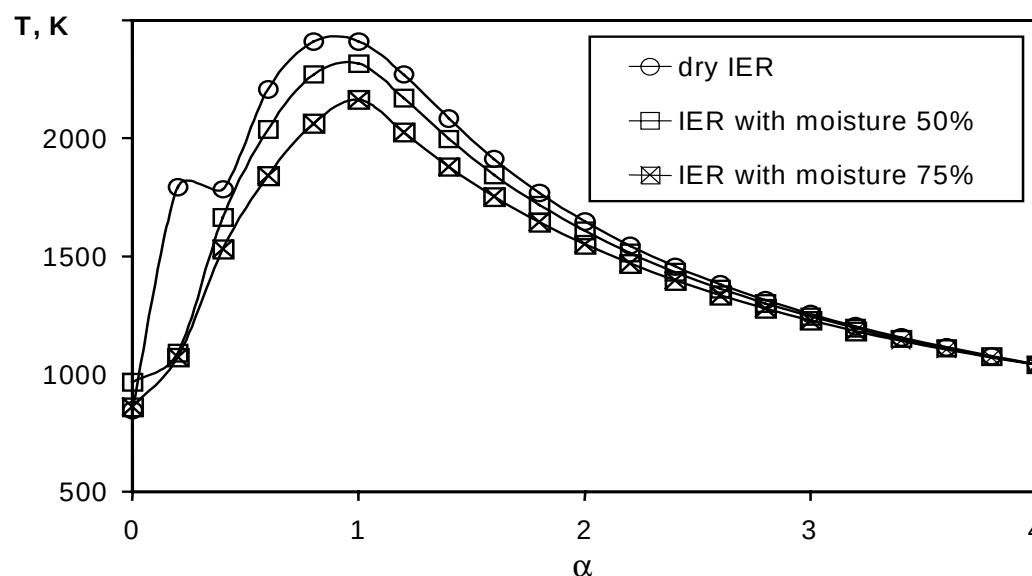


Fig. 2 The equilibrium combustion temperature of a mixture of IER with 20 % PMF vs the air excess coefficient α .

CHEMICAL COMPOSITION OF GASEOUS COMBUSTION PRODUCTS

Equilibrium composition of the gas phase of the combustion products in the combustion zone (with the complete burning of the source mixture) depends on the equilibrium temperature.

For example, let us consider the calculated equilibrium composition of gaseous products from combustion of a resin with the empirical formula $C_{45.83}H_{51.41}S_{4.97}O_{14.9}$ with 75 % moisture mixed with 20 % PMF of MTKD-45 type for different amounts of air involved in the combustion (Tables IV and V). Contents of individual gases are given in mass fractions m_i - kg per 1 kg of a mixture of the combustion products.

The decrease of CO_2 and H_2O contents with α increasing (Table IV) is due to dilution of off-gases with the air. For just this reason O_2 and N_2 contents are rising with α increasing. Content of nitrogen oxide NO in the operating conditions range does not exceed 0.001, and content of nitrogen dioxide NO_2 at all values of α is below 10^{-5} . In this Table the carbon oxide content of the combustion products is given as well. Only for $\alpha < 1.0$ carbon monoxide content exceeds 0.005 and for $\alpha > 1.5$ its content is not over 0.0001.

Among the sulfur-bearing gases HS, H_2S , SO_2 and SO_3 (Table V) occur in the combustion products in detectable amounts with HS and H_2S existed only at $\alpha < 1.0$. In the α range between 2 and 3 SO_2 content is about 0.01 and SO_3 content ranges from 0.0001 to 0.0004.

Table IV. Same gases content of the combustion products at different α .

α	Mass fraction of							
	CO_2	H_2O	O_2	H_2	CO	NO	NO_2	N_2
0.2	1.01E-1	2.62E-1	-	2.32E-2	1.19E-1	-	-	2.33E-1
0.6	8.79E-2	2.40E-1	4.65E-7	6.41E-3	5.75E-2	6.70E-6	-	4.32E-1
1.0	1.21E-1	2.12E-1	4.39E-3	3.30E-4	5.58E-3	1.36E-3	3.92E-7	5.21E-1
1.4	1.01E-1	1.69E-1	4.85E-2	1.28E-5	1.87E-4	2.44E-3	3.49E-6	5.71E-1
1.8	8.35E-2	1.39E-1	8.14E-2	1.09E-6	1.28E-5	1.56E-3	4.54E-6	6.04E-1
2.2	7.10E-2	1.18E-1	1.04E-1	1.21E-7	1.13E-6	8.95E-4	4.53E-6	6.27E-1
2.6	6.17E-2	1.03E-1	1.21E-1	1.60E-8	1.20E-7	5.04E-4	4.16E-6	6.44E-1
3.0	5.46E-2	9.08E-2	1.34E-1	2.36E-9	1.42E-8	2.83E-4	3.66E-6	6.57E-1
3.4	4.90E-2	8.14E-2	1.44E-1	-	1.87E-9	1.60E-4	3.16E-6	6.67E-1
4.2	4.06E-2	6.74E-2	1.58E-1	-	-	6.76E-5	2.50E-6	6.82E-1
5.0	3.47E-2	5.75E-2	1.69E-1	-	-	2.58E-5	1.86E-6	6.93E-1

Table V. Sulfur bearing gases content of the combustion products at different α .

α	Mass fraction of				
	HS	H_2S	SO_2	SO_3	H_2SO_4
0.2	9.20E-5	2.26E-2	6.00E-5	-	-
0.6	3.90E-4	1.62E-3	1.93E-2	1.08E-7	-
1.0	1.99E-7	6.09E-8	1.95E-2	5.69E-6	-
1.4	-	-	1.54E-2	2.94E-5	-
1.8	-	-	1.27E-2	6.62E-5	1.08E-9
2.2	-	-	1.05E-2	1.28E-4	3.22E-9
2.6	-	-	8.84E-3	2.33E-4	9.09E-9
3.0	-	-	7.64E-3	4.15E-4	2.52E-8
3.4	-	-	6.58E-3	7.05E-4	6.70E-8
4.2	-	-	5.91E-4	1.77E-4	3.29E-8
5.0	-	-	9.06E-6	8.20E-6	3.35E-9

Table VI. The ash residue composition at the different α .

α	Mass fraction of			
	MgO	$MgAl_2O_4$	K_2SO_4	$MgSO_4$
0.2	5.94E-2	1.72E-1	-	-
0.6	3.67E-2	1.06E-1	-	-
1.0	2.65E-2	7.70E-2	-	-
1.4	2.08E-2	6.03E-2	-	-
1.8	1.71E-2	4.96E-2	-	-
2.2	1.46E-2	4.21E-2	-	-
2.6	1.26E-2	3.66E-2	7.50E-4	-
3.0	1.12E-2	3.23E-2	8.45E-4	-
3.4	1.00E-2	2.90E-2	7.84E-4	-
4.2	5.00E-3	2.40E-2	6.53E-4	9.73E-3
5.0	3.90E-3	2.05E-2	5.58E-4	9.45E-3

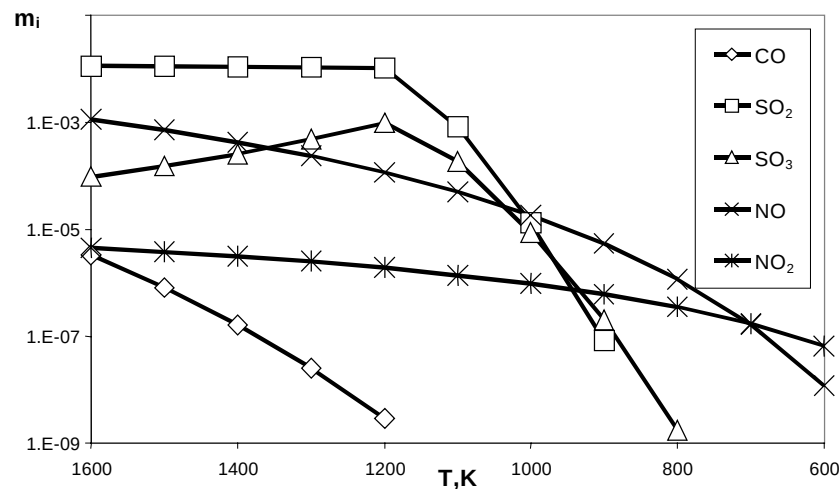


Fig. 3 Behavior of the equilibrium composition of gases in the combustion products on cooling ($\alpha = 2$).

On flow-off from the combustion zone and in further moving through gas-outgoing devices the gases are cooled. Let us use the same source mixture at air excess coefficient $\alpha = 2$ to consider the change of the equilibrium composition of gases on cooling. The change of CO, SO₂, SO₃, NO and NO₂ contents of the gas phase is shown in Fig. 3. As the temperature of the combustion products decreases, SO₂ and SO₃ contents of the gas phase drop sharply which is due to the formation of potassium and magnesium sulfates (K₂SO₄ and MgSO₄) in the condensed phase – ash residue (Fig. 4).

CHEMICAL COMPOSITION OF ASH RESIDUE FROM IER TREATMENT

Equilibrium composition of the ash residue of the combustion products of wet IER mixed with PMF is calculated from those initial data used for the gas phase. The variation of composition of the ash residue depending on the air excess coefficient α is shown in Table VI. Fig. 4 illustrates the variation of the ash residue composition for the source mixture at $\alpha = 2$ and on cooling of the combustion products.

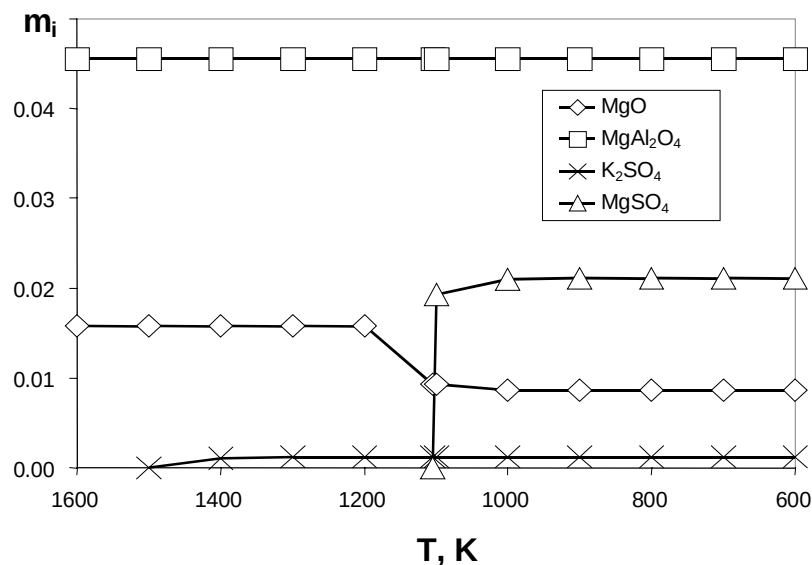


Fig. 4 Variation of equilibrium composition of the ash residue of the combustion products on cooling ($\alpha = 2$).

The condensed combustion products (ash residue) under conditions considered can be seen to consist of magnesium oxide MgO, spinel MgAl₂O₄, sulfates of potassium K₂SO₄ and magnesium MgSO₄. The MgSO₄ appears at $T < 1200$ K binding practically all sulfur contained in the combustion products and a part of magnesium oxide. However, it should be remembered that in practice, this binding is hardly realized in full measure, as the separation of gas phase and ash residue occurs during combustion. Owing to this residence time of sulfur-containing gases in the combustion zone in contact with the condensed products is finite. As to K₂SO₄, the conditions are favorable to its formation, as in the combustion zone potassium compounds with oxygen and hydrogen are in the gas phase and hence interact readily with sulfur-bearing gases.

The results obtained show that during combustion of spent IER containing radionuclides Cs-137 and Sr-90 these latter, by analogy with K and Mg behaviour, will also be transfer into and be confined in the condensed compounds of ash residue. This assumption was verified by Moscow SIA "Radon" investigations (14,15).

EXPERIMENTAL TESTING

Thus, high efficiency of the thermochemical treatment was shown and the range of optimum wet IER-PMF proportions in mixtures was established by the method of thermodynamic numerical simulation. To develop the thermochemical treatment technology, a pilot plant was designed and constructed.

The incinerator in this plant is a vertical metal shaft with diameter of 400 mm and height of 1200 mm. A mixture of 80 % wet IER and 20 % PMF from the mixer is fed into the combustion chamber at the top. Air is injected and ignition is performed at the bottom of the shaft. The temperature of the process, compositions of ash residue and off-gases are controlled in the experiments.

Chemical analysis of gaseous combustion products and comparison of the results with that obtained from the computing simulation show to high non-equilibrium in the combustion products in the point of sampling (at the incinerator outlet). Nevertheless, contents of sulfur and nitrogen oxides in

the gaseous products do not exceed maximum permissible concentrations (PMC) accepted in different countries (Table VII).

Table VII. Hazard gas contents of the combustion products of a mixture of 80 % wet IER (KU-2-8) and 20 % PMF (MTKD-45)

Gas	Content in the combustion products, mg/m ³		PMC accepted in different countries, mg/m ³
	Calculation at $2 < \alpha < 3$	Chemical analysis, average/maximum	
NO	0.03	20 / 50	300...500
NO ₂	0.20		
SO ₂	40	220 / 430	100...2000
SO ₃	24		
CO	< 0.02	< 1.25	50...200

Chemical analysis of ash residue shows that slags confine radionuclides in the fixed form in amounts of 90 % or more of Cs-137 and more than 95 % of Sr-90 and Co-60 (15). Although these results are somewhat exceeded by parameters of the THOR - process (16), rather simplicity of the process proposed and equipment for it allow us to hope that this new technology is competitive. Moreover suggested process can be implemented in a mobile incineration unit which now is in under development at SIA "Radon".

CONCLUSIONS

The results of thermodynamic simulation and the experimental findings have shown high efficiency of the thermochemical treatment of wet ion exchange resins mixed with powder metal fuel. Thus this process may be thought of considerable promise. Of prime importance is its possible realization in a small-sized mobile facility.

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